

**Wrocław University of Technology
Faculty of Chemistry**

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**OF THE 1st
INTERNATIONAL CONFERENCE
ON METHODS AND MATERIALS
FOR SEPARATION PROCESSES**

**SEPARATION SCIENCE
– THEORY AND PRACTICE 2011**



5-9 JUNE, 2011, KUDOWA ZDRÓJ, POLAND

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EDITORS

Anna Jakubiak-Marcinkowska
Andrzej W. Trochimczuk

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Anna Jakubiak-Marcinkowska
Andrzej W. Trochimczuk

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Address:

Faculty of Chemistry

Wroclaw University of Technology

Wybrzeże Wyspiańskiego 27,

50-370 Wrocław, Poland

Phone: +4871 320 3173

Fax: +4871 320 2152

I. LECTURES

- L-1** **Spiro D. Alexandratos, Xiaoping Zhu and Yijia Yang** **18**
ION-SELECTIVE POLYMER-SUPPORTED COMPLEXANTS: DESIGN,
SYNTHESIS, AND THE MECHANISM OF COMPLEXATION
- L-2** **Ecaterina Stela Drăgan, Maria Valentina Dinu, Maria Marinela Perju** **21**
IONIC COMPOSITE MATERIALS AND THEIR INTERACTIONS WITH
IONIC SPECIES
- L-3** **Kazuharu Yoshizuka, Shuhei Tanaka, Akinori Harada, Syouhei Nishihama** **25**
SELECTIVE RECOVERY PROCESS OF PLATINUM GROUP METALS
FROM SPENT AUTOMOBILE CATALYST
- L-4** **Tomasz Chmielewski** **28**
HYDROMETALLURGY AT KGHM POLSKA MIEDŹ SA –
CIRCUMSTANCES, NEEDS AND PERSPECTIVES OF APPLICATION
- L-5** **Piotr P. Wieczorek** **32**
SUPPORTED LIQUID MEMBRANES AS A USEFUL TECHNIQUE FOR
SEPARATION AND PRECONCENTRATION OF ORGANIC COMPOUNDS
- L-6** **V.V. Tepliakov** **34**
IMPACT OF MEMBRANES AND MEMBRANE PROCESSES ON
ENVIRONMENTAL ISSUES
- L-7** **Toyoki Kunitake** **36**
IMPLICATIONS OF NANOMEMBRANES IN SEPARATION SCIENCE

II. SHORT LECTURES

- S-1 **Pavel Kůs, Tomáš Birčák, Kateřina Vonková and Luděk Jelínek** 41
CATION EXCHANGE EQUILIBRIA IN BORIC ACID SOLUTIONS
- S-2 **Dorota Kołodzyńska, Zbigniew Hubicki** 43
POLYMERIC HYBRID SORBENTS IN REMOVAL OF ANIONIC SPECIES FROM WATER AND WASTEWATER
- S-3 **Akinori Jyo, Hiroshi Nakaatari, Ruriko Fujimoto, Masahiro Kitagaki, Hirotaka Matsuura, Masao Tamada, Noriaki Seko** 44
KINETICALLY EXCELLENT NITRATE SELECTIVE ANION EXCHANGE FIBERS DERIVED FROM CHLOROMETHYLSTYRENE GRAFTED POLYOLEFIN FIBER
- S-4 **Maria Marinela Perju, Maria Valentina Dinu, Ecaterina Stela Dragan** 48
REMOVAL OF CATIONIC DYES FROM AQUEOUS SOLUTIONS WITH COMPOSITE HYDROGELS BASED ON POLYACRYLAMIDE AND DEXTRAN SULPHATE
- S-5 **Catherine Branger, Julie Bernard, André Margailan** 52
ELABORATION OF CHELATING RESINS FOR METAL IONS SOLID-PHASE EXTRACTION
- S-6 **Paulina Otremska, Jerzy Gęga** 54
SEPERATION OF NICKEL(II) AND CADMIUM(II) WITH ION-EXCHANGE PROCESS
- S-7 **Grzegorz Wójcik, Violeta Neagu, Ion Bunia** 58
SORPTION STUDIES OF CHROMIUM(VI) ONTO NEW ION EXCHANGER WITH TERTIARY AMINE, QUATERNARY AMMONIUM AND KETONE GROUPS
- S-8 **Hirotaka Matsuura, Hiromi Yonekawa, Akinori Jyo, Masao Tamada, Noriaki Seko and Yuji Ueki** 59
PREPARATION AND PROPERTIES OF BIFUNCTIONAL CHELATING FIBERS CONTAINING IMINODIACETATE AND HYDROPHILIC MOIETIES
- S-9 **Yuliya S. Dzyazko, Ludmila N. Ponomarova, Yurii M. Volfkovich, Valentin E. Sosenkin, Vladimir N. Belyakov** 63
HYBRID ORGANIC-INORGANIC ION-EXCHANGERS FOR REMOVAL OF HEAVY METAL IONS FROM DILUTED SOLUTIONS
- S-10 **Barbara Wionczyk, Wiesław Apostoluk** 67
SEPARATION OF CHROMIUM(III) FROM WASTES OF CHROMIUM-TANNED LEATHERS. EXPERIMENTS AND KINETIC MODELS

S-11	<u>V. N. Belyakov, V. M. Linkov, S. L. Vasilyuk</u> SELECTIVE REMOVAL OF LITHIUM FROM NATURAL WATERS BY INORGANIC SORBENTS AND MEMBRANES	71
S-12	<u>B. Filiz Senkal, Inan Kucukkaya, Erdem Yavuz</u> THE SYNTHESIS OF SULFONAMIDE BASED POLYMERIC SORBENTS FOR SELECTIVE REMOVAL OF MERCURY FROM WATER	75
S-13	<u>Dilek Duranoğlu, Andrzej W. Trochimczuk, Ülker Beker</u> CHROMIUM ADSORPTION ONTO ACRYLONITRILE- DIVINYLBENZENE DERIVED ACTIVATED CARBON	77
S-14	<u>A. Wołowicz, Z. Hubicki</u> INVESTIGATION OF STRONGLY BASIC ANION EXCHANGE RESINS PROPERTIES FOR PALLADIUM REMOVAL FROM ACIDIC SOLUTIONS	81
S-15	Katarzyna Ochromowicz, <u>Wiesław Apostoluk</u>, Tomasz <u>Chmielewski</u>, Barbara Woźniak SOLVENT EXTRACTION OF COPPER AND ACCOMPANYING METALS FROM SULFATE LEACH LIQUORS	85
S-16	K. Wieszczycka, <u>M. Krupa</u>, A. Olszanowski EXTRACTION OF COPPER(II) WITH HYDROPHOBIC PIRYDYL KETOXIMES FROM CHLORIDE AND SULPHATE SOLUTION	89
S-17	<u>Rosa M. Marcé</u>, Dominika Bratkowska, Arlen Davies, Francesc <u>Borrull</u>, Peter A.G. Cormack, David C. Sherrington, Núria <u>Fontanals</u> MIXED-MODE HYPERCROSSLINKED MATERIALS FOR SOLID-PHASE EXTRACTION	93
S-18	<u>Keisuke Ohto</u>, Ryoma Yamaguma, Hidetaka Kawakita PREPARATION OF TRIPODAL PYRIDYL COMPOUNDS FOR PRECIOUS METAL EXTRACTION	96
S-19	<u>Dominika M. Szternel</u>, Magdalena Regel-Rosocka, Maciej <u>Wiśniewski</u> REMOVAL OF LOW-MOLECULAR CARBOXYLIC ACIDS FROM AQUEOUS SOLUTIONS	100
S-20	<u>Piotr Gajewski</u>, Mariusz B. Bogacki INFLUENCE OF ALKYL CHAIN LENGTH IN 1-ALKYL-IMIDAZOLE ON THE CITRIC ACID TRANSPORT RATE ACROSS POLYMER INCLUSIVE MEMBRANE	101

S-21	<u>Piotr Kujawski, Mariusz B. Bogacki</u> MOLECULAR DYNAMICS STUDY OF THE BEHAVIOUR OF TBP-ZINC- CHLORINE COMPLEX AT THE CHLOROFORM/WATER INTERFACIAL SYSTEM	105
S-22	<u>Markku Laatikainen, Katri Laatikainen, Tuomo Sainio and Heli Siren</u> REMOVAL OF VERY SMALL AMOUNT OF NICKEL FROM CONCENTRATED ZINC SULFATE SOLUTIONS - MODELING APPROACH	109
S-23	<u>Jerzy Gęga</u> COMPETITIVE TRANSPORT OF Zn(II) AND Mn(II) IONS THROUGH HYBRID LIQUID MEMBRANES	110
S-24	<u>Vladimir M. Zhdanov, Vjacheslav I. Roldughin</u> THE EFFECT OF SURFACE FORCE ON THE GAS MIXTURE SEPARATION IN NANODIMENSIONAL CAPILLARIES	114
S-25	<u>Wojciech Kujawski</u> MEMBRANE SEPARATION PROCESSES IN THE PRODUCTION OF THE GREEN FUELS	118
S-26	<u>Andrey Yu. Smirnov, Georgy A. Sulaberidze</u> GENERAL MODEL OF MASS TRANSFER PROCESSES IN A CASCADE WITH LOSSES OF WORKING SUBSTANCE	119
S-27	<u>Stanisław Koter</u> RECENT PATENTS ON ION-EXCHANGE MEMBRANES AND ELECTRO-MEMBRANE SEPARATION PROCESSES	120
S-28	<u>Maria Tomaszewska, Agnieszka Mientka</u> PRELIMINARY STUDIES ON CONVERSION OF KCL WITH POST - HYDROLYTIC SULPHURIC ACID INTO KHSO ₄ IN A MEMBRANE REACTOR	122
S-29	<u>Bruce A. Hendry</u> PARADIGM SHIFTS IN PROCESS SCALE IMPLEMENTATION OF NOVEL MULTI-PHASE CONTACTING SYSTEMS	126
S-30	<u>Tatiana Yurchuk, Henry Bergmann</u> DISCONTINUOUS ELECTRO-REGENERATION OF CHROMATE SOLUTIONS FOR ENVIRONMENTALLY-FRIENDLY PLATING PROCESSES	128
S-31	<u>Georgy A. Sulaberidze, Valentine D. Borisevich, Shi Zeng</u> SOME SUPPLEMENTS TO THE CLASSIC THEORY OF IDEAL CASCADES	129

III. POSTERS

- P-1** **Shamshiya K. Amerkhanova, Rustam M. Shlyapov, Farida Zh. Bekkulina** 131
THERMODYNAMIC ASPECTS OF SELECTION OF THE COLLECTORS IN SULPHIDIC ORES FLOTATION
- P-2** **Katarzyna Ochromowicz, Wiesław Apostoluk** 132
THE EFFECT OF POLYMERIC MATRIX ON CHROMIUM(III) TRANSPORT IN SLM SYSTEMS
- P-3** **Anna Bastrzyk, Izabela Polowczyk, Zygmunt Sadowski** 134
ROLE OF HYDROPHOBICITY IN AGGLOMERATION OF DOLOMITE IN CATIONIC-ANIONIC SURFACTANT SYSTEM
- P-4** **Esra Bilgin Şimşek, Dilek Duranoğlu, Ülker Beker** 135
HEAVY METAL ADSORPTION BY MAGNETIC NANO-SORBENT: AN EXPERIMENTAL AND THEORETICAL APPROACH
- P-5** **Aslı Özge Avcı, Dilek Duranoğlu, Ülker Beker** 136
AN ECO-FRIENDLY ADSORBENT FOR HEAVY METAL REMEDIATION IN AQUEOUS ENVIRONMENT
- P-6** **İsmet Gül B. Kaya, Dilek Duranoğlu, Ülker Beker, B. F. Şenkal** 137
REMOVAL OF Cr(VI) BY GRAFT COPOLYMER COATED MAGNETIC NANO-SORBENT: BATCH EQUILIBRIUM AND KINETIC STUDIES
- P-7** **Helena Bendová, Zdeněk Palatý** 139
CONTINUOUS DIALYSIS OF SULPHURIC ACID AND SODIUM SULPHATE
- P-8** **Robert Biernacki, Aleksandra Borowiak-Resterna** 140
THE EFFECT OF HYDROPHOBIC PYRIDINECARBOXAMIDES BASICITY ON COPPER(II) EXTRACTION
- P-9** **Marek Bryjak, Joanna Wolska, Ilona Duraj** 142
UPTAKE OF ENDOCRINE DISRUPTORS BY THE MOLECULARLY IMPRINTED POLYMERS
- P-10** **Butewicz Arleta, Andrzej W. Trochimczuk** 143
GOLD, PLATINUM AND PALLADIUM SORPTION/REDUCTION BY THE IMMOBILIZED EGG SHELL MEMBRANE
- P-11** **Seda Cekli, Erdem Yavuz, Bahire Filiz Senkal** 144
PREPARATION OF SULFONAMIDE CONTAINING CELLULOSE BASED SORBENT FOR REMOVAL OF MERCURY IONS

P-12	<u>Marzena Chorążewska, Piotr Dydo, Marian Turek</u>	145
	PERFORMANCE OF WOVEN AND NON – WOVEN SPACERS IN MEMBRANE SEPARATION PROCESSES	
P-13	<u>Barbara Wionczyk, Anna Mól, Ryszard Cierpiszewski, Krystyna Prochaska</u>	146
	EQUILIBRIUM AND KINETICS OF Cr(III) EXTRACTION FROM AQUEOUS SOLUTION IN THE SYSTEM WITH ALIQUAT 336	
P-14	<u>Anna Jakubiak-Marcinkowska, Sylwia Ronka, Magdalena Pilśniak-Rabiega, Arleta Butewicz, Joanna Czulak, Andrzej W. Trochimczuk</u>	147
	CHANGES OF THE ION CONTENT IN SOIL CONTACTED HYDROGELS	
P-15	<u>Maria Valentina Dinu, Ecaterina Stela Drăgan</u>	148
	STUDY ON HEAVY METALS SORPTION BY IONIC COMPOSITES	
P-16	<u>Diana Felicia Apopei, Ecaterina Stela Dragan</u>	149
	SEMI-INTERPENETRATED COMPOSITE HYDROGELS BASED ON POTATOES STARCH AND THEIR INTERACTION WITH IONIC SPECIES	
P-17	<u>Gabriela Dudek, Roman Turczyn, Anna Strzelewicz, Aleksandra Rybak, Monika Krasowska, Zbigniew J. Grzywna</u>	150
	PREPARATION OF IRON OXIDES - POLYMER COMPOSITES MEMBRANES	
P-18	<u>P. Dydo, M. Turek</u>	151
	THE CONCEPT OF BORON REMOVAL AND CONCENTRATION IN AN INTEGRATED MEMBRANE SYSTEM	
P-19	<u>Janusz Dziak, Jacek Kapłon, Abdirahman Ahmed</u>	152
	APPLICATION OF HYBRID SYSTEM: JET PUMP MIXER-MICROFILTER FOR CRUDE OIL DESALINATION	
P-20	<u>Janusz Dziak, Jacek Kapłon, Lechosław Królikowski, Waleed Abdulsalam</u>	153
	SIMULATION OF THE SEPARATION AND PURIFICATION PROCESS OF LINSEED OIL ETHYL ESTERS	
P-21	<u>Bernadeta Gajda, Mariusz B. Bogacki</u>	154
	SEPARATION PROCESS OF COBALT(II), NICKEL(II), ZINC(II) AND CADMIUM(II) FROM CHLORIDE SOLUTION	
P-22	<u>A. Jakóbiak-Kolon, M. Smolik, H. Jaroszek</u>	155
	EFFECT OF Zr AND Hf SOLUTION PREPARATION STEP ON THEIR SEPARATION ON DIPHONIX® RESIN	

P-23	<u>Anna Jakubiak-Marcinkowska, Andrzej W. Trochiczuk</u> SORPTION OF DI- AND TRIVALENT CATIONS ON MOLECULARLY IMPRINTED POLYMERS	156
P-24	<u>H. Parschová, E. Mištová and L. Jelínek</u> REMOVAL OF HEXAFLUOROARSENATE FROM AQUEOUS SOLUTION	157
P-25	<u>Dorota Jermakowicz-Bartkowiak</u> ANION EXCHANGE RESIN TOWARDS NOBLE METALS SORPTION	158
P-26	<u>Małgorzata Kica, Sylwia Ronka</u> SYNTHESIS OF POLYMER ADSORBENTS BY DIELS- ALDER MODIFICATION OF VINYL GROUPS IN POLY(DIVINYLBENZENE)	159
P-27	<u>E. V. Kirillov, V. N. Rychkov, M. L. Cherny</u> SELECTIVE RECOVERY OF TRACE REE FROM ACIDIC AQUEOUS SOLUTION WITH DIALKYL HYDROGEN PHOSPHORIC ACID IMPREGNATED RESINS	160
P-28	<u>Kanako Kohata, Syouhei Nishihama, and Kazuharu Yoshizuka</u> SEPARATION AND RECOVERY OF LANTHANUM AND CERIUM FROM WASTE AUTOMOBILE CATALYST USING COATED SOLVENT IMPREGNATED RESIN	161
P-29	<u>Dorota Kołodyńska, Marzena Gęca, Zbigniew Hubicki</u> CHITOSAN MODIFIED BY N,N-BIS(CARBOXYMETHYL)GLUTAMIC ACID IN HEAVY METAL IONS SORPTION FROM WATER AND WASTEWATER	162
P-30	<u>B. Konopczyńska, E. Świerkowska, K. Staszak, K. Prochaska</u> REMOVAL OF CHROMIUM(III) IONS FROM AQUEOUS SOLUTION BY MICELLAR-ENHANCED ULTRAFILTRATION PROCESS (MEUF)	163
P-31	<u>Joanna Kończyk, Jolanta Kozłowska, Cezary Kozłowski, Władysław Walkowiak, Małgorzata Deska</u> SOLVENT EXTRACTION OF Pb(II), Cd(II) AND Zn(II) BY CARBOXYLATED RESORCINARENES	164
P-32	<u>Stanisław Koter, Adriana Cuciureanu, Monika Kultys, Jerzy Michałek</u> CONCENTRATION OF SODIUM HYDROXIDE SOLUTIONS BY ELECTRODIALYSIS	165
P-33	<u>Tomasz Bohr, Stanisław Koter</u> PROPERTIES OF SULFONATED PSEBS TRIBLOCK COPOLIMER MEMBRANES FOR ELECTROCHEMICAL APPLICATIONS	166

P-34	<u>A. Kowalik, M. Smolik, K. Mączka</u> THE INFLUENCE OF TEMPERATURE ON THE VALUES OF DISTRIBUTION COEFFICIENTS, $D_{2/1}$ DURING THE CRYSTALLIZATION OF $\text{CoSeO}_4 \cdot n\text{H}_2\text{O}$	167
P-35	<u>Iolanta Kozłowska, Iwona Zawierucha, Małgorzata Deska</u> APPLICATION OF CARBOXYPHENYL DERIVATIVE OF RESORCINARENE FOR SOLID PHASE EXTRACTION OF Pb(II), Zn(II) AND Cd(II) IONS	168
P-36	<u>Monika Krasowska, Gabriela Dudek, Anna Strzelewicz, Aleksandra Rybak, Zbigniew J. Grzywna</u> PERCOLATION BEHAVIOUR OF GAS PERMEABILITY IN POLYMERIC MEMBRANES WITH MAGNETIC PARTICLES	169
P-37	<u>Marta Meller, Wojciech Kujawski, Radosław Kopeć</u> POLYAMIDE-6 PERVAPORATION MEMBRANES FOR ORGANIC-ORGANIC SEPARATION	170
P-38	<u>Monika Kultys, Stanisław Koter</u> PERMEABILITY OF DIVALENT CATIONS ACROSS ANION-EXCHANGE MEMBRANES IN THE PRESENCE OF SULFURIC ACID. PART 1: ELECTRODIALYSIS OF MgSO_4 AND H_2SO_4 MIXTURE	171
P-39	<u>Monika Kultys, Stanisław Koter</u> PERMEABILITY OF DIVALENT CATIONS ACROSS ANION-EXCHANGE MEMBRANES IN THE PRESENCE OF SULFURIC ACID. PART 2: ELECTRODIALYSIS OF ZnSO_4 AND H_2SO_4 MIXTURE	172
P-40	<u>Jana Martinková, Tomáš Weidlich</u> APPLICATION OF TETRAPHENYL AND ETHYLTRIPHENYLPHOSPHONIUM SALTS FOR REMOVAL OF ANIONIC DYES PROCION RED MX-5B AND REACTIVE BLACK 5 FROM AQUEOUS SOLUTIONS	173
P-41	<u>Ireneusz Miesiac, Krzysztof Alejski</u> DESALINATION OF GLYCERINE BY ION EXCLUSION	174
P-42	<u>I. Miesiac, K. Alejski, A. Rogaliński, M. Przewoźna</u> SEPARATION OF SUCCINIC ACID AND GLYCEROL	175
P-43	<u>Marian Turek, Krzysztof Mitko, Marzena Chorążewska</u> ELECTRODIALYTIC SATURATION OF CHLOR-ALKALI DEPLETED BRINE	176
P-44	<u>Syouhei Nishihama, Akane Kawasaki and Kazuharu Yoshizuka</u> ADSORPTION OF TETRAALKYLAMMONIUM HYDROXIDE WITH MESOPOROUS SILICA	177

- P-45** **Łukasz Nowak, Magdalena Regel-Rosocka, Maciej Wiśniewski** 178
TRANSFER OF ZINC(II) AND IRON(III) IONS THROUGH POLYMER INCLUSION MEMBRANES CONTAINING PHOSPHONIUM CHLORIDE
- P-46** **Anna Nowik-Zajac, Cezary Kozłowski, Andrzej Trochimczuk** 179
SELECTIVE TRANSPORT OF Ag^+ AND Cu^{2+} ACROSS PLASTICIZER MEMBRANES WITH CALIX[4]PYRROLE
- P-47** **Keisuke Ohto, Hirotoshi Sadamatsu, Shigemasa Kuwata, Tomoaki Yoneyama, Hideaki Ishibashi, Hidetaka Kawakita** 180
SPECIFIC METAL EXTRACTION WITH CALIX[4]ARENE CARBOXYLIC ACIDS CAUSED BY SODIUM ADDITION
- P-48** **Tadashi Okobira, Naoko Matsuoka, Hiroaki Fujino, Naomi Tajiri and Kazuya Uezu** 181
ESSENTIAL STRUCTURAL FACTOR OF BIS-1,2-DIOL IN POLYOL MOLECULES FOR CAPTURING BORON
- P-49** **Maria Marinela Perju, Maria Valentina Dinu, Ecaterina Stela Dragan** 182
SEMI-INTERPENETRATED IONIC HYDROGELS BASED ON CHITOSAN AND POLYACRYLAMIDE
- P-50** **L. F. Petrik, G. Ndayambaje, O. O. Fatoba, R. Akinyeye, N. T. Van der Walt** 183
SORPTION PROPERTIES OF NATURAL ZEOLITES FOR REMOVAL OF HAZARDOUS ELEMENTS FROM INDUSTRIAL EFFLUENTS
- P-51** **Karol J. Pokomeda, Anna Witek-Krowiak** 184
SEPARATION OF WATER-ETHANOL MIXTURE BY MEANS OF PERVAPOARATION
- P-52** **Beata Pośpiech** 185
SEPARATION OF SILVER(I) AND COPPER(II) FROM AQUEOUS SOLUTIONS BY TRANSPORT THROUGH POLYMER INCLUSION MEMBRANES WITH CYANEX 471X
- P-53** **Ryszard Poźniak, Gryzelda Poźniak** 186
SIMULTANEOUS REMOVAL OF ANILINE AND NITRATE BY MICELLAR ENHANCED ULTRAFILTRATION
- P-54** **Magdalena Regel-Rosocka, Kamila Kicińska, Maciej Wiśniewski** 187
NICKEL(II) AND COBALT(II) EXTRACTION FROM CHLORIDE SOLUTIONS WITH QUATERNARY PHOSPHONIUM SALTS
- P-55** **Sylwia Ronka, Andrzej W. Trochimczuk** 188
DIBENZOTHIOPHENE UPTAKE FROM FUELS BY THE POLYMER-DERIVED CARBON MATERIALS

P-56	<u>Aleksandra Rybak</u>, Gabriela Dudek, Anna Strzelewicz, Monika Krasowska, Zbigniew J. Grzywna	189
	INFLUENCE OF THE MAGNETIC POWDER TYPE AND GRANULATION ON THE AIR SEPARATION PROCESS BY MAGNETIC MEMBRANES	
P-57	Gamze Barim, Erdem Yavuz, M. Sabri Celik, <u>B. Filiz Senkal</u>	190
	GRAFTING OF POLYACRYLAMIDE ONTO CLAY FOR SELECTIVE REMOVAL OF Hg ²⁺ ION FROM WATER	
P-58	<u>Kanako Shibata</u>, Syouhei Nishihama, and Kazuharu Yoshizuka	191
	REMOVAL OF ARSENIC FROM GROUND WATER WITH TITANIUM DIOXIDE	
P-59	<u>Petra Šlapáková</u>, Helena Parschová	192
	SORPTION OF METALS BY COMPOSTIE SORBENTS BASED ON IRON OXIDE	
P-60	<u>M. Smolik</u>, Z. Hubicki, A. JakóbiK-Kolon, T. Korolewicz, Ł. Siepietowski	193
	THE WEIGHT DISTRIBUTION COEFFICIENTS OF Zr(IV), Hf(IV), Ti(IV), Th(IV), Fe(III), Al(III), Cr(III), Y(III), La(III), Cu(II), AND Zn(II) ON DIPHONIX® RESIN IN 0.5 M H ₂ SO ₄ SOLUTION	
P-61	<u>Michał Sowa</u>, Dorota Jermakowicz-Bartkowiak	194
	SORPTION OF NOBLE METAL IONS ON HEXAMETHYLENEIMINE VBC/DVB DERIVED RESIN	
P-62	<u>Katarzyna Staszak</u>, Maciej Staszak	195
	COMPUTATIONAL FLUID DYNAMICS (CFD) MODELING OF POROUS MEMBRANES	
P-63	<u>Łukasz Steczek</u>, Katarzyna Kiegiel, Grażyna Zakrzewska-Trznadel	196
	APPLICATION OF CALIX[6]ARENE FOR EXTRACTION OF URANIUM(VI) FROM WATER SOLUTION	
P-64	<u>P. Szczepański</u>, I. Diaconu, D.A. Radu	197
	KINETIC MODEL FOR p-NITROPHENOL TRANSPORT THROUGH AN AGITATED BULK LIQUID MEMBRANE	
P-65	<u>P. Szczepański</u>, R. Wódzki	198
	NETWORK MODEL FOR DESCRIPTION OF THE BENZOIC ACID PERTRACTION IN AN AGITATED BULK LIQUID MEMBRANE SYSTEM	
P-66	A. Raszowska-Kaczor, R. Wódzki, <u>P. Szczepański</u>	199
	SEPARATION AND RECOVERY OF Zn(II) FROM ELECTROPLATING PLANT WATER BY HYBRID ROTATING PERTRACTO	

P-67	<u>Małgorzata Ulewicz, Elżbieta Radzymińska-Lenarcik</u>	200
	SUPPORTED AND POLYMER MEMBRANES PERTRACTION OF COPPER(II) FROM LIQUID SOLUTIONS BY 1-HEXYL-2-METHYLIMIDAZOLE	
P-68	<u>S. L. Vasilyuk, V. N. Belyakov, A. V. Palchik, G. N. Bondarenko</u>	201
	NEW INORGANIC ION-EXCHANGERS FOR TREATMENT OF NUCLEAR WASTEWATERS CONTAINING ¹³⁷ Cs, ⁹⁰ Sr	
P-69	<u>Barbora Vystrčilová, Libor Dušek, Ladislav Novotný</u>	202
	INDIRECT ELECTROCHEMICAL OXIDIZING DECOLORIZATION WASTEWATER FROM THE PRODUCTION OF AMINOANTRACHINONE DYES	
P-70	<u>Tomáš Weidlich, Jana Martínková</u>	203
	APPLICATION OF TETRAPHENYL- AND ETHYLTRIPHENYL-PHOSPHONIUM SALTS FOR THE SEPARATION OF REACTIVE BLACK 39, REACTIVE RED 45:1 AND H-ACID FROM AQUEOUS SOLUTIONS	
P-71	<u>Joanna Wolska, Marek Bryjak</u>	204
	SORPTION OF PHTHALATES BY MOLECULARLY IMPRINTED POLYMERS	
P-72	Bryjak Marek, Smolińska Katarzyna, <u>Wolska Joanna</u>	205
	SMART MEMBRANE OBTAIN BY PLASMA MODIFICATION	
P-73	<u>Joanna Wolska, Marek Bryjak</u>	206
	MONODISPERSIVE MICROSORBENTS FOR REMOVAL OF SELECTED SPECIES FROM WATER	
P-74	<u>M. Wawrzkievicz, Z. Hubicki, A. Wołowicz</u>	207
	ANION EXCHANGE RESINS AS EFFECTIVE SORBENTS FOR EGACID ORANGE II DYE REMOVAL FROM AQUEOUS SOLUTIONS AND WASTEWATERS	
P-75	<u>M. Wawrzkievicz, Z. Hubicki, M. Greluk, A. Wołowicz</u>	208
	APPLICATION OF WEAKLY BASIC ANION EXCHANGE RESINS FOR REMAZOL BLACK B REMOVAL FROM AQUEOUS SOLUTIONS AND WASTEWATER	
P-76	<u>A. Wołowicz, Z. Hubicki, M. Greluk, M. Wawrzkievicz</u>	209
	COLUMN AND BATCH STUDIES OF Pd(II) IONS SORPTION ON ACRYLIC, GEL TYPE WEAKLY BASIC ANION EXCHANGE RESIN FROM CHLORIDE-NITRATE(V) SOLUTIONS	
P-77	Magdalena Greluk, Zbigniew Hubicki, <u>Anna Wołowicz</u>, Monika Wawrzkievicz	210
	REMOVAL OF REACTIVE DYES FROM AQUEOUS SOLUTIONS USING GEL ANION EXCHANGER	

- P-78** **Marta Woźniak, Katarzyna Staszak, Magdalena Sottek, Krystyna Prochaska** 211
MEMBRANE SEPARATION OF DICARBOXYLIC ACID PRODUCED BY BIOSYNTHESIS
- P-79** **Grzegorz Wójcik, Zbigniew Hubicki, Magdalena Górska** 212
RECOVERY OF GOLD(III) IONS FROM CHLORIDE SOLUTIONS ON THE CARBON ADSORBENT LEWATIT AF5
- P-80** **Gamze Barim, Yesim Gurse, Erdem Yavuz, B. Filiz Senkal, M. Sabri Celik** 213
MODIFICATION OF CLAY WITH N-METYL-D-GLUCAMINE CONTAINING POLYMER FOR REMOVAL OF BORON
- P-81** **Erdem Yavuz, B. Filiz Şenkal, Gülay Bayramoğlu, M. Yakup Arıca** 214
PREPARATION OF HYDRAZINE CONTAINING CORE-SHELL TYPE RESIN FOR REMOVAL OF ALDEHYDES
- P-82** **Iwona Zawierucha** 215
ION EXCHANGE OF Cd²⁺, Zn²⁺ and Pb²⁺ FROM AQUEOUS SOLUTION BY AMBERLITE IR 120
- P-83** **Vladimir M. Zhdanov, Vjacheslav I. Roldughin , Elena E. Sherysheva** 216
EFFECT OF SURFACE DIFFUSION ON THE ASYMMETRY OF GAS TRANSPORT AND MIXTURE SEPARATION IN COMPOSITE MEMBRANES

AUTHORS INDEX

217

I. LECTURES

ION-SELECTIVE POLYMER-SUPPORTED COMPLEXANTS: DESIGN, SYNTHESIS, AND THE MECHANISM OF COMPLEXATION

Spiro D. Alexandratos, Xiaoping Zhu and Yijia Yang

*Hunter College of the City University of New York, Department of Chemistry,
New York, NY 10065 USA
e-mail: alexsd@hunter.cuny.edu*

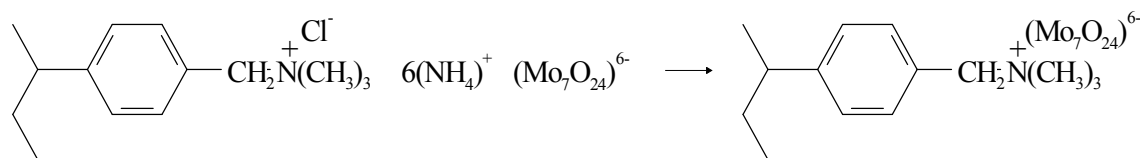
The results of three recent research projects will be detailed. In each case, an ion-selective polymer is developed.

Water in the environment contains dissolved silica from 1 ppm up to 50 ppm. The removal of silica from water is important for use in power plants, desalination units and microelectronics industries. In order to avoid the formation of scale, the silica level must be < 10 ppm in water to reverse osmosis units and < 8 ppm to high pressure boilers.

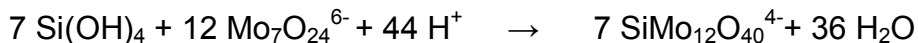
A silicate-selective polymer-supported reagent was developed from the reactivity of silicate to react with heptamolybdate and thus form Keggin anions (1).



The heptamolybdate anion was first electrostatically bound to trimethylammonium ligands on microporous poly(vinylbenzyl chloride) beads to give what was abbreviated the TMAMo resin.



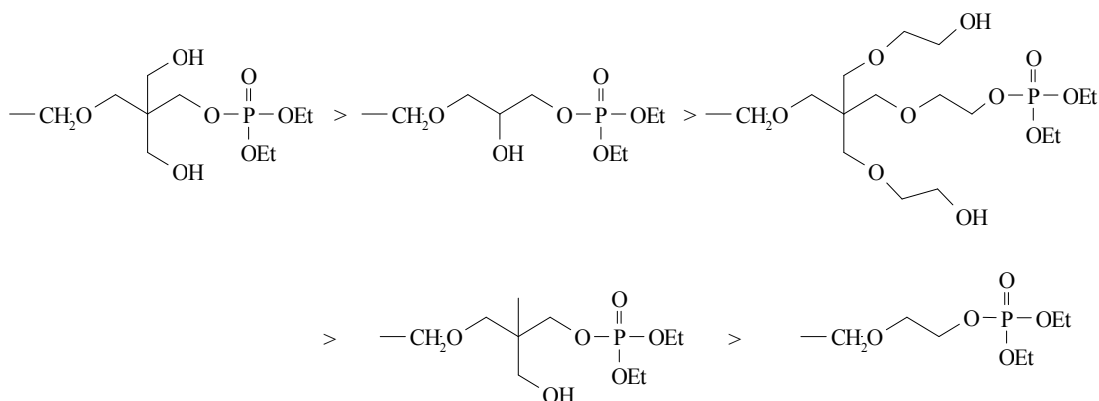
Contacting a solution containing 20 ppm silica at pH 7 with TMAMo removed 94.8% of the silicate. Under the same conditions, the trimethylammonium resin in the chloride form removed 1.2% of the silicate. Complexation by the heptamolybdate resin remained high throughout the pH range 3.8 - 10.7. Sorption was unaffected by the presence of chloride, sulfate, and nitrate ions. The reaction occurring on the polymer is indicated below; it is supported by literature precedent and corresponding FTIR spectra.



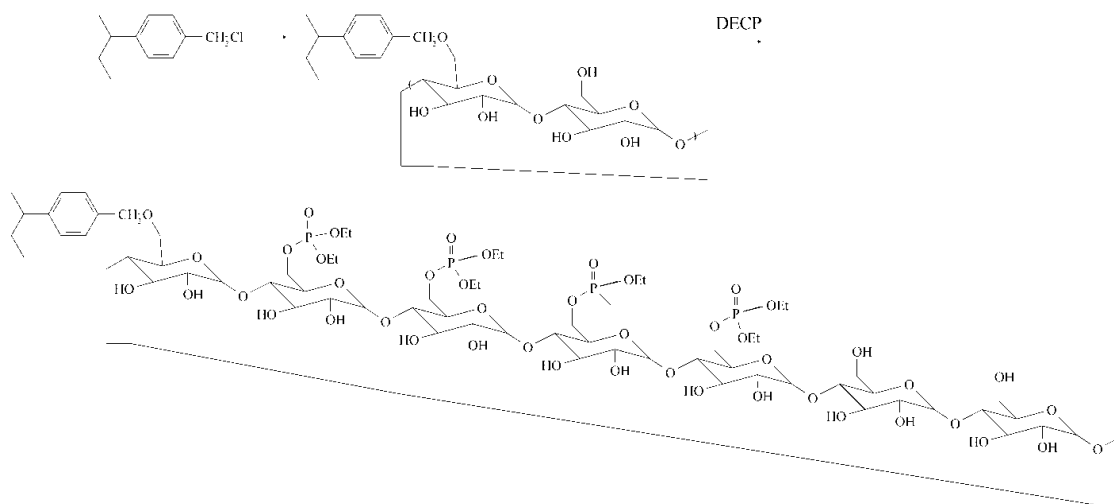
The support structure influences the kinetics of reaction: the microporous polymer requires 24h to complex all of the silicate from a 100 ppm solution while an expanded gel attains that level in 4 h. The rate-limiting step is thus accessibility of the silicate to the heptamolybdate rather than the rate of reaction to form the silicomolybdate.

The effect of polar (auxiliary) groups on a scaffold around a given ligand was studied through a series of phosphorylated polyols bound to a polystyrene support. It was determined that the affinities for a given divalent metal ion

increased along the series phosphorylated pentaerythritol > glycerol > triethoxylated pentaerythritol > trimethylethane > glycol.

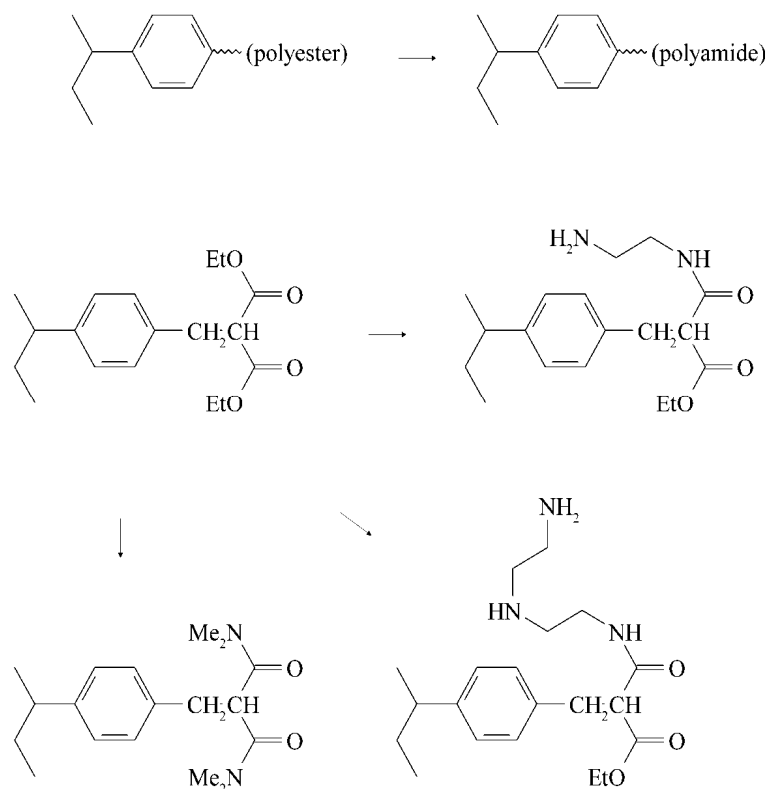


Hydrogen bonding between the -OH groups and the phosphoryl oxygen of the phosphate ligand was postulated to be the cause of the increased affinities. The position of the FTIR band assigned to hydrogen bonding between the -OH and P=O in the region of 890 to 873 cm^{-1} correlates with the metal ion affinities. This was extended with polymer-bound phosphorylated β -cyclodextrin, pCD (2).



The polyol with the highest affinities had been the phosphorylated pentaerythritol (pPE) with a band at 873 cm^{-1} ; pCD, however, was now found to be the most red-shifted of the polyols with a band at 868 cm^{-1} . Consistent with this, pCD had a significantly higher affinity for the uranyl ion than pPE: the percents complexed from a 10^{-4} M uranyl solution in 1.0 N HNO_3 , HCl , and H_2SO_4 were 94.7%, 90.5%, and 93.6%, respectively, for pCD and 68.6%, 52.1%, and 40.1%, respectively, for pPE. This further supports the hypothesis that the strong complexing ability of phosphorylated polyols is due to activation of the phosphoryl oxygen through hydrogen bonding between the P=O and the -OH groups within the polyol.

Amides are an important category of solvent extractants and a versatile class of ligands, along with polyols, that can be immobilized onto polymer supports. A series of polyamides was thus prepared from immobilized esters, beginning with tetramethylmalonamide (TMMA) ligands (3). The affinity of that ligand for lanthanide ions in 0.001 M - 8 M HCl and HNO₃ solutions was studied. The affinity is dependent on the acid concentration. The distribution coefficients are low from 0.001 to 2 M HCl, increase in 4 and 6 M HCl then decrease in 8 M



HCl. A mechanism is proposed: in the low-acid region, the metal ion remains in solution and does not coordinate to the carbonyl groups; as the acid concentration exceeds 2 M, protonation of the amide occurs to form an iminium moiety, electrostatically attracting the anionic lanthanide complex through ion-exchange and releasing waters of hydration; at high acid concentration, the affinity decreases due to competition by the large excess of chloride ions for the

ion-exchange sites. In 6 M HCl, the affinities are Tb > Dy > Eu > Gd > Ho > Sm > Er > Tm > Yb > Lu > Nd > Ce > La. Trends are comparable in HNO₃. There is thus a point of maximum affinity across the lanthanide series rather than a monotonic trend which is evidence of a recognition phenomenon. The reason for recognition is the presence of two opposing mechanisms in the interaction: dehydration of the metal ion and ion / ligand electrostatic attraction.

Acknowledgement: We gratefully acknowledge the support of the U.S. Department of Energy, Office of Basic Energy Sciences, Separation and Analysis Program, through grant DE-FG02-02ER15287.

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IONIC COMPOSITE MATERIALS AND THEIR INTERACTIONS WITH IONIC SPECIES

Ecaterina Stela Drăgan, Maria Valentina Dinu, Maria Marinela Perju

*"Petru Poni" Institute of Macromolecular Chemistry, Grigore Ghica Alley 41A,
700487, Iasi, Romania
e-mail: sdragan@icmpp.ro*

Some results concerning the interactions between ionic species and ionic composite materials based on natural and synthetic polymers are presented in brief. Three types of ionic composites have been selected for discussion: (1) ionic composites based on chitosan (CS) and zeolite and their interactions with metal ions; (2) s-IPN ionic composite hydrogels based on polyacrylamide (PAAm) and dextran sulfate (DxS) and their interactions with cationic dyes and/or biological compounds; (3) s-IPN ionic composite hydrogels based on PAAm and CS and their interactions with proteins.

1. Ionic composites based on CS and clinoptilolite (CPL)

A strong interest has been focused last decades on biosorbents derived from polysaccharides as an alternative to the existing sorbents like activated carbon and synthetic ion exchangers (1-3). Among biopolymers, CS has attracted numerous scientists due to its outstanding biological properties like biodegradability, biocompatibility, and antibacterial activity (1,2). The chelating properties for Cu^{2+} cations were recently investigated and correlated with the physical and chemical modifications of CS (1-3). In this context, we have recently reported on the synthesis of some novel ionic composites by embedding natural zeolite microparticles (CPL) in a matrix of cross-linked CS (4). Their interactions with metal ions (Cu^{2+} , Co^{2+} , Ni^{2+} , UO_2^{2+} and Th^{4+}) as a function of different parameters like: pH, contact time, metal ion concentration will be presented here in brief.

Solution pH can influence the interactions between metal ions and CS-based composites by the modification of both metal ion concentration and the level of ionization of CS. The adsorption capacity at equilibrium, of the cross-linked CS and of the ionic composite containing 20 wt.% CPL for Cu^{2+} , Co^{2+} and Ni^{2+} ions, as a function of pH, was investigated at pH values ranging from 2 to 6 (4,5). It was observed that the amount of ions adsorbed by cross-linked CS and ionic composites slowly increased with the increase of pH, the optimum adsorption pH being located at 5. At low pH, most of the amino groups of CS in the composite were ionized and therefore, the electrostatic repulsion between metal cations and NH_3^+ ions may prevent the adsorption of metal ions onto the composite. This supports the chelation of metal ions on the ionic composites.

In order to examine the controlling mechanism of the adsorption process such as mass transfer and chemical reaction, kinetic models were used to test the experimental data. The kinetics of metal ion adsorption on the ionic composites was determined with three different kinetic models, i.e., the pseudo-first and pseudo-second order and the intra-particle diffusion model. The adsorption process of metal ions obeyed of the pseudo-second order kinetics, supporting

the chemisorption would be the rate-determining step (5). Two isotherm models have been tested namely the Freundlich and Langmuir isotherm models. The equilibrium adsorption data obtained for all metal ions well fitted in the Langmuir model with a maximum theoretical adsorption capacity of 11.32 mmol Cu^{2+} /g, 7.94 mmol Ni^{2+} /g and 4.209 mmol Co^{2+} /g, respectively.

Removal of radioactive ions from the wastewaters is a huge problem because these ions are extremely dangerous for the environment and human health. Adsorption features of UO_2^{2+} and Th^{4+} ions from simulated radioactive solutions onto the ionic composite based on CS and CPL have been investigated and compared with cross-linked CS (6). The adsorption kinetics was well described by the pseudo-second order model (Fig. 1), and the adsorption isotherms were better fitted by the Sips model (Fig. 2). The maximum experimental adsorption capacities were 328.32mg Th^{4+} /g composite, and 408.62mg UO_2^{2+} /g composite.

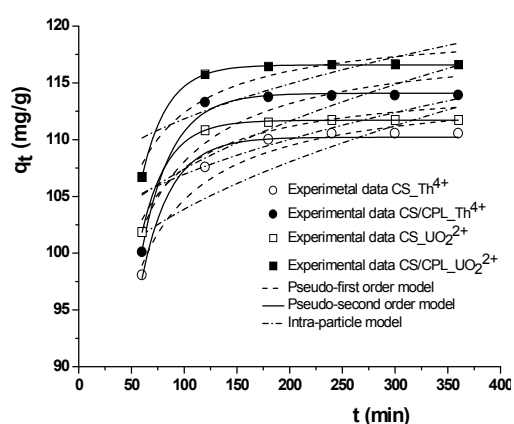


Fig. 1. Plots of q_t vs. t for the adsorption of UO_2^{2+} and Th^{4+} onto cross-linked CS and CS/CPL composite (initial metal concentration of 20 mg/L, mass of sorbent = 0.04 g)

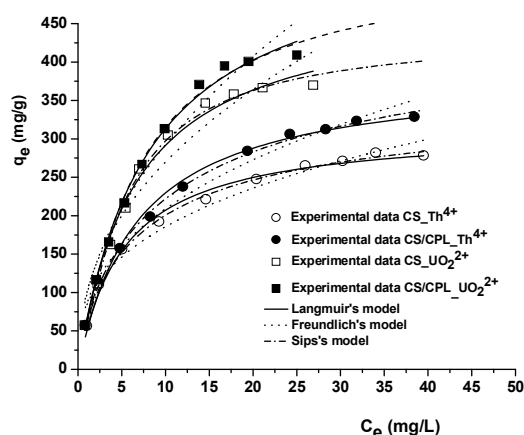


Fig. 2. Comparison of experimental and calculated data for three models for the adsorption of UO_2^{2+} and Th^{4+} on cross-linked CS and CS/CPL composite

The overall adsorption tendency of CS/CPL composite toward UO_2^{2+} and Th^{4+} radiations in the presence of Cu^{2+} , Fe^{2+} and Al^{3+} , followed the order: $\text{Cu}^{2+} > \text{UO}_2^{2+} > \text{Fe}^{2+} > \text{Al}^{3+}$, and $\text{Cu}^{2+} > \text{Th}^{4+} > \text{Fe}^{2+} > \text{Al}^{3+}$, respectively. The desorption level of UO_2^{2+} from the composite, by using 0.1M Na_2CO_3 , was around 92%, and that of Th^{4+} ions, performed by 0.1M HCl , was around 85%, both values being higher than the desorption level of radiations from the cross-linked CS.

2. Ionic s-IPN hydrogels based on PAAm and DxS

Macroporous ionic s-IPNs composite hydrogels based on DxS as a physical entrapped polymer within PAAm 3D network have been prepared by the cryogelation technique. The addition of an anionic biopolymer (DxS), would provide a novel material with potential applications in biomedical, pharmaceutical, and environmental fields. It was considered that the change of the gel preparation temperature, as well as the cross-linker ratio (X) would affect the water diffusion and sorption along with the phase organization. A

superfast swelling responsiveness has been observed for these composites. This particular behavior has been attributed to the spongy-like structure of cryogels, which accommodate a large amount of free water (7-10). Thus, during the hydration process, the interconnected pores dramatically facilitate the diffusion of water and solutes. Fig. 3 illustrates the influence of the synthesis temperature on the morphology of PAAm/DxS composite hydrogels.

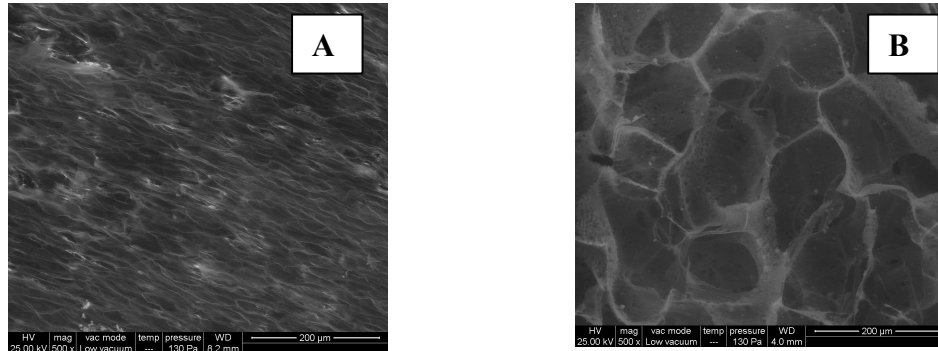


Fig. 3. ESEM images of PAAm/DxS composite hydrogels prepared at +20°C (A), and -18°C (B) at $X = 1/80$. The scaling bars are 200 μm . Mag. = 500x

Swelling rate as a function of the synthesis temperature is obvious in Fig. 4.

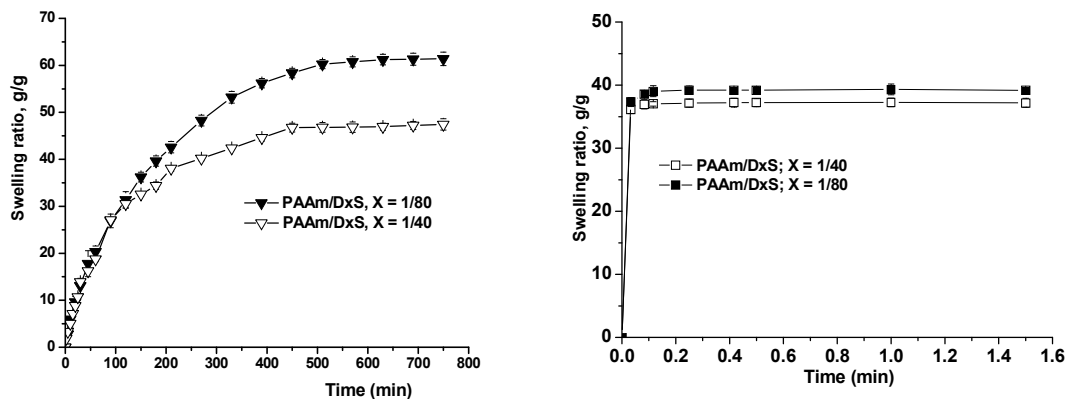


Fig. 4. Swelling ratio in water as a function of contact time for PAAm/DxS composite hydrogels prepared at +20°C (left) and -18°C (right)

As Fig. 4 shows, the time necessary to attain the equilibrium swollen state starting from the dry state was about 500 min, for hydrogel prepared at 20°C, the increase of X decreasing the values of swelling ratios. On the other hand, the PAAm/DxS composite cryogels attained the equilibrium state in water within 15 sec, irrespective of X . The superfast swelling of hydrogels prepared at -18°C are explained by their high permanent porosity. The interaction of the PAAm/DxS composite gels with a cationic dye, methylene blue (MB) showed a faster sorption of the dye on the gel prepared at +20°C than on the cryogel, the amount of the dye adsorbed increasing with the increase of temperature, irrespective of the gel morphology. Because s-IPN composite gels with trapped DxS are negatively charged on the whole range of pH, lysozyme ($M_v = 14$ kDa, $i_{ep} = 11$) has been selected for the tests of protein sorption. It was found a loading in protein of 29 mg protein /g dried gel prepared at +20°C, and 26 mg protein/g dried gel prepared at -18°C, after 48 h. A slow desorption rate has been found both in PBS and at pH 1.5.

3. Ionic s-IPN composite hydrogels based on PAAm and CS

In the synthesis of PAAm/CS s-IPN hydrogels, CS has been used as trapped polymer in a matrix of PAAm, following the influence of X, and the CS molar mass on the gel fraction yield and the fraction of CS trapped in the composite hydrogel. Composite hydrogels were prepared as monoliths by free radical cross-linking copolymerization at 22°C and -18°C. The initial concentration of monomers (AAM + BAAM) has been kept constant (5 wt.%); the redox initiator system used consisted of APS and TEMED. CS is a weak polycation, which provides potential applications in biomedical and environmental fields and it is also expected to induce pH responsiveness of the gels. The gel morphology and the interaction of composite gels with ionic species have been strongly influenced by the synthesis conditions. Fig. 5 illustrates the influence of the synthesis temperature on the morphology of the gel having X = 1/40.

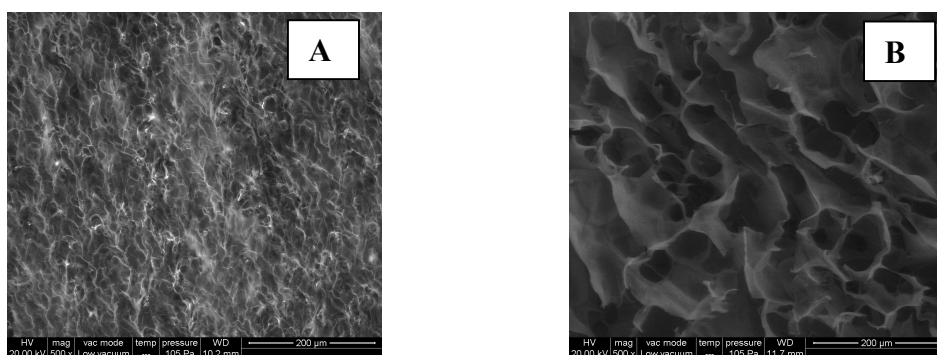


Fig. 5. ESEM images of PAAm/CS composite hydrogels prepared at +20°C (A), and -18°C (B). The scaling bars are 200 µm. Mag. = 500x

Macropores with sizes in the range 30-100 µm can be observed in the image of the composite s-IPN cryogel (B) compared with the gel prepared at +20°C (A), which show only small pores. It was expected as the presence of CS and of the large pores to make the cryogel suitable to absorb large proteins like albumins. The preliminary test of loading/release of bovine serum albumin (BSA) in/from the PAAm/CS cryogel showed a loading capacity of 84.3 mg BSA/g cryogel. Desorption of BSA has been faster at pH 1.5 than in phosphate buffer saline (PBS), pH 7.4, at 22°C, because in acidic pH both CS and protein are positively charged (isoelectric point of BSA being 4.8). The slow release of BSA in PBS recommends this composite for potential application in controlled drug release.

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SELECTIVE RECOVERY PROCESS OF PLATINUM GROUP METALS FROM SPENT AUTOMOBILE CATALYST

Kazuharu Yoshizuka, Shuhei Tanaka, Akinori Harada, Syouhei Nishihama

*Department of Chemical Engineering, The University of Kitakyushu,
Hibikino 1-1, Kitakyushu 808-0135, Japan
e-mail: yoshizuka@env.kitakyu-u.ac.jp*

Platinum group metals (PGMs), such as Pd, Pt, and Rh have high melt point, corrosion resistance, and heat resistance. The PGMs are also used for automotive catalyst, because of their selectivity for hydrogenation and oxidation. Although demand for PGMs is still increasing in recent years, the primary supply of PGMs is restricted to the mines located in a few limited countries. Separation and recovery of the PGMs from waste catalyst called secondary supply is therefore nowadays an active issue (1). The present separation and recover process of the PGMs is based on the solvent extraction. However, solvent extraction is high environmental load, because it requires large amount of organic solvent. Alternative separation process being more environmentally friendly is expected instead of solvent extraction.

In the present work, the separation and recovery of Pd²⁺, Pt⁴⁺, and Rh³⁺ from the spent automobile catalyst is investigated using ion exchange method. In our preliminary experiment, since the three metals can be effectively leached by 5 mol/L HCl solution, the present work is done based on the solution of 5 mol/L HCl. Two kinds of adsorbents, commercial weak acid ion exchange resin (DIAION WA-21) (2) and dihexyl sulfide (DHS) impregnated resin are employed for the chromatographic operation of the metals.

Preparation of DHS impregnated resin

DHS (11.48 g) and DIAION HP2MG (methacrylic acid/ester) (27.26 g) were impregnated in acetone. Since then, DHS impregnated resin was prepared by evaporation of acetone. The impregnation amount was 1.46 mmol/g.

Batch adsorption of PGMs

DHS impregnated resin or DIAION WA-21, and feed solution were contacted and shaken at 25°C for 24 h. Composition of feed solution were coexist metals and PGM that concentration were 50 mg/L, respectively. The concentration of metals was analyzed by ICP-AES (inductively coupled plasma atomic emission spectrometer).

Figure 1 shows the effect of hydrochloric acid concentration on adsorption percentage of

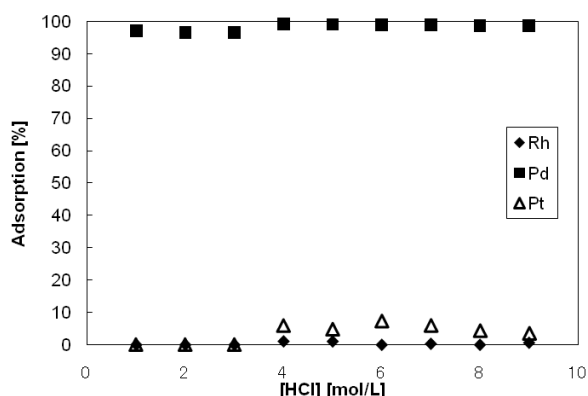


Figure 1. Effect of hydrochloric acid concentration on adsorption percentage of metal ions from ternary metal system with DHS impregnated resin

metal ions from ternary metal system with DHS impregnated resin. only Pd^{2+} was adsorbed at 1~5 mol/L HCl.

Figure 2 shows the effect of hydrochloric acid concentration on adsorption percentage of metal ions from ternary metal system with WA-21 in ternary metal system. three PGMs were adsorbed at 1~5 mol/L HCl. Coexisted metals hardly affect on the selective recovery of PGMs.

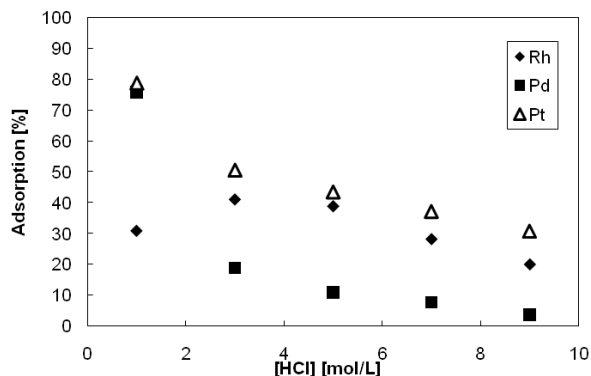


Figure 2. Effect of hydrochloric acid concentration on adsorption percentage of metal ions with WA-21 in ternary metal system

Chromatographic separation of PGMs

Chromatographic separation of PGMs are conducted by using DHS impregnated resin and DIAION WA-21. Each adsorbent was packed into the glass column, and then simulated leaching solution of spent automobile catalyst ($[\text{Pd}^{2+}] = 60 \text{ mg/L}$, $[\text{Pt}^{4+}] = 80 \text{ mg/L}$, $[\text{Rh}^{3+}] = 20 \text{ mg/L}$, $[\text{HCl}] = 5 \text{ mol/L}$) was fed upward to the columns. In the case of DHS impregnated resin, elution was conducted with 0.1 mol/L thiourea / 1 mol/L HCl. The effluent was collected with a fraction collector for measuring the concentrations of the metals by ICP-AES. In the case of WA-21, elution was conducted with 0.1 mol/L thiourea / 1 mol/L HCl in B.V. = 0 ~ 20) and then 1 mol/L H_2SO_4 in B.V. = 20 ~ 120.

Bed volume (B.V.) was calculated by:

$$\text{B.V.} = v \cdot t / V \quad (1)$$

where v is flow rate of feed solution [mL/min], t is supplying time of feed solution [min], and V is wet volume of adsorbent [mL].

DHS impregnated resin can be applied to the chromatographic separation and selective adsorption of Pd^{2+} can be conducted as same as batchwise experiments. Adsorption amount under the chromatographic operation is however lower than maximum adsorption amount of Pd^{2+} obtained in batchwise adsorption isotherm. This seems to be due to the leakage of DHS from the resin, and the leakage percentage is estimated to ca. 5 % from the comparison of maximum adsorption amount. Figure 3 shows the elution curves of the metals from DHS impregnated resin. Pd^{2+} can be selectively eluted with the elution yield of 98 %. In addition,

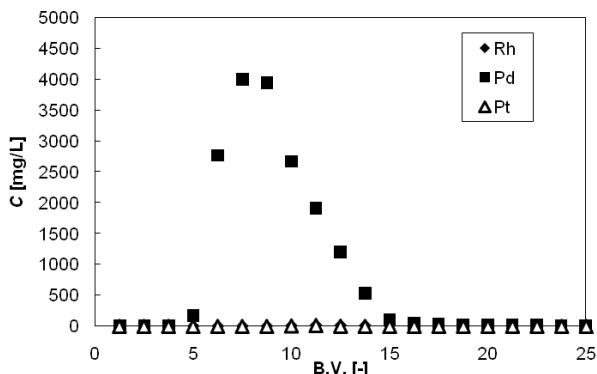


Figure 3. Elution curves of Pd^{2+} , Pt^{4+} and Rh^{3+} from DHS impregnated resin; Eluent: 0.1 mol/L thiourea -1 mol/L HCl)

concentration of Pd^{2+} can be achieved from 60 mg/L to ca. 3500 mg/L by just one cycle of adsorption – elution processing. On the other hand, DHS impregnated resin has no adsorption ability of Pt^{4+} and Rh^{3+} by chromatographic operation.

WA-21 is also applied to the chromatographic separation of PGMs. In adsorption stage, Pt^{4+} is selectively adsorbed, while other two metals (Pd^{2+} and Rh^{3+}) are also adsorbed slightly. Figure 4 shows the elution curves of the metals from WA-21 column. By changing the eluent, Rh^{3+} can be selectively eluted, while elution of Pd^{2+} and Pt^{4+} progresses simultaneously.

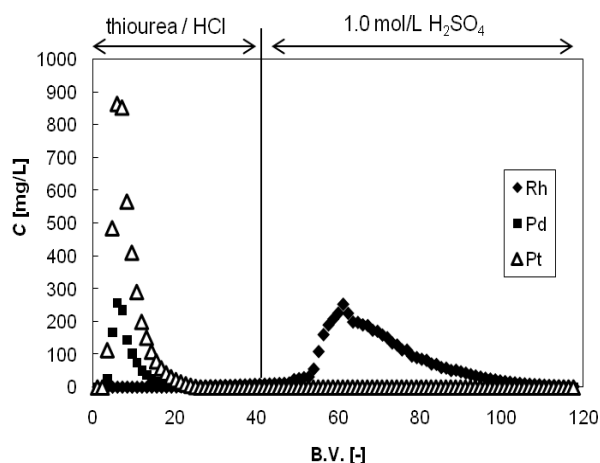


Figure 4. Elution curves of Pd^{2+} , Pt^{4+} and Rh^{3+} from WA-21; Eluents: 0.1 mol/L thiourea / 1 mol/L HCl in B.V. = 0 ~ 20 and 1 mol/L H_2SO_4 in B.V. = 20 ~ 120

By chromatographic separation of PGMs from spent automobile catalyst, DHS impregnated resin has high selectivity for Pd^{2+} against Pt^{4+} and Rh^{3+} , and WA-21 can separate Rh^{3+} from Pt^{4+} at the elution step by changing the eluent. The results indicate the possibility of mutual separation of the three PGMs by the combination of DHS impregnated resin and WA-21. The sequential chromatographic operation as shown in Figure 5 with the columns packed with DHS impregnated resin and WA-21 is expected to separate individual PGM.

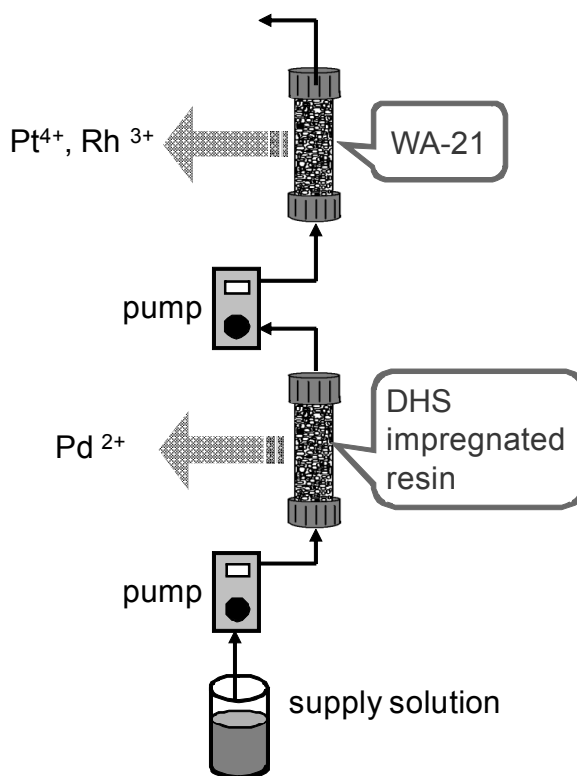


Figure 5. Schematic diagram of the sequential chromatographic operation for recovery of individual PGM

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HYDROMETALLURGY AT KGHM POLSKA MIEDŹ SA – CIRCUMSTANCES, NEEDS AND PERSPECTIVES OF APPLICATION

Tomasz Chmielewski

*Wrocław University of Technology, Faculty of Chemistry, Division of Chemical Metallurgy, Wybrzeże Wyspiańskiego 23, 50-370 Wrocław, Poland
e-mail: tomasz.chmielewski@pwr.wroc.pl*

The presentation discusses the reasons for the growing importance of hydrometallurgical technologies in the processing of copper ores, by-products and concentrates in the world. The conditions and a need of application of hydrometallurgy at KGHM Polska Miedź SA as an alternative for smelting are presented and discussed in details. A particular attention has been paid to the unfavorable changes of composition of copper ores both worldwide and in the Polish copper industry. These changes cause systematic decline of the recovery of copper and accompanying metals, as well as the decrease in the quality of the concentrates, which is particularly critical at Lubin Concentrator, where recovery decreased by more than 4 % and concentrate grade declined by 4.5 % (1). Moreover, some valuable metals (Co, Zn, Mo, V) are currently not recovered from the flotation concentrates produced at KGHM. Additionally, increasing content of organic carbon in flotation products (above 8 % for Lubin concentrate) reduces their application as a feed for flash smelting.

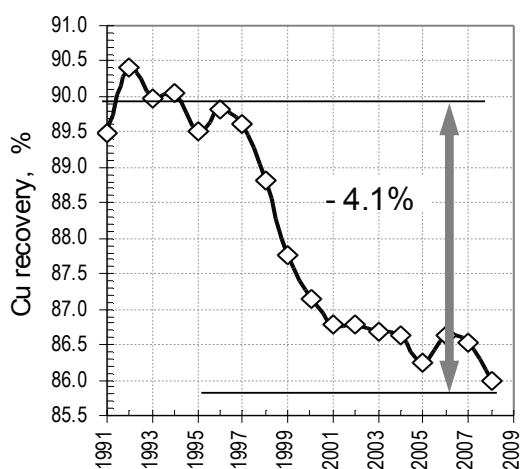


Fig. 1. Decrease of copper recovery at Lubin Concentrator between 1991 and 2008 (1)

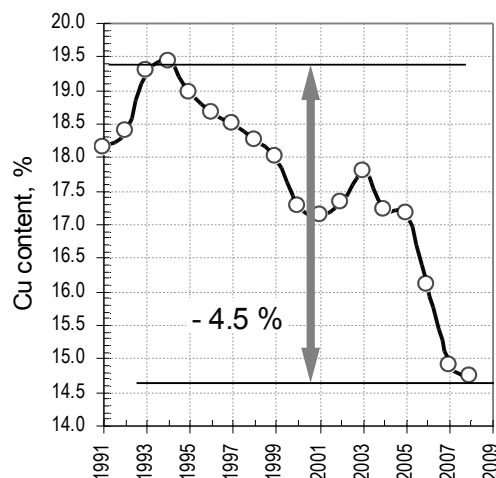


Fig. 2. Decrease of copper content in flotation concentrate at Lubin Concentrator (1)

Characterized were the world-wide tendencies in declining grade of copper ores and growing complexity of the feed for copper smelting. This is the main reason for a search for new and more effective technologies of copper ore and concentrate processing. Hydrometallurgy became recently the only rational and cost effective solution for processing of the small and complex copper resources, both oxidized and sulphidic. The most advanced sulphate-based hydrometallurgical processes were described and characterized (Mt Gordon Process – low temperature pressure leaching (2), Total Pressure Oxidation

Process – high temperature pressure leaching (3-6), Sepon Copper Process – atmospheric leaching in oxidized, acidified Fe(III) solution (7), Las Cruces Copper Process – atmospheric leaching in oxygenated sulphuric acid solutions containing iron(III) (8), BioCop Process – bioleaching with thermophilic bacteria (9). Analyzed were the main parameters influencing the efficiency of copper leaching: temperature, pressure, solid/liquid ratio, particle size distribution, role of oxygen.

The necessity of application of hydrometallurgy as a novel, alternative or complementary method of processing of sulphide flotation concentrates or by-products from the flotation circuits was analyzed in terms of the unique properties of Polish copper deposits from Legnica – Glogow copper basin (LGOM). The presence of three lithological layers: carbonate, shale and sandstone, complex and exceptional mineralogical structure (dominating presence of secondary sulphides), fine dissemination of metal values in carbonate or shale host as well as specific chemical composition of Polish copper ores mined from sedimentary deposits is the principal reason for high and hard-to-accept copper, silver and other metals losses to flotation tailings (10). The occurrence of shale fraction in Polish copper ores creates numerous technical, economical and ecological issues, even though shale is the material with highest concentration of metals (11).

A selective liberation of fine metal - bearing particles of sulphides disseminated in the carbonate or shale host matrix would be the simple way to enhance metals recovery. However, it appears to be ineffective by standard physical methods in the existing milling circuits. Consequently, the hydrophilic gangue-sulphide intergrowths substantially reduce both flotation selectivity and the metal content in the concentrate. Therefore, it can be declared that the existing beneficiation technologies currently applied for processing of Polish copper sedimentary ores have already reached the limit of their technical and economical efficiency.

The application of modern hydro- or biometallurgy, well known and approved in the world for copper recovery, becomes an urgent necessity in Polish copper industry to reverse unfavorable trends in flotation results, particularly at Lubin Concentrator (12). The application of atmospheric leaching with oxygenated solutions of sulphuric acid and in the presence of Fe(III), one of the processing options, has to be considered as a promising, complimentary process for processing of shale flotation by-product or flotation concentrate at ZWR Lubin, which are difficult to beneficiate using existing techniques. This approach, previously applied by the author within the research program of BIOSHALE (13) primarily involved the separation of the most troublesome ore fraction (shale containing middlings) from the commercial flotation circuit and introduction of hydrometallurgical methods for their alternative, effective processing.

Sedimentary copper ores from all three LGOM deposits (Lubin, Polkowice and Rudna) exhibit specific and simultaneously beneficial polymetallic and polymineral composition (14). Bornite and chalcocite are generally dominating copper-bearing sulphides, with chalcopyrite and covellite as a minor components. This is very advantageous for hydrometallurgical treatment, since

chalcocite and bornite are the easiest leachable in contrary to chalcopyrite being the most refractory in leaching. Additionally, Polish copper ores contain pyrite and marcasite, the minerals which are well known as a electrochemical activators in sulphides leaching. Sulphide minerals in Lubin flotation products form vast number of intergrowths, creating intermineral galvanic cells, which remarkably elevate the leaching rate.

A newest technological approach for KGHM concentrate has been currently examined. It comprises application of atmospheric or pressure leaching by means of oxygenated sulphuric acid solutions in order to elevate copper and other metals recovery from the Lubin Concentrator flotation concentrate. The idea has been extensively investigated by the Division of Chemical Metallurgy at the Wroclaw University of Technology within the HYDRO research project financed by the National Center for Research and Development (NCBiR) in the framework of the IniTech Enterprise. The examined process consists of numerous unit operations: feed preparation (grinding, non-oxidative leaching and separation of gypsum, separation of magnesium), atmospheric or pressure leaching, metals separation from solution after leaching (solvent extraction and ion exchange), processing of solid residue for Ag and Pb recovering, removal and stabilization of toxic components (As), waste treatment.

To increase the efficiency of metals recovery from the Lubin ores, the feed to leaching can be both the currently produced commercial flotation concentrate as well as a low grade concentrate of higher metals recovery. According to the technical analysis presented by KGHM a reduction of concentrate grade by about 50% may result in the increase of copper recovery by more than 5%.

In the light of the observed reduction of flotation indices (both metals recovery and concentrate grade), very advantageous sulphidic mineralization of copper, unique mineralization of barren components and easy access to sulphuric acid, the application of hydrometallurgy either to concentrate or to selected flotation products offers a chance for a significant improvement of recovery of copper and accompanying metals. The atmospheric and pressure leaching in oxygenated solutions of sulphuric acid and in the presence of iron(III) ions is considered as the most feasible.

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SUPPORTED LIQUID MEMBRANES AS A USEFUL TECHNIQUE FOR SEPARATION AND PRECONCENTRATION OF ORGANIC COMPOUNDS

Piotr P. Wieczorek

*Opole University, Faculty of Chemistry, ul. Oleska 48, PL-45052 Opole, Poland
e-mail: piotr.wieczorek@uni.opole.pl*

Environmental food or biological samples, due to their matrix complexity, can not be analyzed without preliminary sample preparation. Sample preparation is almost an essential step in every analytical method in which potential interferences should be removed. Additionally the concentration of analytes should be increased for identification and determination at low detection levels, and to overcome the limitation of the detection systems. Many techniques have been used for sample preparation. The most popular techniques in every day analysis are solid-phase extraction (SPE), chromatographic methods, traditional liquid-liquid extraction (LLE) and also membrane techniques. Moreover, membrane separation is in special place due to offering various modes of separation and its flexibility on choice of suitable separation scheme.

From the various membrane techniques supported liquid membranes (SLM) are of special interest because versatility that combines the benefits of liquid-liquid extraction and membrane process. The typical configuration is organic, liquid membrane immobilized in pores of polymeric support that separates two aqueous phases.

The principle of enrichment is the extraction of the analytes from an aqueous donor phase, transport through a hydrophobic liquid membrane, and re-extraction into a stagnant aqueous acceptor phase. The transport through the membrane is forced by concentration gradient of the compound, or their complex with special extractant, across the membrane and results in permeate dissolution in the membrane and its diffusion through the membrane phase. For this reason the solute must be in the donor phase in such a form that is soluble in the organic membrane phase. Whereas, after diffusion to the acceptor phase, the analytes has to be in a form that prevents its diffusion back into the membrane (1). As long as the concentration gradient is preserved, the extraction will continue. In recent years, several trends have emerged, such as the use of smaller initial sample size, small volumes, important in body fluid analysis, or enhancement of the specificity and selectivity, or possibly automation (2).

As a method with great potential for energy saving, low capital and operational cost, and the possibility to use expensive extractants, due to the small amounts of the membrane phase, SLM have been used in various fields including hydrometallurgy, chemical engineering, biotechnology and analytical chemistry. In analytical chemistry SLM is used for transport studies and selective extraction and enrichment of various classes of organic compounds, such as phenolic compounds, amines, organic acids, pesticides and drugs as well as amino acids and their analogues. The presentation gives an overview of the possible transport systems and experimental factors influencing extraction

efficiency of such polar compounds as well as some examples of applications in environmental, food and biological analysis (3).

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IMPACT OF MEMBRANES AND MEMBRANE PROCESSES ON ENVIRONMENTAL ISSUES

V.V. Tepliakov

*A.V. Institute of Petrochemical Synthesis, Russian Academy of Science
e-mail: tepl@ips.ac.ru*

Membranes have gained an important role in chemical technology and are used in a broad range of applications. First of all, the membrane processes are, in principle, the lower energy consuming ones since they do not need energy for phase transition. Secondly, they can provide effective recovery of desired components from the products of modern technology which are as a rule the multi-component mixtures. As a result membrane processes can generate new clean technology based on reusing and/or recycling of by-products.

Main areas of membrane application include (1) water treatment (waste water recycling, desalination, purification from organics, etc.), (2) filtration processes for liquid and gases (microfiltration, ultrafiltration, nanofiltration), (3) gas separation (air separation, hydrogen recovery, natural gas conditioning) and (4) combination with conventional separation techniques. Modern membrane science includes large comprehensive topics covering synthesis of new membrane materials, membrane's preparation, functionalization, characterization, applications, membrane processes, redesign (integration and intensification), modeling, mechanism investigation as well (1-3).

One of the prospective technologies of the production of energy carriers from renewable raw material is biological conversion of organic wastes. The products of this conversion are gaseous (biogas, biohydrogen) or liquid mixtures containing methane and hydrogen or lower alcohols respectively. Such technology is distinguished due to many benefits: low energy consumption, high ecological safety, high level of organic wastes utilization, availability and simplicity of performance and control. Main practical problem of energy carrier's production by microbial treatment of biomass is low calorificity of obtaining gas and liquid mixtures because products of biotreatment are diluted water-organic mixtures and/or gas mixtures containing considerable amounts of ballast CO₂.

Traditional membrane systems are considered and original gas-liquid membrane contactors (MCs) are proposed as prospective systems for energy carrier's recovery (methane, hydrogen) from gas mixtures. MCs do not demand preliminary compression (additional energy consumption) of initial gas mixture. Technical degree methane (>95%) can be obtained after the separation stage of biogas for example, which is possible to supply to gas grid or to receiver. Low energy consumable membrane system is created on the basis of developments of TIPS RAS in cooperation with experts-microbiologists and specialists in mechanical engineering.

Application of such membrane methods as pervaporation and membrane recovery of organic component from vapour phase is also perspective for recovery of liquid energy carriers (bioalcohols) from diluted water-organic

solutions (range of organic substances concentrations is 1-7%) obtained by biofermentation. It is shown that organophilic polytrimethylsilylpropyne (PTMSP) membranes can be successfully applied for processes of continuous recovery of liquid energy carriers from products of biomass treatment.

In whole the potential and prospects of membrane processes application for creation of environmental friendly technology are considered.

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IMPLICATIONS OF NANOMEMBRANES IN SEPARATION SCIENCE

Toyoki Kunitake

*Kitakyushu Foundation for the Advancement of Industry, Science and
Technology, 2-1 Hibikino, Wakamatsu-ku, Kitakyushu, 808-0135, Japan
kunitake@ruby.ocn.ne.jp*

1. Significance and Definition of Giant Nanomembrane

In the biological world, ion channels and other transport functions are essential for maintenance of the living state, and such functions are supported by biological membranes. They consist of organized lipid bilayers and imbedded protein molecules with thickness of 5-10 nm. The basic functional features of biomembranes are similarly important for industrial applications of much thicker membranes. In addition to mimicking intricate organization of biomembranes, macroscopic size and defect-free robustness are usually required for the next-generation industrial membrane. In the past, the development of nanometer-thick (molecular size) membranes with macroscopic mechanical stability has been intensively pursued. Such membranes may be defined as “giant nanomembrane”, being characterized with the following three basic features. First, its thickness is in the range of 1–100 nm. The self-supporting (free-standing) property is the second feature that is required for a membrane to be able to physically separate two spaces. Thirdly, the “giant” nanomembrane should be characterized by aspect ratios of size and thickness greater than 10^6 , that is, if the membrane thickness is 10 nm, its size must be greater than $1\text{ cm} \times 1\text{ cm}$. These features are realized by macroscopic mechanical strength (robustness), and the uniform and defect-free membrane texture over a large area.

2. Major Approaches for Fabrication of Giant Nanomembranes

Electrostatic layer-by-layer assembly, as first demonstrated by Decher (1), is composed of adsorption of polymer ions in solution onto an oppositely-charged solid substrate. When the adsorption produces excess charges on the surface, alternate adsorption of positive and negative polymer ions becomes feasible, and repeated cycles of adsorption give rise to thin films of the two polymer ions. Recent reports include a free-standing hexagonal sheet (10 mm size and 5 nm thick) of alternate polyions, as well as a free-standing ultrathin film that incorporates magnetite nanoparticles. In general, the alternate layer-by-layer assembly could give self-supporting nanomembranes with thickness of sub-100-nm but with rather small sizes.

A more recent, general approach for this purpose is the use of highly cross-linkable materials as precursor. The maintenance of macroscopic robustness in spite of nanometer thickness is the key to fabrication of robust “giant nanomembrane”. It is possible to enhance stress responsiveness of materials by simply reducing their thicknesses, since mechanical stress is more readily released in thin materials. High-density crosslinking has been a general approach toward preparation of hard, strong materials, and such hard matters can be converted to soft, flexible materials by reducing its thickness without

losing satisfactory mechanical strength. Such cases will be discussed in the following.

3. Nanomembrane of Metal Oxides

Common oxide ceramics are made of high-density oxide networks (crosslinking), and are a typical hard matter in the macroscopic size. Therefore, oxide ceramics are a qualified candidate for fabrication of robust nanomembranes. In the sol-gel method, soluble precursor materials are converted to solid ceramic materials by heating or through reaction with water. This process can be applied to the preparation of free-standing nanomembranes of metal oxides by employing proper sacrificial underlayers. The latter facilitates detachment of nanomembrane from substrate by dissolution in appropriate solvent. A poly(vinyl alcohol) (PVA) layer as underlayer provides a hydroxyl-rich surface, and apparently promotes formation of uniform metal oxide layer. As for example, an ultrathin titania layer is formed from titanium *n*-butoxide by spin-coating onto a PVA/photoresist layer on Si wafer. This specimen is isolated as a free-standing, defect-free nanomembrane with 10 to 200 nm thickness (2). This fabrication procedure was later extended to obtain robust nanomembranes from other metal oxides of Al₂O₃, NbO₅, ZrO₂, SiO₂ and La₂O₃. The combination of chemical inertness and physical softness allows interesting applications for these nanomembranes, as mentioned below.

4. Organic Nanomembranes

Fabrication of robust, free-standing nanomembrane is not limited to ceramic components. Thermosetting resins are a representative class of such materials, being insoluble and infusible upon cross-linking by thermal treatment. Epoxy resin is a typical thermosetting resin and has attractive practical properties such as superior adhesiveness, dimensional stability, chemical resistance and electrical inertness. Spin coating of an aged mixture of the two resin precursors gives uniform nanolayers with thicknesses in the range of 10 to 100 nm. Large, flexible 20-nm films with a size of over 5 cm² are formed without any traces of cracks and other defects on the surface (3). This nanomembrane is robust enough to be isolated in solution or in air. Other thermosetting resins, melamine resin, urethane resin, and phthalic resin, give similar nanomembranes, in addition to crosslinked acrylate resins (4). Their mechanical properties appear to reflect those of the corresponding macroscopic (thick) resins. The urethane nanomembrane shows plastic deformation unlike other nanomembranes, when air pressure is applied in the bulge test. Some of the crosslinkable acrylate monomers are also useful as precursors of nanomembrane. When a dilute solution of acrylic precursors (pentaerythritol tetraacrylate [PETA] or bisphenol A-functionalized acrylic oligomer [Kayarad R-280] and a photochemical radical initiator is spin-coated on a suitable underlayer and subjected to UV irradiation, efficient polymerization proceeds and free-standing nanomembranes that behave essentially identical to nanomembranes of the thermosetting resins are formed.

5. Nanomembrane of Organic and Inorganic Hybrids

Robust giant nanomembranes are obtainable as organic and inorganic hybrids.. Simultaneous progress of radical polymerization of bis-acrylate and sol-gel reaction of zirconium alkoxide during the spin-coating process gives free-

standing nanomembranes that contain partially entangled two network structures (5). A 35-nm thick nanomembrane of this kind is shown by SEM observation to be a uniform and defect-free layer (constant thickness $\pm 10\%$). TEM observation indicates formation of a smooth amorphous phase at low (11.2 mol%) zirconium oxide (ZrO_2) fractions, but the presence of regular ZrO_2 lattices with domain sizes of 5 to 10 nm is noted at the ZrO_2 content of more than 20%. When the ZrO_2 component is replaced with SiO_2 , the resulting hybrid nanomembrane possess a smooth, amorphous surface, and the domain formation of the inorganic component is not found even at a high SiO_2 fraction of 35 mol%.

In contrast to such non-covalent entanglement, the two network structures may be covalently connected to give chemical hybridization. This new system is prepared from a epoxy resin precursor that contains amino-group derivatized SiO_2 precursor (3-aminopropyl triethoxysilane) and epoxy-group containing oligomer (poly[(*o*-creyl glycidyl ether)-*co*-formaldehyde]). The physical behavior of this nanomembrane was essentially identical to that of nanomembrane from the conventional epoxy resin.

6. Mechanical and Electrical Properties

The macroscopic robustness of nanomembrane is largely determined by cross-linking density and rigidity of component structure. Macroscopically, nanomembranes in general are extremely flexible, reflecting their ultimate thinness. Such combination of nanoscopic strength and macroscopic flexibility is a result of extremely large aspect ratio. Their mechanical properties (tensile strength and ultimate elongation) was estimated by the bulge test. The experimental setup is shown in Figure 1a. The nanomembrane is attached on a metal plate with a circular hole, and air pressure is applied to the nanomembrane from below through the hole. This behavior is compared for nanomembranes of thermosetting resins in Figures 1b–1d. The nanomembrane deflects as the applied air pressure is increased and finally breaks. The extent of deflection varies with the kind of thermosetting resins and the nanomembrane of urethane resin gives the largest deflection. The tensile strength and ultimate elongation are estimated from balloon shape and applied pressure at the break. It is interesting to note that these mechanical properties are essentially identical to those of the corresponding macroscopic resins after correction for thickness.

The electrical property of the crosslinked nanomembrane appears unchanged from that of the macroscopic counterpart. For a 30-nm thick epoxy (PCGF–PEI) nanomembrane that is transferred onto a p-type silicon wafer, an output leakage current of approximately 90 μA at 0.5 V is obtained, corresponding to a resistivity value of $0.5 \times 10^{11} \Omega\cdot\text{cm}$. This highly insulating character is additional evidence of the defect-free nature, and is not lost upon detachment from the substrate. A conventional bisphenol-A-type epoxy resin gives a similar range of electrical resistivity values (10^{10} – $10^{12} \Omega\cdot\text{cm}$).

7. Separation of Electron, Ions and Molecules

Various applications are conceivable from unique characteristics of giant nanomembrane. For example, free-standing insulating nanomembranes would

be useful for many large-area electronic devices, and giant nanomembranes made of ion-conducting double metal oxides have been used as electrolyte membrane for constructing efficient fuel cells which operate at intermediate-temperature range of 200–400°C. As for separation of molecules, the molecular imprinting technique was used for creating designed cavities in TiO₂ nanomembrane (6). It showed size selectivity in the permeation of several organic molecules.

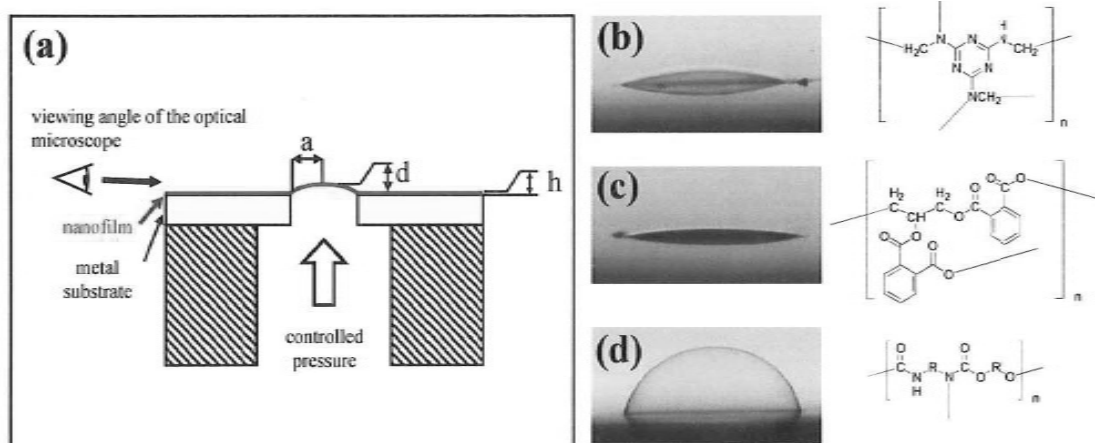


Fig. 1. Set-up of Bulge Test and Behavior of Thermosetting Nanomembrane

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II. SHORT LECTURES

CATION EXCHANGE EQUILIBRIA IN BORIC ACID SOLUTIONS

Pavel Kůs¹, Tomáš Birčák², Kateřina Vonková¹ and Luděk Jelínek²

¹*Research Reactors Section, CV Řež, Husinec-Řež 130, 250 68, Czech Republic*

²*Department of Power Engineering, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic
e-mail: jelinekl@vscht.cz*

In pressurized water reactors that are used in nuclear power stations throughout the Europe, boron, in the form of boric acid and borates, plays an important role of neutron absorber in primary circuits of nuclear reactors. Boron concentration varies throughout the cycle being lowest at the end of the cycle. When reactor is operated on power effect, boric acid concentration drops below the detection limit (1).

The adjustment of the chemical regime of primary circuit is based on the calculation of pH at the reactor operating temperature of 300°C which is kept in the range of 7.0 to 7.2 (1). Apart from alkalization with potassium hydroxide, the composition of primary circuit coolant is also changed when it passes through the ion exchange filters that are used to remove unwanted impurities. These filters operate at the temperature of 40°C. The discrepancy between pH of primary circuit coolant at 300°C and 40°C, increases with decreasing concentration of boric acid (2).

During the operation of VVER-1000 reactor on power effect, uptake of potassium on strong acid cation exchanger (Dowex HCR-S NG) filter was higher than during the normal operation mode (3). Though, the change in sorption of potassium onto cation exchanger is obviously caused by the change of boric acid concentration, we can identify two different effects of boric acid. It can be simple increase of pH at 40°C with decreasing boric acid concentration or formation of the potassium complexes with borates, or possibly polyborates. Considerably stable polyborate species, such as trimer $B_3O_3(OH)_4^-$ (4,5) and tetramer $B_4O_5(OH)_4^{2-}$ (5) are formed in solution at higher borate concentration.

Series of equilibrium and column tests were carried out to elucidate the sorption equilibria of potassium cations on Dowex HCR-S NG strong acid cation exchanger. Results of column experiments were in part published (2) in Czech and are included here for the sake of completeness. Solutions mimicking real primary circuit coolant containing 0 to 0.5 g/L (batch) or 0 to 6 g/L (column) of boric acid, 0 to 4 mg/L of potassium, 0 to 0.35 mg/L of lithium, 0 to 15 mg/L of ammonia and pH ranging from 7.5 to 10.0 at 25°C were used for Batch-wise equilibrium tests. Results of batch-wise tests were compared with column tests at the same conditions. In the column experiments, attention was also paid to the re-establishing of equilibrium after the step change of parameters.

Batch-wise sorption of potassium onto cation exchanger reached equilibrium within 24 hours with reaction half time of within the range of 1–2 hours. The presence of boric acid in the range 0 to 0.5 g/L had no effect on the sorption kinetics and sorption equilibria.

In multicomponent solution containing potassium, ammonia and boric acid, there was pronounced effect of equilibrium pH on potassium sorption, suggesting the most important role of boric acid is pH buffering. However, column experiments showed that in the presence of boric acid, amount of potassium adsorbed onto column is lower than in its absence. In the case of multicomponent (potassium, ammonia and boric acid) column sorption, the presence of boric acid changes lowers the extent of potassium sorption. When the boric acid concentration was lowered, potassium and lithium sorption increased. Under the elevated temperature of 40°C reaction of system to the step changes of inlet solution were faster than at 20°C.

Column experiments with model solution corroborated the anomaly in potassium sorption from primary circuit coolant during the power effect operation. There is however still discrepancy between the result of batch wise and column experiments that needs to be clarified.

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POLYMERIC HYBRID SORBENTS IN REMOVAL OF ANIONIC SPECIES FROM WATER AND WASTEWATER

Dorota Kołodyńska, Zbigniew Hubicki

*Department of Inorganic Chemistry, Faculty of Chemistry,
Maria Curie-Skłodowska University, Maria Curie-Skłodowska Sq.2. 20-031
Lublin, Poland,
e-mail: kolodyn@poczta.onet.pl*

Ion exchangers have been widely used in wastewaters treatment and most of them are commercially available. They are characterized by excellent properties, good sorption capacities, high selectivity towards certain metal ions but they also possess some disadvantages such as poor thermal stability and mechanical strength. The above-mentioned limitations are overcome by introducing the composite organic-inorganic resins. This new class of organic-inorganic materials denoted as the polymer supported nanoparticles (PSNs) combines advantages of porous polymeric materials and nanoscaled inorganic particles. In this group of materials hydrated Fe(III) oxide particles (HFO), Mn(IV) oxides, Fe₃O₄ crystals and elemental Zn⁰ or Fe⁰ are frequently used. Lately, many publications appeared on application of iron oxides and hydroxides in adsorption processes of various types of contamination from natural waters and waste waters such as phosphonates(V), arsenates(III,V) chromates(III,VI).

In the presented paper the results of the sorption of heavy metal ions in the presence of biodegradable complexing agents IDS (iminodisuccinic acid) and EDDS (ethylenediaminedisuccinic acid) from the synthetic aqueous solution as well as Cr(VI), As(V) on commercially available ion exchangers possessing inbuilt nanoparticles of Fe(III) PuroLite Arsen X^{np} and Lewatit FO36 were described. Both impregnated with iron nanoparticles are innovative hybrid adsorbers consisting of combination of a polymeric anion exchange resin and an iron oxide of a goethite structure. The iron oxide is distributed in the pores of the ion exchange resin in a layer a few nanometers thick by a special production process. For comparison the composite ion exchanger obtained by mixing of nickel(II)-potassium hexacyanoferrate(II) and a resin matrix (NiNCF) was also used.

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KINETICALLY EXCELLENT NITRATE SELECTIVE ANION EXCHANGE FIBERS DERIVED FROM CHLOROMETHYLSTYRENE GRAFTED POLYOLEFIN FIBER

Akinori Jyo¹, Hiroshi Nakaatari¹, Ruriko Fujimoto¹, Masahiro Kitagaki¹, Hirotaka Matsuura¹, Masao Tamada², Noriaki Seko²

¹*Department of Applied Chemistry & Biochemistry, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan*

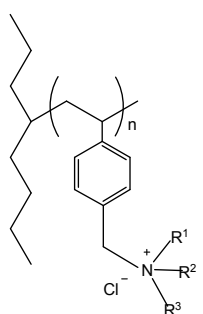
²*Quantum Beam Science Directorate, Japan Atomic Energy Agency, Watanukimachi 1233, Takasaki, Gunma 370-1279, Japan*

e-mail: jyo@gpo.kumamoto-u.ac.jp

1. Introduction

High nitrate concentrations in drinking water bring on infantile methemoglobinemia and are responsible for causing cancers (1). In addition, high nitrate concentrations promote eutrophications in lakes and rivers (2). Therefore, it is important to develop kinetically excellent nitrate selective anion exchangers. In this regard, recently, we reported preparation and properties of three kinds of anion exchange fibers named FTEA, FBDA, and FDMA (3). Their structures are shown in Scheme 1. Unfortunately, these anion exchange fibers did not exhibit the high selectivity toward nitrate; sulphate markedly interferes with uptake of nitrate. However, they have excellent kinetic performances in column-mode uptake of nitrate; breakthrough profiles of nitrate were essentially independent of flow rates of feeds, when the feeds were supplied to the column at the flow rate range from 50 to 3000 h⁻¹ in space velocity (SV). It is pointed out

that an anion exchange resin (P-N⁺R¹R²R³X⁻) prefers sulphate to nitrate when R¹, R², and R³ are methyl and ethyl groups. When R¹, R², and R³ in trialkylammonio methacrylate are butyl and hexyl



Anion exchange fiber	R ¹	R ²	R ³
FTEA	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅
FDMA	CH ₃	C ₂ H ₄ OH	CH ₃
FBDA	CH ₃	n-C ₄ H ₉	CH ₃
FTBA	n-C ₄ H ₉	n-C ₄ H ₉	n-C ₄ H ₉
FTAA	C ₅ H ₁₁	C ₅ H ₁₁	C ₅ H ₁₁
FTHA	C ₆ (4)H ₁₃	C ₆ H ₁₃	C ₆ H ₁₃

Scheme 1. Structures of anion exchange fibers: FTEA, FDMA, FBDA, FTBA, FTAA, and FTHA

groups, these resins take up nitrate in preference to sulphate (4). In this work, we prepared three anion exchange fibers named FTBA, FTAA, and FTHA (Scheme 1) from chloromethylstyrene grafted polyethylene-coated polypropylene fiber. Column-mode uptake of nitrate by these anion exchange fibers was tested by changing the feed flow rate and the influence of competing anions was also studied.

2. Experimental

2.1 Graft polymerization of chloromethylstyrene (CMS) onto polyethylene-coated polypropylene staple fiber (PPPE).

PPPE (1.5 denier, 3.8 cm, 5.0 g) irradiated with electron (2 MV, 200 kGy) was reacted with excess dimethyl sulfoxide solution of CMS (50 wt. %) in air-free

glass tube at 40°C for 10 h. The resulting CMS grafted PPPE (PPPE-*g*-CMS) was washed with acetone and methanol in successive and then dried in vacuum overnight. Yield 9.9 g. Procedures mentioned above were repeated to obtain PPPE-*g*-CMS in which weight of grafted CMS was nearly equal to that of trunk PPPE.

2.2 Functionalization of PPPE-*g*-CMS and characterization of the resulting anion exchange fibers

Dried PPPE-*g*-CMS (1 g) was swollen in absolute ethanol (25 mL) overnight. After removal of adherent ethanol on PPPE-*g*-CMS, it was taken into a glass tube and then absolute ethanol (18.8 mL) and triethylamine (12.5 mL) were added. Then the content in the glass tube was mixed well and the glass tube was set in a stainless steel autoclave. The autoclave was stood in an oil bath at 80°C for 5 h. Then, the autoclave was taken out from the oil bath and allowed to stand overnight for cooling. The resulting fiber named FTAA was washed with acetone, ethanol, and water in successive and then swollen in water for 5 h. After air-drying, it was dried in vacuum. FTBA and FTHA were prepared by almost the same procedures for the preparation of FTAA. The resulting anion exchange fibers were characterized by CHN analysis, FT-IR spectroscopy, and anion exchange capacity measurement.

2.3 Column-mode study

An anion exchange fiber (FTBA, FTAA, or FTHA) was packed into a polyethylene column (i.d. 1.3 cm). Table 1 lists dry weight and wet volume of each fiber in respective columns. First 1 M HCl solution (100 mL) was fed to the column and then the column was washed with milli Q water until the column effluent was chloride free at a flow rate of 5 h⁻¹ in SV. Feeding solution

Table 1. Amount of fibers in columns

Fiber in column	Dry weight	Wet volume
	(g)	(mL)
FTBA	0.40	1.92
FTAA	0.40	1.82
FTHA	0.41	1.47

containing nitrate was fed to the column at a given flow rate. The column effluent was collected in a series of volumetric flasks and ionic

Table 2. Results of chemical analyses of anion exchange fibers FTBA and FTAA

Anion exchange fiber	Nitrogen content (mmol/g)	Anion exchange capacity (meq/g)
FTBA	1.5	1.4
FTAA	1.4	1.2
FTHA	1.3	1.1

Nitrogen was not detected in the precursor PPPE-*g*-CMS.

composition in each flask was determined by means of ion chromatography. After the adsorption operation, the column was regenerated by feeding 1 M HCl (100 mL) and washed with milli Q water at flow rate of 5 h⁻¹ for the next adsorption operation. Detail experimental conditions, such as flow rates and compositions of feeds will be given with results.

3. Results and Discussion

3.1 Characterization of the resulting anion exchange fibers

A strong absorption band at 1260 cm⁻¹ was observed in FT-IR spectrum of PPPE-*g*-CMS but this band was not observed in FT-IR spectrum of FTBA, FTAA, or FTHA. In addition, CHN analysis showed the introduction of nitrogen,

whereas the precursor PPPE-*g*-CMS has no nitrogen as written in Table 2. These results mean the completion of the quaternization of PPPE-*g*-CMS. Anion exchange capacity of each anion exchange fiber in chloride form was measured by eluting chloride with sodium nitrate solution and the subsequent argentometric determination of eluted chloride; the results are in good agreement with nitrogen contents within experimental error of CHN analysis.

3.2 Dependence of breakthrough profiles of nitrate on flow rate of feed

The effect of the flow rate of the feed on breakthrough profiles of nitrate was examined to evaluate kinetic performances of FTBA, FTAA, and FTTHA. Figure 1 shows the results and feed flow rates are given in the inset of each graph. As judged from Figure 1, breakthrough profiles of nitrate are not markedly

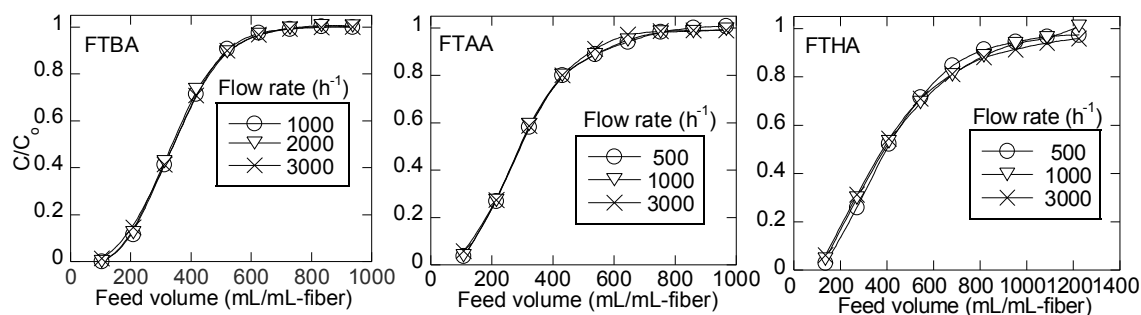


Figure 1. Breakthrough profiles of nitrate. Column: refer to Table 1. Feed: 1.0 mM NaNO₃ for FTBA and FTAA columns, and 0.75 mM for FTTHA column

dependent on the flow rate of the feed up to 3000 h⁻¹ in SV, indicating excellent kinetic performances of these anion exchange fibers. Table 3 summarizes 5% breakthrough capacities for nitrate and total uptake of nitrate. In case of FTBA and FTAA, the total uptake of nitrate is independent of feed flow rate and equal to anion exchange capacities, although 5% breakthrough capacities decrease slightly at the highest flow rate of 3000 h⁻¹. In case of FTTHA, the decrease in 5% breakthrough capacities was observed with an increase in the feed flow rate but the total uptake was nearly constant.

Table 3. Numerical data on Figure 1

Fiber	Flow rate (h ⁻¹)	5% BTC ^a (mmol/g)	Total uptake (mmol/g)
FTBA	1000	0.80	1.4
	2000	0.76	1.4
	3000	0.68	1.4
FTAA	500	0.52	1.2
	1000	0.52	1.2
	3000	0.46	1.2
FTTHA	500	0.42	1.2
	1000	0.37	1.2
	3000	0.28	1.1

^a) 5% Breakthrough capacity

3.2 Effect of competing anions

Bicarbonate, chloride, and sulphide ions are main anions in groundwater, lake water, and river water. Then, the effect of these anions on the breakthrough profiles of nitrate was studied. Some examples of results are shown in Figure 2. Here, feeds containing both nitrate and competing anions were supplied to each column. Table 4 lists flow rates of feeds, ionic compositions of feeds, 5% breakthrough capacities for nitrate and total uptake of nitrate. In case of FTBA, chloride does not markedly interfere with uptake of nitrate when the molar ratio of nitrate to chloride is 1:1. When the nitrate to chloride molar ratio is 1:5, chloride interference becomes to be marked. Sulphate more markedly interferes

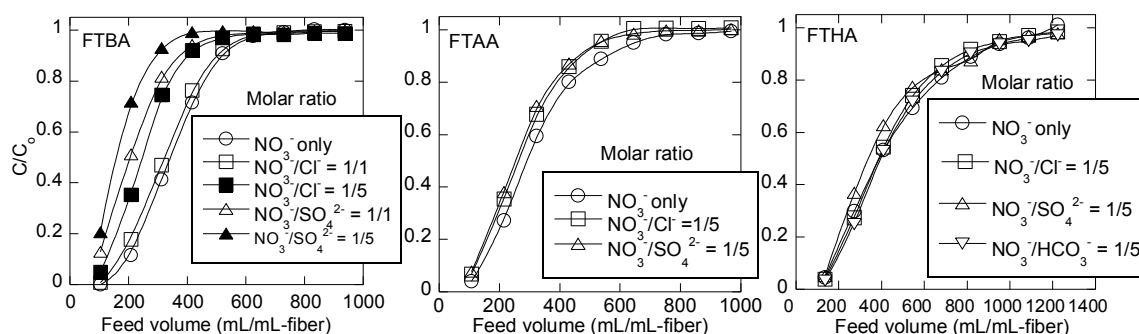


Figure 2. Breakthrough profiles of nitrate in column-mode uptake of nitrate from feeds containing both nitrate and competing anion

with uptake of nitrate than chloride and nitrate uptake decreases significantly when nitrate to sulphate molar ratio is 1:5. However, the nitrate selectivity of FTBA is significantly higher than that of FTAA, FDMA, and FBDA in which R¹, R² and R³ are CH₃, C₂H₅, and/or C₂H₄OH (3). In particular, interfering effect of sulphate is markedly decreased. In case

Table 4. Numerical data on Figure 2

Fiber	Feed ^{a)}		5%BTC ^{c)} (mmol/g)	Total uptake (mmol/g)
	NO ₃ ⁻ (mM)	[X] ^{b)} /[NO ₃ ⁻]		
FTBA	1.0	NO ₃ ⁻ only	0.76	1.4
		Cl ⁻ 1	0.65	1.4
		Cl ⁻ 5	0.49	1.0
		SO ₄ ²⁻ 1	0.41	0.83
		SO ₄ ²⁻ 5	0.38	0.58
FTAA	1.0	NO ₃ ⁻ only	0.52	1.2
		Cl ⁻ 5	0.47	1.1
		SO ₄ ²⁻ 5	0.45	1.0
FTHA	0.75	NO ₃ ⁻ only	0.37	1.2
		Cl ⁻ 5	0.38	1.2
		SO ₄ ²⁻ 5	0.36	1.1
		HCO ₃ ⁻ 5	0.38	1.0

^{a)}Flow rate of feed: 2000 h⁻¹ for FTBA column, 1000 h⁻¹ for FTAA and FTAA columns. ^{b)}X represents a competing anion. ^{c)}5% Breakthrough capacity.

decreased. In case of FTAA and FTAA, sulphate does not significantly interfere with uptake of nitrate even in the case that nitrate to sulphate molar ratio is 1:5; both total uptake of nitrate and 5% breakthrough capacity for nitrate are nearly equal to those in the absence of competing anion. Since PPPE-*g*-CMS is highly hydrophobic, the resulting anion exchange fiber becomes highly hydrophobic when triamylamine or trihexylamine was reacted with PPPE-*g*-CMS. Under such conditions, less hydrated nitrate will be more favoured by the anion exchangers, compared with highly hydrated sulphate.

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REMOVAL OF CATIONIC DYES FROM AQUEOUS SOLUTIONS WITH COMPOSITE HYDROGELS BASED ON POLYACRYLAMIDE AND DEXTRAN SULPHATE

Maria Marinela Perju, Maria Valentina Dinu, Ecaterina Stela Dragan

*“Petru Poni” Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A,
700487 Iasi, Romania
e-mail: sdragan@icmpp.ro*

Abstract

In this study, novel composite semi-interpenetrated polymer networks (s-IPNs) based on polyacrylamide (PAAm) and dextran sulphate (DxS) were synthesized by radical polymerization at two temperatures: +20°C and -18°C for 24 h, using DxS as an ionic physical entrapped polymer, acrylamide (AAm) monomer and N,N'-methylenebis(acrylamide) (BAAm) as cross-linking agent. The PAAm/DxS composites were tested as sorbents for Methylene Blue (MB) from aqueous solutions. The effect of contact time on the adsorption of dye (MB) onto composite hydrogels has been investigated. The modelling of the experimental data by applying different kinetic models was also performed.

1. Introduction

Hydrogels are known for their applications in agriculture, as soil conditioners, to decrease soil erosion, or to control the release of herbicides, and in hydrometallurgy as adsorbents in waste water remediation. The ability of a hydrogel to adsorb ionic species is depending on some of its intrinsic characteristics like: hydrophilic/hydrophobic balance, swelling degree, chemical and mechanical stability. Colored organic effluents are released in environment as a result of different industrial activities. Therefore, dye pollution in water stream is a major environmental problem. However, colored wastewater cannot be discharged without adequate treatment. The methods of dye removal from industrial wastewaters could require many processes such as biological treatment, coagulation, electrochemical techniques, adsorption, and oxidation. Among several chemical and physical methods, adsorption process is one of the effective methods to remove dyes from wastewaters (1-7).

It has been reported that many different types of adsorbents are effective in removing color from aqueous effluents. Natural polymeric materials are gaining more and more interest for application as adsorbents in wastewater treatment due to their biodegradable and non-toxic nature. As a functional biological polymer, DxS offers an interesting set of characteristics, including non-toxicity, biodegradability and biocompatibility. In our investigations, the s-IPNs and cryogelation technique have been adopted to prepare ionic composite hydrogels based on DxS as a physical entrapped polymer within PAAm 3D network. Their efficiency in the removal of MB from aqueous solution, as a function of contact time has been evaluated.

2. Experimental

The DxS with molar mass of 100000 g/mol from *Leuconostoc* ssp purchased from Sigma-Aldrich was used as received. Acrylamide (AAM, Fluka), N,N'-methylenebis(acrylamide) (BAAM, Sigma), ammonium persulfate (APS, Sigma-Aldrich), and N,N,N',N'-tetramethylethylenediamine (TEMED, Sigma-Aldrich) were used as received. All reagents were of analytical grade or highest purity available. APS and TEMED stock solutions were prepared by dissolving 0.2 g of APS and 0.625 mL of TEMED each in 25 mL of distilled water. The BAAM stock solution, prepared by dissolving 0.2527 g of BAAM in 10 mL of distilled water, at 25°C, was used for hydrogels synthesis after 24 h.

Composite hydrogels based on PAAm and DxS were prepared by free radical cross-linking copolymerization in aqueous medium at two temperatures: +20°C and -18°C. The initial concentration of the monomers (AAM + BAAM), C_0 , has been kept constant in all experiments ($C_0 = 5$ wt.-%), and cross-linker ratio $X = 1/40$. The redox initiator system used consisted of APS and TEMED. Study of the dye removal properties of the composite hydrogels was carried out using a batch equilibrium procedure. Thus, 0.01 g of dry composite hydrogels was placed in a flask and contacted with 10 mL of aqueous solution of dye: MB at the concentration of 2×10^{-5} mol/L. For kinetic study, the flask containing the mixture of composite hydrogel and dye solution were placed in a thermostatic bath at 20°C. After adsorption process composite hydrogels were filtered off and the residual concentration of MB remained in the filtrate was measured by the UV-Vis spectroscopy at 665 nm.

3. Results and Discussion

The effect of the contact time on the adsorption capacity of the PAAm/DxS composites hydrogels for MB is shown in Figs. 1 and 2. The contact time varied in the range 0 - 600 min. As Figs 1 and 2 show, the time required to achieve the equilibrium at temperature 20°C was about 240 min.

In order to examine the controlling mechanism of the adsorption process of MB adsorption on the PAAm/DxS composites obtained at +22°C and -18°C such as mass transfer and chemical reaction, three kinetic models were used to test the experimental data: the pseudo-first order, Eq. (1), pseudo-second order, Eq. (2), and the intra-particle diffusion model, Eq. (3):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

$$q_t = k_{id}t^{0.5} \quad (3)$$

where q_e and q_t are the amounts of the dye adsorbed at equilibrium (mmol/g) and at time t , respectively, k_1 is the rate constant of pseudo-first order kinetic (min^{-1}), k_2 is the rate constant of pseudo-second order kinetic ($\text{g}/(\text{mmol} \times \text{min})$), and k_{id} is the intra-particle diffusion rate constant ($\text{mmol}/(\text{g} \times \text{min}^{0.5})$).

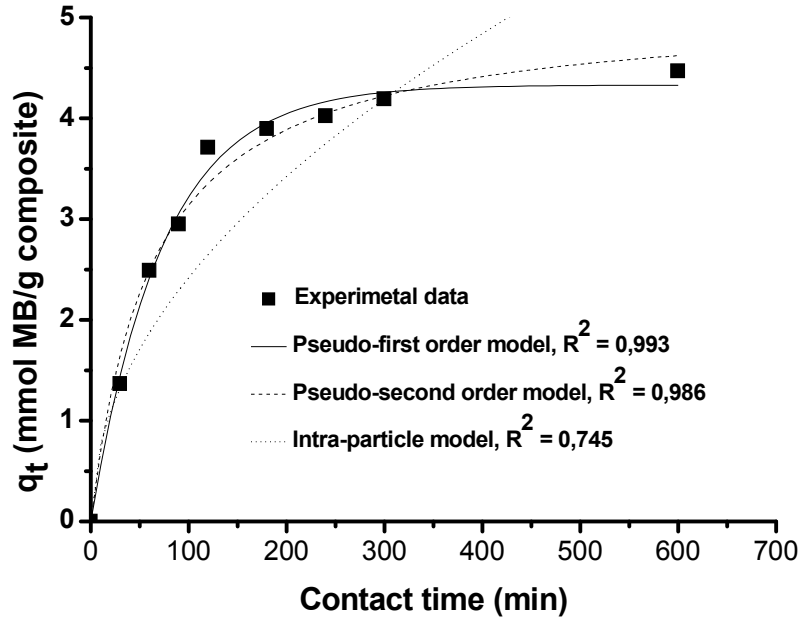


Fig. 1. Comparison of experimental and calculated data for three kinetic models for the adsorption of MB onto PAAm/DxS composites obtained at +22°C with a cross-linker ratio of 1/40

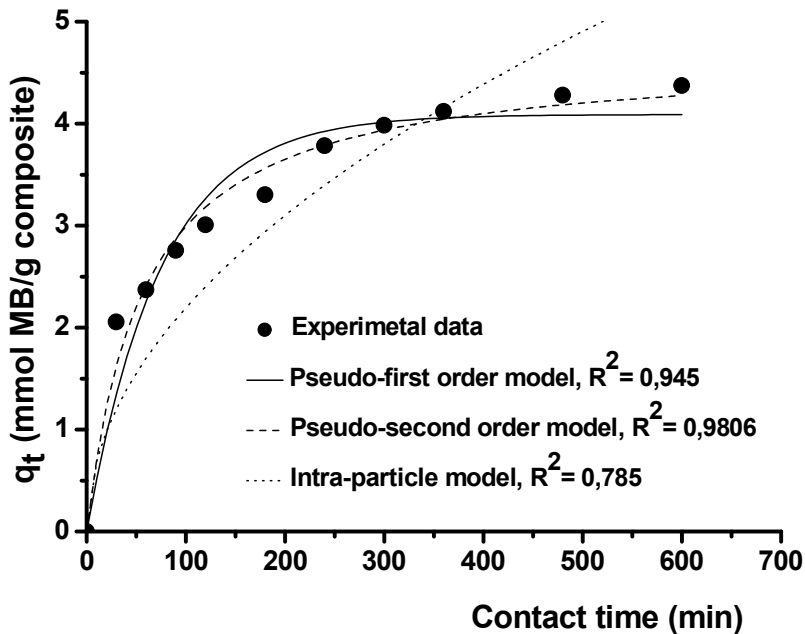


Fig. 2. Comparison of experimental and calculated data for three kinetic models for the adsorption of MB onto PAAm/DxS composites obtained at -18°C with a cross-linker ratio of 1/40

The constants corresponding to the pseudo-first order and pseudo-second order models and the intra-particle diffusion model were calculated with an Origin 7.5 program by applying Eq. (1) for the pseudo-first order model, Eq. (2) for the pseudo-second order model, and Eq. (3) for the intra-particle diffusion model, the values being presented in Table 1.

Table 1. Kinetic data for the adsorption of MB on PAAm/DxS composites

PAAm/DxS composite	$q_{e \text{ exp}}$, mmol/g	Pseudo-first order constants		Pseudo-second order constants		Intra-particle diffusion constants
		$q_{e \text{ calc}}$, mmol/g	k_1 , min ⁻¹	$q_{e \text{ calc}}$, mmol/g	k_2 , g/mmol x min	k_{id} , mmol/g x min ^{0.5}
+22°C	4.47	4.32	0.0136	5.10	3.116×10^{-3}	0.242
-18°C	4.37	4.08	0.0133	4.67	3.8×10^{-3}	0.219

As Table 1 shows, the theoretical $q_{e,calc}$ values estimated from the pseudo-first order model are very close to the experimental values for the PAAm/DxS composite obtained at +22°C, the correlation coefficients being also high (Fig. 1). These results showed that PAAm/DxS composite obtained at +22°C are able to adsorb and trap cationic dyes by electrostatic interactions, i.e., the physical adsorption is the principle mechanism. On the other hand, in the case of PAAm/DxS composite obtained at -18°C, the correlation factors are high for the pseudo-second order model. The pseudo-second order kinetics supports the chemisorption would be the rate-determining step controlling the adsorption process of MB on PAAm/DxS composite obtained at -18°C. The deviation of the straight line from the origin indicates that the intra-particle diffusion is not the rate-limiting step. The values of the correlation coefficients in Figs. 1 and 2 also support this conclusion.

4. Conclusions

In this study, the capacity of PAAm/DxS composite hydrogels obtained at +22°C and -18°C to adsorb MB from aqueous solutions was examined. Kinetic data were successfully fitted by the pseudo-first order equation, which gave the best correlation with experimental data, for the PAAm/DxS composite obtained at +22°C. In the case of PAAm/DxS composite obtained at -18°C, the adsorption process of MB obeyed of the pseudo-second order kinetics, supporting the chemisorption would be the rate-determining step.

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ELABORATION OF CHELATING RESINS FOR METAL IONS SOLID-PHASE EXTRACTION

Catherine Branger, Julie Bernard, André Margailan

*MAPIEM Laboratory – Université SUD Toulon-Var – ISITV,
BP 56 – 83162 La Valette du Var - France
e-mail: branger@univ-tln.fr*

Functionalization of cross-linked polymer resins leads to materials with applications in the field of chromatography, organic synthesis or solid phase extraction (SPE) (1). SPE applied to metal extraction commonly involves poly(styrene-co-divinylbenzene) resins bearing chelating groups (2). Such resins should meet specific criteria in terms of bead sizes, textural properties and chemical stability. We have been working on functionalization of such materials either by introducing a ligand on a commercial resin (Amberlite® XAD-4) or by preparing resin beads containing this ligand by suspension copolymerization. Catechol was chosen for the present study since it allows these two routes.

The first route has been achieved by grafting catechol on Amberlite® XAD-4 via two kinds of links: reduced imine and diazo (Fig. 1). As the synthesis occurred in a heterogeneous medium, a molecular approach has been undertaken to make the resins characterization easier. This approach involved the optimization of the synthetic scheme on a model molecule before its implementation to the grafting process. A special care has been taken to the characterization of grafted resins by FTIR, TGA, EA and catechol titration. Moreover, textural properties were studied at different stages of the grafting: a diminution of the specific area was observed in all cases. This phenomenon could not be explained by a post-reticulation of the polymer network but rather by the blockage of some connections between mesopores.

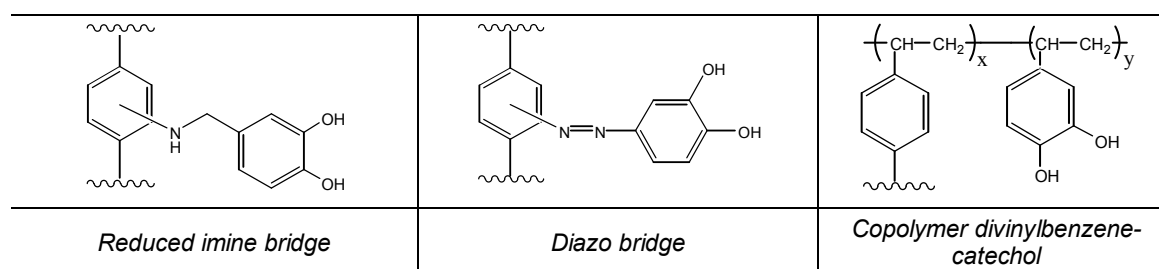


Figure 1. Structures of grafted resins and synthesized copolymers

A monomer bearing protected catechol (3,4-dimethoxystyrene) was copolymerised with divinylbenzene by suspension technique in order to obtain beads of desired size and specific area (3). Porosity was controlled by use of toluene as an inert diluent. Resins were characterized by the same methods as for grafting. Three different compositions were obtained by varying the 3,4-dimethoxystyrene monomer quantity. Catechol was regenerated by deprotection of the methoxy groups (Fig. 1). This induced a post-reticulation of the network and increase of the metal ion retention.

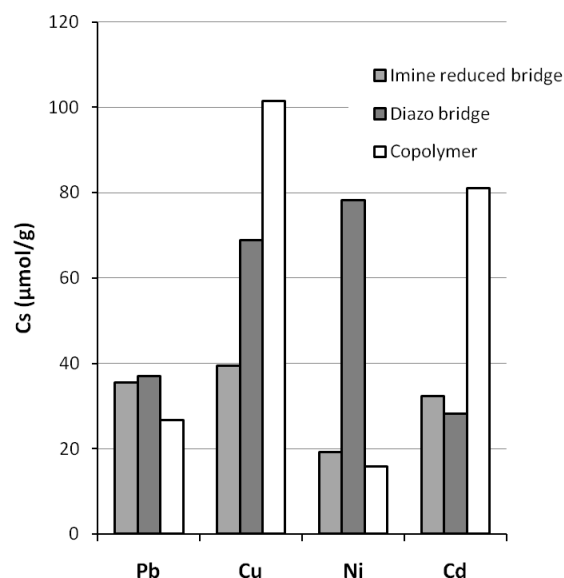


Figure 2. Sorption capacities ($\mu\text{mol/g}$)

The retention properties of the different resins were compared for lead(II), copper(II), nickel(II) and cadmium(II) ions (Fig. 2). It could be concluded that functionalized resins prepared by the copolymerization route were equivalent for metal extraction to the grafted resins. However, this route presents many advantages: the copolymers are easier to prepare, less time consuming and more eco-friendly since their preparation implies less toxic reagents. Moreover, their synthesis is more reproducible and leads to non colored materials. This proves that direct copolymerization is a more attractive route for functionalized materials on the condition that functionalized monomers are easily accessible. Finally, the copolymers have a pale yellow color which changes upon complexation (Fig. 3). This might be helpful for direct determination of metal ions by colorimetry.

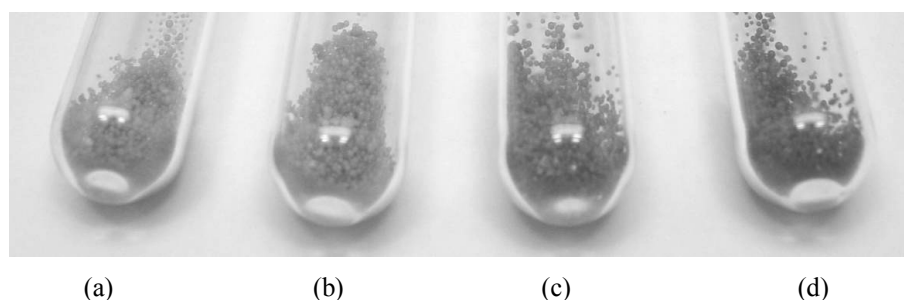


Figure 3. Color variation of DVB-DOH(9/1) resin upon complexation with varying lead concentration solutions: (a) $100\mu\text{g}\cdot\text{L}^{-1}$, (b) $50\mu\text{g}\cdot\text{L}^{-1}$, (c) $500\mu\text{g}\cdot\text{L}^{-1}$, (d) $1000\mu\text{g}\cdot\text{L}^{-1}$

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SEPARATION OF NICKEL(II) AND CADMIUM(II) WITH ION-EXCHANGE PROCESS

Paulina Otremska, Jerzy Gęga

*Częstochowa University of Technology, Department of Chemistry,
19 Armii Krajowej Str., 42-200 Częstochowa, Poland
e-mail: potremska@wip.pcz.pl*

Separation of nickel(II) and cadmium(II) ions from sulphate solution has been studied. The solution has been treated with two ion exchange resins: Lewatit OC-1026 and Lewatit TP 207. Obtained data were compared with data from supported liquid membrane (SLM) experiments.

1. INTRODUCTION

Recovery of heavy metals from low grade ores, purification of wastewaters or treating of industrial wastes has become very important. Both economical and environmental aspect caused constant development of methods for metal separation and recovery. Recovery of heavy metals could be based on pyrometallurgical and hydrometallurgical processes (1,2). The major drawbacks of the first process are energy consumption and need of dust collecting and gas cleaning systems. The second method is more economical and environmentally suitable (1). The other methods like precipitation from the solution are also sometimes used but they have disadvantages especially if they are used when solutions contain metal ions in low concentration (3,4). Flocculation or coagulation are related to precipitation and cause formation of large amounts of sediments containing heavy metal ions (5). Among others, nickel and cadmium have many useful applications in our life but they are also very harmful if discharged into natural water resources. Therefore, it is very important to purify water. These methods should be effective, inexpensive and automated.

In comparison with other common methods ion exchange provides a lot of advantages. Large application of ion exchangers was caused by invention and application of new organic and inorganic exchangers. Improvement in kinetics of process and capability of ion exchanges was enabled by means of macroporous ion exchanges developed in the nineteen seventies (5). In removal of Cd(II) with ion-exchange process resins like: cationic exchanger (Dowex 50Wx8, Amberlit IR-120), chelating ion-exchanger containing phosphonic groups (Duolit ES-463, Diaion CRP-200), aminophosphonic groups (Duolit C-467, Lewatit TP 260, Purolit S-940, Purolit S-950), amphoteric exchanger (Retardion 11A8) and resins with sulphonic and diphosphonic groups (Diphonix) (6) are used. In this work two ion exchange resin: Lewatit OC 1026 and Lewatit TP 207 have been used for sorption of nickel and cadmium ions from sulphate solution.

Membrane processes are also important method used in metal separation because they minimize the need for organic solvents and could be an alternative method of separation and concentration of metal ions. Therefore, the extraction ability of resins was compared with data obtained from SLM.

2. EXPERIMENTAL

Solutions of known metal ions concentration were prepared by dissolving an appropriate salt: nickel(II) sulphate hexahydrate, cadmium(II) sulphate 8/3-hydrate in deionized water. The pH was adjusted by the addition of appropriate volume of sulphuric acid or sodium hydroxide. The resins used were: Lewatit OC 1026 (carry out in Na^+ form by left with 3% NaCl overnight) and Lewatit TP 207 (Na^+ form) both made by Lanxess. Lewatit OC 1026 is a resin based on crosslinked polystyrene matrix with adsorbed di-2-ethylhexylphosphate (D2EHPA) and Lewatit TP 207 is a macroporous resin containing iminodiacetic groups which have chelating properties. As a membrane in SLM experiments a PTFE-filter (Whatman) soaked in D2EHPA (solution in kerosene) was used.

The appropriate volume of metal salt solution and resin were contacted for 30 minutes. In a SLM transport processes of metal ions from a donor phase (i.e. solution of metal salts, pH = 3) to an acceptor solution (0.5 M H_2SO_4) were performed. Concentrations of metal ions were measured by atomic absorption spectrometry (SOLAR 939) with an air/acetylene flame and the appropriate hollow cathode lamps. All experiments were carried out at room temperature.

3. RESULT AND DISCUSSION

The influence of pH as well as kind of functional group of resins on the sorption of nickel(II) and cadmium(II) from sulphate solution are shown in Fig. 1. The results indicate that the highest percent extraction was obtained for resin with iminodiacetic groups (Lewatit TP 207). Percent extraction was almost 100% for both ions at pH = 2 and higher. However, separation of these ions could not be possible. It was found that percent extraction for Lewatit OC 1026 was only about 5.7% for Ni(II) and 38% for Cd(II). Separation of studied ions could be possible over pH = 1 but at pH = 3 this process could be more effective.

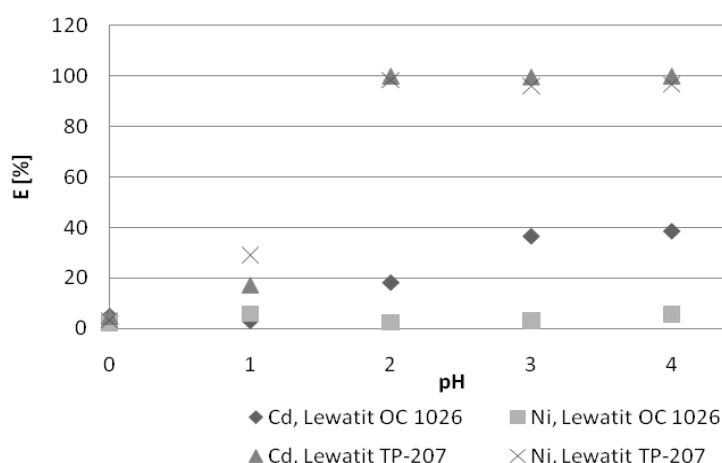


Fig. 1. Percent extraction of nickel(II) and cadmium(II) ions as a function of pH in ion-exchange processes

The effect of H_2SO_4 concentration on ions desorption was also studied. For this study sorption of Ni(II) and Cd(II) ions was made from solution at pH = 1 (Lewatit TP 207) and at pH = 3 (Lewatit OC 1026). The concentration of

nickel(II) and cadmium(II) after desorption process from Lewatit TP-207 resin are shown in Fig. 2. It was found that desorption of nickel(II) depends on concentration of sulphuric acid. The lowest desorption of nickel(II) was for 0.05 M H₂SO₄. However, in this concentration separation Ni(II) from Cd(II) was the highest. Desorption of metal ions from Lewatit OC 1026 was studied for solution at pH = 3. The results are presented in Fig. 3. For this resin H₂SO₄ concentration changes did not result on both ions desorption. The results indicate that for all applied H₂SO₄ concentration separation of Ni(II) from Cd(II) could be possible.

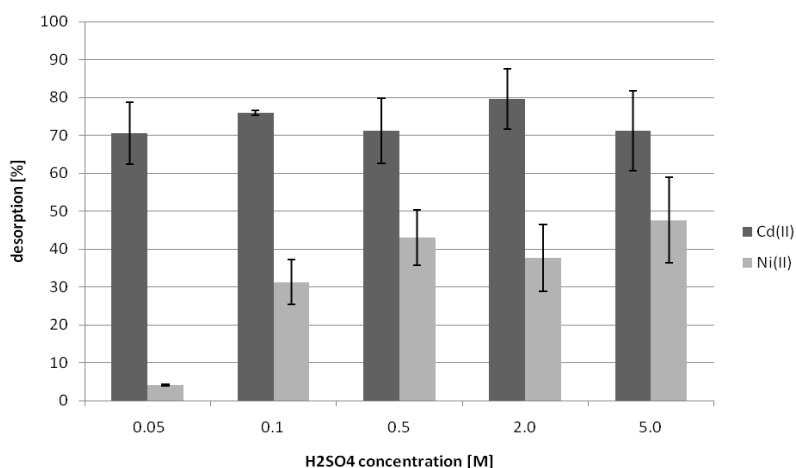


Fig. 2. Percent desorption of nickel(II) and cadmium(II) ions from Lewatit TP 207 resin as a function of concentration of sulphuric acid

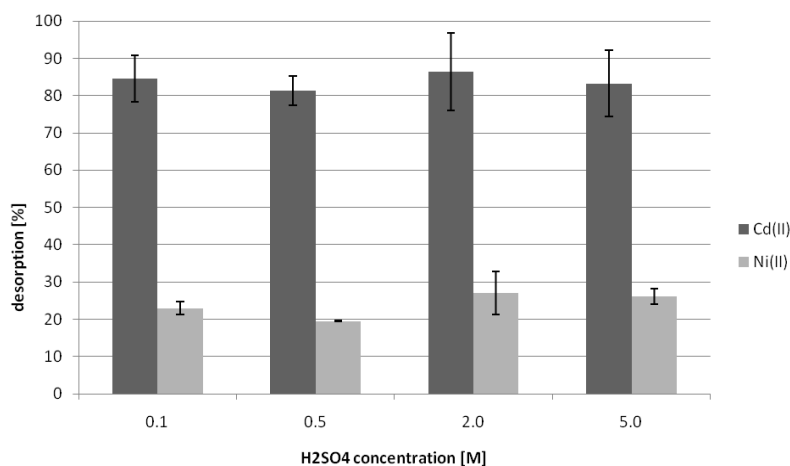


Fig. 3. Percent desorption of nickel(II) and cadmium(II) ions from Lewatit OC 1026 resin as a function of concentration of sulphuric acid

The SLM studies showed that separation of Cd(II) and Ni(II) from sulphate solution at pH = 3 with D2EHPA as an ion carrier was also possible (Fig. 4). The highest percent of extraction was 40% for Cd(II) and around 10% for Ni(II). Of course it was the difference in time used. The SLM extraction required longer time to separate the ions.

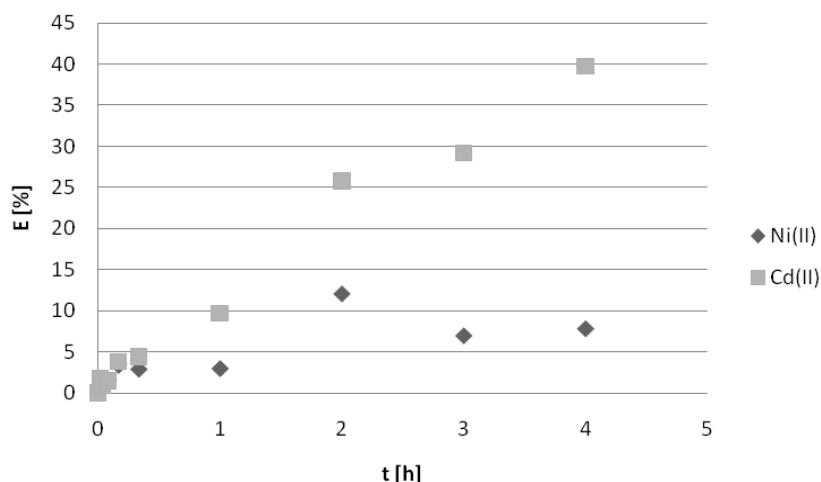


Fig. 4. Percent extraction of nickel(II) and cadmium(II) ions as a function of time [h] in SLM experiment. Donor phase: 0.01 M NiSO₄ and 0.01 M CdSO₄, pH = 3, acceptor phase 0.5 M H₂SO₄, liquid membrane: PTFE-filter soaked with D2EHPA solution in kerosene

Table 1. Comparison of separation of Ni(II) and Cd(II) from sulphate solution by different methods

	Concentration before experiment		Concentration after sorption		Concentration after desorption	
	Ni [mM]	Cd [mM]	Ni [mM]	Cd [mM]	Ni [mM]	Cd [mM]
Lewatit OC 1026	10.00	10.00	9.18	6.38	0.20	3.50
Lewatit TP 207	10.00	10.00	6.65	8.33	0.30	4.72
SLM	10.00	10.00	8.87*	6.60*	n/d**	3.84**

* Concentration in donor phase after 4 hours.

** Concentration in acceptor phase after 4 hours.

n/d - not detected

3. CONCLUSIONS

This paper discusses the possibility of separation of Ni(II) and Cd(II) ions from sulphate solution with both SLM and ion-exchange processes. The best separation Ni(II) and Cd(II) was obtained for SLM transport as was presented in Table 1. The experimental results show that among applied ion-exchangers better separation of metal ions was obtained for Lewatit OC 1026 but higher percent extraction was obtained for Lewatit TP 207. It was also found that desorption from resins used in the experiment is possible.

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SORPTION STUDIES OF CHROMIUM(VI) ONTO NEW ION EXCHANGER WITH TERTIARY AMINE, QUATERNARY AMMONIUM AND KETONE GROUPS

Grzegorz Wójcik¹, Violeta Neagu², Ion Bunia²

¹*University of Maria Curie-Skłodowska, Faculty of Chemistry Department of Inorganic Chemistry Pl. M. Curie-Skłodowskiej 2, 20-031 Lublin, Poland*

²*"Petru Poni" Institute of Macromolecular Chemistry, Gr. Ghica Voda 41A, Iasi, 700487, Romania*

e-mail: grzegorzwojcikumcs@wp.pl

The waste streams from the mining operations, metal-plating facilities, power generation facilities, electronic device manufacturing units, and tanneries may contain heavy metals with the concentrations exceeding the local discharge limits. These waste streams contain toxic heavy metals such as chromium, cadmium, lead, mercury, nickel, and copper. They are not readily removed without specialized or advanced treatment. Chromium is a common pollutant which occurs in the surface or groundwater due to the discharge of a variety of industrial wastewaters. On the other hand, chromium based catalysts are also employed in various chemical processes, including selective oxidation of hydrocarbons. According to the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit for total chromium is 0.05 mg/L.

A new acrylic anion exchanger with both tertiary and quaternary ammonium as well as ketone groups in the structural unit has been prepared by the nucleophilic substitution reaction of aminolyzed vinylacetate : acrylonitrile : divinylbenzene copolymer of porosity structure in the swelling state with 2-chloroacetone as a halogenated compound. The new compound exhibits better qualities of strong base exchange capacity than the weak base anion exchangers. The obtained acrylic anion exchanger was used to remove Cr(VI) from the aqueous solution. Batch adsorption studies have been carried out to determine the effect of contact time, concentration of hexavalent chromium in the solution and pH on the sorption capacity. The kinetic parameters were determined on the basis of the static results. The thermodynamic parameters of Cr(VI) sorption process on the anion exchanger were calculated based on the Langmuir and Freundlich isotherms. Sorption was studied in the pH range of 1.5 to 7 and it was found that it depends on the solution acidity. At the pH values of 3.5 and 7 the anion exchanger exhibited large values of chromium sorption capacity. The speciation of chromium was investigated in the studied pH range by the Diffuse Reflectance Spectroscopy (DRS) method. Reduction of chromium(VI) to chromium(III) under acidic conditions was observed. The performed acrylic strong base anion exchanger is superior compared to the conventional one based on the styrene: divinylbenzene matrix due to its ability for reposition of the long spacer arm for providing exchange sites, hydrophilic character of matrix, and possible hydrogen bonds provided by carbonyl functional groups.

PREPARATION AND PROPERTIES OF BIFUNCTIONAL CHELATING FIBERS CONTAINING IMINODIACETATE AND HYDROPHILIC MOIETIES

Hiroataka Matsuura¹, Hiromi Yonekawa¹, Akinori Jyo¹, Masao Tamada²,
Noriaki Seko² and Yuji Ueki²

¹*Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan*

²*Quantum Beam Science Directorate, Japan Atomic Energy Agency, 1233 Watanuki-machi, Takasaki, Gunma 370-1292, Japan
e-mail: hmatsu@chem.kumamoto-u.ac.jp*

1. Introduction

Chelating resins are useful for selective adsorption of heavy metal ions in water. However, one of their disadvantages is slow kinetics of metal ions uptake. To improve kinetic performances, we prepared fibrous chelating adsorbents having iminodiacetate group (1). More recently, we have developed bifunctional chelating fiber containing aminomethylphosphonate and sulfonate groups (2). The introduction of sulfonate group, which is dissociated even in a strong acid solution, as a second functional group into chelating adsorbents is more effective to improve kinetics in adsorption of metal ions. Indeed, column-mode uptake of Cu(II) was achieved even at extremely high flow rates of feeds up to 7000 h⁻¹ in space velocity (2). In this bifunctional chelating fibers, the metal ion selectivity was governed by both sulfonate and chelating functional groups. In the present study, we prepared two kinds of bifunctional iminodiacetate chelating fibers in which styrenesulfonate or methoxynona(ethylene glycol) methacrylate (MNEGM) was grafted and properties of the resulting bifunctional fibers were studied.

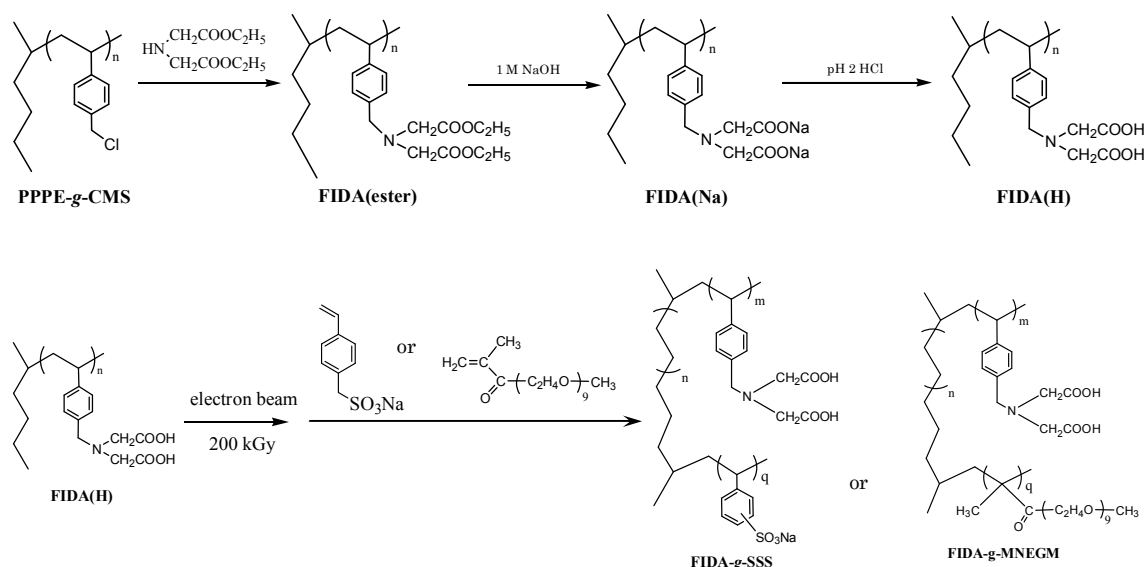
2. Experimental

2.1 Preparation of chelating fibers

Monofunctional iminodiacetate fiber, FIDA, was prepared from polyethylene-coated polypropylene fiber (PPPE) according to the scheme reported in the previous paper (1). Synthetic route of FIDA from PPPE is shown in Scheme 1. PPPE-*g*-CMS was prepared by the graft polymerization of chloromethylstyrene (CMS) onto PPPE after electron beam irradiation. Then, PPPE-*g*-CMS was functionalized with diethyl iminodiacetate, resulted in FIDA-ester. After alkali hydrolysis of ester moieties, the resulting fiber was treated with 1 M HCl and then equilibrated with dilute HCl of pH 2. After air-drying, it was dried in vacuum. Thus, FIDA in the hydrogen ion form was obtained.

Bifunctional iminodiacetate fibers were prepared individually by the graft polymerization of sodium styrenesulfonate (SSS) or MNEGM onto FIDA after electron beam irradiation. The both resulting bifunctional fibers are named FIDA-*g*-SSS and FIDA-*g*-MNEGM, respectively. Synthetic routes of FIDA-*g*-SSS and FIDA-*g*-MNEGM are also shown in Scheme 1. FIDA in the H⁺ form was irradiated with electron (2 MV, 200 kGy) and it was immersed in an aqueous solution of SSS at 40°C for 4, 8, 16, and 24 h to prepare FIDA-*g*-SSS,

and immersed in dimethyl sulfoxide solution of MNEGM at 40°C for 0.5, 1, and 2 h to prepare FIDA-g-MNEGM.



Scheme 1. Synthetic routes of FIDA, FIDA-g-SSS, and FIDA-g-MNEGM

Characterization of FIDA, FIDA-g-SSS, and FIDA-g-MNEGM was performed by determining nitrogen and sulfur contents and acid capacities. Nitrogen contents were determined by CHN analyses. Sulfur was analyzed by ion chromatography after combustion of the fibers. Acid capacities were estimated by determination of NaOH consumed by fibers in H^+ form after immersing them in 1 M NaOH for 24 h. FT-IR analyses were also carried out for characterization of the fibers to investigate their chemical structures. Degree of grafting (dg) of SSS or MNEGM was calculated by the following equation:

$dg (\%) = (\Delta W/W_0) \times 100$, where ΔW means a weight increase of fiber by grafting and W_0 means the weight of fiber before grafting.

2.2 Column-mode adsorption and elution of Cu(II)

FIDA (0.4030 g in dry weight), FIDA-g-SSS1 (0.4018 g in dry weight, dg = 49.58%), FIDA-g-MNEGM1 (0.4024 g in dry weight, dg = 35.55%), or FIDA-g-MNEGM2 (0.4082 g in dry weight, dg = 107.2%) was packed individually into a polyethylene column (i.d. 9 mm). Bed volumes of FIDA, FIDA-g-SSS, FIDA-g-MNEGM1, and FIDA-g-MNEGM2 in each column were 1.30, 1.40, 1.27, and 3.39 mL, respectively. Two polyethylene filters were placed at the bottom of the column and at the top of the fiber bed. Prior to adsorption of Cu(II), each column was conditioned by feeding an acetate buffer (pH 5.3). Then, 0.01 M of Cu(II) solution was supplied to the column at a flow rate of 100 h^{-1} in space velocity (SV). After the column was washed with water, adsorbed Cu(II) on the column was eluted with 1 M HCl. Flow rate of the eluent was 5 h^{-1} in SV. All effluents from the column were collected on a fraction collector. Concentration of Cu(II) in each fraction was determined by ICP-AES.

3. Results and Discussion

3.1 Characterization of FIDA, FIDA-g-SSS, and FIDA-g-MNEGM

In the FT-IR spectrum of FIDA, the band of hydroxyl group was observed around 3400 cm^{-1} . The bands of carboxylic acid and carboxylate anions were observed at 1732 and 1632 cm^{-1} , respectively, indicating zwitterionic structure

of iminodiacetate groups of FIDA in the H^+ form ($-NH^+(CH_2COOH)(CH_2COO^-)$). FT-IR spectrum of FIDA-g-SSS exhibits the band of sulfonate group at 1129 cm^{-1} . Thus, SSS is introduced onto FIDA by the graft polymerization. In the FT-IR spectrum of FIDA-g-MNEGM, the bands of alkyl ether were observed around 1100 cm^{-1} , which may indicate introduction of MNEGM onto FIDA.

Table 1 summarizes properties of FIDA, FIDA-g-SSS, and FIDA-g-MNEGM. Nitrogen content in FIDA was 2.16 mmol/g and acid capacity of FIDA was 4.33 meq/g . Acid capacity was in fairly good agreement with calculated value as twice the nitrogen content. As for FIDA-g-SSS, both degrees of grafting and sulfur to nitrogen molar ratios of fibers increased with an increase in the reaction time. Acid capacities calculated from the sum of twice the nitrogen content and sulfur content are in good agreement with observed ones listed in Table 1, except for FIDA-g-SSS1 (reaction time of 4 h). For column-mode uptake of Cu(II), FIDA-g-SSS1 (degree of grafting: 49.58%) was used because of the smallest sulfur to nitrogen molar ratio. In case of FIDA-g-MNEGM, the longer the reaction time, the higher the degrees of grafting. However, nitrogen content decreases with an increase in the degree of grafting. Acid capacities of FIDA-g-MNEGM listed in Table 1 were almost the same as calculated values. For column-mode uptake of Cu(II), FIDA-g-MNEGM1 (degree of grafting: 35.55%) and FIDA-g-MNEGM2 (degree of grafting: 107.2%) were used.

Table 1 Properties of FIDA, FIDA-g-SSS, and FIDA-g-MNEGM

Fiber	Reaction time (h)	dg (%)	N content (mmol/g-F)	S content (mmol/g-F)	Acid capacity (meq/g-F)
FIDA	-	-	2.16	-	4.33
FIDA-g-SSS1	4	49.58	1.21	1.90	3.54
FIDA-g-SSS2	8	76.45	1.01	2.04	4.03
FIDA-g-SSS3	16	82.80	0.96	2.20	3.81
FIDA-g-SSS4	24	116.6	0.84	2.44	4.21
FIDA-g-MNEGM1	0.5	35.55	1.43	-	2.51
FIDA-g-MNEGM2	1	107.2	1.26	-	2.08
FIDA-g-MNEGM3	2	174.7	0.52	-	1.40

3.2 Column-mode adsorption and elution of Cu(II)

Figure 1 shows column-mode adsorption of Cu(II) by FIDA, FIDA-g-SSS1, FIDA-g-MNEGM1, and FIDA-g-MNEGM2 and Table 2 summarizes numerical data on column-mode adsorption and elution of Cu(II). Breakthrough capacities and adsorbed amounts of Cu(II) on the fibers increased with an increase in the acid capacity. In the present experiment, column-mode uptake of Cu(II) was tested at pH 5.3, in which iminodiacetic acid was negatively charged (monovalent anion) because its pK_{a1} and pK_{a2} are 2.65 and 9.38,

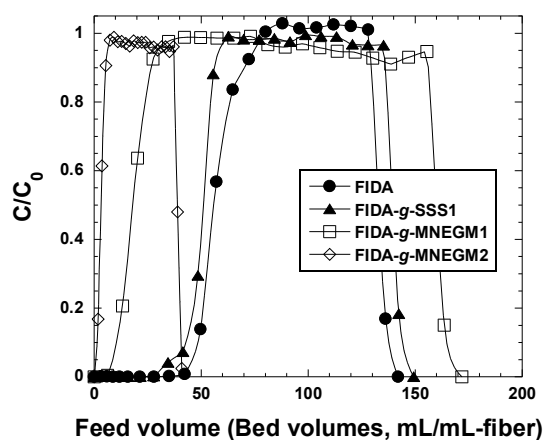


Fig. 1. Breakthrough profiles of Cu(II)
Feed: $0.01\text{ M Cu(NO}_3)_2$
Flow rate: 100 h^{-1} in space velocity

respectively. Thus, Cu(II) was easily adsorbed on even a monofunctional chelating fiber FIDA due to the effect of electrostatic repulsion between negatively charged iminodiacetate groups. Total uptake of Cu(II) on FIDA was estimated 88% of the amount of iminodiacetic acid in it. As for FIDA-*g*-SSS, 1.5 mmol/g of Cu(II) was adsorbed, which was larger than the amount of iminodiacetic acid (1.21 mmol/g), indicating that both iminodiacetate and sulfonate groups were related to Cu(II) uptake on FIDA-*g*-SSS. On the other hand, both FIDA-*g*-MNEGM1 and FIDA-*g*-MNEGM2 adsorbed less amount of Cu(II) compared to the former two fibers. Because of the introduction of uncharged hydrophilic functional group, negative charge density of FIDA-*g*-MNEGM1 and FIDA-*g*-MNEGM2 were lower than that of FIDA and FIDA-*g*-SSS. This may result in the differences of swelling ratios among the fibers. Therefore, it is difficult to discuss the results only from viewpoints of the amounts of iminodiacetate.

Iminodiacetic acid will be protonated at pH less than 2 and result in the decrease of negative charge density of the fibers. Evaluation of kinetic performances of the fibers should be further studied and is now in progress under strongly acidic conditions (pH less than 2) in order to investigate the roles of hydrophilic groups in the bifunctional chelating fibers.

Table 2 Summary of column-mode adsorption and elution of Cu(II) by FIDA, FIDA-*g*-SSS, and FIDA-*g*-MNEGM

Fiber	5% Breakthrough point (ml/ml-F)	5% Breakthrough capacity (mmol/g-F)	Adsorbed amount of Cu(II) (mmol/g-F)	Eluted amount of Cu(II) (mmol/g-F)	Recovery (%)
FIDA	48	1.6	1.9	1.8	97
FIDA- <i>g</i> -SSS1	36	1.1	1.5	1.5	99
FIDA- <i>g</i> -MNEGM1	7.9	0.21	0.67	0.55	83
FIDA- <i>g</i> -MNEGM2	0.8	0.02	0.21	0.19	92

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HYBRID ORGANIC-INORGANIC ION-EXCHANGERS FOR REMOVAL OF HEAVY METAL IONS FROM DILUTED SOLUTIONS

Yuliya S. Dzyazko¹, Ludmila N. Ponomarova¹, Yurii M. Volfkovich²,
Valentin E. Sosenkin², Vladimir N. Belyakov¹

¹*V.I. Vernadskii Institute of General & Inorganic Chemistry, Palladin Ave. 32/34, 03142, Kiev, Ukraine*

²*A.N. Frumkin Institute of Physical Chemistry & Electrochemistry, Lenin Pr. 31, 119991, Moscow, GSP-1, Russia*
e-mail: dzyazko@ionc.kiev.ua

Hybrid materials based on organic and inorganic ion exchangers demonstrate better functional properties comparing with those for individual components, namely high protonic conductivity up to 423 K (1) and selectivity towards toxic ions (2). Moreover modification of polymers with inorganic nanoparticles is known to result in improvement of their stability against fouling with organic substrates and bacteria (3). Swollen polymeric ion-exchangers include gel-like fields, when nanosized clusters (so called mesopores) and more narrow channels (meso- and micropores) are localized (4). Void volume between these fields are related both to mesopores and macropores. Nanoparticles of inorganic ion-exchangers can occupy gel-like fields as well as the voids between them. Functional properties of hybrid materials are undoubtedly influenced by localization of the inorganic constituent.

A number of hybrid ion-exchangers has been obtained by modification of strongly acidic gel-like cation-exchange resin Dowex HCR-S (Dow Chemical) with amorphous zirconium hydrophosphate (ZrPh), which was deposited from $ZrOCl_2$ solution by H_3PO_4 . The deposition occurred directly inside the resin particles. The ZrPh content in the polymer matrix was varied during the synthesis procedure. The inorganic constituent has been found to exist in the form of non-aggregated nanoparticles (4-20 nm) and their aggregates (Fig. 1), which size is up to several μm . Single nanoparticles are placed evidently inside clusters and channels, at the same time the aggregates are localized between the gel-like fields.

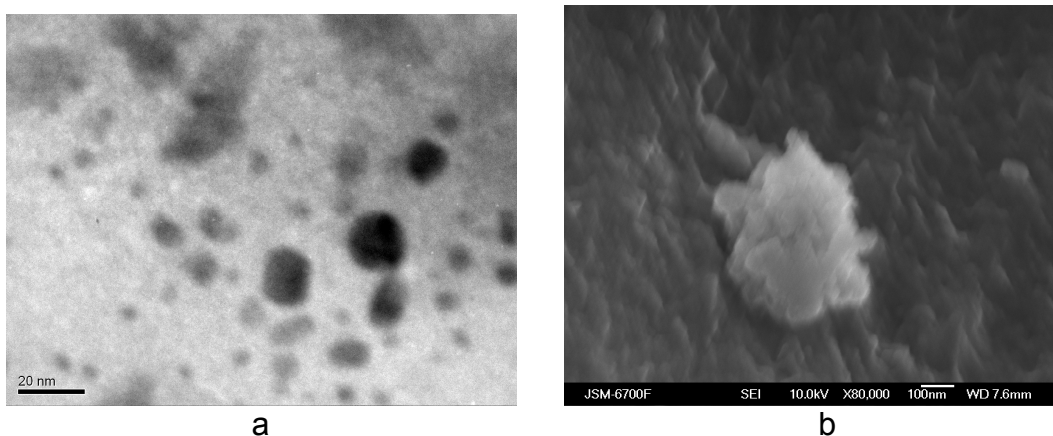


Fig. 1. TEM (a) and SEM (b) images of organic-inorganic ion-exchangers

During the synthesis procedure the void space between the gel fields is filled first by ZrPh aggregates (the mass increase is about 35%). Then the aggregates play a role of a barrier against co-ions (Cl^- , H_2PO_4^- and HPO_4^{2-}), thus the uptake of excess of counter-ions (ZrO^{2+} and H^+) is impossible. As a result, the aggregate formation is stopped, and non-aggregated nanoparticles are deposited preferably in the clusters of gel phase. This deposition provides only a small increase of mass (up to 3 %).

Porous structure of the modified matrix has been investigated with a standard contact porometry method, which can be applied to ion-exchange polymers (5). The measurements were carried out using water as a working liquid, the samples were previously vacuumized at 353 K. This temperature cannot provide removal of water, which is bonded with ZrPh surface as well as free water inside aggregate mesopores. Thus, only polymer structure has been recognized. As seen from the porogrammes, insertion of ZrPh into the matrix causes a decrease of mesopore volume (Fig. 2) probably due to corking of the cluster and channel mouths by the nanoparticles. Simultaneously, the maximum at 10 nm becomes wider indicating stretching of the clusters under the influence of inorganic constituent. Increase of macropore volume is evidently due to their stretching caused by the nanoparticle aggregates. Pores, which are attributed to the aggregates, allow water penetration to the matrix macropores during the porometric measurements as opposed to non-aggregated nanoparticles (they form a barrier against water in clusters and channels).

Stretching and corking of meso- and macropores of the polymer are two competitive factors, which cause maxima on the dependencies of swelling (for H-form) as well as shrinkage (for Na- and Cd-forms) vs ZrPh content (Fig. 3). In the case of H- and Na-forms the maxima evidently indicate the end of aggregate formation in the clusters. As for Cd-forms, the maximum is shifted towards higher ZrPh content.

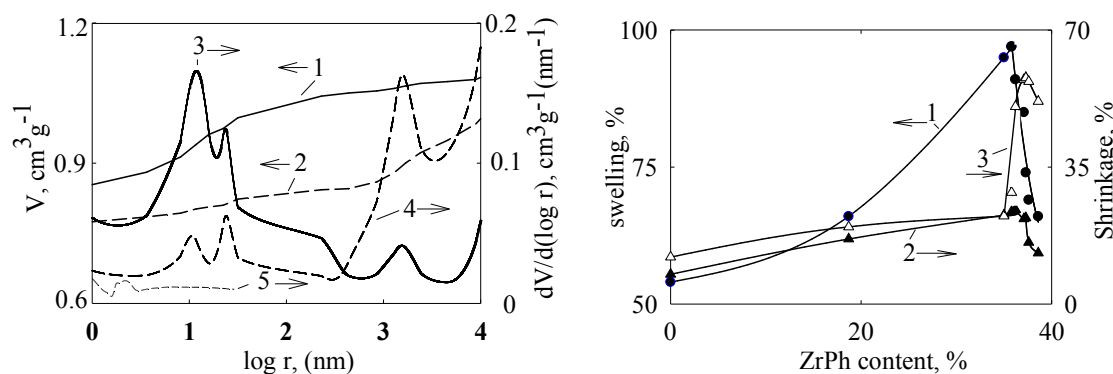


Fig. 2. Integral (1, 2) and differential (3-5) pore distribution obtained for initial (1, 3), modified polymer matrix (2, 4) and ZrPh (5)

Fig. 3. Swelling of H⁺-form (1), shrinkage of Na- (2) and Cd- (3) forms comparing with H⁺-forms as functions of ZrPh content in the matrix

Kinetics of $\text{Cd}^{2+} \rightarrow \text{H}^+$ exchange has been investigated using a "thin layer" method similarly to (6). Particle diffusion was found to be a rate-determining stage, thus the following equation (7):

$$B\tau = 2\pi - \frac{\pi^2}{3}\beta - 2\pi\left(1 - \frac{\pi}{3}\beta\right)^{0.5}, \quad (1)$$

can be applied. Here β is the degree of process completion, τ is the time, B is the kinetic parameter, $B = \frac{4\pi^2 \bar{D}}{\bar{d}^2}$, where \bar{D} is the diffusion coefficient, \bar{d} is the particle diameter. In the case of isotope exchange the plot of $B\tau - \tau$ is linear, the \bar{D} value is attributed to the self-diffusion coefficient (\bar{D}'). When different ions are exchanged, no linearity is observed (Fig. 4). Thus the Helfferich model is valid (8):

$$\bar{D}_{Cd,H} = \frac{\bar{D}'_{Cd} \bar{D}'_H (z_{Cd}^2 \bar{C}_{Cd} + z_H^2 \bar{C}_H)}{\bar{D}'_{Cd} z_{Cd}^2 \bar{C}_{Cd} + \bar{D}'_H z_H^2 \bar{C}_H}, \quad (2)$$

Here \bar{C} is the concentration and z is the valence. $\bar{D}_{Cd,H}$ corresponds to \bar{D}'_{Cd} at $\bar{C}_{Cd} \rightarrow 0$.

Larger values of Cd^{2+} self-diffusion coefficient were found for the modified samples, though the interaction with functional groups of inorganic constituent had been expected to be a brake of diffusion. This is evidently due to stretching of the polymer. Moreover a small size of ZrPh particles incorporated into the matrix results in higher rate of ion exchange comparing with that for individual inorganic material (the order of \bar{D}'_{Cd} value is $10^{-13} \text{ m}^2 \text{ s}^{-1}$).

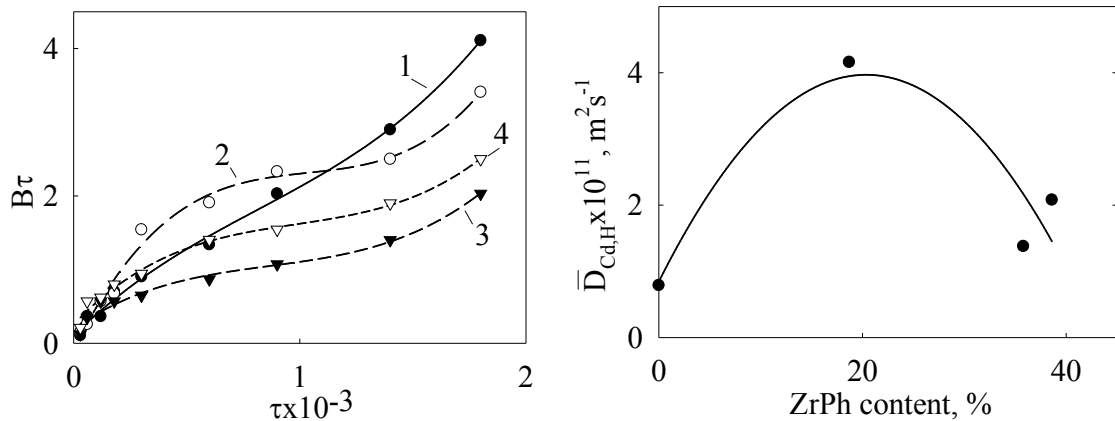


Fig. 4. Time dependencies of $B\tau$ for initial (1) and modified resins containing 19 (2), 36 (3) and 39 (4) mass % ZrPh

Fig. 5. Self-diffusion coefficient of Cd^{2+} as a function of ZrPh content in the matrix

Higher selectivity towards Cd^{2+} ions comparing with Ca^{2+} was found for modified samples. Ion-exchange capacity has been also estimated theoretically using corresponding data for individual components as well as their content in the samples. The experimental data are higher than calculated ones. Thus the nanocomposites show synergism of ion-exchange properties, which is evidently

caused by ZrPh surface development in the polymer. This compensates a decrease of matrix micro- and mesoporosity. "Strong sorption centers" of the nanocomposite can be related to pores in the aggregates, which are formed during the first synthesis stages. This assumption is confirmed by Langmuir isotherms (Fig. 7): a slope of the lines is independent on ZrPh content, which is regulated by a number of modification procedure cycles.

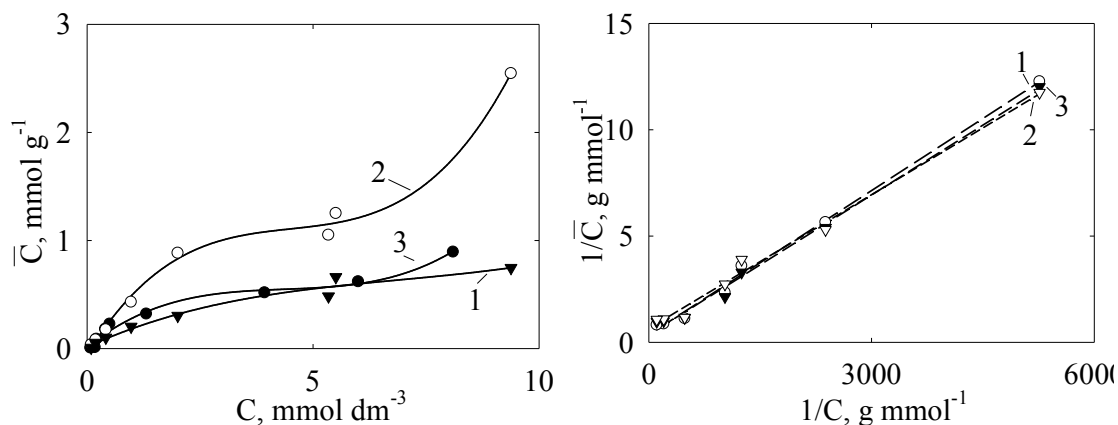


Fig. 6. Calculated (1) and experimental isotherms of $\text{Cd}^{2+} \rightarrow \text{H}^+$ (1, 2) and $\text{Ca}^{2+} \rightarrow \text{H}^+$ (3) for the modified ion-exchanger

Fig. 7. Langmuir Isotherms of $\text{Cd}^{2+} \rightarrow \text{H}^+$ exchange for the samples containing 19 (1), 36 (2) and 39 (3) mass % ZrPh

Thus the ion-exchange resin modified with nanoparticles of ZrPh shows synergism of ion exchange properties, which is a result of surface development of the inorganic constituent on the one hand and transformation of the polymer porous structure on the other hand. Insertion of inorganic material into the polymer leads also to increase of ion exchange rate. Preferable Cd^{2+} uptake as well as relatively low shrinkage after loading with Cd^{2+} have been found for the samples, which contain up to 30 mass % ZrPh in the form of non-aggregated and aggregated nanoparticles. No aggregate formation is during further insertion of ZrPh, the nanoparticles, which are deposited in the clusters, results in increase of shrinkage degree and does not influence on selective Cd^{2+} uptake.

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SEPARATION OF CHROMIUM(III) FROM WASTES OF CHROMIUM-TANNED LEATHERS. EXPERIMENTS AND KINETIC MODELS

Barbara Wionczyk¹, Wiesław Apostoluk²

¹*Institute of Leather Industry, Zgierska 73, 91-462 Łódź, Poland,*

²*Division of Chemical Metallurgy, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland;
e-mail: wionczyk@ips.lodz.pl*

INTRODUCTION

The leather industry generates large amounts of liquid and solid wastes both containing chromium(III) and free of its compounds. Total quantities of different solid chromium(III) wastes depend on applied technology and on kind of produced leathers. The recovery of chromium(III) from the solid tannery wastes has both ecological and economical consequence because reduces contamination of environment and may prevent losses of large amounts of chromium(III) compounds and also collagen proteins that could be reused in other industrial processes. From literature it comes that many different methods have been examined for separation of chromium(III) from solid tannery wastes, especially from wastes of chromium-tanned leathers. Generally, biochemical, hydrometallurgical, and thermal methods as well as their combination have been studied on the removal of chromium(III) from such wastes. Process used in this work us for separation of chromium(III) from selected wastes of chromium-tanned leathers consists of two the main stages, namely: (i) the alkaline hydrolytic decomposition of the leather wastes under which chromium(III) passes, without oxidation, from the wastes to an alkaline solution in the form of soluble hydroxocomplexes and (ii) the separation of chromium(III) from the resulting alkaline protein hydrolyzate by the solvent extraction with Aliquat 336 and stripping operation with sulphuric acid. We also show kinetic analysis of alkaline decomposition of the chromium leather waste under isothermal conditions with the application of some important kinetic models used usually for analysis of heterogeneous processes (1).

EXPERIMENTAL

Chromium-tanned leather wastes were obtained by grinding of various useless pieces of uncolored finished leathers. They contained 2.2% of Cr(III) and 12.1% of total nitrogen with reference to dry matter. The leather wastes were hydrolyzed with 0.2 M and 0.3 M NaOH solutions at the liquid/solid phase ratio (V/m) equal to 80 cm³/g and at different constant temperatures from 303 K to 343 K.

In the extraction: feed aqueous phases were freshly obtained alkaline protein hydrolyzates and the organic phases were 0.05 M solutions of trioctylmethylammonium chloride (Aliquat 336) in heptane, modified with 1%(v/v) of 1-decanol. The effect of time, temperature and volume phase ratio on the Cr(III) extraction from hydrolyzate was examined. Chromium(III) was stripped from the loaded organic phase with 0.5 M sulphuric acid at 25°C and at volume phase ratio equal to 1.

RESULTS AND DISCUSSION

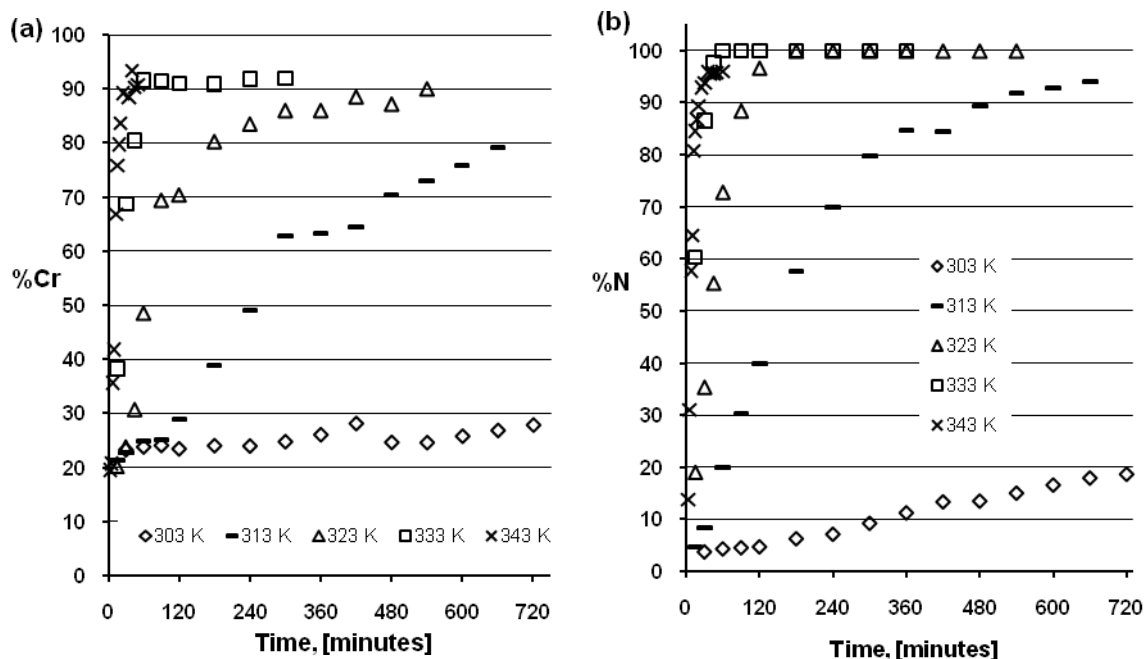


Fig. 1. The effect of time and temperature on percent of (a) - Cr(III) and (b) collagen proteins which went in some soluble forms from the leather wastes to 0.2 M NaOH solution at the ratio of liquid/solid phases equal to 80 cm³/g

Results in Figure 1 indicate that longer time of hydrolysis and elevated temperature affected positively the hydrolytic decomposition of the wastes of chromium leathers with 0.2 M NaOH. Moreover, our studies proved that application of NaOH solution of higher concentration (0.3 M) shorten the time needed for complete decomposition of the wastes at constant temperature.

The evaluation of kinetic parameters {activation energy (E) and frequency factor (A)} is difficult if the reaction mechanism is unknown. The different models/rate equations and corresponding to them mechanisms/factors limiting the total rate of a process are proposed in literature (1). In Table 1 the symbols of some of the most important models and related to them mechanisms are shown. Each symbol and mechanism is represented by appropriate rate equation in its integral, $g(\alpha)$, and differential, $f(\alpha)$, form, where α denotes the extent of reaction/process. The extent of hydrolytic decomposition of the leather wastes in the studied heterogeneous system was measured by dimensionless degree of "transformation" of the each of two main components that are present in the wastes of leathers, namely by fractions of Cr(III) (α_{Cr}) and of the total nitrogen (α_N) dissolved in alkaline solution after the defined time of hydrolysis at different constant temperatures from 313 K to 343 K. The results at 303 K were omitted in kinetic analysis because studied process was at the beginning (see Fig. 1). Then, the mechanism of the reaction/process was determined by testing the accuracy of mathematical fit of the experimental data (α_{Cr} , α_N) to the relationships between: α vs. time { $g(\alpha) = kt$ } and $d\alpha/dt$ vs. α { $d\alpha/dt = kf(\alpha)$ }, expressed, respectively, by the integral and differential forms of models that symbols are given in Table 1. The linearity of these dependencies was checked by the multiple regression analysis using the standard statistical criteria. It was found that the alkaline leaching of chromium(III) from the wastes is best

described by more than one of the models (D2-D4; R3; F1; F2). So, it means that this process is probably limited by several factors, and their contribution changes in a random way with temperature. Consequently, the diffusion and chemical reaction at phase boundary substrate-product (contracting volume and reaction order) may have a significant influence on kinetics of the dechromation of the leather wastes. The contracting volume and the first order rate equations (R3; F1) are the best descriptions of the experimental data (α_N) observed for hydrolysis of collagen of the leather wastes, and then, these factors limit the total rate of this process. From the best fitted models the rate constants (k) were determined for the leaching of Cr(III) and hydrolysis of collagen at different constant temperature within the range of 313 – 343 K. After that, the activation energies and the frequency factors were found out for the both processes from relation of the rate constants vs. reciprocal of absolute temperature (Arrhenius equation). Moreover, it was established that increasing concentration of NaOH solution used for decomposition of the leather wastes leads to the increase of the rate of both the chromium(III) leaching and the collagen hydrolysis. This positive effect is reflected in values of the frequency factors (A) but does not affect the activation energies (E) of both processes.

Table 1. Some of the most important models proposed for kinetic analysis of heterogeneous processes (1)

Kind of kinetic model	Symbol	Mechanism
Deceleratory α -time		
Geometrical models	R2	phase boundary controlled reaction (contracting area)
	R3	phase boundary controlled reaction (contracting volume)
Diffusion models	D1	one-dimensional diffusion
	D2	two-dimensional diffusion
	D3	three-dimensional diffusion (Jander equation)
	D4	three-dimensional diffusion (Ginstling-Brounshtein equation)
'Order of reaction' models	F0	zero order
	F1/ A1	first order /Avrami-Erofeev equation, n=1
	F2	second order
Sigmoid α -time		
	A2	random nucleation and growth of nuclei through different nucleation and nucleus growth models (Avrami-Erofeev equation, n=2)
	A3	Avrami-Erofeev equation, n=3
	A4	Avrami-Erofeev equation, n=4
	B1	Prout-Tompinks equation

Our previous studies revealed that Aliquat 336 effectively extracted Cr(III) from both the model alkaline solutions (2-5) and industrial spent tanning chromium baths (6). The positive results of those studies empowered us to examine of this method for separation of Cr(III) from the alkaline protein hydrolyzate obtained

by hydrolytic decomposition of the wastes of chromium-tanned leathers. It was found that the chromium(III) extraction with Aliquat 336 from the hydrolyzate at 50°C does not depend on shaking time from 15 to 150 minutes and on the aqueous/organic phase volume ratio from 1/1 to 5/1. Elevated temperature positively affected the extraction of Cr(III) in this system while an increase of NaOH concentration in the aqueous phase reduced slightly the quantity of Cr(III) extracted to the organic phase.

CONCLUSIONS

The average values of the activation energies (E) and the frequency factors (A) determined for the kinetic models describing the best the alkaline leaching of Cr(III) and the hydrolysis of collagen of the leather wastes are as follows:

$E_{Cr} = 122 \pm 2 \text{ kJ/mol}$; $\ln A_{Cr} = 34.4 \pm 1.8 \text{ s}^{-1}$, and $E_N = 96 \pm 3 \text{ kJ/mol}$; $\ln A_N = 25.5 \pm 0.3 \text{ s}^{-1}$, respectively.

At temperature 50°C and at the aqueous/organic phase volume ratio equal to 5/1, chromium(III) is effectively removed (99%) with Aliquat 336 from the alkaline hydrolyzate originating from the decomposition of the wastes of chromium leathers.

It was demonstrated that during one cycle of alkaline hydrolysis followed by the extraction and stripping operations, chromium(III) is separated from the source leather wastes with the total yield over 90%. The final products are: the protein hydrolyzate contaminated with traces of Cr(III) (less than 5 ppm) and the solution containing on the average 4.4 g/dm³ of Cr₂(SO₄)₃ and small quantities of protein substances.

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SELECTIVE REMOVAL OF LITHIUM FROM NATURAL WATERS BY INORGANIC SORBENTS AND MEMBRANES

V. N. Belyakov¹, V. M. Linkov², S. L. Vasilyuk¹

¹*Vernadsky Institute of General and Inorganic Chemistry NAS Ukraine
Palladin av. 32/34, Kiev 03142, Ukraine*

²*University of the Western Cape, Modderdam Road, Bellville 7535,
Republic of South Africa
e-mail: belyakov@ionc.kiev.ua*

Lithium plays an important role in industrial development of modern society. Lithium is used in a wide array of applications including batteries, glass ceramic, refrigerants and systems of air drying, energy, special oils and lubricants as metals and light structural alloys, etc. The demand for lithium metal and new lithium compounds will continue to grow. For example, the consumption of lithium for the production of batteries is increasing annually by more than 20%, encourages the search for new sources of raw materials and the developing of effective methods for lithium extraction. As promising sources of lithium raw materials currently being considered: seawater (one (metric) ton of seawater holds 0.17 grams of lithium on the average), brines after the desalination of sea water, groundwater and mine waters. A distinctive feature of such raw materials is a significant content of other metals salts. Effective extraction of lithium from these solutions is possible with the help of modern sorption-membrane methods, such as electrodeionization. However, the main condition for the efficiency is use of selective ion-exchanges and membranes.

It is known relatively long time that for the improving of selective properties of the inorganic sorbents and membranes relative to lithium ions the method of thermal modification can be used. Accordingly to this method, amorphous sorption-membrane matrix saturated predetermined ions during the synthesis and heat treatment is carried out. The result is changes in the structure of the material due to the inclusion of ions to the inorganic matrix. The subsequent removal of introduced ions from the matrix leads to the formation of structurally organized centers of selective sorption. Special feature of these sorption centers is the three-dimensional interaction of adsorbed ions with the matrix of the sorbent. The energy of this interaction includes not only the Coulomb forces, but also the possibility of solvation of the adsorbed ion by functional groups of the sorbent.

The ability of hydrated Mn(IV) oxide to the ion-thermal formation by Li⁺ ions, was shown at the synthesis of inorganic ion exchanger ISMA-1, which has high selectivity and capacity characteristics for the adsorption of these ions from various solutions, including natural highly mineralized waters (1,2). However, the widespread use of such ion-exchange materials based on manganese dioxide did not get that, probably due to their low mechanical properties. It can be assumed that poor strength of materials connected to the fact that their synthesis is usually leads through a stage of precipitation. In the 2000's, such studies have been reviewed (3-5). Problem of mechanical strength and, in

particular, granulation of ion-exchangers, was eliminated by the use of polymeric binders, while losing sorption capacity.

Another way to obtain such materials could be synthesis through the stage of gelation. However, the lack of literature reference on the synthesis of a hydrated Mn(IV) oxide through the stage of gelation and the negative results, obtained while attempted to develop such a synthesis methods, showed that only introduction of manganese dioxide into the gel of other polyvalent metals can be possible way for the increasing of mechanical properties of manganese containing ion-exchange materials. In this case, one should bear in mind that the decrease of the sorption capacity per unit mass in a two-component system does not happen if the gelation component also has the adsorptive capacity towards Li^+ ions.

The possibility of synthesis of hydrated titanium dioxide through the stage of gelation and property of this material to improve the sorption ability relative to the Li^+ ions, as a result of a heat treatment, gave grounds to expect that a combination of titanium dioxide and manganese oxide in an inorganic ion-exchange material would provide the ion-exchanger having good mechanical properties and improved, compared with sorption properties of titanium dioxide, towards lithium ions. A specially designed synthesis method allowed us to obtain titanium-manganese oxide materials in the form of solid granules (2-4 mm) and to study an influence of their sorption properties at the ion-thermal modification.

Figure 1 shows the effect of heat treatment of materials saturated with lithium ions on the sorption capacity towards lithium ions.

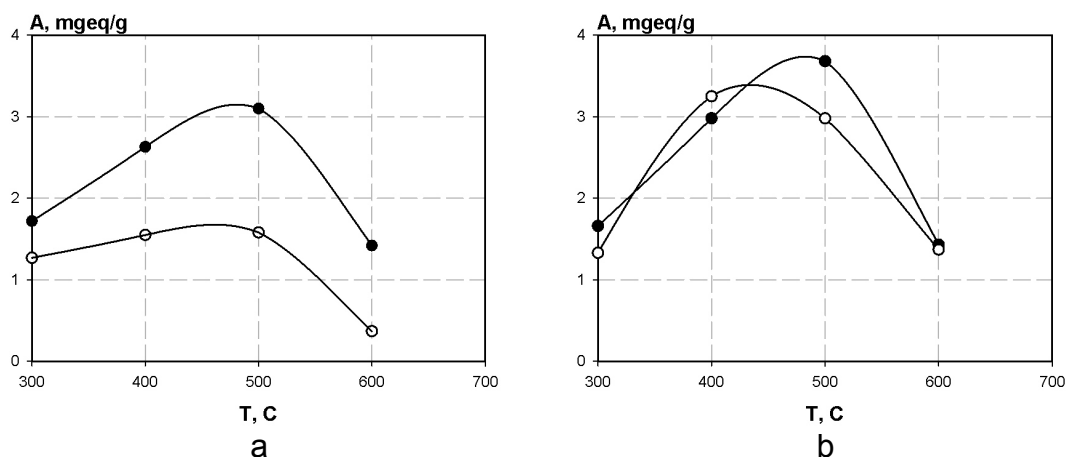


Fig. 1. The dependence of ion-exchange capacity for Li^+ ions at its sorption from 0.1 N LiCl solution at pH 8 (a) and pH 11 (b) from the temperature of formation of hydrated oxides Ti(IV) (○) and Ti(IV)-Mn(IV) (●)

It was found that the process of thermal modification leads to a significant increase in sorption capacity relative to lithium ions when heat treatment temperature was increased. In this case, as follows from the Figure 2, the selectivity of sorption of lithium ions towards sodium ions increases significantly.

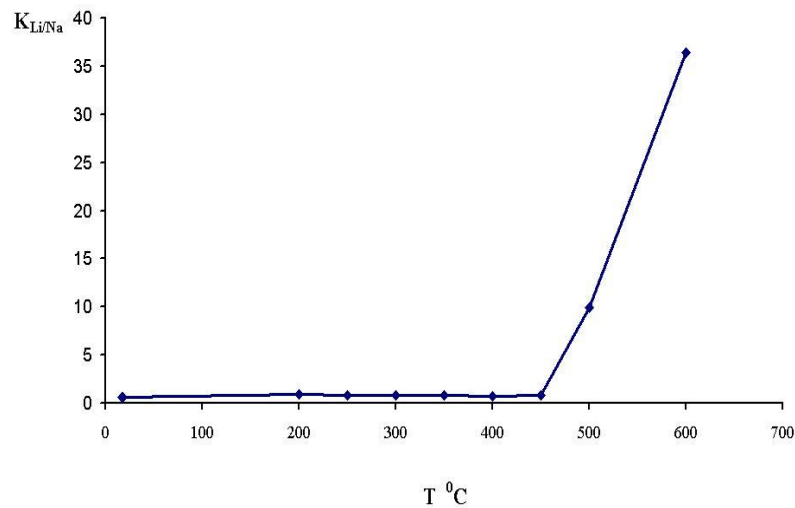


Fig. 2. Effect of heat treatment on the sorption selectivity coefficient of lithium ions relative to sodium ions for the oxide materials $TiO_2-MnO_2 = 1:1$ type

Another example of the selectivity for obtained materials is shown in Figure 3.

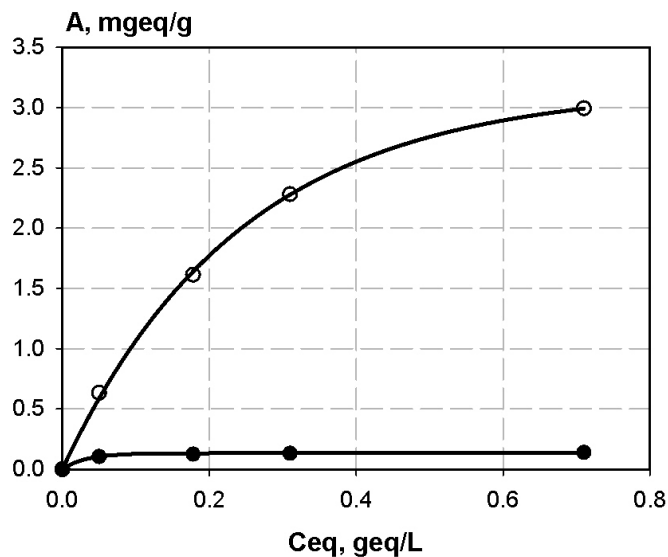


Fig. 3. Sorption isotherm of Li^+ ions (\circ) from 0.5 N NaCl solution at specifically formed ion-exchange materials based on $TiO_2 - MnO_2$ (\bullet sorption of Na^+ ions)

As can be seen from the curves in Figure 3, the selectivity of sorption of Li^+ ions in the presence of significant amounts of Na^+ ions by binary oxide material passing a specific formation is high - the material practically does not adsorb sodium ions.

To developed material based on TiO_2-MnO_2 effect sorption of Li^+ ions in presence of Na^+ ions has been studied. This experiment simulated the sorption of Li^+ ions from a solution containing 0.5 mol/L NaCl and 0.0176 mol/L LiCl. The results are shown in Figure 4.

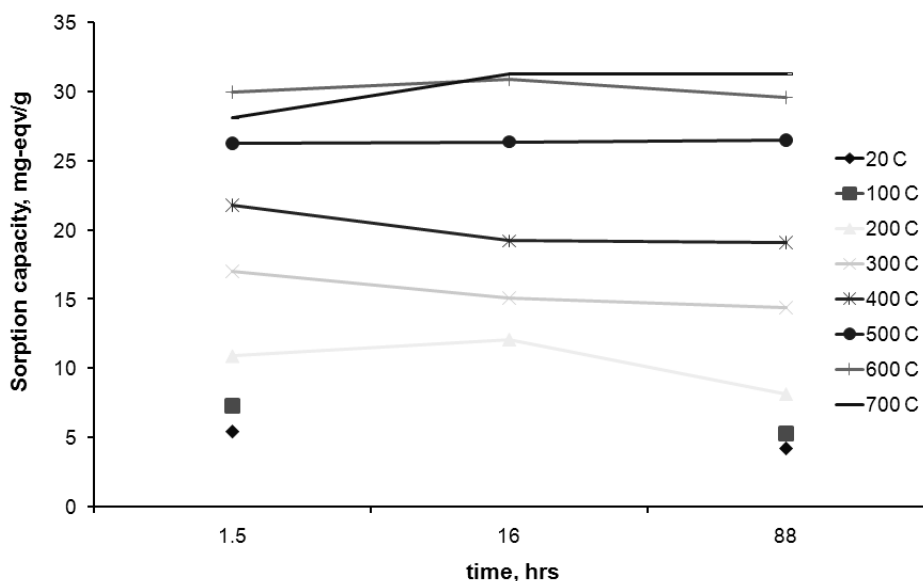


Fig. 4. Sorption capacity of the ion-exchanger relative to the lithium ions on a background of sodium ions depending on the time of the interaction ion-exchanger-solution

Described experimental results confirmed the perspective of the chosen direction in the choice of sorption materials for selective extraction of lithium ions from aqueous solutions.

Based on these results, were synthesized lithium-selective ceramic membranes, which are currently being investigated.

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THE SYNTHESIS OF SULFONAMIDE BASED POLYMERIC SORBENTS FOR SELECTIVE REMOVAL OF MERCURY FROM WATER

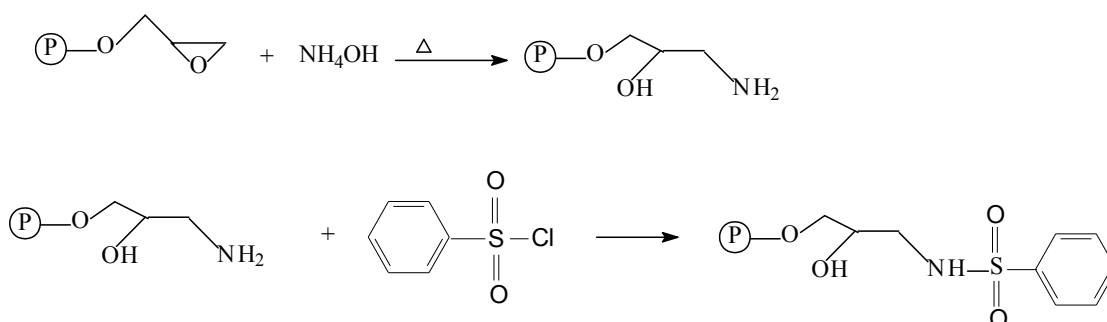
B. Filiz Senkal, Inan Kucukkaya, Erdem Yavuz

*Department of Chemistry, Istanbul Technical University, Maslak-Istanbul 34469, Turkey
e-mail: bsenkal@itu.edu.tr*

Mercury represents a serious environmental problem because it is widely used in many industries and applications. Among these, paper industry, paints, cosmetics, thermometers, manometers, fluorescent lamps and mercury batteries (1).

The use of polymer-bonded ligands in selective mercury removal has been the subject of many research articles (2,3) and reviews (4,5). Two common ligand types, sulfur and amide are being used currently in the design of polymer sorbents for binding mercuric ions selectively.

In this study, new polymeric resins with sulfonamide pendant functions have been prepared for the selective extraction of mercuric ions. Crosslinked poly(glycidylmethacrylate)(PGMA) – ethyleneglycol dimethacrylate (EGDMA) resin was prepared by using suspension polymerization method. The resin was treated with ammonia to obtain amine functional group. The resulting resin was reacted with benzene sulfonyl chloride to obtain sulphonamide pendant methacrylates based sorbent (resin 1).

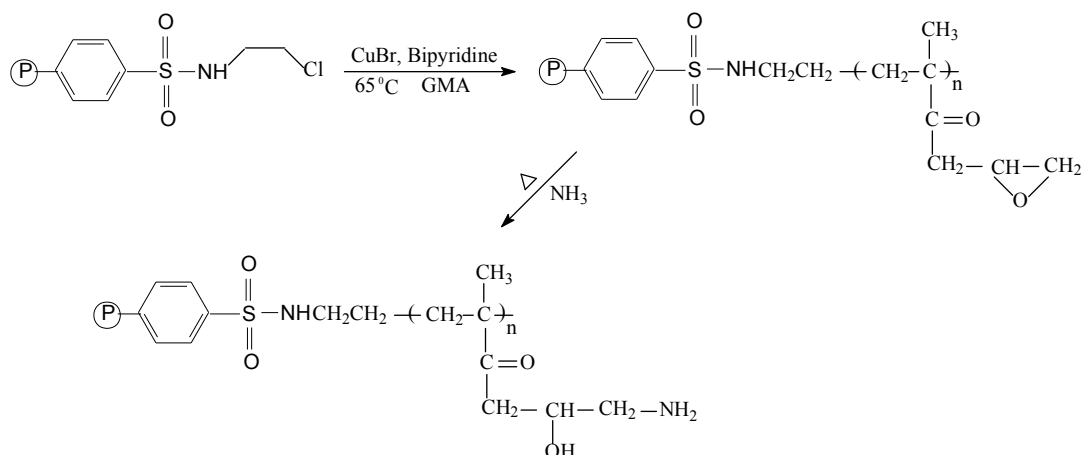


Scheme 1. Preparation of sulfonamide based resin (resin 1)

Linear polymers grafted onto crosslinked polymer resins offer numerous potential applications due to the combination of the non-solubility of resin and the flexibility of the graft polymer side chains as the functional group carrier.

The surface-initiated atom transfer radical polymerization (SI-ATRP) technique has attracted great interest for the surface grafting of high-density polymer brushes with controlled molecular weight, molecular weight distribution, and well defined structure (6–8).

Poly(glycidyl methacrylate) was grafted onto crosslinked poly(styrene) beads through the 2-chloroethyl sulphonamide groups present in the resin using ATRP polymerization method described in the literature (9).



Scheme 2. Preparation of sulfonamide containing core-shell type resin (resin 2)

The resin 1 and resin 2 are efficient sorbents for removal mercury through the sulfonamide groups. On the basis of the basic reaction of the mercuric ions with sulfonamide groups, this yielded covalent mercury–sulfonamide linkages.

The mercury loading capacity of the resin were found as about 1.50 and 1.60 mmol·g⁻¹ resin 1 and resin 2, respectively. Also, mercury uptake kinetic measurement studies for these resins were performed. To investigate the efficiency of the resins in the presence of trace quantities, batch kinetic sorption experiments were performed with highly diluted HgCl₂ and Hg(CH₃COO)₂ solutions. The sorbed mercury in these resins can be eluted by repeated treatment with HCl without hydrolysis of the sulfonamide groups.

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CHROMIUM ADSORPTION ONTO ACRYLONITRILE-DIVINYLBENZENE DERIVED ACTIVATED CARBON

Dilek Duranoğlu¹, Andrzej W. Trochimczuk², Ülker Beker¹

¹*Yildiz Technical University, Chemical Engineering Department, Davutpasa Campus, Esenler 34210, Istanbul, Turkey*

²*Faculty of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
e-mail: dilekdur@gmail.com; dduran@yildiz.edu.tr*

Chromium compounds are widely used in industries such as leather, textile, metal plating, battery and pigments. Chromium exists in the aqueous media mainly in two states: Cr(III) and Cr(VI). The hexavalent form is considered to be more hazardous due to its carcinogenic properties. Contact with chromium can cause severe health problems from simple skin irritation to lung carcinoma (1). It is therefore essential to remove Cr(VI) from wastewater before disposal. The permissible limit for Cr(VI) in potable water is 0.05 mg/L in Turkey. Similarly, American Environmental Protection Agency (EPA) limits this value to 0.05 mg/L (2). There are various methods including chemical precipitation, ion exchange, membrane processes, electrodialysis and adsorption for removing chromium compounds from aqueous media (1, 3-6). Among them adsorption by activated carbon is very effective because of high specific surface area and pore volume plus specific surface functionalities.

Activated carbons can be produced from many carbonaceous materials available at low cost, both naturally occurring and synthetic (7). In contrast to activated carbons obtained from natural products, the pore structure of polymer-derived carbons can be better controlled by the proper choice of the precursor material i.e. its own porosity, chemical composition and pore size distribution. Polymer-derived carbons display considerable high adsorption capacity due to high specific surface area and are more stable and mechanically resistant than other types of carbonaceous materials. Also, polymers in the shape of beads received some attention due to good hydrodynamic properties of the resultant carbons in fix bed/fluidized bed type separation applications.

It was aimed to evaluate Cr(VI) adsorption from aqueous solution in batch system by using new activated carbon developed from acrylonitrile-divinylbenzene copolymer in this work. Acrylonitrile-divinylbenzene copolymer beads (AN/DVB) were prepared by suspension polymerization method with hexadecane and toluene (1:9 w/w) as diluents. Polymerization mixture consisted in one third from monomers and in two thirds of inert diluents. The level of crosslinker was set at 40 wt.-%. Full details of the polymerization were given in (8). The activation of AN/DVB beads was performed in two successive stages: air oxidation at 300°C and final carbonization at 850°C under inert atmosphere. Detailed production conditions of polymer based activated carbon were reported previously (9). The produced polymer based activated carbon was abbreviated as ANDVB-AC. The some characteristics of produced activated carbon are given in Table 1.

Cr(VI) adsorption has been investigated at different process parameters like pH, carbon dosage, contact time and temperature. Cr(VI) sorption capacity of carbon samples was strongly dependent on pH of the solution. It can be seen from Figure 1, maximum Cr(VI) sorption capacity was obtained at pH 2 and it was decreased with increasing pH. The high Cr(VI) sorption capacity at low pHs could be explain that the electrostatic attraction between positively charged groups on carbon surface and HCrO_4^- ions.

Table 1. Characteristics of ANDVB-AC (9)

	ANDVB-AC
Product yield (%)	46
BET surface area (m^2/g)	579
Pore volume (cm^3/g)	0.300
Micropore volume (cm^3/g)	0.234
Acidic groups (meq/g) ^a	0.8802
Basic groups (meq/g) ^a	0.4918
Point of Zero Charge (PZC) ^b	8.2
Isoelectric Point (IEP) ^c	4.8
C (%)	82.29
H (%)	1.38
O (%)	11.85
N (%)	4.485
N (mmol/g) ^d	3.35

^a Measured by Boehm Method, ^b Obtained from potentiometric titration data, ^c Obtained from zeta potential measurements,

^d Measured by Kjeldahl Method

It is very important to evaluate the adsorption equilibrium and dynamics characteristics by using theoretical models in order to design and control the adsorption process units. For that reason, equilibrium adsorption data were applied to Langmuir and Freundlich adsorption model and pseudo first and pseudo second order rate equations were used to describe adsorption kinetics. All experimental isotherm curves show typical Type 1 shapes according to IUPAC classification at pH 2 and 4 (Fig. 1a, b, e, f). As shown in figure Cr(VI), Freundlich equation is well represent the adsorption of Cr (VI) ions onto ANDVB-AC.

The kinetic experiments were carried out at different temperature in order to investigate the effect of temperature on adsorption rate and to calculate the activation energy. As can be seen from Table 2 the correlation coefficients for the linear plots of pseudo first order model are 0.828 and 0.877, which indicates the poor correlation of Cr(VI) adsorption onto ANDVB-AC. Application of a pseudo second order model provides much better correlation coefficients, which is 0.999. Moreover, there is an excellent correlation between the calculated q_e values from the pseudo second order kinetic model and the experimental q_e values. Cr(VI) adsorption onto polymer based activated carbon follows the pseudo second order kinetic model. The pseudo second-order kinetic model suggests that the sorption process involves chemisorption mechanism (10,11).

Therefore, it may be concluded that Cr(VI) adsorption onto obtained adsorbents could consist of chemical adsorption.

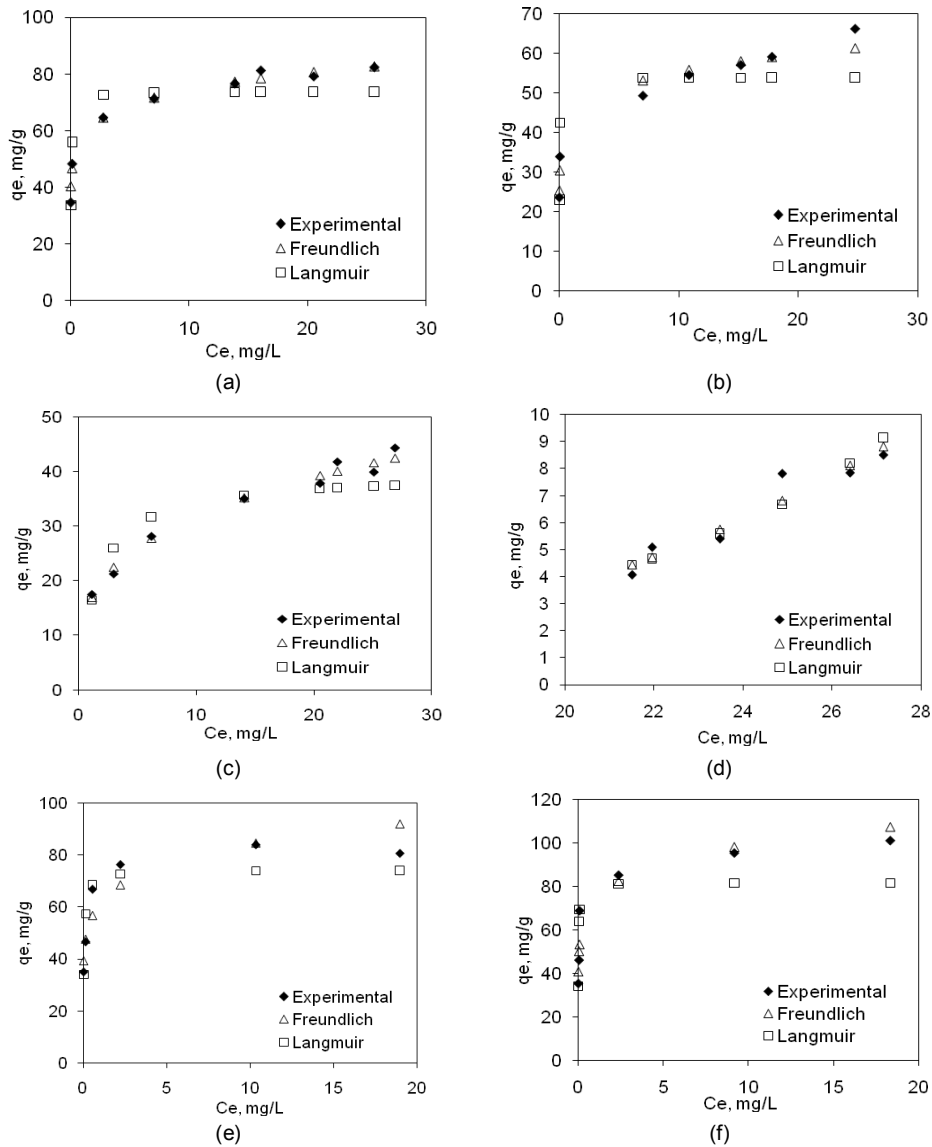


Fig. 1. Comparison of the experimental and theoretical adsorption isotherms (a) C_i :30ppm, pH:2, T:295K (b) C_i :30ppm, pH:4, T:295K (c) C_i :30ppm, pH:6, T:295K (d) C_i :30ppm, pH:8, T:295K (e) C_i :30ppm, pH:2, T:305K (f) C_i :30ppm, pH:2, T:318K

Table 2. Pseudo second order kinetic model parameters

T, K	Experimental capacity q_e , mg/g	Theoretical capacity q_e , mg/g	Rate constant k_2 , g/mg.sa	Initial rate h^* , mg/g.dak	R^2	R^{2**}
295	46.69	48.86	0.1085	4.316	0.999	0.857
305	47.79	47.97	0.1240	4.756	0.999	0.877
318	47.53	47.68	0.2319	8.788	0.999	0.828

* $h = k_2 \cdot q_e^2(12)$; ** correlation coefficients of pseudo first order kinetic model

The activation energy of Cr(VI) adsorption onto AN/DVB-AC was calculated by using Arrhenius equation as 26.2 kJ/mol. The mean free sorption energy which was calculated by using Dubinnin-Radushkevich adsorption isotherm model was > 22 kJ/mol at pH 2. The mean free sorption energy for ion exchange processes is between 8-16 kJ/mol (12-14) and activation energy of physical adsorption is not higher than the value of 4.184 kJ/mol (15). Furthermore, Cr(VI) adsorption heat was calculated about 73.6 kJ/mol which is approximately same magnitude as the heat of chemisorption, which is generally in the range of 80 to 200 kJ/mol (16). It can be concluded that the whole adsorption heat and energy calculations indicate that the chemical interaction between the carbon surface and hydrogen chromate anions occurs.

As a conclusion, macroporous acrylonitrile-divinylbenzene copolymer have been successfully converted to microporous activated carbons and the produced carbon could be evaluated as potential adsorbents to remove Cr(VI) from aqueous media effectively.

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INVESTIGATION OF STRONGLY BASIC ANION EXCHANGE RESINS PROPERTIES FOR PALLADIUM REMOVAL FROM ACIDIC SOLUTIONS

A. Wołowicz, Z. Hubicki

*Maria Curie-Skłodowska University, Faculty of Chemistry, Department of Inorganic Chemistry, Maria Curie-Skłodowska Square 2, 20-031 Lublin, Poland
e-mail: annamyrt@poczta.onet.pl*

Abstract: Strongly basic anion exchange resins such as Amberlyst A-29, Amberlit IRA-458, Dowex MSA-1 and Dowex MSA-2 applicability in palladium(II) removal from the chloride-nitrate(V) solutions were described. Batch and continuous systems were applied. Additionally, kinetic analysis of the obtained data has been fitted to various sorption models and the results indicate that the Pd(II) sorption process using SBA resins followed the pseudo-second order kinetic equation. On the other hand, the breakthrough curves of Pd(II) were obtained for the Pd(II) ions using the fixed bed columns packed with SBA resins. The highest column sorption capacity was found for Dowex MSA-2 – 0.0238 g/cm³ (0.9 M HCl – 0.1 M HNO₃ – 100 mg/dm³). AFM pictures of the surface of Dowex MSA-2 before and after the sorption process were also obtained.

Introduction: From an economic point of view, recovery of palladium and other precious metals from different types of scrap materials such as recyclable products: spent industrial catalysts from e.g. oil refining and petroleum industry, electronic scraps e.g. mobile phones, printed circuit boards, spent automotive catalysts e.g. end-of life car catalysts, by-products: e.g. from non-ferrous industry e.g. anodic slimes from copper industry, drosses from lead smelters and others: precious metal bearing raw materials e.g. photographic residues, fuel cells etc. is very important and necessary nowadays (1). In the past two decades, the most active research area concerning the recovery of precious metals from their primary and secondary sources has been hydrometallurgical techniques e.g. (2-7). Before the separation and purification procedures palladium and other noble metals must be brought into solutions using series of acids and caustic leaches (8-9). Precipitation of impurities, solvent extraction, adsorption and ion-exchange are the effective methods to isolate and concentrate the precious metals of interest.

Ion exchange finds wide application in analytical chemistry, hydrometallurgy, chemical processing and environmental-pollution control as a technique for recovery and refinement of soluble metallic species. Synthetic ion exchange resins of different types based on polystyrene-divinylbenzene, methacrylic or acrylic acid crosslinked with various divinyl monomers are frequently used in palladium and other noble metal ions preconcentration. The literature data concerning applicability of the strongly basic anion exchange (SBA) resins are still incomplete. Application of SBA resins such as: 717 (10) – Ag(I), Au(III), Pd(II), Pt(IV) adsorption from the chloride solutions, Dowex 1-X10 (11) – Pd(II) and Pt(IV) recovery from road dust, Bio-Rad AG1-8X (12) – Pd(II), Pt(IV) and Au(II) recovery from silicate rocks, ores, road dusts, Dowex 1-X8 and Amberlite

IRN-78 (13-16) Pd(II) removal from nitric acid solutions and Pd(II), Rh(III) and Ru(III) recovery from radioactive wastewaters, Amberlite IRA-900, Amberlite IRA-400 (17-19) – Pd(II), Pt(II), Ru(III), Rh(III), Au(III), Ir(IV) removal from the chloride and nitrate solutions and wastewaters, Amberlite IRA-958, Lewatit MP-500A, Purolite A-850 (20-21), Wofatit SZ-30 (22), PUFIX (23), Cellex T (24), Amberlite CG-400 (25), Bio-Rad AG-1X2 (26), PS-PDHC (27) is described in literature.

Experimental: Batch and column method were applied in the investigations of Pd(II) removal using the SBA resins. The batch sorption experiments were performed using the initial Pd(II) solutions – 100 mg/dm³ and 0.5 g SBA resin (mass of the SBA resin ratio to volume of Pd(II) initial solutions = 0.5g/0.05 dm³) by shaking the samples from 1 min to 12 h (amplitude = 8, shaking rate = 180 strokes per minute). Continuous sorption studies were carried out in glass columns (column length = 25 cm, diameter = 1 cm). The columns were packed with 10 cm³ of swollen SBA resin (flow rate = 0.4 cm³/min).

Characteristics of the obtained parameters based on the breakthrough curves and the effect of phases contact time are presented in Table 1. The data of Pd(II) sorption on the SBA resins were fitted using the pseudo-first and pseudo-second kinetic order equations.

Table 1. Characteristics of sorption parameters

Methods	Sorption parameters			
	Parameters	Symbol	Equations	Plots
Batch	Amount of palladium (II) complexes sorbed	q_t [mg/g]	$q_t = (C_o - C_t)V/W$ (1)	q_t vs. t
	Working ion exchange capacity	C_r [g/cm ³]	$C_r = (V_p \cdot C_o)/V_j$ (2)	
Column	Weight distribution coefficient	D_w	$D_w = (U - U_o - V_v)/m_j$ (3)	C/C_o vs. V
	Bed distribution coefficient	D_v	$D_v = D_w d_z$ (4)	

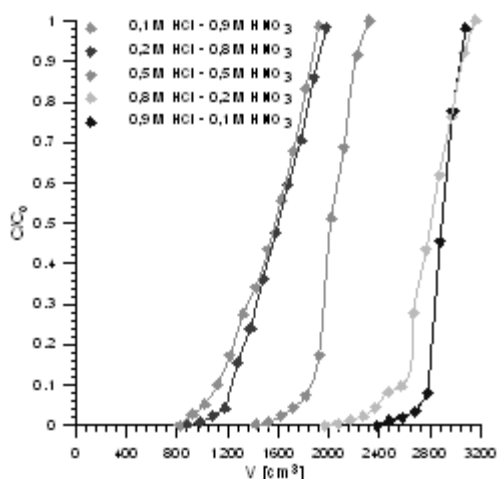


Fig. 1. Breakthrough curves for Dowex MSA-2

Kinetics: In this study, two models have been used for fitting the sorption data obtained by means of the batch method. To model kinetic data, the pseudo-first and pseudo-second kinetic order equations were selected (see Table 2).

Results and discussion: Only chosen examples of the obtained results were presented here. The breakthrough curves for Dowex MSA-2 are shown in Fig. 1. and the calculated sorption parameters are presented in Table 3.

Table 2. Characteristics of kinetic parameters.

Pseudo-first order equation				
Rate constant of Lagergren equation	k_1 [1/min]	$\log(q_e - q_t) = \log q_e - (k_1 / 2.303)t$ (5)		$\log(q_e - q_t)$ vs. t
		$k_1 = -2.303 \times \text{slope}$ (6)		
Sorption capacity of Pd(II)	q_e [mg/g]	$q_e = 10^{\text{intercept}}$ (7)		
Pseudo-second order equation proposed by Ho				
Rate constant of Ho equation	k_2 [g/mg min]	$t / q_t = 1 / k_2 q_e^2 + 1 / q_e t$ (8)		
		$k_2 = \text{slope}^2 / \text{intercept}$ (9)		
Sorption capacity of Pd(II)	q_e [mg/g]	$q_e = 1 / \text{slope}$ (10)		t/q_t vs. t
Initial sorption rate	h [mg/g min]	$h = k_2 q_e^2$ (11)		

All sorption parameters decrease with the decreasing nitric acid concentrations. It is a result of competition between anions which form in this type of solutions. Moreover, the amount of Pd(II) ions sorbed on the SBA resins increases with the increasing phases contact time (Fig. 2).

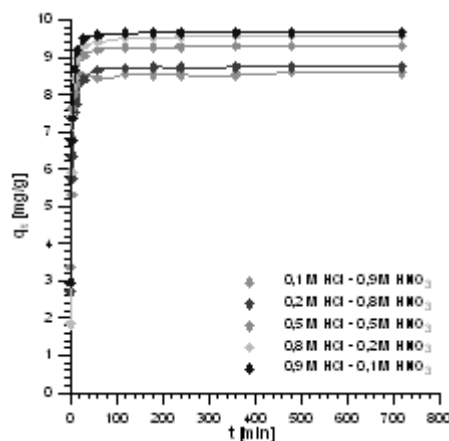


Table 3. Comparison of sorption parameters obtained for the SBA resins.

Fig. 2. Effect of phases contact time on Pd(II) sorption.

Systems	SBA resins	D_w	D_v	C_w [g/cm ³]
0.1 M HCl – 0.9 M HNO ₃	Amberlit IRA-458	197.6	56.5	0.0030
0.2 M HCl – 0.8 M HNO ₃		242.7	69.4	0.0040
0.5 M HCl – 0.5 M HNO ₃		293.0	83.8	0.0040
0.8 M HCl – 0.2 M HNO ₃		369.6	105.7	0.0060
0.9 M HCl – 0.1 M HNO ₃		388.8	111.2	0.0060
0.1 M HCl – 0.9 M HNO ₃	Amberlyst A-29	495.0	152.0	0.0070
0.2 M HCl – 0.8 M HNO ₃		490.7	150.7	0.0070
0.5 M HCl – 0.5 M HNO ₃		626.2	192.3	0.0090
0.8 M HCl – 0.2 M HNO ₃		756.1	232.2	0.0140
0.9 M HCl – 0.1 M HNO ₃		875.0	268.7	0.0170
0.1 M HCl – 0.9 M HNO ₃	Dowex MSA-1	544.5	149.2	0.0086
0.2 M HCl – 0.8 M HNO ₃		585.4	160.4	0.0090
0.5 M HCl – 0.5 M HNO ₃		782.5	214.4	0.0135
0.8 M HCl – 0.2 M HNO ₃		998.2	273.5	0.0220
0.9 M HCl – 0.1 M HNO ₃		1110.2	304.2	0.0226
0.1 M HCl – 0.9 M HNO ₃	Dowex MSA-2	564.4	156.8	0.0082
0.2 M HCl – 0.8 M HNO ₃		572.7	159.1	0.0088
0.5 M HCl – 0.5 M HNO ₃		722.8	200.8	0.0132
0.8 M HCl – 0.2 M HNO ₃		1007.9	280.0	0.0197
0.9 M HCl – 0.1 M HNO ₃		1037.8	288.3	0.0238

AFM analysis:
The AFM picture of Dowex MSA-2 resin surface before and after the sorption process was obtained (Fig 3). This resin shows high porosity of its surface before and after Pd(II) sorption, but as can be easily seen after the sorption process the surface of Dowex resin becomes more

smooth, the pores are blocked.

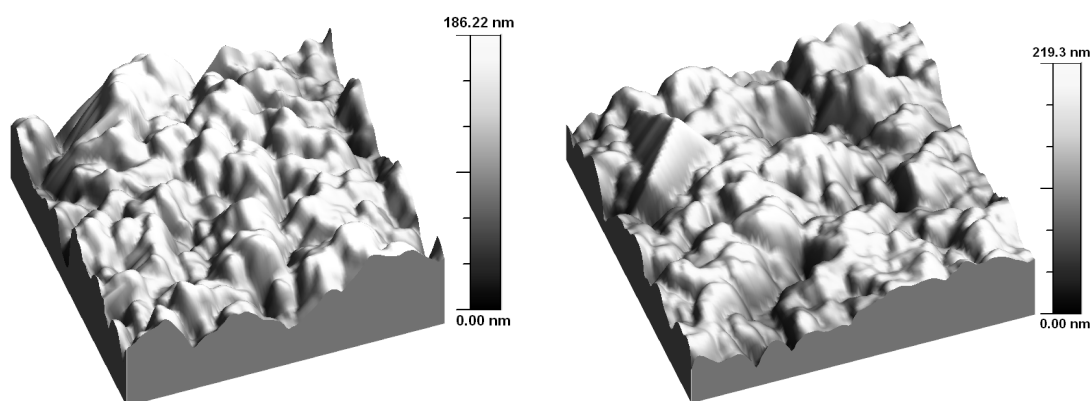


Fig. 3. AFM pictures of Dowex MSA-2 surface a) before and b) after the sorption of Pd(II).

Conclusions: (i) The SBA resins can find application in Pd(II) recovery from acidic solutions. Dowex MSA-2 shows the highest capacity for Pd(II) ions. The selectivity series of SBA resins toward Pd(II) can be presented as follows:

Dowex MSA-1 ≈ Dowex MSA-1 > Amberlyst A-29 > Amberlit IRA-458;

(ii) Pd(II) sorption process using the SBA resins followed the pseudo-second order kinetic equation;

(iii) SBA resins are characterized by good kinetic properties – sorption process is fast, after about 30 – 180 min depending on the SBA resins used.

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SOLVENT EXTRACTION OF COPPER AND ACCOMPANYING METALS FROM SULFATE LEACH LIQUORS

Katarzyna Ochromowicz, Wiesław Apostoluk, Tomasz Chmielewski,
Barbara Woźniak

*Wrocław University of Technology, Faculty of Chemistry,
Division of Chemical Metallurgy, Wybrzeże Wyspiańskiego 23, 50-370 Wrocław
e-mail: wieslaw.apostoluk@pwr.wroc.pl*

Introduction

Hydrometallurgical processing of copper ores, by-products and concentrates has been intensified in recent years, due to decreasing grade of flotation feed and declining metals recovery by means of standard flotation – smelting – refining techniques. About 25 % of copper is currently produced by hydrometallurgy and the successes of this method are mainly limited by separation of metals from leaching solution, mainly by solvent extraction.

Depending on the composition of processed feed material, type and concentration of leaching agent and leaching parameters, the composition of pregnant leach solutions (PLS) is diversified in pH and concentrations of valuable (Cu, Zn, Co, Ni, Ag) and unwanted (Fe, As, Ca) metals. Sulfate leach liquors can be obtained by a simple atmospheric or high pressure leaching of non-sulphidic metal bearing materials with sulfuric acid at ambient or elevated temperature. Sulfate leach liquors can be also obtained by leaching of sulphide ores, concentrates and byproducts with oxygenated or/and $\text{Fe}_2(\text{SO}_4)_3$ solutions acidified with sulfuric acid. Typically, copper sulfate leach solutions contain from 10 to 60 g/dm³ Cu, 0,5 to 30 g/dm³ Fe, different quantities of other metals (Co, Ni, Zn, As, Mg, Ca), while their acidity usually changes in the pH range from 1 to 2.

Presently, the solvent extraction (SX) is a mature separation process widely used in the industrial scale for recovering of valuable metals from various pregnant leach solutions (1-5). A key role in solvent extraction processes plays the organic phase composed of metal extractant, organic diluent (usually hydrocarbon diluents) and extraction modifiers. The composition of organic phase is strictly dependent on the composition of leach liquor. Therefore, the efficient separation of metals from leach solution requires proper selection of extraction system, compatible with given PLS (6).

In the present paper the key factors influencing SX operations are considered and few examples of metal extraction from sulfate leach liquors are also discussed.

Organic phase composition

A suitable preparation of organic solution containing properly selected metal extractant, diluents, and modifier is the essential step of solvent extraction procedure. The correctly selected properties of diluent assure a good solubility of extractant and neutral complexes or ionic pairs of extracted metal. It is desirable that organic phase, especially loaded, had relatively low viscosity,

because disengagement of aqueous and organic phase is fast at that time. On the contrary, too low surface tension of organic phase and interfacial tension between the phases of the system is unwanted, because they may result in formation of emulsion which makes disengagement of both phases considerably difficult.

Extraction of M^{n+} cations with acidic extractant (HA) follows the chemical reaction:



where subscripts (a) and (o) refer to aqueous and organic phase, respectively. The reaction (Eq. 1) is reversible towards hydrogen ions. Different metal cations are extracted under specific pH regions, therefore the efficiency of extraction and reextraction, as well as selectivity of their separation is largely dependent on pH of aqueous phase.

The plot of extraction efficiency (% E) vs. equilibrium pH enables the comparison of the results of metals extraction with the selected extractant. The results of extraction of different metal ions with di(2,4,4-trimethylpentyl) phosphinic acid (Cyanex® 272) are presented in Fig. 1. Such dependencies are useful in preliminary determination of initial extraction conditions for given metal, while the known value of pH_{50} can be used to estimate the possibility of its effective separation from the metal ionic species present in leach solution.

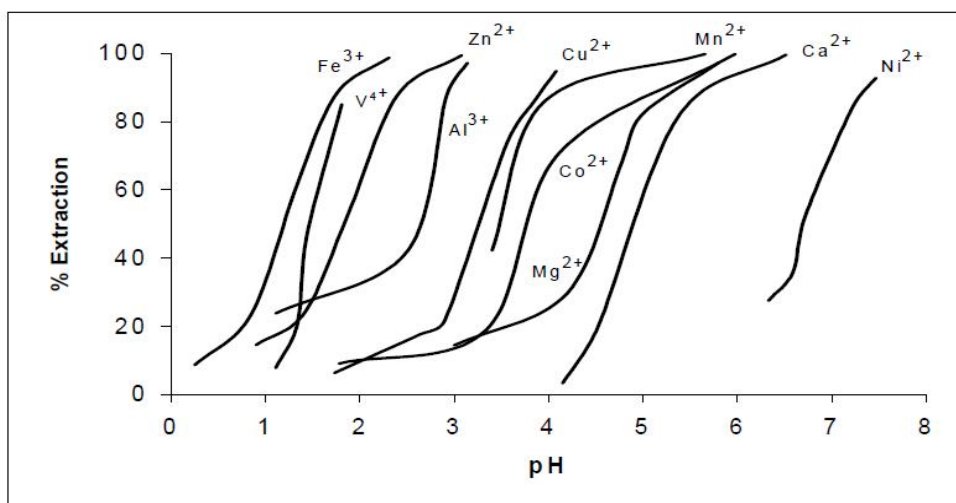


Fig. 1. Dependence of pH of aqueous phase on metals extraction with Cyanex 272 from sulfate solutions (7)

Metal cations are effectively extracted with several acidic extractants, usually hydrophobic organic acids, like:

- 5,8-dinonylnaphthalene sulfonic acid (DNNSA);
- aliphatic carboxylic acids, preferably with branched chain structure, i.e. Versatic 10, Versatic 9-11;
- organophosphorous base acids (Cyanex 272, Cyanex 301, Cyanex 302);
- hydroxyoximes of aromatic aldehydes and ketones;
- β -diketones;
- 8-hydroxyquinoline derivatives.

Extractants are usually dissolved in properly selected hydrocarbon diluent.

From the apparent reasons, an organic diluent should exhibit possibly high boiling and ignition temperatures as well as low solubility in aqueous solutions. For industrial application purposes, the mixtures of higher aliphatic hydrocarbons (C_nH_{2n+2}), alicyclic (C_nH_{2n}) and aromatic hydrocarbons are used as diluents. The characteristic of commercial diluents is given in Table 1.

Type of diluent, type and concentration of extractant and loading of organic phase with metal – extractant complex, are the factors influencing the viscosity of organic phase. The newest generation of LIX series extractants by Cognis, labeled by LV symbol, is modified with additives ensuring low viscosity of organic phase. It is advisable to use LV diluents when extractant concentrations are high (50% vv), for example in copper extraction from sulfate solutions after high pressure leaching of sulfide concentrates. Low viscosity extractants, for example LIX® 612N-LV i LIX® 6422N-LV ensure better extraction and reextraction efficiency comparing to regular extractants. Moreover, their application is reasonable from the economical, technical and ecological point of view (8).

Table 1. Characteristics of commercial diluents

Diluent	Boiling temp., °C	Ignition temp., °C	Hydrocarbons content, % vv		
			aliphatic	alicyclic	aromatic
Isopar L	189	62	92.7	7.0	0.3
Isopar M	207	78	79.9	19.7	0.3
Escaid 100	191	76	56.5	23.4	20.0
Escaid 110	193	76	39.9	57.7	2.4
Escaid 200	196	69	97.9	1.1	0.6
Napoleum 470	210	79	48.6	39.7	11.7
DX 3641	183	57	45.0	49.0	6.0
Naphtezol M	-	-	45.0	55.0	-
Shellsol D70	198	74	60.0	40.0	-
Solvesso 150	171	67	-	3.0	97.0

Very frequently the specific compound, called extraction modifier, is added to the organic phase. Usually in this function, hydrophobic aliphatic alcohols, alkylphenols and some esters, e.g. 1-decanol, tridecanol, nonylphenol, 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB) are used. They prevent third phase formation (liquid or solid) in extraction systems, weaken too strong bonding in complexes between extractants and metal ions allowing thereby for effective regeneration of extractants and stripping of metal ions (1-5, 7, 9).

SX applications

Specific problems of metal extraction from sulfate PLS with acidic extractants have been presented and broadly discussed:

- copper extraction with aromatic hydroxyoximes and Cu/Fe separation (1,2);
- high acidity of PLS (10,11);
- iron extraction and Fe/Zn separation with diesters of phosphoric acid (12-14);
- cobalt and nickel separation with organophosphorous based acids (15-17).

A number of extraction systems have been suggested for valuable and unwanted metals separation. Each system shows some advantages and disadvantages and the choice of an appropriate system depends on many factors, including among others, the PLS composition and the metal to be extracted. Despite enormous knowledge and experience in this field the diversity and specific composition of pregnant leach solutions does not allow for introduction of ready-made solution.

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EXTRACTION OF COPPER(II) WITH HYDROPHOBIC PIRYDYL KETOXIMES FROM CHLORIDE AND SULPHATE SOLUTION

K. Wieszczycka, M. Krupa, A. Olszanowski

Poznań University of Technology, Institute of Chemical Technology and Engineering, Pl. Marii Skłodowskiej-Curie 2, 60-965 Poznań, Poland
e-mail: marta.krupa@doctorate.put.poznan.pl

Solvent extraction is one of the most important processes to separate the metal ions, which is applied in hydrometallurgy (1). A lot of extractants for copper recovery from different solutions were investigated: for the extraction of copper(II) from chloride solutions - Acorga CLX-50® (*bis*(isodecyl) pyridine-3,5-dicarboxylate and Acorga ZNX-50 (derivatives of benzimidazole), for the extraction of copper(II) from sulphate solutions - the chelating extractants: LIX 64N (mixture of α -hydroxyoxime and benzophenone oxime), LIX 84I (2-hydroxy-5-nonylacetophenoneoxime), MOC 45 (2-hydroxy-5-nonyl acetophenone oxime) or LIX 860 (5-nonylsalicylaldoxime) and their mixtures with phosphoorganic extractant (2).

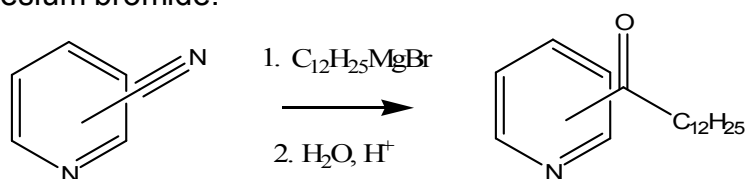
The hydrophobic pyridylketoximes have been proposed as an extractant to recovery of Cu(II), Fe(III), and Cd(II) ions from chloride solutions (3-5). The extraction of copper(II) from chloride solution with oxime of 1-(2-pirydył)tridecan-1-one does not depend on pH and concentration of chloride ions in the aqueous solutions. After extraction the loaded organic phase was stripped in 100% in two stages process with aqueous solutions of NH_3 and H_2SO_4 . Other results were obtained for 1-(4-pirydył)tridecan-1-one oxime; the copper extraction increased with increasing Cl^- concentration and the stripping was realized using water (100% recovery in two stages) (5).

In this paper the extraction of copper(II) from sulphate and sulphate/chloride solutions with oxime of 1-(2-pirydył)tridecan-1-one, oxime of 1-(3-pirydył)tridecan-1-one and oxime of 1-(4-pirydył)tridecan-1-one were investigated. The influence of Cl^- and SO_4^{2-} ions concentration, the extractant and the metal concentration and pH of aqueous phases on copper(II) extraction were studied.

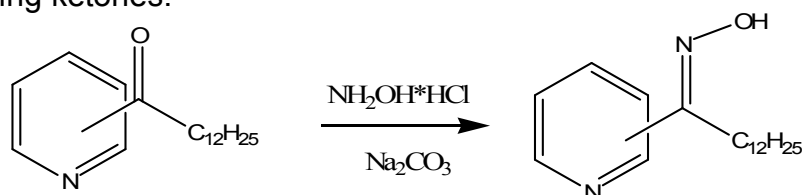
1. Experimental

1.1. Synthesis of extractant

As model extractants the hydrophobic 2-, 3- and 4-pirydyłketoximes with C-12 alkyl chain were synthesized in two stages reaction (5). In the first stage, ketones were synthesised by treating appropriate pyridyl cyanide with dodecylmagnesium bromide.



In the second stage, oximes were synthesised by adding hydroxylamine to the corresponding ketones.



The yields of oximes were 30-80%. Purities of ketones and oximes were 98.9% (HPLC/MS). NMR (^1H , ^{13}C) spectra proved the structure of synthesised compounds.

1.2. Extraction procedure

The oximes of 1-(2, 3- or 4-pirydyl)tridecan-1-one were dissolved (0.1 mol/L) in toluene with 10 vol.% addition of decan-1-ol.

A sulfate feed solutions were prepared by dissolving $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ and Na_2SO_4 (or Na_2SO_4 and NaCl) in de-ionized water. The pH of the aqueous solution (3.5 for chloride and 5.0 for sulphate solutions) was adjusted (713 pH Meter, Metrohm) to a desired value by adding 0.2% solutions of H_2SO_4 or HCl and NaOH . The extractions from chloride solution was carried out at constant water activity $a_w = 0.835$ using appropriate amounts of NaCl , NaNO_3 and LiNO_3 (6). The basic studies were carried out at a constant copper(II) concentration equal to 0.01 mol/L. The organic and aqueous phases (O/W 1:1) were shaken at room temperature (23-25°C) using a bio-mix BWR 04. The metal concentration in the aqueous phase was analysed by Mettler Toledo T50 titrator using EDTA as a titrant.

2. Results and discussion

The copper(II) extraction with 1-(3-pirydyl)tridecan-1-one oxime, similar like 4-pirydylketoxime, depends on the concentration of chloride ions. The removing of copper from aqueous solutions increased from 30% for 0.1mol/L to 56% for 4 mol/L Cl^- . From the loaded organic phases, copper were stripped with de-ionized water (70% reextraction).

The copper(II) extraction from sulphate solution with 3PC12 and 4PC12 is not efficient. During the extraction with 3PC12 white emulsion was formed. The concentrations of copper(II) in aqueous phases were analysed but the results are not satisfactory: the extraction with 3PC12 and 4PC12 was less than 6% (Table 1). For 2-pirydyl ketoxime the extraction of copper(II) was also observed but the formation of the emulsion did not allow to separate phases, even after one week.

K. Klonowska-Wieszczycka et al. (5) obtained good results of copper(II) extraction from chloride solution using 1-(2-pirydyl)tridecan-1-one oxime and 1-(4-pirydyl)tridecan-1-one oxime. Therefore, the addition of NaCl to sulphate solution of copper(II) ions was studied (Table 2).

Table 1. The extraction of Cu(II) from sulphate solution with oximes of 1-(2-pirydy)tridecan-1-one (2PC12), 1-(3-pirydy)tridecan-1-one (3PC12) and 1-(4-pirydy)tridecan-1-one (4PC12) in toluene with 10% decan-1-ol as diluents

The concentration of sulphate ions [mol/L]	The extraction of copper(II) ions [%]		
	2PC12	3PC12	4PC12
0.01	*	5.1	4.6
0.1	*	5.6	3.7
0.5	*	4.8	3.5
1	*	5.4	3.3

* emulsion

The preliminary results were obtained when the molar ratio of chloride and sulphate ions was 1:1. 2-pirydyketoxime removes from sulphate/chloride solution (above 0.01 mol/L NaCl) almost all copper(II) ions. When the concentration of NaCl was increased the extraction of copper(II) also increased, however, for 0.1 and 0.5 M NaCl the precipitation of complexes was noted. The emulsions were also observed for 1-(3-pirydy)tridecan-1-one oxime, when the concentration of NaCl was below 0.1 mol/L. The extraction of copper(II) ions from sulphate/chloride solution by 1-(3-pirydy)tridecan-1-one oxime was observed only for solution containing 1 mol/L Cl⁻. Oxime of 1-(4-pirydy)tridecan-1-one seems to be better extractant than 1-(3-pirydy)tridecan-1-one oxime. However, the extraction of copper(II) from solution containing both 1 mol/L Cl⁻ and SO₄²⁻ is not higher than 11%.

Table 2. The extraction of Cu(II) from sulphate/chloride solution with oximes of 1-(2-pirydy)tridecan-1-one (2PC12), 1-(3-pirydy)tridecan-1-one (3PC12) and 1-(4-pirydy)tridecan-1-one (4PC12) dissolved in toluene with 10% decan-1-ol

Na ₂ SO ₄ [mol/l]	NaCl [mol/l]	The extraction of copper(II) ions [%]		
		2PC12	3PC12	4PC12
0.01	0.01	*	*	0
0.1	0.1	96 _p	*	0
0.5	0.5	94 _p	0	6
1.0	1.0	100	7	11

* emulsion

p - precipitate

The change of the composition of aqueous phases, where the constant concentration of sulphate ions (1 mol/L Na₂SO₄) and various concentration of Cl⁻ were tested, improved the copper(II) extraction. The removing of metal from sulphate/chloride solutions by 3- and 4-pyridylketoximes increases with increasing of Cl⁻ concentration achieving 33% and 68% extraction of copper(II) at 2 mol/L Cl⁻ for 3PC12 and 4PC12, respectively. The 100% extraction of copper(II) by oxime of 1-(2-pirydy)tridecan-1-one was determined and the results did not depend on concentration of Cl⁻ ions. From the loaded organic phase, copper(II) was stripped with de-ionized water in 60% (3PC12) and 70% (4PC12). In the case of copper(II) complexes with 2PC12 more drastic reagents

are needed for the stripping than after the extraction of copper(II) from chloride solutions (5).

Table 3. The extraction of Cu(II) from 1 mol/L sulphate solution with various concentration of Cl⁻ by oximes of 1-(2-pirydy)tridecan-1-one (2PC12), 1-(3-pirydy)tridecan-1-one (3PC12) and 1-(4-pirydy)tridecan-1-one (4PC12) dissolved in toluene with 10% decan-1-ol

Na ₂ SO ₄ [mol/l]	NaCl [mol/l]	The extraction of copper(II) ions [%]		
		2PC12	3PC12	4PC12
1.0	0.1	100	0	0
1.0	0.5	100	1	4
1.0	1.0	100	7	11
1.0	2.0	100	33	68

3. Conclusions

The copper(II) extraction from sulphate solution by hydrophobic pirydyketoximes is not efficient. The addition of Cl⁻ ions allows to extract copper(II) from initial sulphate solutions. Oxime of 1-(2-pirydy)tridecan-1-one removes all copper(II) ions from solution and the extraction does not depend on concentration of Cl⁻.

For the pyridineketoximes with oxime group at 3 and 4 position in pyridine ring the extraction of copper(II) was observed only when the total concentration of Cl⁻ and SO₄²⁻ ions were minimum 2 mol/L.

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MIXED-MODE HYPERCROSSLINKED MATERIALS FOR SOLID-PHASE EXTRACTION

Rosa M. Marcé¹, Dominika Bratkowska¹, Arlen Davies², Francesc Borrull¹, Peter A.G. Cormack², David C. Sherrington², Núria Fontanals¹

¹*Department of Analytical Chemistry and Organic Chemistry, Universitat Rovira i Virgili, i Campus Sescelades, 43007 Tarragona, Catalonia, Spain*

²*Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow, G1 1XL, Scotland, UK
e-mail: rosamaria.marce@urv.cat*

Solid-phase extraction (SPE) is considered to be the most used extraction technique for liquid samples, mainly due to the availability of different sorbents. The ideal sorbent should balance capacity and selectivity (1). However, it has not appeared yet the ideal sorbent able to retain with both high capacity and selectivity, necessary in fields such as environmental analysis. Those sorbents that possess high retention (i.e. hypercrosslinked sorbents) lack selectivity, which other kinds of sorbents possess, such as molecularly imprinted polymers.

Recently, it has been marketed sorbents with mixed-mode technology, which combine the reversed-phase interactions from the polymer basis with the ionic interactions from the ionic functional groups, which modify the sorbent. By using these sorbents in SPE one can tune the capacity and selectivity of the extraction process in one single step (1,2).

We present a step further in the mixed-mode technology with the synthesis of different resins on spherical low-micron size hypercrosslinked particles and further modified with such groups as piperazine, carboxylic, sulfonic, dimethyl butylamine so that these resins behave as ion-exchange sorbents to improve the selective SPE.

The properties of these resins with the combination of enhance reversed-phase and ionic interaction envisaged us to test them as successful material to selectively extract a group of pharmaceuticals from complex environmental water samples. Thus, on one hand, the cation-exchange hypercrosslinked resins successfully extract basic pharmaceuticals, and eliminate the acidic pharmaceuticals and interferences in the washing step. On the other hand, the anion-exchange hypercrosslinked resins selectively extract acidic compounds, while washing out the basic ones and interferences.

For the synthesis of most of the materials, the vinylbenzyl chloride (VBC) and divinylbenzene (DVB) based hypercrosslinked resin (HXL) was first synthesized (3). For strong anion-exchange resin (SAX) the resin was further reacted with dimethylbutylamine (4). For the strong cation-exchange resin (SCX), it was used a similar procedure but the resin was further reacted with the lauroyl sulfate and the sulfonic group was introduced (5). For the weak anion-exchange (WAX) both piperazine and ethylenediamine were introduced to the resins (6). For the weak cation-exchange resin (WCX), the precursor polymer was first

synthesized using as monomer precursor methacrylic acid (7), VBC and DVB and then it was hypercrosslinked using conditions similar to those used for HXL (3). The chemical structure of the sorbents is shown in Figure 1.

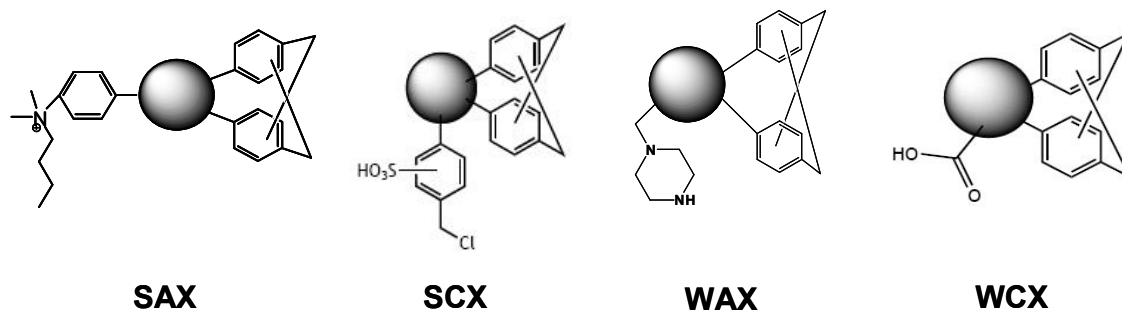


Figure 1. Chemical structures of the sorbents

Once the materials were synthesised, a key point in their application to reach the maximum selectivity are the SPE conditions. First, they were applied to off-line SPE and some of them were also used in on-line SPE-liquid chromatography. Therefore, for each sorbent, they were carefully optimized in order to get the highest selectivity and sensitivity. Critical conditions are the sample and volume pH, the solvent used and its volume for washing step and the elution conditions, both solvent, pH and volume.

These conditions were optimised for each sorbent and the optimum conditions were: for SAX, sample at pH 7, 10 ml of methanol as cleaning solvent and 10 ml of 10% acetic acid in methanol (MeOH); for SCX, sample at pH 3, 5 ml of MeOH as cleaning solvent, and 5 ml of 5% of NH_4OH in MeOH as elution solvent; for WAX, sample at pH 7, 4 ml of MeOH as cleaning solvent and 2 ml of 2% NH_4OH in MeOH and for WCX, sample at pH 7, 2 ml of MeOH as cleaning solvent and 5 ml of 2% of TFA in MeOH as elution solvent.

The studies of these sorbents in on-line SPE-liquid chromatography also demonstrated that they can be used in this format which enables low sample volumes to be extracted and lower limits of detection to be obtained (8).

The hypercrosslinked mixed mode resins presented good capacity and selectivity. The high capacity, which enables high sample volume to be extracted, is due to the hypercrosslinked structure of the resins; whereas the high selectivity, which enables the selective extraction of basic pharmaceuticals, is due to the specific retention of these compounds by ion-exchange interactions, which enables a clean-up step with an organic solvent. This clean-up step eliminates other organic contaminants present in the sample and mainly retained by reversed phase interactions.

These resins were successfully applied to different environmental water samples (river, STP effluent and STP influent) which cover different degree of complexity, and high recovery were obtained as well as very clean

chromatograms. The comparison of these hypercrosslinked mixed-mode sorbents with those commercially available, which are macroporous, demonstrated the higher performance of the hypercrosslinked resin since their microporous structure enhances their interactions with the analytes.

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PREPARATION OF TRIPODAL PYRIDYL COMPOUNDS FOR PRECIOUS METAL EXTRACTION

Keisuke Ohto, Ryoma Yamaguma, Hidetaka Kawakita

Department of Chemistry and Applied Chemistry, Saga University
1-Honjo, Saga 840-8502, Japan
e-mail: ohtok@cc.saga-u.ac.jp

Introduction

In order to mutually separate, recover and remove valuable or toxic metals ions, separating reagents play an important role. In our group, various types of extraction reagents based on macrocycles and pseudo-macrocycles, such as calixarenes and tripodal compounds have been prepared for metal separation (1). The tripodal compounds show some advantages in use as the extraction reagents (2). 1) Alkyltrimethylols as starting materials are easily prepared by condensation reaction of the corresponding aldehyde and formaldehyde in the presence of a base. 2) They have sp^3 carbon, shows C_3 symmetry, and the same three functional groups can be introduced in. 3) Chemically modified alkyltrimethylol compounds provide coordination sites with certain sizes for selective metal recognition. 4) The compounds have plural functional groups in a single molecule, consequently they show high coordination ability due to the chelate effect and the aggregating effect of functional groups.

In the present study, we report synthesis of two pyridino derivatives of the tripodal compounds with pyridino nitrogens at different position for precious metals. The chemical structures of the tripodal compounds in the present study are shown in Fig.1.

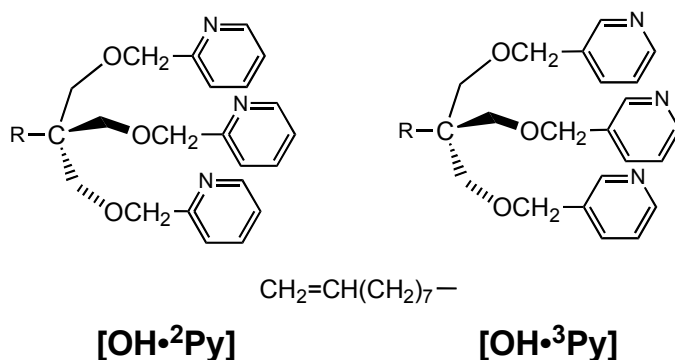


Fig. 1. Chemical structures of the tripodal compounds in the present study

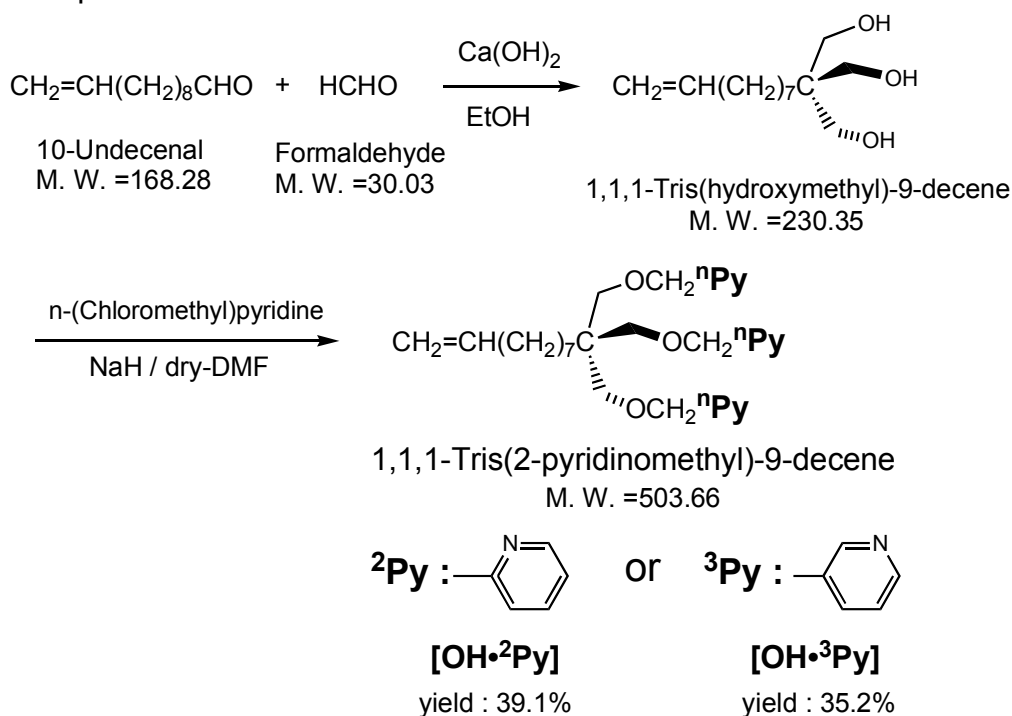
Experimental

Two pyridino compounds have been prepared by two steps, synthesis of 1,1,1-tris(hydroxymethyl)-9-decene as a framework and introduction of pyridyl groups. The products were confirmed to be desired compounds by 1H -NMR and IR spectra. The synthetic reaction of the pyridino tripodal compounds is shown in Scheme 1.

The investigation of the extractant leakage into aqueous solution was carried out. The organic phases were prepared by dissolving each extractant in

chloroform to 5 mM ($M = \text{mol}\cdot\text{dm}^{-3}$). The aqueous solution was prepared by arbitrarily mixing 0.1 M hydrochloric acid (or nitric acid) and 0.1 M HEPES (2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid) as buffer solution. Equal volumes (5.0 cm^3) of both phases were mixed and gently shaken at 303 K for approximate time to reach equilibrium. After phase separation, the equilibrium pH and the extractant concentrations were measured by pH meter (TOA-DKK, HM-30R) and UV-VIS (HITACHI, U-3310), respectively.

Next, metal extraction was carried out. The organic phases were prepared by dissolving each extractant in chloroform to 5 mM. The aqueous solution was prepared by dissolving each chloride or nitrate salt in 0.1 M hydrochloric acid or 0.1 M HEPES buffer. Equal volumes (5.0 cm^3) of both phases were mixed and gently shaken at 303 K for approximate time to reach equilibrium. After phase separation, the equilibrium pH and metal concentration in the aqueous phase were measured by pH meter and ICP-AES (Shimadzu, ICPS-8100), respectively. Metal concentration in the organic phase was calculated from the mass balance between the initial and equilibrium metal concentrations in the aqueous phase.



Scheme 1. Synthetic reaction of the pyridino tripodal compounds

Results and Discussion

Leakage of the present extractants into aqueous phase was preliminarily investigated before the extraction. Effect of pH on percentage leakage of the present extractants into aqueous phase is shown in Fig.2 . The percentage leakage is defined by eq. (A).

$$\% \text{ Leakage} = 100[\text{OH}\cdot^{\text{nPy}}]_{\text{aq}} / [\text{OH}\cdot^{\text{nPy}}]_{\text{ini}} \quad (\text{A})$$

where $[\text{OH}\cdot^{\text{nPy}}]_{\text{ini}}$ and $[\text{OH}\cdot^{\text{nPy}}]_{\text{aq}}$ are the initial extractant concentration in organic phase and the equilibrium extractant concentration in the aqueous phase, respectively. As expected, significant leakage for both extractants at low pH region was observed. Since both extractants have three pyridine nitrogen

atoms easily protonated at low pH region, they were gradually leaked into aqueous solution with decreasing pH. For the corresponding monopodal pyridino compounds, only little leakage into the aqueous phase was observed, the leakage was mainly affected by tri-functionality. Different leakage percentage between two extractants may be attributed to basicity and the difference of hydration degree based on the position of nitrogen atoms. Since both extractant leaks into aqueous phase at lower pH, the extraction was carried out at pH above 3 for OH^{•2}Py and above 4 for OH^{•3}Py.

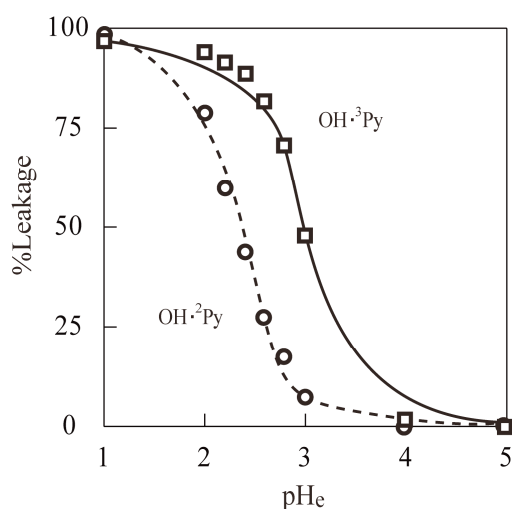


Fig. 2. Effect of pH on % leakage of the extractants into aqueous phase

Effects of pH on percentage extraction of precious metals with OH^{•2}Py and OH^{•3}Py in nitrate media are shown in Figs.3(a) and (b). The percentage extraction is defined by eq. (B).

$$\% \text{ extraction} = 100 [\text{Metal}]_{\text{org}} / [\text{Metal}]_{\text{ini}} \quad (\text{B})$$

where [Metal]_{ini} and [Metal]_{org} are the initial metal concentration in aqueous phase and the equilibrium metal concentration in the organic phase, respectively.

The extractant, OH^{•2}Py shows higher extraction ability than OH^{•3}Py. It is related to the percentage leakage. The extractant, OH^{•2}Py provides higher electric density and more suitable coordination site than OH^{•3}Py. Among previous metals, silver, palladium, and the other ions are effectively, moderately and slightly or hardly extracted with the present extractants. Each metal ion exists as cation species in nitrate media and the present extractants extract cations by coordination with counter anions. Consequently, low charge ions are preferably extracted with the present extractants. Furthermore, the coordination sites of the extractants, especially OH^{•2}Py seem to fit size of silver ion. It is supported that other thioether derivative of tripodal compound also selectively extract silver ion among many ions (3).

Since the extractant, OH^{•2}Py shows high selectivity to silver ion, extraction behavior of silver with OH^{•2}Py was investigated. Little pH dependency was observed and stoichiometry of OH^{•2}Py and silver was determined to be 1 : 1 by the result of Job's method. Finally, the extraction reaction was determined to be solvation as expected.

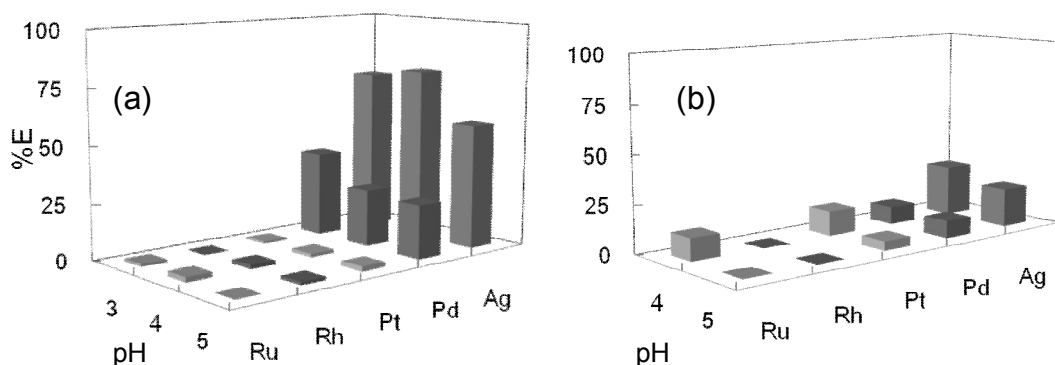


Fig. 3. Effects of pH on percentage extraction of precious metals with (a)OH•²Py and (b)OH•³Py in nitrate media

In order to determine at which silver is extracted, ¹H-NMR spectra change of OH•²Py before and after silver loading in nitrate media was investigated. The spectra before and after silver loading are shown in Fig.4. After the loading of silver, the obvious peak shift not only for pyridyl protons but also methylene ones in OH•²Py was observed. Therefore, the coordination site would be mainly pyridyl nitrogen atoms and complementarily alkoxy oxygen atoms.

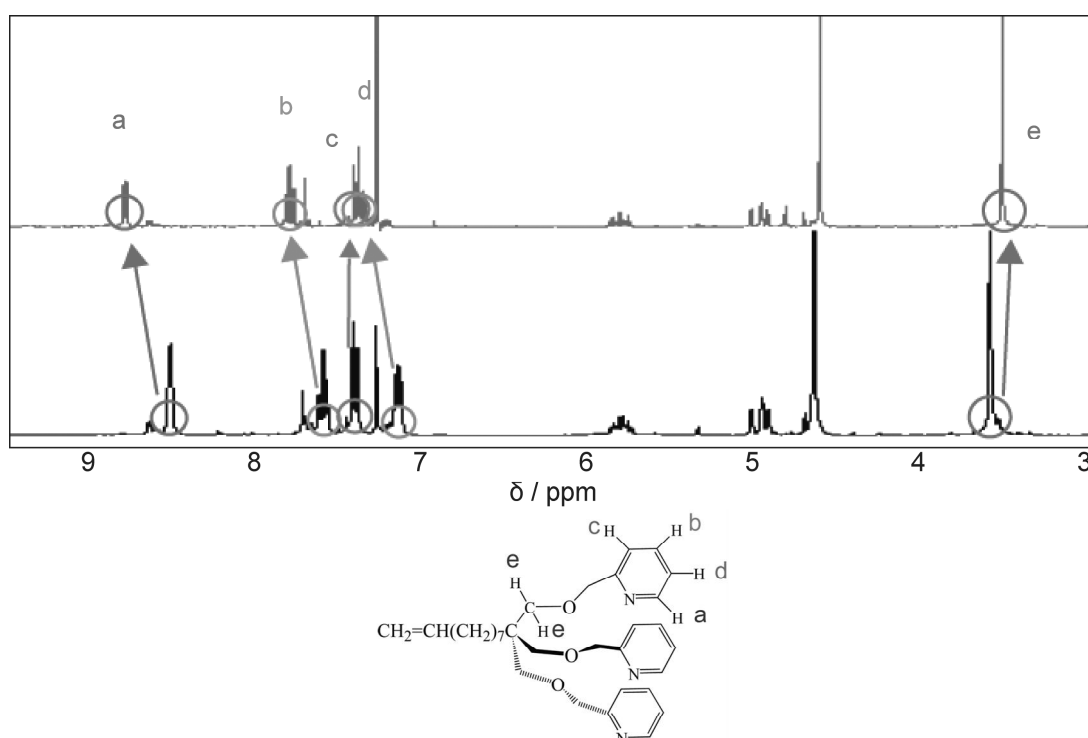


Fig. 4. ¹H-NMR spectra change of OH•²Py before (top) and after (bottom) silver loading in nitrate media

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REMOVAL OF LOW-MOLECULAR CARBOXYLIC ACIDS FROM AQUEOUS SOLUTIONS

Dominika M. Szternel, Magdalena Regel-Rosocka, Maciej Wiśniewski

*Poznan University of Technology, Institute of Chemical Engineering and Technology, Pl. M. Skłodowskiej-Curie 2, 60-965 Poznań
e-mail: dominika.a.szternel@doctorate.put.poznan.pl*

Nowadays, fermentation as process technology for the production of chemicals and organic acids in particular, has become of great interest with increase in demand for environmentally friendly materials (1-3). Biological production of organic acids from biomass by fermentation has become of great importance in today's industry (food, chemical and pharmaceutical) because of its environmentally friendly character and a wide variety of applications for its natural and renewable products (3,4).

The recovery of these products from fermentation broths must be energy-efficient, economy-preferable and must produce a high-purity product (3-5). Among many recovery processes, liquid - liquid extraction is favoured as one of the promising and attractive method if the appropriate extractant is used. Moreover, it is a low energy consuming process (4,6).

Extraction of carboxylic acids, C₂-C₆ (e.g., fumaric, maleic succinic, crotonic, citric) from the aqueous phase, with various extractants (e.g., tributyl phosphate, trioctylamine, Cyanex[®]923) and diluents (such as Exxsol D 220/230, octanol) was studied. Extraction experiments were carried out in a typical way at room temperature. Equal volumes (5 cm³) of phases were mechanically shaken in separatory funnels, then left to stand for phase separation. The distribution ratio and extraction efficiency were determined. Additionally, extraction equilibria of organic acids with solvating and base extractants, and the effect of pH of the organic acids solutions on extraction efficiency were studied. The effect of the addition of sodium chloride into the aqueous phase on the extraction efficiency was determined. As a result, extraction isotherms were presented indicating differences in extraction equilibria of the acids studied. Additionally, kinetics of extraction was investigated.

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INFLUENCE OF ALKYL CHAIN LENGTH IN 1-ALKYL-IMIDAZOLE ON THE CITRIC ACID TRANSPORT RATE ACROSS POLYMER INCLUSIVE MEMBRANE

Piotr Gajewski, Mariusz B. Bogacki

*Poznań University of Technology Institute of Chemical Technology and Engineering, pl. M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland
e-mail: piotrgajewskitch@wp.pl*

1. Introduction

Citric acid is one of the most common applied organic acids in the world. It is used mainly as antioxidant, acidity regulator and effervescent agent with hydrogen carbonate. Due to its antioxidative and preserving properties it is most commonly used in food industry.

Actual technology of citric acid production takes advantage of fermentation using applicable kinds of fungus (1,2). In this method after fermentation step citric acid is precipitated in lime citrate form, cleaned and dissolved in sulfuric acid(VI). This production method causes forming of appreciable amount of discarded lime sulfate, is energy-consuming and does not allow continuous production of acid (1). Therefore, other methods are being searched for, which could be used to release this acid during production. One of the possibilities is application of extraction process (3,4). Other usable method that could be used to release citric acid during and after fermentation is membrane technique.

During last years more attention is given to membrane technique that makes use of polymer inclusive membrane (PIM) (5). This process is investigated mainly from the point of view of ion metal transport across PIM (6,7) but lately also publications that give attention to application of this kind of membrane to separation of organic compounds appeared (8-11).

The main purpose of this research is investigation of citric acid transport through PIM with application of 1-alkyl-imidazoles and tri-octylamine as carriers and orto-nitrophenyl octyl ether as plasticizer. As polymer matrix cellulose acetate was used.

2. Experiment

2.1. Experimental apparatus

In research the experimental apparatus consisting of two glass chambers was used. One chamber with feeding phase and second with receiving phase were separated by PIM membrane (Figure 1). Both feeding and receiving phases were constantly and intensively stirred. Volume of both phases was the same and equal to $V = 45 \text{ cm}^3$. The membrane surface was equal to $A = 4.15 \text{ cm}^2$. Membrane consisted of polymer matrix – cellulose acetate (CTA), plasticizer – orto-nitrophenyl octyl ether (ONPOE) and one of the active compounds – tri-octylamine (TOA) or 1-alkyl-imidazole with alkyl chain length of 10, 11, 12, 14 and 16 carbon atoms (Imi10-Imi16). 1-alkyl-imidazoles were prepared as described earlier (12).

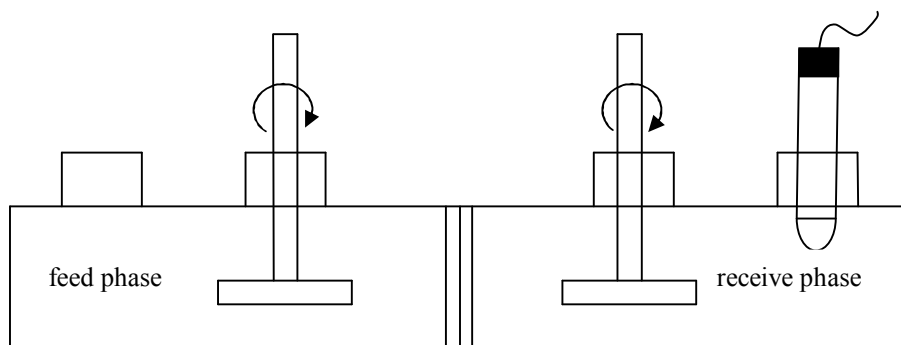


Fig. 1. Experimental apparatus diagram

2.2. Measurement procedure

Solution of citric acid on 0.1M concentration was used as feeding phase. As a receiving phase deionized water ($R \approx 1.5 \text{ M}\Omega$) was applied. Research was conducted at constant temperature equal to $T = 25^\circ\text{C}$. Process run for 50h. In order to determine citric acid concentration during process, conductivity of receiving phase was measured every 15 minutes. The conductivity was converted to concentration of acid in this phase. Before process the thickness of all membranes was measured.

3. Results

In Figure 2 change of citric acid concentration in receiving phase against time was plotted. In case when TOA was used as a carrier the best results were obtained and concentration of citric acid after process was repeatedly higher compared to transport process with 1-alkyl-imidazoliums (Imi11-Imi16) as carriers. In this case, citric acid concentration in receiving phase, after 50h of process, averaged to $0.012 \text{ [mol/dm}^3\text{]}$. It was 25% of equilibrium state. In case of imidazoles, only 1-decylimidazole gave good results, repeatedly better then rest of imidazoles. Comparing the rest four of the imidazoles, a limited ability of citric acid transport was observed.

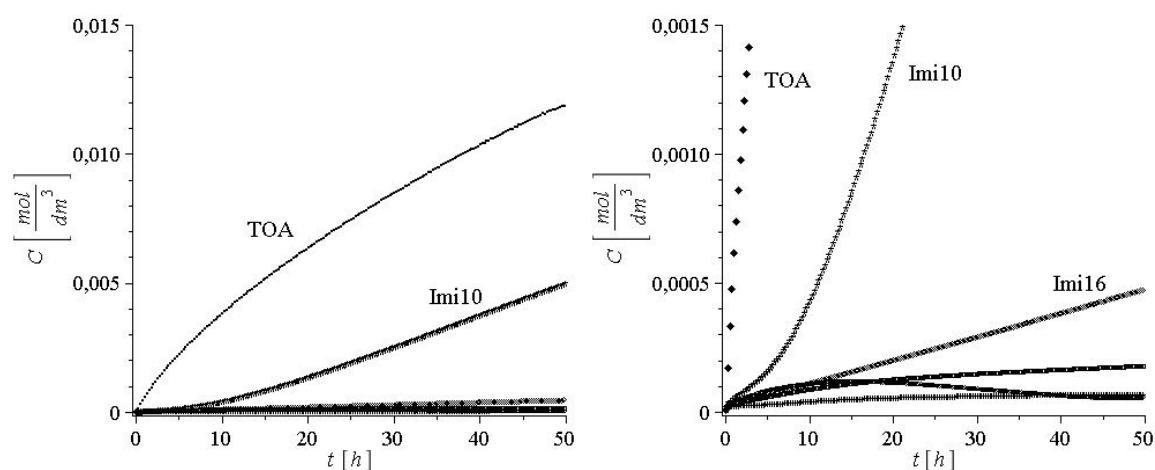


Fig. 2. Dependence of time of process on citric acid concentration in receiving phase

Beginning with fundamental relationship (first Fick's law) it is possible to derive simplified formula that describes transport of citric acid across membrane:

$$-\frac{1}{2} \ln \left(1 - \frac{2 \cdot C}{C_0} \right) = P \cdot t,$$

where P is permeability coefficient $P = \frac{D}{d} K$.

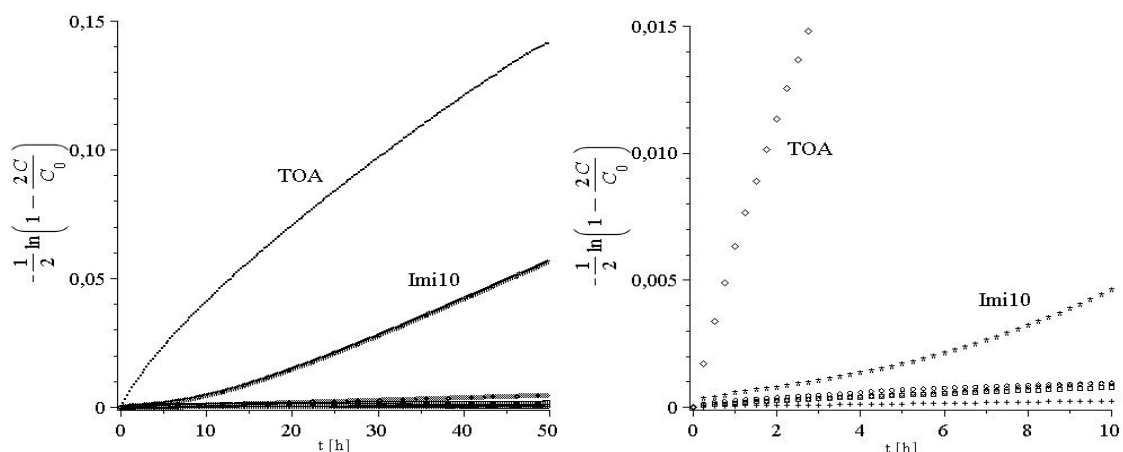


Fig. 3. Dependence of time of process on logarithm of citric acid concentration

In Figure 3 dependence of time on concentration was presented. According to presented formula, this relationship should be a straight line, especially at the initial time, when process is far away from equilibrium state. On the basis of this, it is possible to determine a slope of straight line corresponding to a permeability coefficient P. Having membrane thickness and permeability coefficient, it is possible to calculate diffusion coefficient assuming that $K = 1$. For all measurements mole flux was also calculated.

Table 1. Parameters characterizing transport trough PIM's

	P [m/s] * 10^8	J [mol/m ² *s] * 10^7	d [m] * 10^5	D [m ² /s] * 10^{13}
Imi10	1.06	9.89	3.71	3.94
Imi11	0.186	1.75	4.34	0.81
Imi12	0.076	0.72	3.56	0.27
Imi14	0.307	2.93	4.96	1.52
Imi16	0.294	2.79	4.41	1.29
TOA	8.89	85.4	5.41	48.1

Analyzing results of calculations (Table 1) it is possible to observe that value of permeability coefficients, mole fluxes and diffusion coefficients are more than ten times higher for TOA compared to Imi11-Imi16. In case of Imi10 results are near ten times higher than for rest of the imidazoles. Comparing TOA and Imi10, it is possible to notice slightly better results for amine. Simultaneously, it is showed that thickness of membrane with TOA as a carrier is higher than thickness of the rest of membranes. Analyzing the effect of alkyl chain length in imidazoles it was found out that only imidazole with ten carbon atoms (Imi10)

gives good results. The rest of the imidazoles did not show any influence of alkyl chain length on transport.

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MOLECULAR DYNAMICS STUDY OF THE BEHAVIOUR OF TBP-ZINC-CHLORIDE COMPLEX AT THE CHLOROFORM/WATER INTERFACIAL SYSTEM

Piotr Kujawski, Mariusz B. Bogacki

*Institute of Chemical Technology and Engineering, Poznań University of Technology, Pl. M. Skłodowskiej – Curie 2, 60-965 Poznań,
e-mail: piotr_kujawski@wp.pl*

In this work we report a series of molecular dynamics simulation of the TBP-Zinc-Chloride complex at the water-chloroform interface as well as in mixture of these two compounds. At this interfacial system TBP complexes molecules were placed differently: in pure organic phase, at the interface, and in pure aqueous phase. Pure solvent simulations allow us to define the interface as 5,5 Å thick area. Simulations of TBP at the water/chloroform interface demonstrate the adsorption and orientation of TBP at the interface – where phosphoryl dipoles of TBP molecule are pointed towards the aqueous phase and the alkyl chains are pointed towards organic phase.

1. INTRODUCTION

Phosphoorganic extraction solvents belong to the significant group of chemical compounds, which are used in many technological processes for selective separation and metal ion extraction from polymetallic solutions e.g. zinc, cobalt extraction by D2EHPA or TBP. Natural compounds such as TBP or trialkyl-phosphine oxides with different alkyl-substituents are a very important group of compounds among phosphoorganic extraction solvents. This group of chemistry compounds such as many others extraction solvents belong to amphiphile compounds. They are able to modify interface and this property is used for interpretation of extraction mechanism.

For many years quantum molecular modelling methods have been applied to analyse and describe effects, which proceed in the reactive extraction process (1-3). Many articles describe effects at the interface: water phase/organic phase (4,5) as well as behaviour of the metal complex in different phases.

The aim of this work is to answer several significant questions from the extraction mechanism point of view. First of all we would like to define behaviour of the TBP-Zinc-Chloride complex molecule at the water/chloroform interface and in pure organic phase as well as in pure aqueous phase. How do they move, do molecules try to change their orientation and location? Another question is: What is the orientation of hydrophobic and hydrophilic parts of the TBP molecule?

2. TBP-ZINC-CHLORIDE COMPLEX

Zinc, in chloride solutions, is able to create four different chloride complex: $ZnCl^+$, $ZnCl_2$, $ZnCl_3^-$, $ZnCl_4^{2-}$. Tri-Buthyl-Phosphate is strongly alkaline extractant. Phosphoryl oxygen (P=O) has two free electron pairs thanks to it, this oxygen atom is able to create hydrogen-bonds. TBP can replace even water particles at hydrates of inorganic salt solutions. One form of the zinc-

chloride complex is complex solvated by TBP molecules. This entire unit has tetragonal structure (Fig. 1).

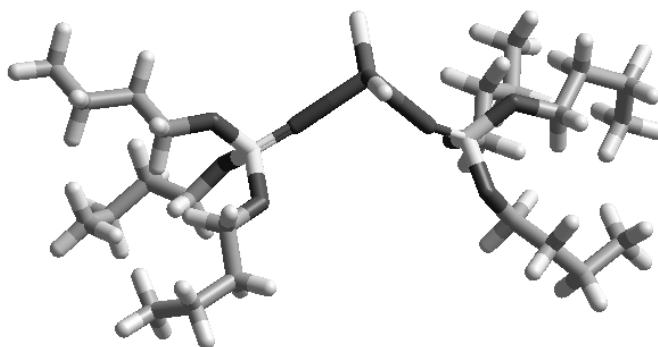


Fig. 1. Structure of $ZnCl_2(TBP)_2$

3. COMPUTATIONAL METHODS

3.1. MOLECULAR DYNAMIC

Molecular dynamic calculations were preformed using Amber 10 software (6) with following representation of the potential energy. Potential energy (E.1) is the sum of energy terms that describe the deviation of bond length, bond angles and torsion angles away from equilibrium values, plus terms for non-bonded pairs of atoms describing van der Waals and electrostatic interactions.

$$V(r) = \sum_{\text{bonds}} K_b (b - b_0)^2 + \sum_{\text{angles}} K_\Theta (\Theta - \Theta_0)^2 + \sum_{\text{dihedrals}} \sum_n \frac{V_n}{2} (1 + \cos(n\varphi - \gamma)) + \sum_{\text{bonds } i \neq j} \left(\frac{q_i q_j}{r_{ij}} - \left(\frac{B_{ij}}{r_{ij}} \right)^6 + \left(\frac{A_{ij}}{r_{ij}} \right)^{12} \right) \quad (1)$$

Before molecular dynamic simulations the entire system of molecules was energy mineralized. Mineralization of the simulation was carried out in three steps. At the beginning we mineralized water and chloroform phase independently. In the next step mineralization of all molecules was preformed. This calculations was done with periodic boundary conditions factor.

Molecular dynamic simulations were divided into two parts. During the first part the temperature of entire system was equilibrated. This part of the simulation was preformed under the following conditions: constant volume, temperature range from 0 to 300 K, Langevin thermostat NTT = 3, shake algorithm = 2, cutoff = 10. Time of simulation 20 ps. The first part of the simulations was preformed in three steps. In the first step water and chloroform phases were equilibrated independently, in the second, equilibration of entire system was preformed. During the second part of the molecular dynamic simulations density of entire system was equilibrated. This simulation was preformed for entire system under the following conditions: constant temperature = 300 K, Langevin thermostat NTT = 3, shake algorithm = 2, cutoff = 12. Time of simulations 2000 ps.

3.2. WATER/CHLOROFORM INTERFACE AND MIXTURE SYSTEMS

Structures of complex and chloroform were created on HyperChem v7.0 software. TBP-Zinc-Chloride complex was created from two the most stable molecules of TBP and than entire molecule was optimized. In HyperChem

each type of molecule is optimized by using semi-empirical method – PM3. Optimization was performed under the following conditions: Algorithm Fletcher-Reeves, termination condition: RMS gradient of 0,001 kcal/(Å·mol) or 10000 of maximum cycles function in vacuo – on. Optimized molecules were used as base molecules for further calculations – conformational search. We chose conformer with most stable heat of formation value to further molecular dynamic simulations.

Water/chloroform interface was created under the following conditions: Numbers of water particles = 1645, numbers of chloroform particles = 373. The particles were placed in a box of the following dimension: $x = 40+40$ Å, $y = 35$ Å, $z = 35$ Å. Interface crosses along z axis for the x coordinate = 40. Minimal distance between molecules is equal to 2 Å (Fig. 2.).

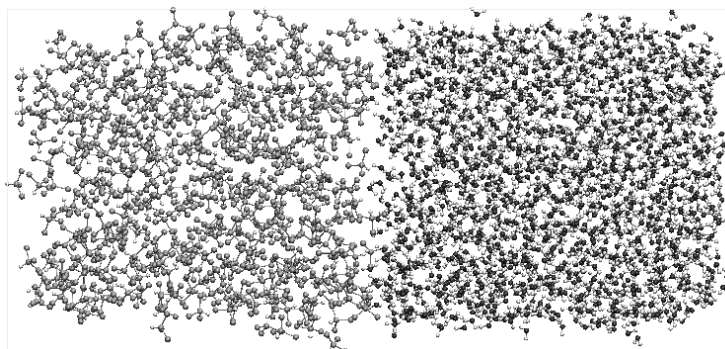


Fig. 2. Water/Chloroform interface. Water phase (right), organic phase (left)

Similar conditions were used to create water/chloroform mixture system. However interface was not defined. Molecules were placed by random in a box of the following dimension: $x = 80$ Å, $y = 35$ Å, $z = 35$ Å.

4. RESULTS

4.1. MIXTURE SYSTEM OF PURE SOLVENTS

Separation of chloroform and water molecules took about 2ns. After simulation we can distinguish three phases: in the middle – organic phase, and at its both sides water phases (“Three layers effect” is the result of periodic boundary conditions.). Results of molecular dynamic simulations allow us to describe the density profile for each solvent. Final density of solvents phases correspond to real value of water and chloroform density.

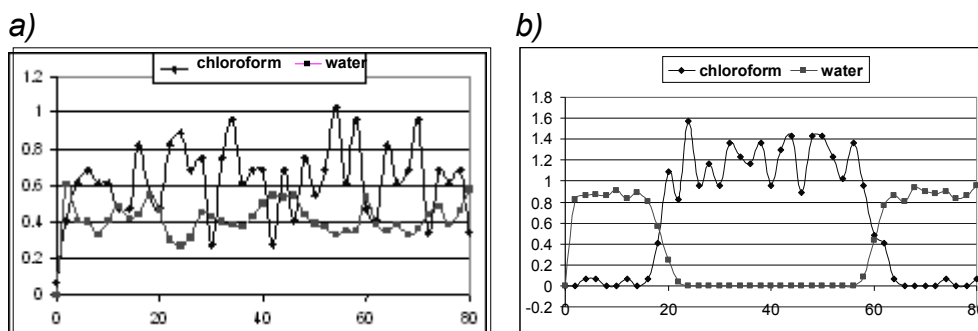


Fig. 3. Water/Chloroform mixture: a) Density profile time = 0 ns. b) Density profile time = 1.5 ns

Thickness of interface can be determined as the distance between two areas where the density of water molecules changes from 10% to 90%. This assumption allows us to state that the interface area is very sharp and its thickness is approximately 5,5 Å. A cross-section through interface shows that particles of the solvent are placed by random. However they have tendency to form associates bounded by hydrogen-bonds.

4.2. SIMULATIONS WITH TBP-ZINC-CHLORIDE COMPLEX

To research TBP-Zinc-Chloride behaviour at the interface we preformed several simulations. First of all we placed three complex molecules in three different way. In system with defined interface one complex molecule was placed in pure chloroform phase, second one at the interface and the last one was placed in pure aqueous face. Moreover we carried out simulation with TBP complexes in the chloroform/water mixture system.

Separation of the mixture system took about 2ns and at the end of simulation we can observe that all three TBP complexes are present at the chloroform/water interface. The alkyl chains of TBP molecule are pointed towards organic phase while more polar part of molecule are pointed towards the aqueous phase.

Molecular dynamic simulation of interfacial system shows that complex molecule which had been placed in pure chloroform phase is less mobile compared to two others. During simulation we can observe that complex which had been placed at the interface, moved deep into organic phase while third complex absorb itself at the "one" of the water/chloroform interfaces.

5. CONCLUSIONS

Our research concludes that TBP-Zinc-Chloride molecules behave in various way depending on the entire system. Complex molecules in organic phase are less mobile than in aqueous phase. Moreover complexes placed at the interface move deep into organic and they are replaced by complexes which had been placed in water phase. Thanks to molecular modelling we can also observe the absorption manner of these complexes at the interface as well as we are able to define thickness of the interface between the solvents.

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REMOVAL OF VERY SMALL AMOUNT OF NICKEL FROM CONCENTRATED ZINC SULFATE SOLUTIONS - MODELING APPROACH

Markku Laatikainen¹, Katri Laatikainen², Tuomo Sainio¹ and Heli Siren²

¹*Lappeenranta University of Technology, Laboratory of Industrial Chemistry,
P.O. Box 20, FI-53851 Lappeenranta, Finland*

²*Lappeenranta University of Technology, Laboratory of Chemistry,
P.O. Box 20, FI-53851 Lappeenranta, Finland
e-mail: markku.laatikainen@lut.fi*

Removal of impurity metals to very low concentrations is essential part of the hydrometallurgical zinc refining process. Use of chelating adsorbents in removal of copper from the highly concentrated zinc sulfate solution has been recently shown to be a realistic alternative for conventional methods (1,2). At the same time, however, selectivity for other impurity metals (nickel, cobalt, cadmium) proved to be insufficient.

Separation of the impurity metals in a fixed-bed system has been modeled with a dynamic model, where the equilibrium binding has been described using the NICA (non-ideal competitive adsorption) model (3). Parameters of pure electrolytes estimated from experimental equilibrium data are used to predict the behavior of multi-component solutions. This approach works well for copper but fails for nickel. This result can be explained by the affinity difference between the impurity metal and zinc. The difference is relatively small for nickel and zinc, and therefore the effect of zinc concentration on nickel uptake is much stronger than predicted by the NICA model.

In this communication, the break-through behavior of nickel is analyzed using experimental data measured with different Ni/Zn ratios. An additional term is included in the equilibrium model to account for the inhibition effect of zinc. Moreover, the possibility of Ni binding kinetics as the rate determining step is discussed.

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COMPETITIVE TRANSPORT OF Zn(II) AND Mn(II) IONS THROUGH HYBRID LIQUID MEMBRANES

Jerzy Gęga

*Czestochowa University of Technology, Department of Chemistry,
19 Armii Krajowej Str., 42-200 Częstochowa, Poland
e-mail: gega@wip.pcz.pl*

Selective separation and concentration of metal ions from water solutions is a significant problem for the analytical procedures and some industrial processes. The use of liquid membrane containing a metal ion carrier is an alternative method to the solvent extraction and ion exchange processes used for removal of metal ions from aqueous solutions (1-5). The processes with such membrane involve the selective transport of the ionic species from a source aqueous solution across a liquid organic phase into an aqueous receiving solution. The liquid membranes are characterized by high separation ability and fast transfer of metal ions. On the other hand they are unstable since the transfer of the ionic carrier as well as an organic solvent into the contacting aqueous phases is observed. The instability of these systems often produces a problem to the practical industrial applications. Thus, the solving of liquid membrane stability is an important issue.

For improvement of liquid membrane stability several methods has been proposed, for example: gelation of liquid phase, polymerization of membrane top layer and others (6-10). Among them an application of hybrid liquid membrane has been described (11-17). The concept of the method is the introduction of liquid organic layer between two solid polymeric membranes, which are permeable for metal ions (e.g. ion-exchange membrane). In this situation the solid membranes physically separate organic and aqueous liquid phases simultaneously allowing diffusion of ions. In this paper the application of hybrid liquid membranes for separation of Zn(II) and Mn(II) mixture is presented.

Separation processes of an initial equimolar mixture of zinc(II) and manganese(II) sulphates with hybrid membranes were studied in the system:

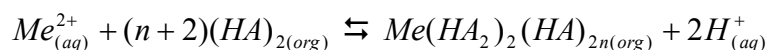
aqueous feed solution (Zn(II), Mn(II))	solid polymeric membrane	organic phase – ionic carrier solution in kerosene	solid polymeric membrane	aqueous receiving solution (H ₂ SO ₄)
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In the role of solid polymeric barrier two kinds of membranes were applied:

1. cation exchange membrane Nafion 117 (CEM)
2. polymeric inclusion membrane (PIM), made with cellulose triacetate as a support, o-nitrophenyl octyl ether as a plasticizer and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) as an ionic carrier.

In the liquid organic phase the same ionic carrier at concentration of 0.10 M was used.

Cyanex 272 is well known extractant of several metal ions (14,18-20). In the case of divalent ions complexation, the reaction can be written as (14):



For all applied membranes the transport of both metal ions was observed. The representative kinetic curves at pH of aqueous feed solution equal to 2.0 for hybrid membranes with CEM (HLM-CEM) as well as hybrid membranes with PIM (HLM-PIM) are shown in Fig. 1. For comparison the results of transport through CEM and PIM alone are presented also.

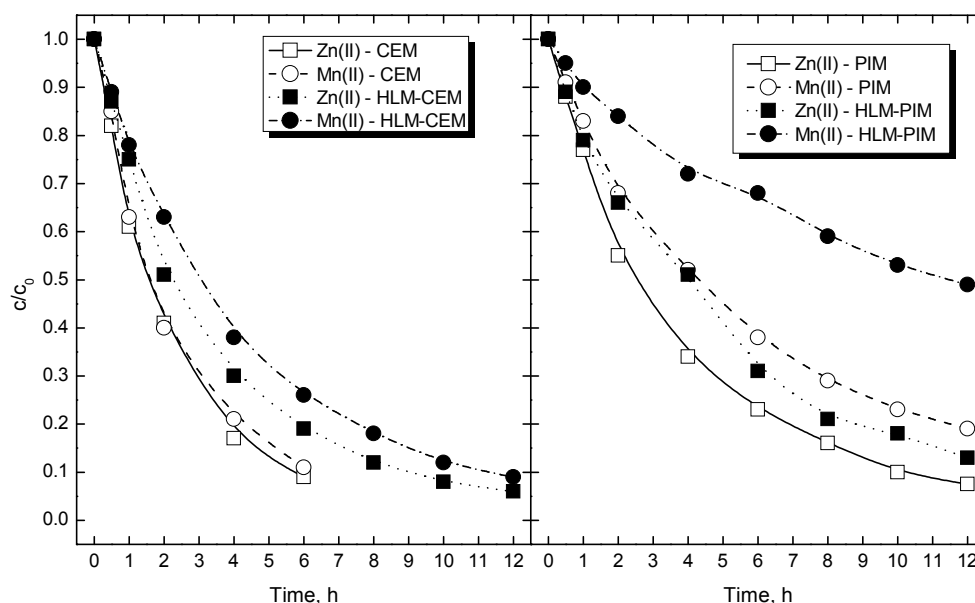


Fig. 1. Kinetics of Zn(II) and Mn(II) transport through different kind of membranes. Aqueous feed phase: 10 mM ZnSO₄ and MnSO₄, pH = 2.0. Receiving phase: 2.0 M H₂SO₄. Description of membranes – see text

It can be seen that no significant differences between the transport of Zn(II) and Mn(II) ions through membrane Nafion 117 (CEM). For other membranes the results indicate that Zn(II) ions are transported faster than Mn(II). The largest differences are observed for hybrid membrane HLM-PIM.

For comparison of the transport rate through all kinds of membranes the initial fluxes of both metal ions were calculated. Kinetic curves obtained at different pH of aqueous feed solution in the range from 0 to 6 are typical for first order equation, i.e. dependence of $\ln(c/c_0) = f(\text{time})$ is linear and its slope (corresponding to constant rate k of transport) can be used for calculation of the flux.

The influence of feed phase acidity (pH) on Zn(II) and Mn(II) initial fluxes is presented in Fig. 2. It can be seen that with the pH increase the flux grows in cases of all used membranes. For Nafion 117 membrane the fluxes for both ions are similar and changes across pH range are small. In the case of hybrid membrane with cation exchange membrane (HLM-CEM) fluxes of both metal ions are increasing to constant values at pH above 5. Zn(II) ions are transported faster than Mn(II) ions in all pH range. For PIM and HLM-PIM membranes strong increasing of both metal ions fluxes with pH increase were observed but

differences between flux of zinc(II) and manganese(II) ions are bigger than in the case of membranes with CEM.

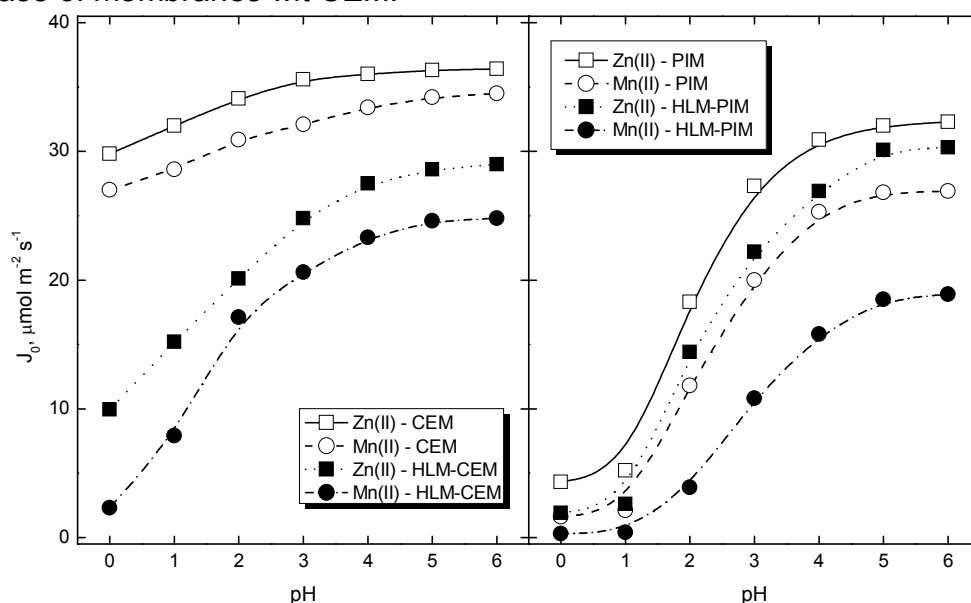


Fig. 2. Initial flux of Zn(II) and Mn(II) ions as a function of feed phase pH. Aqueous feed phase: 10 mM ZnSO₄ and MnSO₄. Receiving phase: 2.0 M H₂SO₄

For description of separation ability of the investigated membranes the separation factor $S_{Zn/Mn}$ was calculated as a ratio of initial fluxes of metal ions and is presented in Fig. 3. As can be concluded from this figure for CEM separation factor reach value about 1 and do not depend on feed solution pH. For other membranes $S_{Zn/Mn}$ is decreasing with pH increase. The highest values of separation factor were achieved for hybrid membrane with polymer inclusion membranes (HLM-PIM).

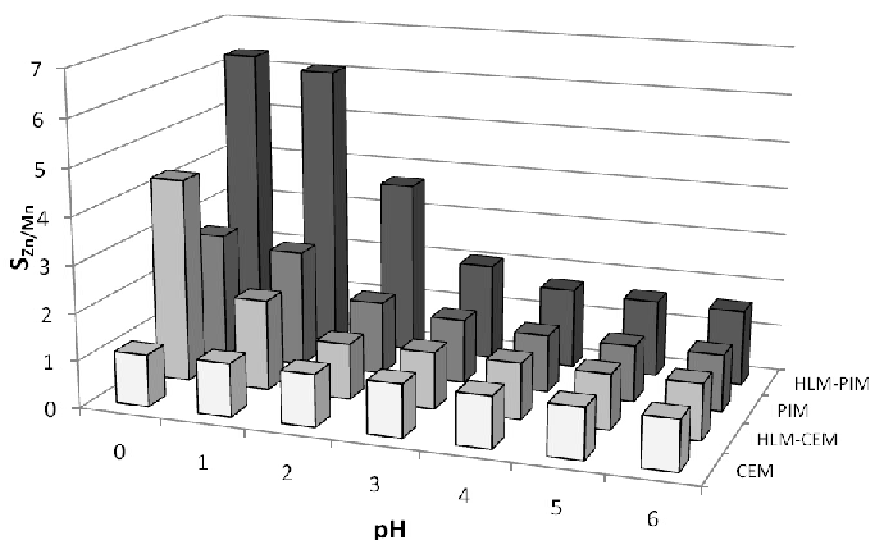


Fig. 3. Separation factor of Zn(II) vs. Mn(II) as a function of feed phase pH. Aqueous feed phase: 10 mM ZnSO₄ and MnSO₄. Receiving phase: 2.0 M H₂SO₄

CONCLUSIONS

Presented results show the possibility to use of hybrid membranes obtained by combination of liquid membrane with cation exchange membrane (HLM-CEM) or polymeric inclusion membranes (HLM-PIM) for separation of Zn(II) and Mn(II) from sulphate solutions at different pH. For all investigated systems Zn(II) ions were transported faster than Mn(II) ions. Membranes with CEM transported ions faster than those with PIM. Membranes HLM-PIM allowed to separate of equimolar mixture of Zn(II) and Mn(II) with the highest efficiency. Efficiency of separation was lowering with feed phase pH increasing.

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THE EFFECT OF SURFACE FORCE ON THE GAS MIXTURE SEPARATION IN NANODIMENSIONAL CAPILLARIES

Vladimir M. Zhdanov¹, Vjacheslav I. Roldughin²

¹*National Research Nuclear University "MEPhI", Kashirskoe shosse, 31
115409, Moscow, Russia*

²*Frumkin Institute of Physical Chemistry and Electrochemistry, Russian
Academy of Sciences, Leninsky prospect, 31, 119991, Moscow, Russia
e-mail: VMZhdanov@mail.ru*

1. Introduction

It is well known, that there is a separation of a gas mixture under the action of pressure and temperature gradients during the flow of mixture in fine capillaries (1,2). The separation effect occurs due to the difference in masses, cross-sections or accommodation coefficients of mixture species.

It was shown that the effects related to the surface forces acting on the molecules in the vicinity of capillary surface should be taken into in consideration of free molecular gas flow in nanosize capillaries under the action of temperature gradient (3,4). These forces appear naturally in the left-hand side of the Boltzmann kinetic equation for the gas which is non-uniform in temperature.

The surface forces significantly effect the flow rate due to the temperature gradient and the termomolecular pressure drop (TPD) between the vessels connected with a package of nanosize capillaries under the steady state (4). The molecules of different species have different potentials of gas/surface interaction, so the surfaces forces can affect the separation of components of gas mixture flowing in ultrafine capillary.

In the present report the effects of the surface forces on the non-isothermal gas mixture flow in nanosize capillaries are considered. The possibility is shown of the gas mixture separation due to the difference in the potentials of molecule/wall interaction for mixture components in the presence of temperature gradient. The explicit expressions for the TPD and separation effects were obtained for the stationary conditions corresponding to the vanishing integral diffusion fluxes of mixture species. The possibility is discussed of the determination of gas/surface interaction parameters by combined measuring the TPD and separation effects.

2. Average velocities of mixture components in a capillary

Consider the flow of multicomponent gas mixture in a cylindrical capillary in the presence of pressure ∇p , temperature ∇T and concentration ∇y_α , gradients all directed along the z axes of a capillary (indexes α indicate species numbers). Let us assume that the gas molecules interact with the surface of capillary wall being in the field with potential $U_\alpha(r)$, where r is the distance from the center of the capillary. Potential $U_\alpha(r)$ is other than zero in the neighborhood of the walls, i.e., at $r \approx R$, where R is the capillary radius.

The state of gas mixture is described by distribution functions $f_\alpha(r, z, v_\alpha)$ of mixture molecules over velocities v_α . We assume that distribution functions $f_\alpha(r, z, v_\alpha)$ can be represented as $f_\alpha(r, z, v) = f_\alpha^{(0)}(1+\varphi_\alpha)$, where φ_α are corrections to local Maxwell-Boltzmann distributions $f_\alpha^{(0)}$.

As the analysis implies the surface force effects are significant only for ultrafine capillaries, which diameter is less than the mean free path of gas molecules under the normal conditions (4). This corresponds to the free- molecular or Knudsen flow of gas and enables one to ignore the collision integral in the right-hand side of kinetic equation. The linearized kinetic equation in our case can be represented as (4,6):

$$\bar{v}_{\alpha r} \frac{d\varphi_\alpha}{d\bar{r}} = -v_{\alpha z} \left(\frac{mv_\alpha^2}{2kT} - \frac{5}{2} \right) \tau - v_{\alpha z} k_\alpha - v_{\alpha z} \frac{U_\alpha(r)}{kT} \tau, \quad (1)$$

where $\tau = \nabla T / T$, $k_\alpha = \nabla p_\alpha / p_\alpha$, p_α is the partial pressure of component α , \bar{r} is two-dimensional vector in the cross-section plane.

The expression for φ_α is obtained if we integrate equation (1) along the characteristics (6). The macroscopic velocities of the mixture species fluxes are defined as:

$$u_\alpha(r) = \int v_\alpha \varphi_\alpha \exp\left(-\frac{m_\alpha v_\alpha^2}{kT}\right) d\bar{v}_\alpha = -\left(\frac{2kT}{m_\alpha}\right)^{1/2} \frac{1}{4\pi} \left\{ \left(k_\alpha - \frac{1}{2}\tau\right) \int_0^{2\pi} \sqrt{(R^2 - r^2 \sin^2 \vartheta)} d\vartheta + \tau \int_\Sigma \frac{U_\alpha(\bar{r}')}{kT} \frac{d\Sigma}{|\bar{r} - \bar{r}'|} \right\}$$

where Σ is the channel cross-section.

The averaged over the cross-section flux of mixture species α through the capillary can be written as

$$G_\alpha = n_\alpha \langle u_\alpha \rangle \pi R^2 = -\frac{2}{3kT} \bar{v}_{\alpha t} \pi R^3 \left[\nabla p_\alpha - \frac{1}{2} \frac{p_\alpha}{T} \nabla T (1 + b_\alpha) \right] \quad (2)$$

where

$$b_\alpha = -\frac{3}{8\sqrt{\pi}} \frac{1}{R} \frac{1}{Q_\alpha} \int_0^R \exp\left(-\frac{U_\alpha(r)}{kT}\right) r \int_\Sigma \frac{U_\alpha(\bar{r}')}{kT} \frac{d\Sigma}{|\bar{r} - \bar{r}'|} dr$$

$$Q_\alpha = \int_0^R \exp\left(-\frac{U_\alpha(r)}{kT}\right) r dr$$

Here $\bar{v}_{\alpha t} = (8kT/\pi m_\alpha)^{1/2}$ is the mean thermal velocity of molecules of species α . One can see from equation (2) that velocities of the mixture species fluxes is determined not only by their masses (multiplier $\propto \sqrt{1/m_\alpha}$), but also by the potentials of their interaction with capillary surface (parameter b_α). Since each component has its own surface force potential, the surface forces give different contribution to the fluxes of species under the action of temperature gradient.

In general case the calculation of $\langle u_\alpha \rangle$ at given $U_\alpha(r)$ can be carried out only numerically.

3. Thermomolecular pressure drop and effect of mixture separation

Let us consider the case when there is a fixed temperature drop between the vessels I and II connected by a package of nanosize capillaries. The transfer of mixture components caused by the temperature gradient results in a pressure difference between the vessels which varies in time. The steady state pressure drop is established when the total fluxes G_α of mixture components through the capillaries cross sections vanish. Under this condition, we have

$$\nabla p_\alpha - \frac{1}{2} \frac{p_\alpha}{T} (1 + b_\alpha) \nabla T = 0, \quad (3)$$

Summing Eq. (3) we have

$$\nabla p = \frac{1}{2} \frac{p}{T} (1 + \sum_\alpha y_\alpha b_\alpha) \nabla T \quad (4)$$

Integration of this equation results in the relation between the ratios of pressures and temperatures in the vessels

$$\frac{p_I}{p_{II}} = \left(\frac{T_I}{T_{II}} \right)^{\beta_T/2}, \quad \beta_T = 1 + \sum_\alpha y_\alpha b_\alpha. \quad (5)$$

The result obtained shows that surface forces effect the TPD.

Now, let us consider the stationary concentration difference in the vessels established for binary mixture (separation effect). It is known, that in the absence of surface forces, there is no thermodiffusion separation of gas mixture flowing in a capillary in the free molecular regime (1). In our case, putting $p_1 = y_1 p$, where subscript 1 refers to the lighter component of mixture, and using equations (3) and (4) we find

$$\nabla y_1 = \frac{1}{2} (b_1 - b_2) y_1 y_2 \frac{1}{T} \nabla T. \quad (6)$$

From (6) it follows that the separation effect is determined by the difference in coefficients b_α , directly related to the potentials characterizing the interaction of gas molecules with capillary surfaces. Expressions (5) and (6) give the base for quantitative determination of the parameters of surface force potentials using the measurements of TPD and separation effects.

Let us estimate the contribution of the surface forces to the effects discussed. We assume that the surface van der Waals' forces of attraction fall in accordance with the power law with an increase in the distance $x = R - r$ from the surface of channel walls and take advantage of the following expression (5)

$$U_\alpha(x) = - \frac{\hbar \omega_0 \alpha_\alpha \alpha_s N_s}{x^3}, \quad (7)$$

Where \hbar is Planck's constant, ω_0 is characteristic frequency of electron transitions ($\hbar \omega_0$ is approximately equal to ionization potential), α_α, α_s are the

polarizabilities of molecules of kind α and the matter of channel walls, respectively, N_s is the number of atoms per unit volume of solid.

Assuming that x is equal to a mean value $\langle x \rangle \approx 0.5$ nm, the capillary radius is 10 nm and taking the corresponding values of the polarizability for argon and glass (6), we have for the coefficient b_α at room temperature:

$$b_\alpha = \frac{\langle x \rangle}{R} \frac{\hbar \omega \alpha_\alpha \alpha_s N_s}{\langle x \rangle^3 kT} \approx 0.1. \quad (8)$$

Even having in mind some indefiniteness of parameter $\langle x \rangle$, one can easily see that accounting for the surface forces results in noticeable increase in the effects discussed. As the temperature decrease, the effect of surface forces rises. Note also that relation (8) gives the lower estimate of the correction.

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MEMBRANE SEPARATION PROCESSES IN THE PRODUCTION OF THE GREEN FUELS

Wojciech Kujawski

Faculty of Chemistry NCU, 7 Gagarina Street, 87-100 Toruń, Poland
e-mail: kujawski@chem.umk.pl

Since the 1970s, the world market has been facing massive fluctuations in the availability and prices of conventional motor fuels. Moreover, due to excessive emissions of carbon dioxide and other greenhouse gases, environmental changes associated with global climate warming are accelerating. Since the 1980s, ethanol has been considered as one possible alternative fuel in many countries. In Brazil, fuel ethanol is produced on a large scale since 1970s, whereas in EU countries development started in 2003 only as a result of 2003/30/EC Directive. This Directive suggested that a minimum proportion of biofuels and other renewable fuels placed on national markets should be 2% by the end of 2005, 5,75% by the end of 2010 and targeting at 20% by 2020.

In general, the biofuels can be classified into four groups or generations:

- I generation of biofuels is produced directly from food crops (oil, ethanol).
- II generation of biofuels has been developed to overcome the limitations of first generation biofuels. Such biofuels are produced from non-food crops such as wood, organic waste, food crop waste and specific biomass crops, therefore eliminating the main problem with first generation biofuels.
- III generation of biofuels is based on improvements in the production of biomass. It takes advantage of specially engineered energy crops such as algae.
- IV generation of biofuels is aimed not only at producing sustainable energy but also a way of capturing and storing carbon dioxide.

The lecture will overview the potential of the application of various membrane techniques (e.g. enzymatic membrane reactors, micro-, ultra- and nanofiltration, gas separation and pervaporation) in the production of ethanol (as an example of I and II generation of biofuels) and by-products management (Fig. 1). Special attention will be given to pervaporation. This membrane separation technique can be used for the removal of ethanol from the fermented broth, dehydration of ethanol and dehydration of fusel oils.

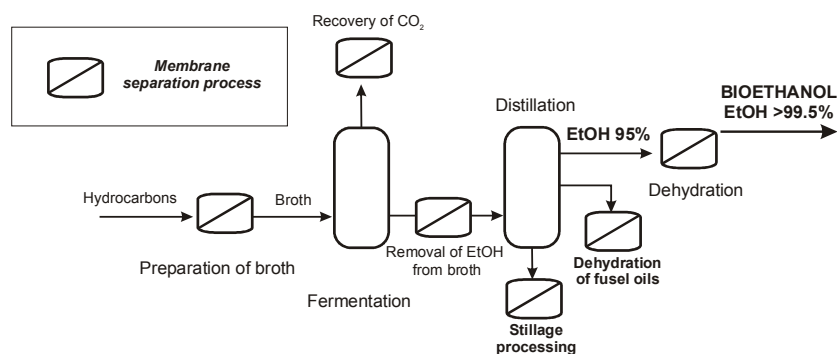


Fig. 1. Membrane separation processes in the ethanol production

GENERAL MODEL OF MASS TRANSFER PROCESSES IN A CASCADE WITH LOSSES OF WORKING SUBSTANCE

Andrey Yu. Smirnov, Georgy A. Sulaberidze

*National Research Nuclear University "MEPhI", 115409, Russia, Moscow,
Kashirskoe shosse, 31
e-mail: a.y.smirnoff@rambler.ru*

For separation of both binary and multicomponent molecular mixtures one often uses so-called separation cascades (multistage separation installations). In most cases gaseous mixtures are used as a working substance in the cascades.

Before construction of the cascade for separation of some mixtures it is necessary to estimate the operational characteristics of such installation (number of stages, number of separation elements, required values of external cascade flows and etc.). The problem of cascade calculation may be complicated due to the following reasons (1,2):

1. destruction of the working substance inside the separation cascade;
2. formation of a new gaseous component out of destruction products;
3. leaking of extraneous gaseous component (for example, water vapour) inside the separation cascade because of slight defects of vacuum system.

All these effects may take place in practice of molecular mixtures separation in cascades. Thus, it is necessary to take them in account during estimation of the operational and economic characteristics of separation factory.

This paper is devoted to analysis of mass transfer regularities in cascades for separation of multicomponent mixtures with account of the whole set of factors such as destruction of the working substance, leaking of extraneous gaseous component and formation of a new gaseous component inside the cascade.

The effect of above-listed factors on external cascade parameters is estimated. Regularities of a distribution of the new component along the cascade are analysed.

All calculations were done based on both the theory of model cascades and the mathematical model widely applied in practice squared-off cascade (the feed flows of each stage are the same).

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RECENT PATENTS ON ION-EXCHANGE MEMBRANES AND ELECTRO-MEMBRANE SEPARATION PROCESSES

Stanisław Koter

*Nicolaus Copernicus University, Faculty of Chemistry, 7 Gagarina St., PL-87100
Toruń, Poland
e-mail: skoter@umk.pl*

A review of patents on polymer ion-exchange membranes and electro-membrane separation processes (excluding the proton- or anion-exchange membrane fuel cells) published in the last 6 years is given. Thousands of patents (mostly from China and Japan) show that these processes are concerned as economically effective and environmentally friendly.

In the first part of work the patents on the methods of formation of cation- (CEM) and anion-exchange membranes (AEM) are discussed. The most numerous are the patents on the membranes obtained by filling a porous polymer film with an ion-exchange material and by modification of polymer films. A few patents describe how to obtain the membranes with profiled surface; this should increase the limiting current and/or eliminate the use of ion-exchange resins or ion-conductive spacers. Some other patents are devoted to the mechanically stable membranes or of increased resistance to fouling, alkaline environment, heat. The methods for manufacturing AEMs without using carcinogenic materials, hollow fiber AEMs, and the improvement of membranes designed for chlorine-alkali electrolysis can also be found.

In the second part of work the patents concerning the following membrane processes are presented: classical electrodialysis (ED), ED with a bipolar membrane (EDB), metathesis ED, electro-electrodialysis (EED), and electrolysis. The applications of ion-exchange membranes are diverse and can be divided into the following groups: desalination and purification, removal of harmful substances, recovery of valuable substances, regeneration of spent solutions, production of new compounds. Apart from the desalination of water or removal toxic substances (fluorine, arsenic, boron, chromium) one can mention the desalination of glycerol-rich solutions (byproducts from biodiesel production), purification of pharmaceutical solutions or the food raw materials, removal of fermentation inhibiting substances. Many patents concern the application of EDB for the conversion of salt solutions into the acid and base solutions. Examples of acids (apart from mineral ones) and bases produced in the EDB or EED cells include gulonic, acetic, hydriodic, 3-hydroxypropionic, glutamic acids, LiOH, NaOH, KOH, NH₃, etc. By that method also a spent absorption solution from flue gas desulfurization is regenerated. Some patents are devoted to the production of compounds by ion exchange (metathesis ED), e.g.: production of monosodium glutamate solution from monoammonium glutamate and sodium salt solutions, the preparation of choline salts, the production of highly soluble oxidizing agents (e.g. magnesium permanganate, calcium permanganate, ammonium peroxydisulfate) from oxidizing agents of limited solubility (e.g. potassium permanganate, potassium peroxydisulfate),

preparation of organic quaternary ammonium fluorides from quaternary ammonium salts and metal fluorides.

Single membrane electrolytic cells (mainly with a CEM) also appear in the numerous patents. They are used in the production of: H_2/O_2 , benzaldehyde, p-hydroxybenzaldehyde, persulfuric acid (H_2SO_5), hydrogen peroxide, chlorine dioxide, high-grade lithium hydroxide, 1,5-diaminonaphthalene, aminoanisole, 4-fluoroaniline, sodium dichromate, etc. These cells are used for metal deposition, for etching or plating solutions regeneration, cleaning of wastewaters (e.g. aniline or nitrobenzene degradation, ammonium and nitrate ions removal) and gas mixtures (e.g. chlorine recovery/removal).

Further development of electro-membrane processes is limited by the lack of membranes selective towards specific ions – no patents solving that problem have been found. Still, more selective CEMs in strongly alkaline solutions and more selective AEMs in acidic solutions, especially multiprotic acid solutions, are needed.

PRELIMINARY STUDIES ON CONVERSION OF KCl WITH POST – HYDROLYTIC SULPHURIC ACID INTO KHSO₄ IN A MEMBRANE REACTOR

Maria Tomaszewska, Agnieszka Mientka

*West Pomeranian University of Technology, Institute of Chemical and Environment Engineering,
ul. Pułaskiego 10, 70-322 Szczecin, Poland
e-mail: maria.tomaszewska@zut.edu.pl*

Introduction

The potassium sulphate is well known inorganic compound which has found great utility in many areas, for example, as a fertilizer and as an intermediate for the production of useful products. In one common procedure, potassium sulphate was prepared by the reaction of KCl and sulphuric acid (1,2). The reaction occurs in two steps:



Another method of K₂SO₄ production was proposed to be performed at lower temperature (3).

The results of our experiments shown that the membrane distillation (MD) process could be applied to the conversion of KCl with H₂SO₄ into KHSO₄ and for simultaneous separation of HCl from the reaction mixture (4,5). HCl is a volatile product of the KCl and H₂SO₄ conversion. Therefore, it can be continuously separated from the liquor to shift the equilibrium of this reaction using membrane distillation.

The aim of the presented work was the investigations of the influence of composition of sulphuric acid obtained from TiO₂ production on the HCl separation and purity of KHSO₄ formed in the membrane reactor integrated with the direct contact membrane distillation (DCMD).

Materials and methods

The investigations were performed using a module equipped with the capillary membranes made from polypropylene (Accurel PP S6/2, Membrana GmbH, Germany) with $d_{in}/d_{out} = 1.8/2.6$ mm. The membranes were characterised by the pore size with a maximum and nominal diameter of 0.6 μm and 0.2 μm, respectively, and the porosity of 73%. The working area for capillary module was 0.0127 m². The studies were performed using sulphuric acid formed during TiO₂ production. The concentration of the acid was about 25 wt%. The acid also contained salts of Fe, Al and Mg. The conversion process was performed using the solutions containing KCl and H₂SO₄ in the molar ratio equal to 1:1. The feed flowed inside the capillaries, whereas the distillate flow through the intercapillary space. The temperature of the reaction mixture at the module inlet amounted to 343 K, whereas the inlet temperature of distillate was kept at 293 K. The reaction mixture were concentrated close to the saturated state, when a salt

was precipitated from the feed solution after cooling. After the separation of the precipitate, the remained mother liquor was again concentrated.

The changes of volume of the cold distillate were measured every hour to calculate the volume permeate flux. Simultaneously, the changes of the solutes concentrations in the feed and distillate were analysed. The formed precipitates were characterized by means of chemical analysis and the X-ray diffraction method (X'Pert PRO, Philips with Cu α lamp). The HCl flux was calculated from the material balance of HCl in the distillate performed every hour taking into account the changes in the volume and the acid concentrations in the distillate as was described in (6).

Results and discussion

Potassium bisulphate and HCl are formed during acidulation of KCl by H_2SO_4 (1). The sulphuric acid obtained from TiO_2 production contained salts of Fe^{2+} up to 4% and Mg, Al in minor concentrations. The process of conversion with HCl removal from the reaction mixture was performed in a membrane reactor integrated with DCMD. The chemical reactor comprises a feed tank and the warm loop of the DCMD installation. The influence of the reaction mixture composition on the HCl flux through the hydrophobic membrane in MD module and the precipitate composition was studied. During the MD process water vapour and hydrogen chloride were transferred from the reaction mixture to the distillate through the membrane pores. Whereas, the ions present in the solution, such as K^+ , SO_4^{2-} , Fe^{2+} , Mg^{2+} , Al^{3+} were completely retained in the feed. The concentration of Fe^{2+} ion as the major component of impurities present in post – hydrolytic sulphuric acid was determined. Retention coefficient of the non-volatile compounds amounted to 100%, thus H_2SO_4 and the salts were concentrated continuously.

The results of the continuous concentration of the reaction mixture containing KCl and post-hydrolytic sulphuric acid at the molar ratio equal 1 to 1 by DCMD are presented in Fig. 1. The figure shows the changes of concentrations of sulphates as an example of the ions retained by the membrane and periodically removed from the feed in a precipitate form and chlorides, freely transported through the membrane as HCl. Initially, the concentrations of components were gradually increased. The sulphates concentration in the feed at the point close to the supersaturation state of potassium salt achieved the value which was four times greater (455.58 g/dm^3) than that in the starting solution. After cooling of the feed to 293 K and the separation of a precipitate formed from the supersaturated feed, the sulphates concentration decreased to 386.58 g/dm^3 . The mother liquor left after the precipitate removal was again concentrated by MD. The further changes of the SO_4^{2-} concentration in the mother solution were associated with its concentration by MD and precipitation of the conversion product. In comparison with the process performed using a model solution (7) the whole conversion process performed in four series was nearly two times longer and lasted 26 hours. The reason could be lower permeate flux in the conversion with post – hydrolytic acid resultant from the presence of additional salts in the acid.

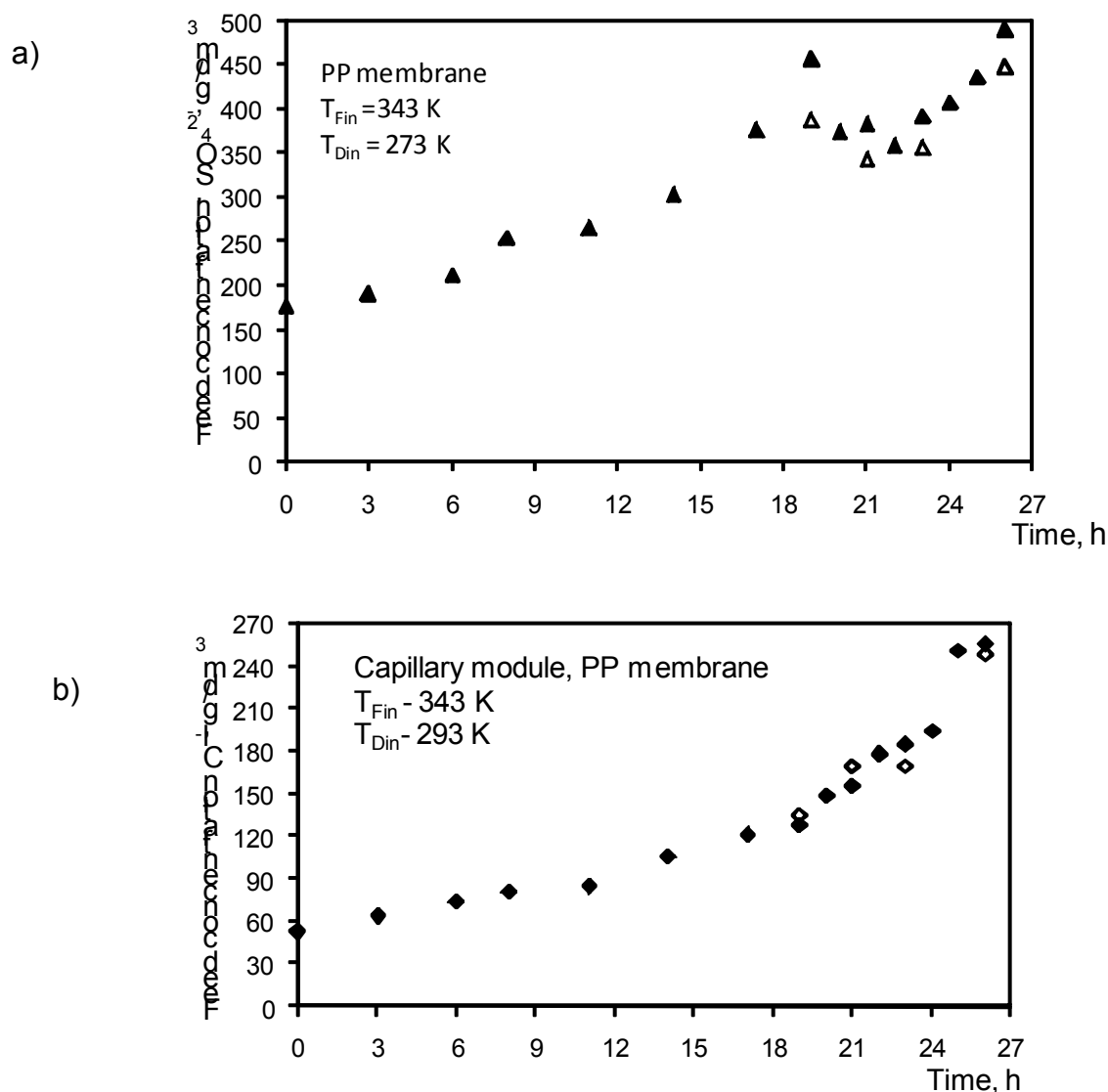


Figure 1. Changes in the ions concentrations in the reaction mixture containing 1 mole KCl and 1 mole H_2SO_4 in the form of post – hydrolytic sulphuric acid in the membrane reactor integrated with MD as a function of reaction time – a) SO_4^{2-} and b) Cl^- (Δ or \diamond – the symbol of the ion concentration in the feed after the precipitate removal)

The K^+ ions similarly as SO_4^{2-} ions were gradually concentrated up to the point close to supersaturation state. The precipitation of a salt caused a decline of the potassium ions concentration in the feed, what indicated that the precipitate contained potassium ions besides sulphates. Every time after separation of the precipitate, the concentration of K^+ in the feed was decreased. Thus, the concentration of potassium ions in the feed was lower at the beginning of subsequent series of the MD concentration.

Since the sulphuric acid from TiO_2 production contained salts of Fe, Al, Mg, changes of Fe(II) concentration were also examined during these experiments. The concentration of Fe ions in the solution increased in three series of MD. It could mean, that Fe^{2+} did not enter into composition of salt precipitated from the mother solution. However, its concentration in the mother solution from the fourth series was decreased after salts precipitation. It could mean that the Fe(II) ions were co-precipitated with potassium ions and complex salts were

formed. The ICP and X-ray analysis confirmed that the precipitate contained also Fe(II).

Fig. 1b present changes of Cl^- during conversion of KCl into KHSO_4 . HCl is the second product of the conversion KCl with H_2SO_4 , according to the reaction (1). The volatile HCl is transported through the PP membranes together with the water vapour from the feed to distillate side. The character of curves indicated that the concentration of HCl on feed side continuously increased, despite of its transfer through the membrane. The transfer of HCl through the pores of PP membrane during the process indicated on the progress in the conversion reaction KCl to KHSO_4 . Simultaneously, it demonstrated that the partial pressure of HCl over the feed despite of comparatively low HCl concentration in the feed was sufficient to transfer the gaseous HCl across the membrane together with the water vapour. It was result of high concentration of non-volatile components in the feed (desalting effect) as well as the increasing HCl concentration in the feed. The presence of salts and sulphuric acid in the feed decreased the solubility of gaseous HCl and favoured its desorption (8). Therefore, HCl concentration in the receiving phase with an increase of the concentration of non-volatile components in the feed was continuously grown. The HCl concentration in the distillate (receiving phase) increased to 12.76 g/dm^3 during the MD process. The molar HCl flux through the membrane increased to $117 \text{ mol/m}^2\text{d}$.

The water vapour pressure was decreased with an increase of solute concentration in the feed, thus the resultant permeate flux was also decreased. Moreover, a decline of the permeate flux was caused by increasing density of the feed and the influence of polarisation phenomena. The permeate flux in the concentration process for model solution without salts Fe (II) was higher than at concentration of the real solution (7).

The composition of the precipitate was determined by the XRD analysis. It was found that KHSO_4 was the main phase in the precipitate obtained in the first three series of the MD process. However, after the fourth series of the concentration of feeding solution a complex salt containing of Fe^{2+} was present in the precipitated solid phase. Obtained KHSO_4 was practically free of chlorides.

Conclusions

The membrane reactor integrated with DCMD was successfully applied for the conversion of KCl into KHSO_4 with diluted H_2SO_4 from TiO_2 production. The precipitated KHSO_4 was free of chlorides and would be applied in agriculture. The presence of the salt and H_2SO_4 in the feed caused an increase in the molar flux of HCl through the hydrophobic membrane during MD.

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PARADIGM SHIFTS IN PROCESS SCALE IMPLEMENTATION OF NOVEL MULTI-PHASE CONTACTING SYSTEMS

Bruce A. Hendry

*Department of Chemical Engineering, Cape Peninsula University of Technology, Symphony Way, Bellville, Cape Town, South Africa 7535
e-mail: hendryb@cput.ac.za*

Regarding development of novel materials and chemical methods for separation processes, some practical considerations in the field applications may narrow down their potential usefulness for separations. This paper will attempt to focus our attention on some the paradigm shifts that engineers and scientists will be making in their collective thinking as such new materials become commonly applied.

The paper will refer to the water and wastewater treatment field which is of particular interest to the author. It is currently an important target application for new technology developments and the ideas will be easily transferred to other process application fields. Type or classes of contact between selective media and aqueous solutions will be broadly defined to compare packed beds, fluidized beds, membranes and 'nanofluids'. The paper will consider the transition of design philosophy from packed beds of adsorptive or reactive media through the adoption of fluidized media contacting to membrane systems including hybrid systems involving conventional resins. The size of the selective media is a major parameter in design and performance of these types of contacting operations. Particle size influences pressure drops for fluid flow in the systems, equipment size, media inventories and rates of mass transfer.

In considering the impending transition to nanoparticles and nanofluids and molecular scale reagents, the reduced size of the selective media is frequently the perceived advantage and target but may also present a potentially confounding factor when it comes to designing equipment and process installations that will compete with conventional technology in terms of first cost, operating cost, reliability and sustainability and the operational skills required.

It would be important for inventors and exploiters of new selective media to find an emerging trend to guide and concentrate R&D effort and expenditure. However, the possibilities for new knowledge creation and the wide range of potential applications in sustainable chemical industries in the present age would not be easily tolerant of such restrictions on scientific endeavours and knowledge creation!

Across the wide range of adsorptive and extractive contacting processes (from liquid extraction to flotation and from porous particles to membranes) improved process efficiency is most often sought by enhancing the selectivity and rates of mass transfer of the media. While the chemistry advances and selective and fast media are invented, engineers might tend to continue thinking in terms of established contacting systems such as packed columns. Changes in design and specification are often dependent on vendors' experience and guarantees. Think of how the learning curve in the adoption of membrane processes for

seawater desalination has progressed since the first commercial seawater RO plants of the mid 1970's era.

On the other hand, many of the chemists developing new media are exploring 'smaller' particles and are extending their interest into the very wide range of 'nano' particles of various shapes and morphological characteristics (dense spheres to nanotubes) and have to consider the rheological properties of these materials and how they will behave in the fluid systems of industrial scale operations. Other chemists are exploring 'larger' extractant molecules supported by surfaces where the spatial interactions affecting both selectivity and rates are important, for example in membrane and polymer supported reagents. So much successful commercial technology rests on polymer supports that the new developments can rather soon make established technology applications outdated or cause them to be reserved for particular niches. For example, analytical chromatography electrophoresis is very reliant on capillary rather than gel media in many situations. Membrane bioreactors and aeration are replacing conventional activated sludge and conventional aeration and providing significant operating benefits. Chemists will need to interact with engineers and other technologists to support the knowledge development required in the applications engineering and marketing fields. This also applies to the production of the new materials.

If we think of the possibility that nanofluids might one day replace particulate resins in ion exchange processes we can see that the mass transfer limitations of pore diffusion may be greatly altered by effectively turning the particle 'inside-out'. All that vast surface area of adsorbent particles (that we enjoy amazing our uninitiated students with in our adsorption lectures) is now on the 'outside'. Thus, the functional groups become directly exposed to the bulk fluid and the forces involved have different effects. Mass transfer rates would be expected to be faster since pore diffusion limitations will largely disappear. However, there will remain stagnant boundary layers and different fluid dynamics models will be applicable in determining overall and film mass transfer coefficients.

To add to the above shifts in technology, there is also increasing interest in 'hybrid' contacting concepts, mainly represented by microfiltration and nanofiltration combined with particulate or dissolved extractant media (1). Within the membrane arena there is continued interest in processes employing particulate materials such as the seeded membrane crystallization ('SPARRO' process). A recent illustration of the latter may be found in (2). How will these, possibly competing, developments reveal their advantages and disadvantages in the quest for a greener planet?

The paper will seek to stimulate discussion of the present and future trends and of the many questions that might arise regarding the directions research and development will take, rather than to offer any specific answers.

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DISCONTINUOUS ELECTRO-REGENERATION OF CHROMATE SOLUTIONS FOR ENVIRONMENTALLY-FRIENDLY PLATING PROCESSES

Tatiana Yurchuk, Henry Bergmann

Anhalt University, FB 6/7, Bernburger Str. 55, 06366 Koethen/Germany
e-mail: T.Yurchuk@emw.hs-anhalt.de

Ion exchange is state of the art system in ion removal from rinse and other waters at $\text{mmol}\cdot\text{dm}^{-3}$ level of concentration. The use of regeneration chemicals, a higher need in working power and automation requirements are amongst the disadvantages of the method. To avoid these, electrodeionization (EDI) was developed. Electrodeionization is a technology combining the principles of ion exchange and electrodialysis for continuous operation in the loading/regeneration of ion exchangers. Initially, EDI was used for the production of ultra-pure water. However, it must be emphasised that rinse waters may significantly differ from ultra-pure water systems. The electrical conductivity of rinse waters or similar systems is often 1-2 orders of magnitude higher than in ultra-pure water. This is one of the reasons for the preferred ion transport through the electrolyte phase of the resin bed in an electrical field similar to electrodialysis (1).

Project work was carried out for feasibility and possible design of semi-industrial electro-regeneration units for diluted waters typical for rinse water systems in electroplating industry. Firstly, one subject of interest was the removal of CrO_4^{2-} ions in the concentration range between 0.06 and $2.3\text{mol}\cdot\text{m}^{-3}$. Ion exchange capacity of several resins under room temperature conditions was tested. A 2-compartment cell with diaphragm was found to be a suitable construction for electrochemical resin regeneration after previous discontinuous loading. The determination of resin conductivities and transport numbers was also part of the studies. Results showed sufficient high current efficiencies up to 70%. Nevertheless, low ion mobility in the resin may limit the removal rate for continuous electrodeionization. In this case, stepwise operation mode in loading and regenerating the resin bed is the only solution. Energy consumption can be lowered by using catholytes of previous electro-regeneration steps. Specific energy consumption until 0.3 kWh per treated cubic meter is to be expected. The method suggested is applicable to many other processes in the metal finishing and plating industry. Additional technological variants were developed and patented by the authors (2).

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SOME SUPPLEMENTS TO THE CLASSIC THEORY OF IDEAL CASCADES

Georgy A. Sulaberidze¹, Valentine D. Borisevich¹, Shi Zeng²

¹*National Research Nuclear University “MEPhI”, Kashirskoe shosse 31,
115409, Russia, Moscow,*

²*Tsinghua University, 100084, P.R.China, Beijing
e-mail: sula39@mail.ru*

The results of the research complementing and broadening the theory of ideal or in other words “no-mixing” cascades are reviewed in the paper. For the case of the binary mixture separation these results are summarized as follows:

- The infinite number of ideal cascades composed of separation stages with constant no small overall separation factors can be designed to provide the given concentration of a key-component in the product and waste flows. They are characterized by the value of the cut θ_1 at the first stage of a cascade which is a parameter of optimization in the search of an ideal cascade type basing on the specified optimization criterion.
- The concepts of the ideal and optimum in a total flow cascades do not coincide in a common case. The reason of this difference and a value of their discrepancy are analyzed in the paper.

The following supplements are added to the theory of the quasi-ideal cascades for the multicomponent mixtures separation:

- It is proved the existence of the best in the total flow quasi-ideal cascade for the given concentration of a key-component in the product and waste flows.
- The possibility to use the parameters of the quasi-ideal cascade as an initial guess in the optimization procedures for the squared and squared-off cascades separating multicomponent mixtures is demonstrated.

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III. POSTERS

THERMODYNAMIC ASPECTS OF SELECTION OF THE COLLECTORS IN SULPHIDIC ORES FLOTATION

Shamshiya K. Amerkhanova, Rustam M. Shlyapov, Farida Zh. Bekkulina

*E.A. Buketov Karaganda State University, ul. Universitetskaya, 28,
Karaganda, Kazakhstan, 100028
e-mail: amerkhanova_sh@mail.ru*

Recently the attention of leading technologists and scientists in the field of coordination chemistry is concentrated on the questions concerning the influence of physical structure and chemical properties of collectors on a complex forming ability (1). However, there is still lack of research in the literature on the thermodynamic functions of processes of linkage of metal ions devoted to the analysis of various flotoreagents and their applications to the highly concentrated solutions. Therefore, definition of thermodynamic characteristics of complexes formation processes of economically and strategically important metals with sulfur containing collectors is becoming more important.

From the data obtained by potentiometric method it (2) follows, that for phosphorus containing collectors the greatest affinity to the metal ions possesses potassium dibutylditiophosphate, among the metal ions there is Co^{2+} ion (3). For other metal ions the complex forming ability changes depending on the type of ligand. Further series of thermodynamic stability of metal ions complexes with anion collectors were obtained: for potassium and sodium dibutylditiophosphate, sodium diisopropylditiophosphate $\text{Co} > \text{Ni} > \text{Fe}; \text{Ag} > \text{Cu}$; the reference of a series in case of the subgroup of copper for potassium butyl xanthate, is caused by oxidation processes such as restoration and coincides with the change of potential size of cation ionization. The series specified above are in symbate dependence with $\Delta_{\text{h}}\text{S}_{\text{T}}^0 (\text{Me}^{\text{n}+})$ (4). Series $\text{Ni} > \text{Co} > \text{Fe}; \text{Ag} > \text{Cu}$ for ammonium dibutylditiophosphate is according to $\Delta_{\text{f}}\text{H}_{\text{T}}^0 (\text{Me}^{\text{n}+})$. Obtained series for Co^{2+} ion is: potassium butyl xanthate $>$ potassium dibutylditiophosphate $>$ sodium dibutylditiophosphate $>$ sodium diisopropylditiophosphate $>$ ammonium dibutylditiophosphate. It is shown that potassium dibutylditiophosphate is suitable for flotation of copper-nickel, iron, and argentiferrous ores, and potassium butyl xanthate for cobalt containing ones, thus energy of hydration of d-metal ions, and also effects connected with influence of aliphatic radical are among defining factors.

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THE EFFECT OF POLYMERIC MATRIX ON CHROMIUM(III) TRANSPORT IN SLM SYSTEMS

Katarzyna Ochromowicz, Wiesław Apostoluk

*Chemical Metallurgy Division, Department of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 23, 50-370 Wrocław, Poland
e-mail: wieslaw.apostoluk@pwr.wroc.pl*

Introduction

In the supported liquid membrane systems (SLM) organic phase separates two aqueous phases: feed and receiving solutions and controls solute transport between them. Organic solution fills pores of polymeric matrix, which acts as its support. Metal concentration and ionic strength of feed phase, carrier type and concentration, and diluent type in organic phase, strength and type of an acid in receiving phase are well-known and well-described parameters affecting metal transport in SLM systems. However, knowledge of a transport should be completed with data regarding polymeric matrix. Different researchers use different materials as a liquid membrane support, therefore full comparison of results is not always possible. The most common materials used as a support are hydrophobic materials of high stability, like: polypropylene (Celgard, Accurel), polysulfone (Gore-Tex), polytetrafluoroethylene and polyvinylidene fluoride (Durapore). These materials differ in chemical and physical properties, which affect the transport through the membrane.

Here, the effect of porosity, tortuosity and hydrophobicity of different polymeric support on chromium(III) transport in SLM systems with di-(2-ethylhexyl)phosphoric acid (D2EHPA) is presented. Additionally, the stabilities of two most hydrophobic materials were compared. The effect of other parameters affecting transport rate and efficiency was described elsewhere (1-3).

Experimental

Chromium(III) feed solution was prepared from chromium(III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and sodium perchlorate (NaClO_4). The ionic strength of the initial feed solution containing 0.0048 M of Cr(III) was equal to 1.0 mol/dm^3 . pH of the feed solution was adjusted to 4 – 4.5 by means of 1 M NaOH solution. As a receiving phase 1.5 M H_2SO_4 solutions were used. Di-(2-ethylhexyl)phosphoric acid was used as chromium(III) carrier. The characteristic of investigated materials is presented in Table 1. Hydrophobicity of investigated materials was measured as wetting angles by feed and receiving phase solutions.

Results

The obtained results showed that chromium(III) transport was the most efficient when using two materials, namely Celgard 2500 and Durapore. Measured wetting angles by feed and receiving phases proved that Durapore is more hydrophobic than Celgard 2500. We can assume that greater thickness and hydrophobicity of Durapore matrix results in slower transport of Cr(III), while its

greater porosity and smaller tortuosity comparing to Celgard 2500 affect favourably the efficiency of chromium(III) pertraction. On the other hand lower porosity and higher tortuosity of Celgard 2500 contribute to its greater stability.

Table 1. Properties of investigated materials

Material	Trade name	Thickness δ_m μm	Porosity ϵ %	Pore size μm	Wettability
Polypropylene	Celgard 2500	25	55	0.22	Hydrophobic
Polypropylene	Celgard 2400	25	37	0.22	Hydrophobic
Polyethylene	Celgard 2730	21	43	0.22	Hydrophobic
Polypropylene	Celgard 3400*	25	37	0.22	Hydrophobic
Polyvinylidene fluoride	Durapore	125	75	0.22	Hydrophobic

* coated with wetting agent

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ROLE OF HYDROPHOBICITY IN AGGLOMERATION OF DOLOMITE IN CATIONIC-ANIONIC SURFACTANT SYSTEM

Anna Bastrzyk, Izabela Polowczyk, Zygmunt Sadowski

*Wroclaw University of Technology, Faculty of Chemistry, Department of
Chemical Engineering, Wybrzeze Wyspianskiego 27,
e-mail: anna.bastrzyk@pwr.wroc.pl*

Oil agglomeration is a size enlargement process, which facilitates the separation operation of mineral processing (filtration, flotation, sedimentation). This technique belongs to physicochemical processes, called “colloidal methods”, where hydrophobic particles are agglomerated in aqueous medium by bridging liquid (oil), whereas, hydrophilic ones remain in suspension (1). To provide the hydrophobization of particle surface, surfactants are often used (2).

In traditional procedure of oil agglomeration the oil is directly introduced to the minerals suspension (1,2). In this study the modified the procedure oil agglomeration was carried out, where the emulsion of bridging liquid and cationic surfactant solution was added to the mineral suspension (3). In such system non-modified carbonates particles possess negative zeta potential (ζ) and oil droplets have positive ζ value. According to DLVO theory these two objects should create oil/particle agglomerate. However, our earlier studies showed that in the absence of anionic surfactant, which adsorbs onto mineral surface agglomeration of particles did not occur or was not effective (4). So, we can assume that this process is correlated with the hydrophobicity and wettability of particles similarly to traditional methods. The hydrophobicity of particles was defined by surface energy and contact angle. Our results are in line with Laskowski and co-workers (5) observation that the emulsified oil droplets in cationic surfactant solution can operate as hydrophobic lattice, which aggregates only with hydrophobic particles. This finding prompted the investigation on the role of particles hydrophobicity on the course of oil agglomeration process in such system.

The aim of this work was to investigate the oil agglomeration behaviour of dolomite mineral by the contact angle, zeta potential and surface energy measurements. We revealed the relationship between the investigated parameters and oil agglomeration as well as shear coagulation. The mechanism of oil agglomeration of hydrophilic particles in cationic/anionic surfactant system has been proposed. We concluded that oil droplets rather interact with aggregates of particles modified by anionic surfactant than the single mineral particles as was explained for naturally hydrophobic particles.

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HEAVY METAL ADSORPTION BY MAGNETIC NANO-SORBENT: AN EXPERIMENTAL AND THEORETICAL APPROACH

Esra Bilgin Şimşek¹, Dilek Duranoğlu², Ülker Beker²

¹Yalova Engineering Faculty, Chem.& Process Eng. Dept., 77100 Yalova/Turkey

²Yildiz Tech. Univ., Chem. Eng. Dept., Davutpasa Campus, Esenler Istanbul/Turkey; e-mail: ubeker@gmail.com

Magnetic sorbents have the potential to remove heavy metals from aqueous solutions due to their high surface area, and selectivity for As, Cu, Cd and Pb species. In this study, a magnetic nano-adsorbent was developed by treating Fe₃O₄ nanoparticles with copolymer to remove heavy metal ions from aqueous solutions. The hydroxyl group of the magnetic adsorbent can act as a weak acid or base and gain or lose proton due to the solution pH. For that reason, it can be used for the adsorption of Pb²⁺ and Cu²⁺ ions via the complexation which means that N atoms are that main electron donors to coordinate with Cu²⁺ or Pb²⁺ and Cu or Pb atoms are electron acceptors. The magnetic nano-adsorbent appeared to uptake more Pb²⁺ than Cu²⁺ in the bimetal solution. The adsorption capacity of polymer adsorbent is 26.39 mg·g⁻¹ for Pb²⁺ and 7.93 mg·g⁻¹ for Cu²⁺ whereas it is increased to 45.81 mg·g⁻¹ for Pb²⁺ and 25.64 mg·g⁻¹ for Cu²⁺ by using magnetic nano-adsorbent. It is relevant to note that the electro negativity of Cu²⁺ is 1.90 while the electro negativity of Pb²⁺ is 2.33. The higher electro negativity tends to hinder the binding of metal ions to the negative sites on the adsorbents. From the results, it appears that magnetic nano-adsorbent has stronger affinity for Pb²⁺ than Cu²⁺. The results showed that Langmuir and Freundlich equations could well interpret the adsorption of polymer adsorbent and magnetic adsorbent, respectively. The parameters of Langmuir and Freundlich adsorption isotherms, evaluated from the linear plots, are presented in Tables 1 and 2 along with the correlation coefficient.

Table 1. The isotherm model of metal ions adsorption on polymer sorbent

Me	Langmuir			Freundlich		
	Q mg·g ⁻¹	b L·mg ⁻¹	(R) ²	K _F mg·g ⁻¹	1/n	(R) ²
Cu	7.93	5.08	0.99	10.87	0.47	0.98
Pb	26.19	20.82	0.99	30.76	0.2	0.98

Table 2. The isotherm model of metal ions adsorption on magnetic nano-adsorbent

Me	Langmuir			Freundlich		
	Q mg·g ⁻¹	b L·mg ⁻¹	(R) ²	K _F mg·g ⁻¹	1/n	(R) ²
Cu	25.64	4.97	0.98	31.76	0.46	0.99
Pb	45.81	33.21	0.97	55.57	0.25	0.98

The Langmuir isotherm model was found to be the most suitable one for adsorption. The 1/n values were between 0 and 1 indicating that the adsorptions of Cu²⁺ and Pb²⁺ onto adsorbents were favorable at studied conditions. The similar results were reported for Cu²⁺ and Pb²⁺ adsorption on different adsorbents by several authors (1,2).

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AN ECO-FRIENDLY ADSORBENT FOR HEAVY METAL REMEDIATION IN AQUEOUS ENVIRONMENT

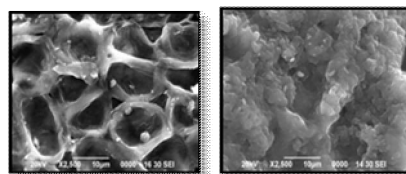
Aslı Özge Avcı, Dilek Duranoğlu, Ülker Beker

Yildiz Tech. Univ., Chem. Eng. Dept., Davutpasa Campus,
Esenler Istanbul/ Turkey
e-mail: ubeker@gmail.com

Apricot stones were carbonised and activated after impregnation with phosphoric acid (1,5:1) at 400°C for 2 h. The physical and chemical properties of the sample produced, as well as their characteristics for liquid-phase adsorption to remove Cr(VI) from aqueous solutions were investigated. Textural characterization, determined by nitrogen adsorption at 77 K shows that mixed microporous and mesoporous structures activated carbon (AC) with high surface area (>1000m²/g) and high pore volume (up to 1.19 cm³/g) can be obtained. As shown in Table 1 the surface area of carbonized carbon sample was increased from 25 m²/g to 1.462 m²/g in the case of acid impregnation. The surface chemical properties of the samples were investigated by Boehm titration. FTIR spectrum analysis revealed that O-H and C-O groups were the leading Cr(VI) binding groups.

Table 1. Properties of adsorbents

	AC	IAC
BET surface area (m ² .g ⁻¹)	25	1462
Total pore volume (cm ³ .g ⁻¹)	0.017	0.638
Carboxyl groups (meq.g ⁻¹)	0.0605	0.763
Lactonic groups (meq.g ⁻¹)	0.24432	0.305
Phenolic groups (meq.g ⁻¹)	0.8898	0.632
Total Capacity (meq.g ⁻¹)	1.1947	1.701
pH _{ZPC}	2.5	1.670
pH _{IEP}	7.62	1.000



Activated carbon sample

Impregnated activated carbon sample

Fig. 1. SEM micrographs of samples

Hexavalent chromium exists primarily as H₂CrO₄, HCrO₄⁻ and CrO₄²⁻ depending on the pH. H₂CrO₄ predominates at pH less than about 1.0, HCrO₄⁻ at pH between 1.0 and 6.0. Batch adsorption experiment was conducted to observe the effect of pH (2-6) on the activated carbon. The optimum uptake occurred when initial pH was 2.0 when 98.68% of the Cr(VI) was removed from the solution with impregnated activated carbon and 21,32% with activated carbon samples. The maximum chromium adsorption capacity for 30 mg.L⁻¹ initial concentration was obtained at pH 2.0 as 12 and 155 mg .g⁻¹, at pH 4.0 as 5 and 50 mg.g⁻¹ and at pH 6.0 as 1.5 and 25 mg.g⁻¹ for activated carbon and impregnated activated carbon samples, respectively. The decrease in the adsorption with increase in solution pH may be due to the decrease in electrostatic force attraction between the sorbent and the sorbate ions. The experimental adsorption isotherms of these molecules on the activated carbon were as well analyzed using isotherms: the Freundlich and Langmuir isotherms. The results obtained from the application of the equations show that the best fits were achieved with the Freundlich equation accurately.

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REMOVAL OF Cr(VI) BY GRAFT COPOLYMER COATED WITH MAGNETIC NANO-SORBENT: BATCH EQUILIBRIUM AND KINETIC STUDIES

İsmet Gül B. Kaya¹, Dilek Duranoğlu¹, Ülker Beker¹, B. F. Şenkal²

¹*Yildiz Tech. Univ., Chem. Eng. Dept., Davutpasa Campus, Esenler Istanbul/Turkey*

²*Istanbul Tech. Univ., Department of Chemistry, 34469, Maslak-Istanbul, Turkey
e-mail: ubeker@gmail.com*

In this study, the adsorption of Cr(VI) from aqueous solutions using the poly(glycidyl methacrylate) graft copolymer (IEX) and Fe oxide-coated IEX sorbent (MIEX) has been studied. Poly(glycidyl methacrylate) was grafted onto crosslinked polystyrene beads through the 2-chloroethyl sulphonamide groups present in the resin using ATRP polymerization method, as it was previously done according to the literature (1). MIEX adsorbent has higher Cr(VI) adsorption capacity comparing to IEX, due to the combining effects of Fe oxides and amine groups. Cr(VI) anions can exchange with OH⁻ from the surface of the hydrolyzed Fe oxides. The maximum Cr(VI) adsorption capacities of IEX and MIEX were determined at pH 4 as 132.5 and 162.86 mg/g, respectively. With increasing pH, maximum adsorption capacity of IEX reduced to 42 mg/g and that of MIEX was found as 65 mg/g at pH = 10. The sorbents produced have considerably high Cr(VI) sorption capacities. The rapid sorption and fast complexation of metal ions by the adsorbents would be useful for practical use, providing a short solution adsorbent contact time in the actual process. The uptake of Cr(VI) was quite high at the beginning, followed by a much slower subsequent removal and at last leading to a steady state. Approximately 56% of Cr(VI) was removed by PGMA in 5 minute and after 30 min, removal efficiency of Cr(VI) was 80% (Fig. 1).

Table 1. Kinetic parameters for the removal of Cr(VI) by PGMA and PGMAFe

Pseudo-first-order					
	$q_{e,exp}$, mg/g	$q_{e,cal}$, mg/g	k_1 , 1/min	R^2	
IEX	65.00	43.18	0.999	0.9026	
MIEX	77.35	60.94	0.217	0.9903	
Pseudo-second-order					
	$q_{e,exp}$, mg/g	$q_{e,cal}$, mg/g	k_2 , 10 ⁻³ g/mg.min	h , mg/g.min	R^2
IEX	65.00	68.18	5.09	23.67	0.9998
MIEX	77.35	79.72	8.40	53.41	0.9997

The correlation coefficients for the linear plots of pseudo-first-order model were 0.9026 and 0.9903, which indicates the poor correlation, for IEX and MIEX, respectively (Table 1). Besides, it can be seen that the experimental values of q_e are not in good agreement with the theoretical values calculated from pseudo-first order model. Application of a pseudo-second order model provides much better correlation coefficients, which is 0.9998 and 0.9997 for IEX and MIEX, respectively. Moreover, there is an excellent correlation between the calculated q_e values from the pseudo-second-order model and the experimental

q_e values. Therefore, it may be concluded that Cr(VI) adsorption onto produced adsorbents consist of chemical adsorption.

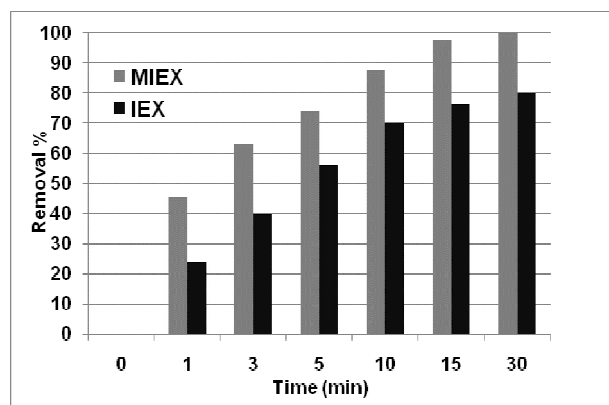


Fig. 1. Effect of contact time on Cr(VI) removal by IEX and MIEX

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CONTINUOUS DIALYSIS OF SULPHURIC ACID AND SODIUM SULPHATE

Helena Bendová, Zdeněk Palatý

*Institute of Environmental and Chemical Engineering, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-532 10 Pardubice
e-mail: Helena.Bendova@upce.cz*

The simultaneous transport of sulphuric acid and sodium sulphate through an anion-exchange membrane Neosepta-AFN was investigated in a counter-current continuous dialyzer for various acid/salt concentration ratios and volumetric liquid flow rates. The basic transport characteristics – the acid recovery, the rejection coefficient of salt and the overall dialysis coefficient of acid – were evaluated from the measurements at steady state.

The initial sulphuric acid concentration in model mixtures was changed in the limits from 0.1 to 1.0 kmol·m⁻³, while that of sodium sulphate in the limits from 0.1 to 0.5 kmol·m⁻³. The volumetric liquid flow rate of the inlet streams was in the limits from 8 × 10⁻⁹ to 24 × 10⁻⁹ m³·s⁻¹.

Under the experimental conditions given, the acid recovery was found to be in the limits from 52% to 86% for dialysis of mixture H₂SO₄/Na₂SO₄. The maximum acid recovery can be reached at the low volumetric liquid flow rates of the feed and low initial salt concentrations. For all the acid and salt mixture tested, the acid recovery markedly decreases with an increasing volumetric liquid flow rate.

The rejection coefficient of salt is in range from 73% to 89%. The values of rejection coefficient always increase with an increasing volumetric liquid flow rate and they are practically independent on the initial acid concentration and initial salt concentration.

The overall dialysis coefficients of acid are in the limits from 4.3 × 10⁻⁷ m·s⁻¹ to 1.8 × 10⁻⁶ m·s⁻¹ and they always increase with an increasing volumetric liquid flow rate. The expressive decrease of the overall dialysis coefficients with an increasing initial salt concentration is obvious, the effect of this parameter is major for low acid concentrations. For higher initial salt concentrations, the increase of overall dialysis coefficients with increasing initial acid concentration is observed.

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THE EFFECT OF HYDROPHOBIC PYRIDINECARBOXAMIDES BASICITY ON COPPER(II) EXTRACTION

Robert Biernacki, Aleksandra Borowiak-Resterna

*Institute of Chemical Technology and Engineering, Poznań University of Technology, Pl. M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland
e-mail: biernacki.robert@wp.pl*

Copper is one of the most strategic metals. In the environment, it occurs in the form of sulphide, oxide, carbonate, silicate ores, and very rarely in pure form as native copper. Due to limited presence of copper in the environment, this metal is also recovered from mine waters and by the recycling of copper wastes. Hydrometallurgy of copper is mainly used in the processing of poor oxide ores. Greater difficulties are encountered in the hydrometallurgical processing of sulphide ores, from which after effective leaching concentrated chloride solutions of ion metals are obtained. Hydrophobic derivatives of pyridinecarboxylic acids, esters and amides, are proposed for the extraction of copper(II) from acidic chloride solutions (1-4). The introduction of electron-acceptor substituent to the pyridine ring reduces the basicity of pyridine nitrogen, and facilitates the decomposition of a complex with Cu(II) in the process of re-extraction.

The ability of pyridine extractants to form complexes with copper(II) and other metal ions largely depends on their basicity. The basicity of the pyridine nitrogen has a significant influence on the extraction process and its performance. Only values of dissociation constants of hydrophilic pyridine derivatives are available in literature so far. The aim of this study was to estimate the basicity of hydrophobic pyridinecarboxamides, potential extractants of copper(II) from chloride solutions, and to investigate the effect of these compounds basicity on copper(II) extraction.

With the use of potentiometric method, values of K_a for pyridine-3(and -4)-carboxamides and their alkyl derivatives in dioxane–water diluent (3:1 v/v) were estimated. The values of K_a in water found earlier by the authors for pyridine-2-carboxamide and its N,N-diethyl derivative are approx. 25 times as high as those obtained for similar pyridine derivatives with an amide substituent at position 3 (3,4). Significant differences in basicity between derivatives having a substituent at positions 2 and 3 were found also in a mixed diluents. The values of pK_a in the dioxane-water system for pyridine-3-carboxamide and its hydrophobic derivatives are from 2.17 to 2.65. For pyridine-2-carboxamides it was not possible to find the values of pK_a because they were very low in the mixed diluents. Such notable differences in the basicity of the two groups of amides are reflected in their ability to extract Cu(II) ions.

For low concentrations (0 – 3 M) of chloride ions, extraction by means of the N-(2-ethylhexyl)pyridine-2-carboxamide (EH2) is not very pronounced. An increase in the concentration of ions Cl^- above 3 M is accompanied by the percentage extraction, reaching a peak value for 6 M Cl^- . The extractant EH3, which is more basic, exhibits a much better ability to complex Cu(II) ions in

chloride solutions and is able to remove more than 50% metal ions from an aqueous medium at as a low Cl^- ion concentration as 0.5 M. Large differences in the extracting properties have been observed also for N,N-dihexylpyridine-2(and-3)-carboxamides (DH2 and DH3, respectively). The percentage extraction of Cu(II) by means of the dialkylamide DH2 is not higher than 5% over the entire tested range of the chloride ion concentrations while the amide DH3 shows a very good ability to extract Cu(II) ions for $[\text{Cl}^-] \geq 3 \text{ M}$ (Fig. 1). Lesser differences both in the extracting properties and basicity are observed for pyridine derivatives having an amide substituent at position 3 or 4. The value of $\text{p}K_a$ for the amide DH4, when the substituent in the pyridine ring is at position 4, is only slightly higher than that of $\text{p}K_a$, obtained for the amide DH3. The course of the extraction curves (Fig. 1) indicates that DH4 shows also a higher potential for the extraction of Cu(II), compared with DH3, which is especially evident in the chloride concentration range of 1-3 M and may result not only from a small difference between the basicity of the two extractants but also from the difference between the structures of their complexes with CuCl_2 .

The extracting properties of pyridine-3-carboxamides (Fig. 1) as well as the estimated values of $\text{p}K_a$ diminish in the following order: EH3 \gg DB3 $>$ DH3 $>$ DO3. The monoalkylamide EH3 shows markedly stronger complexing properties, compared with dialkylamides, which is due both to the higher basicity of its molecules and to their association ability. The formation of intermolecular hydrogen bonds between the molecules of the monoalkylamide complex with CuCl_2 improves their stability while reducing the solubility of the complex in organic diluents.

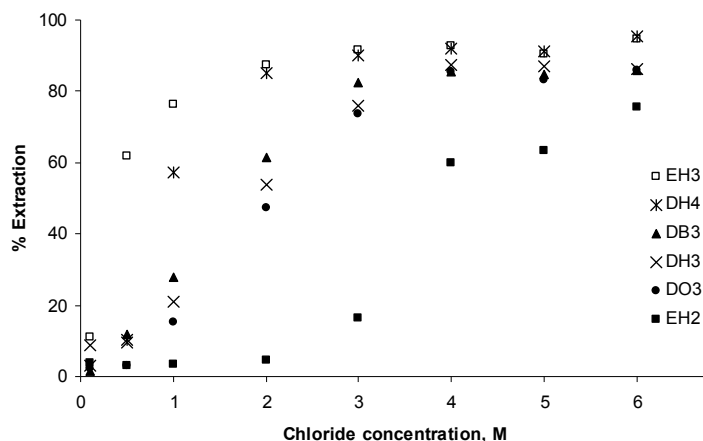


Fig. 1. Extraction of copper(II) from chloride solutions with pyridinecarboxamides N-(2-ethylhexyl)pyridine-2-carboxamide (EH2), N-(2-ethylhexyl)pyridine-3-carboxamide (EH3), N,N-dibutylpyridine-3-carboxamide (DB3), N,N-dihexylpyridine-3-carboxamide (DH3), N,N-dioctylpyridine-3-carboxamide (DO3), N,N-dihexylpyridine-4-carboxamide (DH4)

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UPTAKE OF ENDOCRINE DISRUPTORS BY THE MOLECULARLY IMPRINTED POLYMERS

Marek Bryjak, Joanna Wolska, Ilona Duraj

*Faculty of Chemistry, Division of Polymer and Carbonaceous Materials,
Wrocław University of Technology, Wyb. Wyspiańskiego 27,
50-370 Wrocław, Poland
e-mail: marek.bryjak@pwr.wroc.pl*

Endocrine disruption refers to the interference of endocrine system functions by chemicals. Numerous substances such as dioxins, polychlorobiphenols and phthalates have been suspected of working through endocrine-disruptive mechanisms (1). As a rule these substances are poorly removed from water by conventional methods of water treatment. Due to refractory content of endocrine disruptors in water bodies it is hardly to control a content of such pollutants as well as to develop the efficient methods for their removal (2). The presented studies are focused on preparation of molecularly imprinted polymer sorbents for selective recognizing of endocrine disruptors, such as dimethyl phthalate (DMP).

The molecularly imprinted particles were obtained by block copolymerization of styrene and divinylbenzene, S/DVB, with different amount of crosslinking agent. In all cases azoisobutyronitrile (AIBN) was used as initiator. The amount of templates varied from 1 to 9 % wt. As the references, the samples obtained without DMP were synthesized. The different combination of solvents were used to obtain porous materials. To determine the capacity of obtained polymers, the batch-mode sorption studies were performed and sorption isotherms were evaluated for the best materials. The imprinted materials showed higher sorption capacity towards DMP than their off-template analogues. The uptake of dimethyl phthalate on synthesized resins is depended on the composition of the reaction mixture. Preliminary trials have shown that the nature and composition of solvents used during polymerization appears to be most important. The amount of template used during the synthesis is critical also.

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GOLD, PLATINUM AND PALLADIUM SORPTION/REDUCTION BY THE IMMOBILIZED EGGSHELL MEMBRANE

Arleta Butewicz, Andrzej W. Trochimczuk

*Faculty of Chemistry, Wrocław University of Technology,
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
e-mail: andrzej.trochimczuk@pwr.wroc.pl*

In recent years, much attention has been focused on the use of various industrial wastes, agricultural byproducts, and biological materials for the preparation of biosorbents. In this study we present the use of immobilized eggshell membrane for the sorption/reduction of gold, platinum and palladium. Hen egg is the very popular food in the world. Eggshell membrane (ESM) is the innermost portion of eggshell which comprises inner and outer layers and eggshells can be readily obtainable in large quantities as waste from kitchens and industry. ESM sorption property of precious metals can be attributed to the presence of amino, amido and carboxyl functional groups in its structure.

ESM was prepared by suspending raw hen eggshells in hydrochloric acid. The biomass was then dried, ground, sieved and subsequently used for experiments. For immobilization of the biomass, a 10% (w/v) solution of polysulfone was prepared in N,N-dimethyl formamide (DMF) solution. After stirring the mixture for 24h, the ESM powder (5%) was mixed with the polysulfone slurry, with the resultant slurry dripped in water/acetone mixture, where beads were formed by a phase inversion process. The beads were then washed with deionized water and dried. So prepared product was used for gold, platinum and palladium sorption/reduction from the acidic solutions.

The biosorption experiments were carried out in batches as follows: known weight (~0.050g) of immobilized ESM were added to 100ml solutions of gold ($C_0=16.5\text{mg/L}$ / 0.1M HCl), platinum ($C_0=32.8\text{mg/L}$ / 0.5M HCl) and palladium ($C_0=10.6\text{mg/L}$ / 0.1M HCl) and shaken. Maximal sorption for gold, platinum and palladium was 26.9mg/g, 30.1mg/g, 11.6mg/g respectively.

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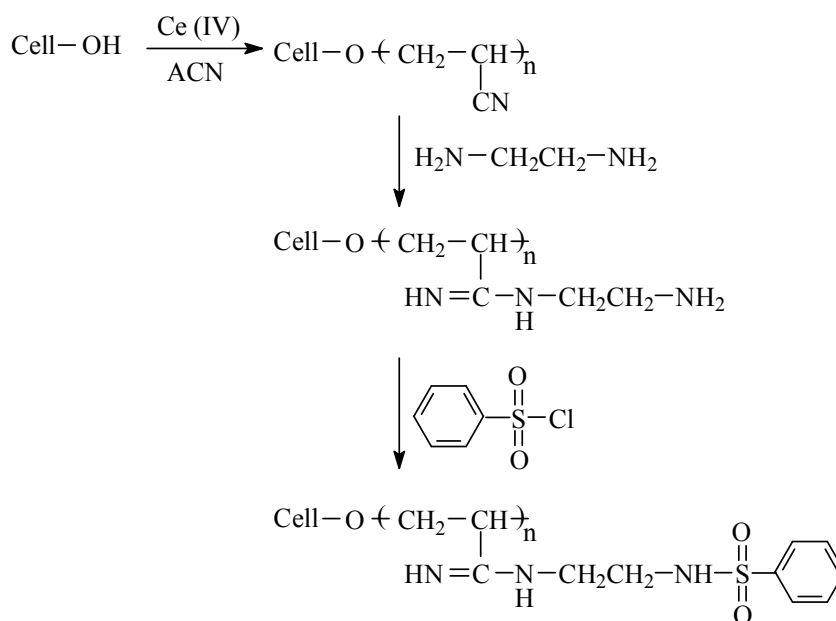
PREPARATION OF SULFONAMIDE CONTAINING CELLULOSE BASED SORBENT FOR REMOVAL OF MERCURY IONS

Seda Cekli, Erdem Yavuz, Bahire Filiz Senkal

*Department of Chemistry, Istanbul Technical University, Istanbul 34469, Turkey
e-mail: ceklis@itu.edu.tr*

Mercury is used in a wide variety of industries such as electrical, paints, fungicides, chlor-alkali, paper and pulp, pharmaceutical, etc. (1). All mercury compounds are known to be highly toxic chemicals. The use of polymer-bonded ligands in selective mercury removal has been the subject of many research articles (2,3) and reviews (4,5).

In this study, poly(acrylonitrile) (PAN) has been grafted onto cotton cellulose by redox polymerization method. Then, PAN grafted cellulose reacted with ethylene diamine and benzene sulfonyl chloride respectively to obtain sulfonamide containing sorbent. The mercury sorption capacity of the sorbent was found as 1.96 mmol/g.



Scheme 1. Preparation of the sulfonamide containing sorbent

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PERFORMANCE OF WOVEN AND NON – WOVEN SPACERS IN MEMBRANE SEPARATION PROCESSES

Marzena Chorążewska, Piotr Dydo, Marian Turek

*Silesian University of Technology, Faculty of Chemistry, ul. B. Krzywoustego 6,
44-100 Gliwice, Poland*

e-mail: Marzena.Chorazewska@polsl.pl

One of the most often applied modules in pressure driven membrane processes is spiral wound module (SWM). SWM consists of a membrane, feed and permeate channels filled with feed spacer and permeate carrier respectively, a perforated permeate tube and a membrane housing (1). The role of the feed spacer is creating the space between the membrane layers, promoting flow unsteadiness and enhancing mass transport (2). Promotion of mixing between the bulk of the fluid and fluid adjacent to the membrane surface keeps membrane surface relatively clean but in the same time increased flow resistance is observed (3). Effective spacer should be generally characterized by high permeate flux (high mass transfer coefficient) and low pressure drop. Additionally, spacers should have small number of places, which may form stagnant flow regions. Thus, in order to operate membrane processes in supersaturation conditions spacers with short mean residence time of solute and with low dispersion should be applied.

Six different spacers were examined. The spacers differ from each other with thickness and design. In the group of examined spacers we can distinguish three woven with thickness 0.19 mm, 0.26 mm and 0.35 mm and two non-woven with thickness 0.2 mm and 0.27 mm. Additionally, commercial non-woven spacer with 0.45 mm thickness was tested.

The highest flux values were obtained for 0.26 mm woven spacer. Its value at cross - flow velocity equal to 0.05 m/s was about 24% higher than flux obtained for 0.27 mm non-woven spacer. The performances of 0.35 woven and 0.45 mm non-woven spacers were similar. Woven spacers indicated smaller pressure drop exhibited than non – woven ones with similar thickness. Woven spacer with 0.35 mm thickness generated the smallest pressure drop in all measurement range. Taking into account mass transfer coefficient and pressure losses the spacer mass transfer efficiency was calculated. It was found that woven spacer with 0.35mm thickness was distinguished by the most effective mass transfer efficiency. The mean residence times t_{av} and its variances σ^2 evolve as follows:

$$t_{av(0.35mm)} < t_{av(0.45mm)} < t_{av(0.26mm)} < t_{av(0.19mm)} < t_{av(0.20mm)} < t_{av(0.27mm)}$$
$$\sigma^2_{(0.35mm)} < \sigma^2_{(0.45mm)} < \sigma^2_{(0.26mm)} < \sigma^2_{(0.19mm)} < \sigma^2_{(0.20mm)} < \sigma^2_{(0.27mm)}$$

Acknowledgement: This work was partially financed by Polish Ministry of Science and Higher Education, grant No. N N209227738.

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EQUILIBRIUM AND KINETICS OF Cr(III) EXTRACTION FROM AQUEOUS SOLUTION IN THE SYSTEM WITH ALIQUAT 336

Barbara Wionczyk¹, Anna Mól³, Ryszard Cierpiszewski², Krystyna Prochaska³

¹*Institute of Leather Industry, ul. Zgierska 73, 91-462 Łódź, Poland*

²*Poznań University of Economics, Faculty of Commodity Science,
al. Niepodległości 10, 60-967 Poznań, Poland*

³*Poznań University of Technology, Institute of Chemical Technology and
Engineering, pl. M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland
e-mail: R.Cierpiszewski@ue.poznan.pl*

Although chromium is a toxic metal it is widely applied in industry, mainly in electroplating and tanning. Effluents and solid wastes containing chromium(III) create an environmental hazard and a risk for the humane health when they discharged into the landfill or rivers. Therefore, recovery and removal of Cr(III) from solid and liquid wastes have both ecological and economical aspects. As it is well known the solvent extraction is one of the most efficient method for concentration and separation of various metal species and as was demonstrated in the literature it can be used for removal of Cr(III) from aqueous solutions.

Our investigations described in this paper were focused on the interpretation of the influence of composition of an aqueous phase as well as the concentration of separated metal ions and the concentration of hydrophobic extractant in the organic phase on the rate of Cr(III) extraction in systems with commercial reagent Aliquat 336 used as extractant.

The kinetics experiments Cr(III) extraction have been investigated by a Lewis-type cell. The apparatus provided a constant interfacial area of 16.6 cm² and the same volume (95 ml) of the aqueous and organic phases. n-heptane was used as the organic diluent. The rotation number of the stirrers were kept in the range of 30÷120 rpm. to maintain a flat and stable interface. Chromium(III) concentration in the aqueous phase was determined by atomic absorption spectroscopy using a Varian SPECTR AA800.

Obtained results allowed to compare the rate of Cr(III) extraction from aqueous solutions of KCr(SO₄)₂, Cr(NO₃)₃ and Cr(ClO₄)₃. Moreover the effect of stirring speed in the Lewis cell on the initial rate of the chromium(III) extraction from aqueous phases of different compositions was shown.

It was found that the extraction rate of chromium(III) ions is affected by the composition of aqueous phase, concentration of extractant in the organic phase and the mixing rates. Especially high value of extraction rate was observed for aqueous solution containing 0.005 M chromium(III) potassium sulphate. Independently on the composition of the aqueous phase the concentration of Cr(III) ions in the organic phase increases almost linearly with the time in the period up to ca. 30 minutes. From the slope of these linear relations the fluxes of chromium(III) ions transferred from the aqueous phase to the organic one were determined. Additionally, the obtained results showed that the initial rate of Cr(III) extraction was approximately proportional to the stirring speed.

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CHANGES OF THE ION CONTENT IN SOIL CONTACTED HYDROGELS

Anna Jakubiak-Marcinkowska, Sylwia Ronka, Magdalena Pilśniak-Rabiega, Arleta Butewicz, Joanna Czulak, Andrzej W. Trochimczuk

*Faculty of Chemistry, Wrocław University of Technology,
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland,
e-mail: andrzej.trochimczuk@pwr.wroc.pl*

Hydrogels are 'soft matter' polymeric materials, which are characterized by the high swelling in aqueous solutions. This property of hydrogels is used in various fields, like biomedical, biotechnology and also in agriculture and forestry. In the latter fields the hydrogels are used to provide sufficient amount of moisture to young trees and shrubs. Hydrogels are able to accumulate water after the rain and slowly release it to the root system of the plants. However, the ability of water retaining is strongly dependent on the ionic form of the hydrogel and on the type and amount of crosslinking agent. Also the ionic strength and pH of the aqueous external solution influences the water uptake by the hydrogel.

The aim of this work was to examine the influence of the ionic forms of the hydrogels contacted with soil and with fertilizers and to determine the water content in hydrogels before and after the use in plant growing. One commercially available hydrogel was used – Aquaterra, a copolymer of acrylic acid and undisclosed crosslinker, which is supplied as sodium salt.

After contact with soil the ionic composition has been changed drastically, the main cations present in the polymer structure are Fe(II) and (III), Ca(II). This changes very strongly the water uptake of polymer from the initial ca. 200 g of water/g of polymer to few grams of water/gram of polymer.

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STUDY ON HEAVY METALS SORPTION BY IONIC COMPOSITES

Maria Valentina Dinu, Ecaterina Stela Drăgan

*"Petru Poni" Institute of Macromolecular Chemistry, Grigore Ghica Alley 41A,
700487, Iasi, Romania
e-mail: vdinu@icmpp.ro*

Removal of heavy metal ions from the wastewaters is a huge problem because these ions are extremely dangerous for the environment and human health by their high toxicity even at very low concentrations. Among the conventional techniques commonly used in the removal of heavy metals from wastewaters, the adsorption process is perhaps the most widely utilized, being mainly preferred either when the enrichment of trace metal amounts or a high selectivity for a certain metal are required (1-3).

Natural polymeric materials have attracted considerable interest for removal of heavy metals due to their biodegradability and non-toxic nature. Chitosan-based composite materials have been reported to exhibit enhanced mechanical, thermal or adsorption properties comparative with any of its components used alone. In our recent studies, we have reported on the synthesis of some novel composites with enhanced adsorption capacity for copper ions by embedding zeolite microparticles in a matrix of cross-linked chitosan (4).

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. Therefore, in this study, the adsorption features of Cu^{2+} , Co^{2+} , Ni^{2+} , UO_2^{2+} and Th^{4+} ions from aqueous solutions onto a chitosan-based composite, containing 20 wt.% of zeolite, as a function of temperature were investigated (5,6). Standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) were evaluated by applying the van't Hoff equation. The negative values of ΔG° indicated the feasibility of the process and the spontaneous nature of the adsorption of metal ions on the chitosan-based composite. The positive values of ΔS° reflect the affinity of the ionic composite for cations and suggest the increased randomness at the solid–solution interface during adsorption.

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SEMI-INTERPENETRATED COMPOSITE HYDROGELS BASED ON POTATOES STARCH AND THEIR INTERACTION WITH IONIC SPECIES

Diana Felicia Apopei, Ecaterina Stela Dragan

*“Petru Poni” Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A,
700487 Iasi, Romania
e-mail: sdragan@icmpp.ro*

Environmental pollution caused by toxic heavy metals in industrial effluents is one of the most severe problems in many densely populated cities worldwide. The use of synthetic resins for the removal of metal ions or ionic dyes in wastewater is a possible approach for preventing the environmental pollution. However, numerous investigations have been recently performed in order to develop cheaper and more effective adsorbents containing polymers coming from the renewable resources (1-4). Among these, polysaccharides such as starch and their derivatives received more and more attention.

To control the diffusion of solutes, various multicomponent networks as interpenetrated polymer networks (IPN) have been designed (5,6). Semi-IPNs (s-IPN) hydrogels are typically produced in a single step by synthesizing a hydrophilic polymer matrix around the preexisting water soluble polymer chains considered the trapped polymer. Numerous water soluble polymers have been used as trapped polymer in the synthesis of s-IPN hydrogels. In our investigations, potatoes starch (PS) has been used as a trapped polymer in a matrix of either poly(acrylamide) (PAAm) or poly(dimethylaminoethyl methacrylate) (PDMAEM) to prepare s-IPN composite hydrogels. The influence of the synthesis temperature on the gel properties has been evaluated. The swelling ratio and the interaction of the composite gels with some ionic species such as metal ions and dyes have been followed.

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PREPARATION OF IRON OXIDES - POLYMER COMPOSITES MEMBRANES

**Gabriela Dudek, Roman Turczyn, Anna Strzelewicz,
Aleksandra Rybak, Monika Krasowska, Zbigniew J. Grzywna**

*Faculty of Chemistry, Department of Physical Chemistry and Technology of
Polymers, Silesian University of Technology, ul. Strzody 9, 44-100 Gliwice
e-mail: gmdudek@polsl.pl*

In last years membrane processes have become competitive to other separation methods, especially because of low capital costs, high energy efficiency, thermal, mechanical and chemical stability, good separation properties and lack of necessity for membrane regeneration (1-4). The development of new membranes or the modification of existing ones for gas separation usually involves a compromise between their permeability and selectivity. Polymers can be modified by various reactions, like: carboxylation, bromination, acylation, sulfonylation, sulfonation, benzoylation and silylation. All these alterations improve their chemical and thermal resistance. In our previous papers (5,6) polymeric membranes containing magnetic powder were presented. This paper focuses on preparation of polymer membranes with oxide magnetic nanoparticles. The preparation of polymer films, containing dispersed ferromagnetic clusters has been of great interest because of both its practical and fundamental importance (7-9). Iron oxides-polymer composites membranes were prepared by adding mixture of Iron(II) and Iron(III) salts (oxalates, chlorides) to ethylcellulose solution (EC) or poly(*p*-phenylene oxide) solution (PPO). The membranes were made by pouring solutions into a Petri dish and the subsequent solvent evaporation at room temperature. Obtained membranes were further processed in order to transform iron salts to iron oxides. Permeation measurements using such prepared membranes before and after magnetization in a field magnet were carried out. Magnetic induction of this field was approximately 2 T.

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THE CONCEPT OF BORON REMOVAL AND CONCENTRATION IN AN INTEGRATED MEMBRANE SYSTEM

P. Dydo, M. Turek

*Silesian University of Technology, Faculty of Chemistry
B. Krzywoustego 6, 44-100 Gliwice, Poland
email: Piotr.Dydo@polsl.pl*

The authors propose an integrated electro dialysis (ED) – reverse osmosis (RO) system for boron removal and concentration from aqueous systems of high boric acid or borate content and moderate salinity. In the proposed system boron removal and simultaneous boron compound concentration is being realized with the use of RO membranes, which have shown superior boron rejection only at high feedwater pH, e.g. higher than pH of 9.0, feedwater pH at which boron rejection coefficients higher than 90% are observed almost exclusively (1,2). Boron rejection coefficients may be further enhanced in the presence of polyols such as D-mannitol, thanks to the formation of boric acid esters also stable only under alkaline conditions (3). According to the authors' data the boron compound rejection in the presence of D-mannitol may achieve values higher than 98 % at feedwater pH close to 11. Moreover, so high rejection in the presence of D-mannitol remains constant in a wide feedwater recovery range up to approx. 90% thus assures successful concentration and high RO permeate yield. This abovementioned RO concentration step at high feedwater pH requirement constitute, however, a fundamental limitation to the applicability of the proposed system in the case of feedwater containing some cations such as calcium and magnesium as well as bicarbonate, since under alkaline conditions severe carbonate or hydroxide scaling would be observed. Therefore, prior to high feedwater pH reverse osmosis concentration step, a deep softening or most likely demineralization step utilizing electro dialysis or electro dialysis reversal is suggested. It was previously shown that aqueous solution of moderate salinity of approx. 2 g/L TDS and of relatively high boric acid concentration 75 mg B/L can be deeply demineralized (99% reduction in salinity) without a significant boron compounds removal (4). So deeply demineralized ED diluate may be then concentrated under alkaline conditions without a scaling risk.

Acknowledgements: This work has been partially supported by Polish Ministry of Science and Higher Education grant No. N5601/B/T02/2010.

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APPLICATION OF HYBRID SYSTEM: JET PUMP MIXER-MICROFILTER FOR CRUDE OIL DESALINATION

Janusz Dziak, Jacek Kapłon, Abdirahman Ahmed

*Department of Chemical Engineering, Faculty of Chemistry,
Wrocław University of Technology, Norwida 4/6, 50-373 Wrocław, Poland
e-mail: janusz.dziak@pwr.wroc.pl*

Crude oil extracted from the earth usually possesses some amount of salt. The salt exists in crystalline form or in droplets of salty water, which are suspended in the oil (1). Salted oil could not be processed in the refinery installation because of the salty oil corrosivity. There are several methods applied in the industry for crude oil desalination, which are described in the literature (2). Many of them consume large quantities of water and there is a need for minimization of that consumption. Water is used for dissolving salt as well as for dilution of salt concentrated water solution that exists in form of droplets inside oil. It is important to distribute the water, that washes the oil, uniformly in the bulk of oil to make the process of desalination effective. The water-oil emulsion that is created during the process of water with oil mixing should be subsequently separated and it is in many cases the crucial stage of crude oil desalination. Demulsifiers (3) and cross-flow microfiltration (4) could be used for water in oil emulsions separation.

An innovative method of crude oil desalination is presented in the paper. The installation is composed of a jet pump mixer and microfiltration device. Jet pump, which characteristics was presented elsewhere (5), is very effective in water with oil mixing and microfilter (10-50 μm pore size) destroys the emulsion.

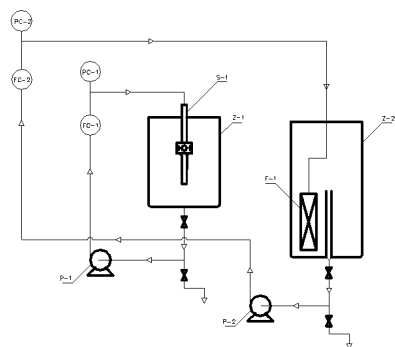


Fig. 1. Installation for crude oil desalination

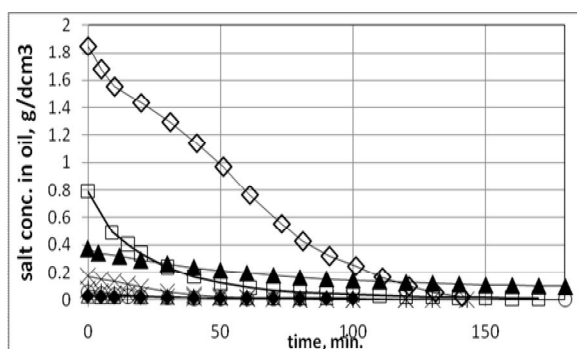


Fig. 2. Concentration of salt in the oil as a function of time of desalination

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SIMULATION OF THE SEPARATION AND PURIFICATION PROCESS OF LINSEED OIL ETHYL ESTERS

**Janusz Dziak, Jacek Kapłon, Lechośław Królikowski,
Waleed Abdulsalam**

*Department of Chemical and Process Engineering, Faculty of Chemistry,
Wrocław University of Technology, Norwida 4/6, 50-373 Wrocław, Poland
e-mail: janusz.dziak@pwr.wroc.pl*

In the process of ethanol transesterification of linseed oil the ethyl esters of higher saturated and non-saturated fatty acids are obtained. They are valuable nutritional supplement because of the significant content of ethyl ester of α -linolenic acid (from omega-3 group).

Separation of ester fraction from reaction mixture requires applying of multistage vacuum flash distillation and phase separation processes. The proposal of installation for the ethyl esters separation is presented in Fig. 1.

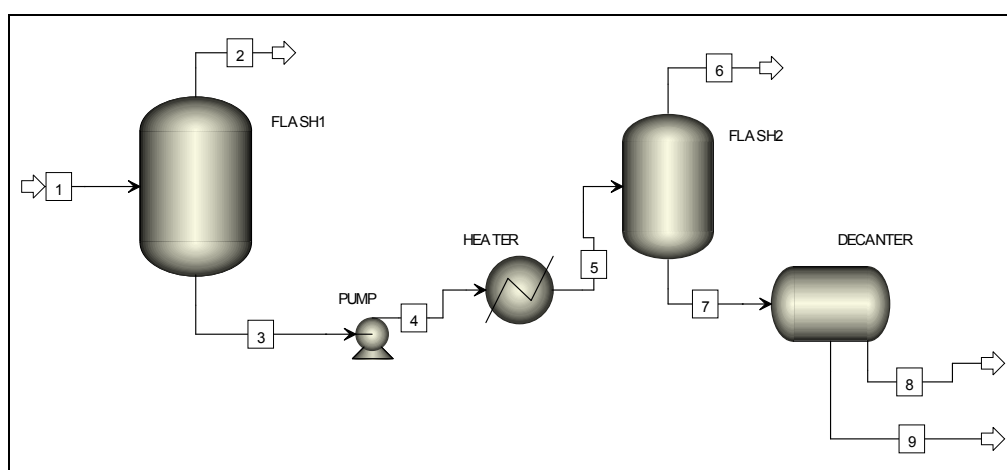


Fig. 1. Scheme of the process

The purification of esters fraction requires ethanol and glycerol removing. The simulation process of ethanol removal from a mixture obtained after transesterification and glycerol removal by mechanical phase separation was performed applying ASPEN PLUS® software. Two-staged flash distillation process was applied under 10 kPa pressure. This guarantees obtaining the product, in which the concentration of ethanol is less than 2.5% mass.

Simulation results of the ethanol separation process could be used in plant design pilot-scale.

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SEPARATION PROCESS OF COBALT(II), NICKEL(II), ZINC(II) AND CADMIUM(II) FROM CHLORIDE SOLUTION

Bernadeta Gajda¹, Mariusz B. Bogacki²

¹*Department of Metal Extraction and Recirculation, Częstochowa University of Technology, Armii Krajowej 19, 42-200 Częstochowa, Poland,*

²*Division of Process Engineering, Poznań University of Technology, Pl. M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland
e-mail: gajda@wip.pcz.pl*

Cobalt, nickel, zinc and cadmium are important elements known as industry useful metals. Main sources of them are sulfur or oxides ores. Other source of them is ocean in which many metal ions are dissolved or present in the concrete form. That source will be very useful in the future when traditional ores of many metals will be exhausted.

Last two decades we have observed growing interest of application of polymer inclusive membranes (PIM) for metal ion separation. PIM membranes have better mechanical strength and chemical resistance than liquid membranes. Plasticizer additive in polymer membrane cause their good or even very good flexibility properties. Membrane contained plasticizer has also good ability for miscible ion carrier in polymer. Today several ion carriers are used as metal extractants such as phosphoric acids, trioctylamine or crown ethers.

In the last ten years also some imidazolium derivatives were also used for ion separation. Imidazolium compounds have two nitrogen atoms in aromatic ring. One nitrogen atom has free electron pair, efficient in coordination bond and we observe reactions of complex formation of imidazolium compounds with metal chlorides MCl_2 .

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EFFECT OF Zr AND Hf SOLUTION PREPARATION STEP ON THEIR SEPARATION ON DIPHONIX[®] RESIN

A. Jakóbk-Kolon, M. Smolik, H. Jaroszek

Silesian University of Technology, Faculty of Chemistry, ul. B. Krzywoustego 6, 44-100 Gliwice, Poland; e-mail: agata.jakobik@polsl.pl

Zirconium and hafnium are widely used in the nuclear industry. However, due to their opposing nuclear characteristics, reactor grade Zr must contain less than 100 ppm of Hf. This requirement is not easily obtained, as hafnium occurs in all zirconium ores and both elements are exceptionally difficult to separate due to their close chemical properties. Complicated chemistry of their aqueous solutions causes additional problems in the separation. Hf and Zr, strong Pearson acids, easily react with strong Pearson bases – ligands with oxygen atoms (H₂O, OH⁻), creating aqua complexes, which, acting as Bronsted bases, polymerize to polynuclear species, i.e. tetramers [Zr₄(H₂O)₁₆(OH)₈]⁸⁺, [Zr₃Hf(H₂O)₁₆(OH)₈]⁸⁺. Additionally, pentamers and species with 8 and more coordination centers were also observed (1). The polymerization degree of studied elements in aqueous solution depends on concentration and type of the mineral acid, concentration of Zr(IV) and Hf(IV) ions, storage time and conditions (temperature), initial Zr(Hf) compound type and origin, thus obtained solution cannot be fully characterized by acid and Zr(Hf) concentration only (2). The polymerization degree may be a critical factor in Zr and Hf separation, thus some authors (3) recommend heating the solution of Zr and Hf in sulfuric acid to white fumes of SO₃ in order to depolymerize the solution before ion exchange separation. Pakalns obtained depolymerized solution by heating the ZrOCl₂·8H₂O or Zr(SO₄)₂·4H₂O (1 M) in 1.25 or 1.75 M H₂SO₄, respectively (4). In our previous work we proposed a method for removal of hafnium from zirconium by ion exchange using Diphonix[®] resin (5). The hafnium content in zirconium decreased from 2.4% to 0.24%.

The aim of this work was to study the effect of Zr and Hf solution preparation step on their separation by ion-exchange. Application of the depolymerization methods mentioned above did not improve investigated separation. Significant improvement of separation efficiency was obtained using solution prepared as follows: zirconium sulphate was converted into zirconium fluoride complexes (considered as monomers), which were next decomposed and HF was completely removed by heating with concentrated sulphuric acid. Obtained slurry was diluted with water to proper acid concentration. Passing obtained solution through Diphonix[®] resin column resulted in decreasing the hafnium content in zirconium from 2.47% to 0.015%.

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SORPTION OF DI- AND TRIVALENT CATIONS ON MOLECULARLY IMPRINTED POLYMERS

Anna Jakubiak-Marcinkowska, Andrzej W. Trochimczuk

*Department of Polymer and Carbonaceous Materials, Faculty of Chemistry,
Wrocław University of Technology, Wybrzeże Wyspiańskiego 27,
50-370 Wrocław, Poland
e-mail: anna.jakubiak@pwr.wroc.pl*

Molecular imprinting (MI) is one of the most promising method to design and synthesize synthetic molecules able to specific molecular recognition of target molecules. The main idea of this approach is formation of assembly of a cross-linked polymer matrix around templating moieties and after removal of the templates the creation of binding cavities complementary in functionality and shape to the original analyte.

The crucial issue in rational design of selective cavities is selection of an effective driving force for binding between monomers and template molecules (covalent, non-covalent, semi-covalent and coordinative). The coordination with metal ions becomes very advantageous for design of MI polymers with various applications in aqueous and non-aqueous media. Coordinative bonds are formed spontaneously and efficiently, they show flexibility in strength and have inherent catalytic properties. They are simultaneously thermodynamically stable and kinetically labile, what facilitates ligands exchange. Due to different metal oxidation states in complexes they may be easily characterized by various spectroscopic methods (1). According to this properties coordinative bonds are mainly applied in catalysis (1,2), sensors (3) and sorption processes (4,5).

The aim of our work is to present the possible application of coordinative imprinting of chosen metals for obtainment of materials able to sorb of various di- and trivalent metal ions. As the exemplary template Cu(II) and Fe(III) ions and their interactions with nitrogen in complexing monomer 4-vinylpyridine have been chosen.

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REMOVAL OF HEXAFLUOROARSENATE FROM AQUEOUS SOLUTION

H. Parschová, E. Mištová and L. Jelínek

*Department of Power Engineering, Institute of Chemical Technology, Prague
Technická 5, 166 28 Prague 6, Czech Republic
e-mail: jelinekl@vscht.cz*

Arsenic is currently one of the most feared inorganic pollutants of drinking water due to its toxic and carcinogenic effects. Arsenic usually occurs in the oxidation states(III) and (V). Compounds of As(III) are about five to twenty times more toxic than compounds of As(V) (1).

In surface waters, arsenic is present mainly in the form of arsenate. However, in some cases hexafluoroarsenate may be the main arsenic species. The presence of hexafluoroarsenate is usually related to waste waters from the glass industry (2). In addition, $KAsF_6$ has been also used as a selective herbicide and as a pesticide (3).

Arsenic (III) or (V) in the form of arsenites and arsenates can be effectively removed from aqueous solutions by various methods such as coagulation and filtration, reverse osmosis (4), sorption on ion exchange resins, polymeric/inorganic hybrid sorbents (5) and sorbents based on hydrated ferric oxide. However, hexafluoroarsenate (6) shows completely different behavior compared to commonly occurring arsenite and arsenate.

Arsenic removal from aqueous solutions containing hexafluoroarsenate or arsenate by strong and weak base anion exchangers was studied by dynamic column tests that were carried out using solution containing $5 \text{ mg}\cdot\text{L}^{-1}$ of arsenic and $100\text{-}1000 \text{ mg}\cdot\text{L}^{-1}$ of accompanying anions (chlorides and sulfates). The breakthrough capacity of arsenic (limit concentration $< 0.1 \text{ mg}\cdot\text{L}^{-1}$) and the effect of concentration of accompanying anions on the sorption of arsenic were studied. The specific flow rate of solution was $6 \text{ BV}\cdot\text{h}^{-1}$. Desorption of arsenic was carried out by $1 \text{ mol}\cdot\text{L}^{-1}$ NaOH or $2 \text{ mol}\cdot\text{L}^{-1}$ KSCN. All the studied anion exchangers performed well in the absence of accompanying anions. In the presence of chlorides and sulfates studied exchangers showed high selectivity towards hexafluoroarsenate in contrast to arsenate.

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ANION EXCHANGE RESIN TOWARDS NOBLE METALS SORPTION

Dorota Jermakowicz-Bartkowiak

*Department of Polymer and Carbonaceous Materials,
Wrocław University of Technology,
50-370 Wrocław, Wybrzeże Wyspiańskiego 27, Poland
e-mail: dorota.jermakowicz-bartkowiak@pwr.wroc.pl*

Synthetic ion exchangers are used for many years for concentration of valuable and/or toxic metals from industrial wastes. The preparation of functionalized polymers with various ion-selective ligands allows to use sorption technology for recovery of valuable metals, as gold, platinum, palladium, silver, and rhenium or for removal of toxic ions as arsenic from metallurgical or hazardous waste water. Since the choice of ligand attached to the resin plays such an important role in getting proper selectivity, a variety of functional groups were used that could be selectively loaded with targeted ions (1).

A wide family of ion-exchange resins, bearing chelating and coordinating ligands, was synthesized in our laboratory in a program for development of new selective resins (1). The polymer matrices crosslinked with divinylbenzene were synthesized on the basis of vinylbenzyl chloride during suspension polymerization (1).

The aim of this work is to present abilities of synthesized resins in selective sorption of gold, platinum, palladium from multicomponent acidic solutions.

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SYNTHESIS OF POLYMER ADSORBENTS BY DIELS-ALDER MODIFICATION OF VINYL GROUPS IN POLY(DIVINYLBENZENE)

Małgorzata Kica, Sylwia Ronka

*Faculty of Chemistry, Wrocław University of Technology,
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
e-mail: sylwia.ronka@pwr.wroc.pl*

Functional polymers are widely used in separation processes and analysis. With the intention of getting specific polymer adsorbents with active and stable functional groups poly(divinylbenzene) beads were synthesized in radical polymerization using suspension polymerization, and modified with maleic anhydride in Diels-Alder reaction. Both gel and porous polymers were prepared. The properties of the polymeric beads, such as porosity and surface area were controlled by using mixture with different content of porogens: *n*-heptane and toluene. The surface area obtained using the BET method was up to 851 m²/g, average pore size 7,0 nm. Using *non*-solvent (*n*-heptane) caused worse solvation of polymer, pore size became higher, what caused lower surface area. Using toluene as a porogen resulted in smaller pores and higher surface area. Content of pedant vinyl groups was assayed by FTIR as described in (1). With the object of increasing amount of pedant vinyl groups time of polymerization was reduced from 9 to 5 hours. Although slight change was observed, impact of reaction time was not significant.

In Diels-Alder cycloaddition poly(divinylbenzene) can participate either as a dien or dienophile, depending on reagents and conditions (2). In described modification maleic anhydride, which is good dienophile, bind to pedant vinyl groups of poli(divinylbenzene), which reacts as a dien. For the purpose of opening maleic acid ring samples were treated with aqueous base. Neither increasing temperature, nor mixing during hydrolysis had influence on amount of acidic groups. As shown by FTIR and back titration the prepared adsorbents contained up to 2.6 mmol of acid groups /g dry polymer. Due to high degree of crosslinking the modification could take place only on the polymer surface, so that the most satisfying result was acquired for polymer with the highest surface area.

In consequence of acidic groups presence on the polymer surface synthesized products can interact with selected substances by hydrogen bond, and so that can be employed as specific sorbents. Moreover, it can be used in process of ion-exchange. High surface area and possibility of bonding of chosen substances provide wide range of application, for example adsorption of herbicides, especially triazines from water.

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SELECTIVE RECOVERY OF TRACE REE FROM ACIDIC AQUEOUS SOLUTION WITH DIALKYL HYDROGEN PHOSPHORIC ACID IMPREGNATED RESINS

E. V. Kirillov, V. N. Rychkov, M. L. Cherny

Ural Federal University, Department of Rare Metals, 19, Mira St., 620002, Ekaterinburg, Russia, tel. +7 343 2190419, e-mail: ugin@gala-decor.ru

Recently, rare earth elements (REE) have received much attention due to increasing demand, especially in electronic, optical and ceramic industries. REE are distributed in trace amounts in several kinds of ores, including monazite, titanous magnetites, tin stone and uranium ore. Currently, REE are recovered as a by-product in the metallurgical process of these ores. However, the metal contents in the ores are intrinsically low (10^{-1} - 10^{-3} %) and, more importantly, separation from a large amount of matrix elements creates technological problems.

Solvent extraction technology has been applied to the recovery of REE from wolframite residue using dialkyl hydrogen phosphate (D2EHPA) as an extractant. On the other hand, for the concentration of trace metals in a large quantity of an aqueous solution, a column separation process using an appropriate stationary phase has greater advantages over a liquid-liquid extraction system owing to the high concentration efficiency and operational convenience.

We have prepared a metal ion selective resin simply by impregnation of dialkyl hydrogen phosphoric acid (D2EHPA) into macroporous resin. It has been demonstrated that the impregnated resin is effective as a column stationary phase for the chromatographic pre-concentration of rare earth elements. In the present study, we examined the distribution behavior of metal ions including lanthanides, iron, aluminum and yttrium toward the impregnated resin and then applied the resin for the recovery of REE from sulphate technological solution and tin slag.

SEPARATION AND RECOVERY OF LANTHANUM AND CERIUM FROM WASTE AUTOMOBILE CATALYST USING COATED SOLVENT IMPREGNATED RESIN

Kanako Kohata, Syouhei Nishihama, and Kazuharu Yoshizuka

*Department of Chemical Engineering, The university of Kitakyushu,
Hibikino 1-1, Kitakyushu 808-0135, Japan
e-mail: m10a0501@hibikino.ne.jp*

Solvent impregnated resin (SIR) has been developed to apply extractant for solvent extraction to ion exchange process. One disadvantage of SIR is that the reuse of SIR is limited because the extractant impregnated is leaked from the resin. A coating method of SIR with crosslinked polyvinyl alcohol (PVA) to prevent leakage of quaternary ammonium salt type extractant was reported (1). Recently, increase in the importance of rare earth metals makes the separation and recovery of rare earth metals from waste materials active issues. In the present work, solvent impregnated resin of 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) coated with crosslinked PVA was prepared to apply the adsorbent to the recovery of La^{3+} and Ce^{3+} from waste automobile catalyst.

The adsorption ability of La^{3+} and leakage of PC-88A were investigated by batchwise adsorption. In the case of uncoated SIR without coating, ca. 3 % of PC-88A is leaked from SIR by one batchwise operation. The coated SIR crosslinked PVA by divinyl sulfone (DVS) or glutaraldehyde (GA) can suppress leakage lower than 1 %. In the case of crosslinking with DVS, however, the adsorption of La^{3+} is significantly sifted to higher pH region. GA is therefore concluded as a suitable crosslinker of PVA for this SIR.

Coated SIR was then applied to column operation. The coated SIR can be used for quantitative adsorption and elution of La^{3+} and Ce^{3+} (Figs. 1 and 2). The separation of La^{3+} and Ce^{3+} is however difficult with the present operational conditions. The eluent should be gradually changed during elution step (gradient mode) to separate two metals. The repeated experiments based on the column operation revealed the present coated SIR can be reused without decrease in the adsorption property at least 3 cycles.

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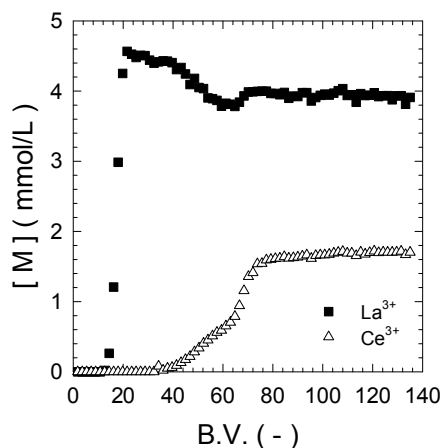


Fig. 1. Breakthrough curves of La and Ce using coated SIR

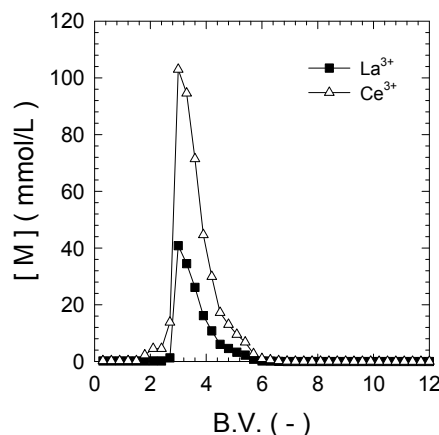


Fig. 2. Elution curves of La and Ce using coated SIR

CHITOSAN MODIFIED BY N,N-BIS(CARBOXYMETHYL)GLUTAMIC ACID IN HEAVY METAL IONS SORPTION FROM WATER AND WASTEWATER

Dorota Kołodyńska, Marzena Gęca, Zbigniew Hubicki

*Department of Inorganic Chemistry, Faculty of Chemistry,
Maria Curie-Skłodowska University, Maria Curie-Skłodowska Sq.2. 20-031
Lublin, Poland, Tel.: +48 (81) 5375736; Fax: +48 (81) 5333348,
e-mail: kolodyn@poczta.onet.pl*

Chitosan (CS) is a polysaccharide, which due to its reactive properties can produce numerous derivatives having a wide range of applications. Chitosan readily undergoes numerous modifications – both physical and chemical with the aim of preventing from polymer dissolution during sorption of metal ions in acidic solutions, causing increase in its sorption capacity and selectivity. The most frequently used modifying agents are: polyvinyl alcohol (PVA), glutaraldehyde (GLA), epichlorhydrin (EPI), ethyleneglycol diglycidyl ether (EGDE), disodium citrate (CitNa), pentasodium tripolyphosphate (TTP), sodium alginate (NaAlg). It can be readily formed into various shapes: globules, fibres, capsules, membranes and others. The research results reported in the literature confirm complex creating action of chitosan towards metal ions. Therefore, chitosan is mainly applied as sorbent for removal of the heavy metal ions: Cu(II), Zn(II), Cd(II), Pb(II), Hg(II), Cr(III,VI), As(III,V), and recovery of the noble metals: Pt(IV), Pd(II), Ag(I) and Au(III) (1-3). Guibal et al. (2-3) have extensively studied the effect of chitosan properties on the adsorption of metals, dyes and organic compounds such as phenols.

In the presented paper the effect of CS modification by preparing of the beads cross-linked by glutaraldehyde and epichlorhydrin in the presence of N,N-bis(carboxymethyl)glutamic acid were presented. The obtained gel beads were used for sorption of heavy metal ions i.e. Cu(II), Zn(II), Cd(II) and Pb(II). Among different factors that influence the sorption process, the following were studied in detail: solution pH, initial concentration, phase contact time, temperature and effect of competitive ions. The most important factor influencing the effectiveness of sorption was pH and metal ions concentration.

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REMOVAL OF CHROMIUM(III) IONS FROM AQUEOUS SOLUTION BY MICELLAR-ENHANCED ULTRAFILTRATION PROCESS (MEUF)

B. Konopczyńska, E. Świerkowska, K. Staszak, K. Prochaska

*Poznań University of Technology, Institute of Chemical Technology and Engineering, Pl. M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland,
e-mail: beata.konopczynska@doctorate.put.poznan.pl*

Chromium has a wide range of applications in chemical and metallurgical industry, in tanning, and in the refractory industry. The widespread application and production of many compounds of chromium causes the generation of sewage pollutions, dust and solid waste containing this element.

The principal techniques for recovery or removal of Cr from wastewater are chemical precipitation, ion exchange, coagulation-flocculation, flotation and adsorption. In recent years, a search for new non-classical separations techniques has been observed. Among them the micellar-enhanced ultrafiltration (MEUF) has been found to be a promising method for the removal of metal ions as: Cd^{2+} , Cu^{2+} , Cr^{3+} , Ni^{2+} and Zn^{2+} from waste streams. MEUF is a hybrid process that combines classical ultrafiltration technique with the ability of surfactants to solubilize.

The paper presents results of our research on removal of chromium(III) ions from the model aqueous solutions using the MEUF technique. A laboratory-scale ultrafiltration system (SEPA CF, OSMONICS, USA) was used in the study. The transmembrane pressure was equal to 0.2 MPa. The usefulness of three polymeric membranes (Membranes SEPA, Osmonics, USA) made of cellulose acetate (CA), polyvinylidene fluoride (PVDF) and polyethersulfone (ER) with an effective area of 0.0155 m² were compared. Initial concentration of aqueous solution of Cr(III) was: 0.01, 0.05 and 0.1 g/dm³. In the experiments two surfactants were considered: sodium dodecyl sulfate (SDS) and Rofam10 as a non-ionic surfactant which is a product of rape-seed oil fatty acids ethoxylation of the general formula $\text{R-CO}(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$ ($\text{R} = \text{C}_{12} - \text{C}_{24}$ is a fatty acid hydrocarbon chain and $n = 10$ is a number of oxyethylene segments). Moreover, the mixtures of both surfactants in the different molar ratios were used. The metal concentration in the permeate flux was determined by UV spectroscopy using a UV VIS SPECORD 40, Analytic Jena, Germany.

The obtained results allowed to analyse the influence of Cr(III) ions concentration in the feed solution, the type of surfactant and the membrane material on the separation efficiency of chromium(III) from aqueous solutions by MEUF technique. It was found that in systems containing a mixture of SDS and Rofam 10, the retention (R) of Cr(III) ions is close to 100% and what is important, R slightly increased in comparison with that obtained for the MEUF system with SDS only. It is worth noting that in the presence of nonionic surfactant Rofam 10 in MEUF system the total concentration of surfactants is much lower so the separation process becomes more environmentally friendly.

Acknowledgements: The work was supported by DS- 32/067/2011.

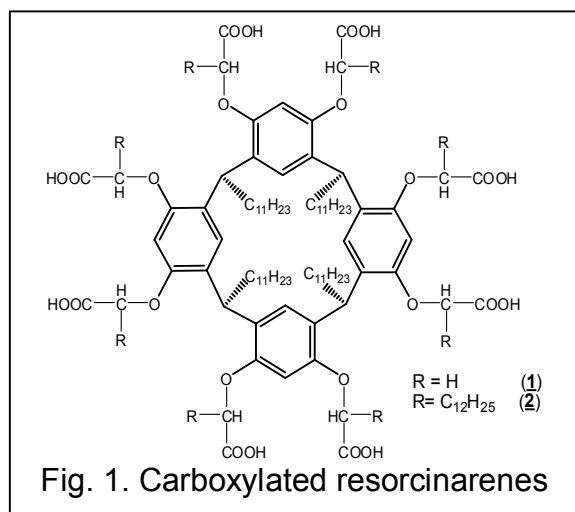
SOLVENT EXTRACTION OF Pb(II), Cd(II) AND Zn(II) BY CARBOXYLATED RESORCINARENES

**Joanna Kończyk¹, Jolanta Kozłowska¹, Cezary Kozłowski¹,
Władysław Walkowiak², Małgorzata Deska¹**

¹*Institute of Chemistry, Environment Protection and Biotechnology, Jan Długosz University of Częstochowa, 42-201 Częstochowa, Armii Krajowej 13/15 Street, Poland;*

²*Chemical Metallurgy Division, Faculty of Chemistry, Wrocław University of Technology, 50-370 Wrocław, Wybrzeże Wyspiańskiego 27, Poland
e-mail: j.konczyk@ajd.czyst.pl*

Carboxylated derivatives of resorcinarenes **1** and **2** (Fig.1) were synthesized by reaction of undecylresorcinarene with α -bromoalkylcarboxylic acid and NaH in dry THF adopted from procedure described in paper.



Separation system was successfully developed in the solvent extraction from $5.0 \cdot 10^{-4}$ M Pb(II), Zn(II) and Cd(II) ions aqueous solutions into chloroform phase containing $1.0 \cdot 10^{-3}$ M resorcinarene as an extractant were investigated.

The obtained values of percent extraction prove that **1** and **2** can be used for selective removal of Pb(II) and affectivity of the process decreases with decreasing length of alkyl chain attached to upper ring. Both resorcinarenes selectively remove Pb(II) over Cd(II) and Zn(II)

ions. The relatively high separability of Pb(II) ions was observed in competitive solvent extraction with resorcinarenes **1** and **2** from aqueous solution in pH range 4 – 6 (Fig. 2). The efficiency and selectivity of metal ions extraction decreased in the sequence Pb(II) \gg Cd(II) > Zn(II). Pb(II) ions were quantitatively removed influencing for separation ability of the ion recognition processes, *i.e.* best fitting of large cations to cavity of resorcinarenes ring.

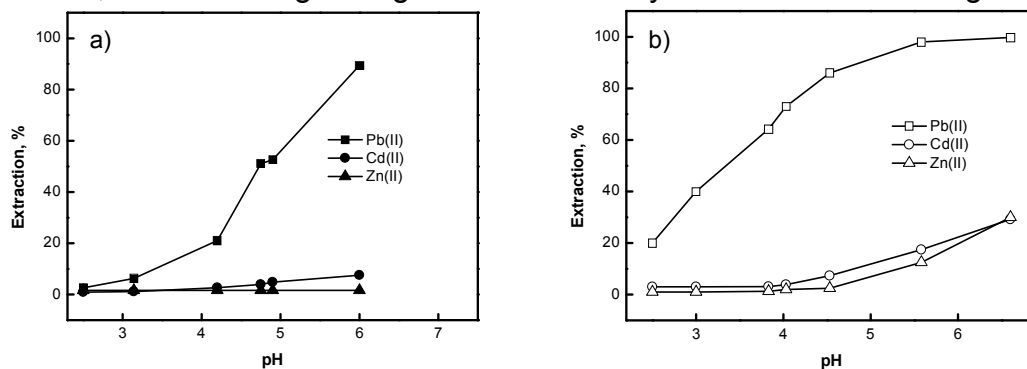


Fig. 2. The effect of pH aqueous phase on the capacity of extraction by **1** (a) and **2** (b)

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CONCENTRATION OF SODIUM HYDROXIDE SOLUTIONS BY ELECTRODIALYSIS

Stanisław Koter¹, Adriana Cuciureanu², Monika Kultys¹, Jerzy Michałek³

¹*Nicolaus Copernicus University, Faculty of Chemistry, 7 Gagarina St., PL-87100 Toruń, Poland*

²*University Politehnica Bucharest, Faculty of Applied Chemistry and Materials Science, Polizu Str, no. 1-7, Bucharest, Romania*

³*CHEMIPOZ Sp. z o.o., ul. Raszyńska 14/4, 60-135 Poznań, Poland
e-mail: skoter@umk.pl*

Sodium hydroxide is used in many technological processes. The basic method of NaOH production is electrolysis of sodium chloride, including membrane electrolysis. However, using that method a high concentration of NaOH is obtained (up to 50%). In some cases, however, there is a need to concentrate a waste dilute solution of NaOH to about 15-20%. One of the methods is to concentrate it by evaporation. The alternative method to be considered is electrodialysis (ED). In that case, a highly selective cation-exchange membrane is needed, whereas an anion-exchange membrane should be resistant to the strong alkali media. Its selectivity is of less importance because the mobility of OH⁻ anions is of much higher than that of Na⁺ cations. Both types of membranes should show low diffusional permeability against NaOH.

In this work we determined the current efficiency and the selectivity of some commercial cation-exchange membranes including Nafion ones in the electrolysytic concentration of NaOH solutions up to 5 M. Also, one type of anion-exchange membrane resistant against NaOH was tested. It was found that at the investigated concentration range two-layer Nafion membranes showed rather unsatisfactory current efficiency (*CE*). Other investigated cation-exchange membrane showed substantially higher *CE*. Regarding the anion-exchange membrane – the diffusional flux of NaOH substantially diminished the current efficiency. The process was modeled using the extended Nernst-Planck equation and the Donnan equations for the membrane transport description. Two model parameters were sufficient to fit the experimental results with adequate accuracy.

PROPERTIES OF SULFONATED PSEBS TRIBLOCK COPOLIMER MEMBRANES FOR ELECTROCHEMICAL APPLICATIONS

Tomasz Bohr, Stanisław Koter

*Nicolaus Copernicus University, Faculty of Chemistry, 7 Gagarina St.,
PL-87100 Toruń, Poland
e-mail: skoter@umk.pl*

A series of sulfonated poly(styrene-ethylene-butylene-styrene) (S-PSEBS) triblock copolymer membranes were prepared using acetyl sulfate as the sulfonating agent according to (1,2). Three types of S-PSEBS copolymer were prepared using different ratios of sulfonating agent to styrene monomers. Cation-exchange membranes were prepared from the S-PSEBS by the solvent evaporation method. They were characterized regarding possible membrane applications like electrolysis, electro dialysis or PEM fuel cells. The influence of sulfonation degree on the following membrane properties was determined:

- ion exchange capacity,
- solvent sorption,
- electric conductivity,
- transport number, and also
- mechanical strength, thermal and chemical stability.

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THE INFLUENCE OF TEMPERATURE ON THE VALUES OF DISTRIBUTION COEFFICIENTS, $D_{2/1}$ DURING THE CRYSTALLIZATION OF $\text{CoSeO}_4 \cdot n\text{H}_2\text{O}$

A. Kowalik, M. Smolik, K. Mączka

*Faculty of Chemistry, Department of Chemistry, Inorganic Technology and Fuels; Silesian University of Technology,
Bolesława Krzywoustego 6, 44-100 Gliwice, Poland
e-mail: Anna.Kowalik@polsl.pl*

Distribution coefficients $D_{2/1}$ (Henderson, Kracěk, Chlopin) are important indicators of the effectiveness of crystallization as a method of purification. They are very useful in preparation of high-purity inorganic salts and therefore they are often determined in various crystallization systems. Selenate crystallization systems are less examined on that score (only a few distribution coefficients for these systems are available and generally for comparable amounts of co-crystallizing salts).

The released data show that during the crystallization from aqueous solutions in the range of 12°C – 100°C cobalt selenate forms four various hydrates differing from each other with crystal structures, which may affect values of $D_{2/1}$ coefficients of M^{2+} ions cocrystallizing with them. The investigation of the character of this influence is the purpose of this presentation.

Coefficients, $D_{2/1}$ of co-crystallization of low amounts of M^{2+} ions $\{M^{2+} = \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Cu}^{2+}, \text{Mg}^{2+}, \text{Cd}^{2+}, \text{Mn}^{2+}\}$ with cobalt selenate have been determined by the method of isothermal levelling of supersaturation at four temperatures: 40°C, 50°C, 68°C and 80°C, which have been selected taking into account the crystal systems of stable in these temperatures hydrates of cobalt selenate as well as hydrates of cocrystallizing selenates ($\text{MSeO}_4 \cdot n\text{H}_2\text{O}$).

The obtained $D_{2/1}$ coefficients are very diverse and strongly affected by the temperature of crystallization. At elevated temperatures they generally drop and in some cases achieve significantly lower values than those determined at 25°C (1) (eg. $D_{\text{Cu}/\text{CoSeO}_4 \cdot 4\text{H}_2\text{O}}$ at 50°C is 15 times lesser than $D_{\text{Cu}/\text{CoSeO}_4 \cdot 6\text{H}_2\text{O}}$ at 25°C). Moreover the influence of some chemical, physicochemical and crystal chemical factors (such as solubility of cocrystallizing salts, their number molecules of crystallization water and crystal structure, as well as ionic radii of cocrystallizing M^{2+} ions, their hardness, electron configuration, and crystal field stabilization energy) on their values have been analysed. The coefficients are most affected by some of them and therefore they can be estimated by the simple empirical formulae.

On the basis of obtained data, it is possible to propose the way of such lowering $D_{2/1}$ coefficients of M^{2+} ions to accomplish essential purification of CoSeO_4 by crystallization.

Acknowledgements: This work was partially financed by Polish Ministry of Science and Higher Education grant No. N N209 409537.

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APPLICATION OF CARBOXYPHENYL DERIVATIVE OF RESORCINARENE FOR SOLID PHASE EXTRACTION OF Pb(II), Zn(II) AND Cd(II) IONS

Jolanta Kozłowska, Iwona Zawierucha, Małgorzata Deska

*Institute of Chemistry, Environmental Protection and Biotechnology, Jan Długosz University of Częstochowa, Armii Krajowej 13/15, 42-200 Częstochowa, Poland
e-mail: j.jablonska@ajd.czest.pl*

The derivatives of calix[4]resorcinarenes has also been used for various ion-exchange methods for metal ions separation, namely as an additive in liquid membrane (1), solvent extraction (2), and sorption (3). However, the use of calix-[4]resorcinarenes as a heavy metal cation adsorbent is still very limited.

The C-4(carboxyphenyl)calix[4]resorcinarene **1** was synthesized by the acid-catalyzed cyclocondensation reaction of resorcinol and *p*-carboxybenzylaldehyde (4). A study on the adsorption characteristics of Pb(II), Zn(II) and Cd(II) ions onto **1** in batch system has been conducted. Batch experiment was conducted by adding 0.05 g of **1** into 20 cm³ of Pb(II), Zn(II) and Cd(II) ions sample solution (10 mg/dm³ each) having various pH values. The effect of pH on the extraction of Pb(II), Zn(II) and Cd(II) ions by **1** was studied in the pH range of 5 to 6.5 and the results are shown in Fig. 1. The amount of Pb(II) extracted increased consistently with the increase of initial pH, and it reached optimum value at initial pH value of 6.5. When the initial pH was high (about 6), there was only limited amount of H⁺ from deprotonation of carboxylic group in lower ring. Accordingly, the interaction occurred in the system was dominated by the interaction between carboxylic group with Pb(II) by fitting of cavity size and large cation. This is the reason why the amount of Pb(II) extracted at relatively high pH value was significantly high than Cd(II) and Zn(II). However, increasing initial pH to a value higher than 6 is not a good selectivity as there has been increase of Cd(II) and Zn(II) extraction capacity.

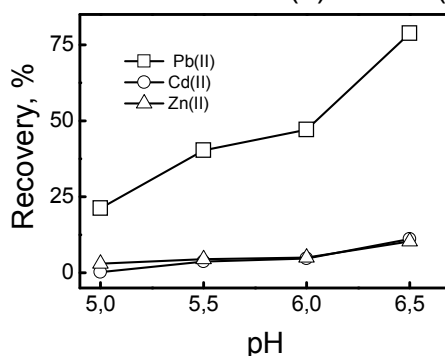


Fig.1. The effect of pH solution on the metal ions separation with **1**

Acknowledgements: This work is part of the project no. N N209 441539 financially supported by Ministry of Science and Higher Education.

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PERCOLATION BEHAVIOUR OF GAS PERMEABILITY IN POLYMERIC MEMBRANES WITH MAGNETIC PARTICLES

**Monika Krasowska, Gabriela Dudek, Anna Strzelewicz,
Aleksandra Rybak, Zbigniew J. Grzywna**

*Faculty of Chemistry, Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, ul. Strzody 9, 44-100 Gliwice
e-mail: mkrasowska@polsl.pl*

In many fields of separation polymeric membranes with additional particles are used. These materials are of great interest because of mixed components with different properties. Mixing the various components can help to overcome the respective drawbacks like low selectivity or low permeability of separating chemical species (1). In our paper, we consider the influence of structural properties of a polymer membrane with magnetic powder on the gas transport through this object (2-3). This process can be considered as percolation process (4). In Fig. 1 we present scanning microscope image of polymeric membrane with magnetic powder, where percolation paths were observed.

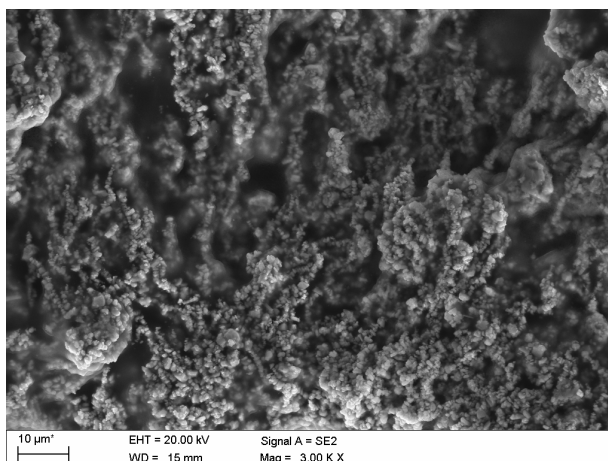


Fig. 1. Scanning microscope image (with representative penetrant – scale gaps) of polymeric membrane with magnetic powder

The physico-chemical structure of polymer affects the percolation threshold and the percolation concentration. Membranes with various amount and granulation of magnetic powder have different topological structures and may lead to different behaviours of the penetrant.

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POLYAMIDE-6 PERVAPORATION MEMBRANES FOR ORGANIC-ORGANIC SEPARATION

Marta Meller, Wojciech Kujawski, Radosław Kopeć

*Faculty of Chemistry NCU, 7 Gagarina Street, 87-100 Toruń, Poland
e-mail: kujawski@chem.umk.pl*

Pervaporation is a membrane separation process used to separate liquid mixtures. Pervaporation is already used in many practical applications like organics dehydration, water purification or beverage processing. Despite the large number of applications, the nowadays research in pervaporation is still focused on new membrane materials as well as and on the optimization of the process. A lot of membranes made from different polymers have been tested for separation of water/organic and/or organic/organic solutions by pervaporation but there are only few reports on the applications of polyamide-6 (PA-6) membranes.

The objective of this work was to prepare composite pervaporation membranes based on polyamide-6 and to determine their pervaporation performance in the separation of organic-organic mixtures.

Several PA-6 membranes of different morphology were prepared. The ultrafiltration support was prepared by the phase inversion method (Fig. 1). The selective layer was cast on the top of the UF support. Pure PA-6 as well as PA-6 filled with inorganic nanoparticles (TiO_2 , Al_2O_3 , ZrO_2) were used to prepare the selective layer. The transport and separation properties of these membranes in contact with organic-organic mixtures of different polarity (e.g. methanol-MTBE, methanol-DMC) were determined. It was found that more polar component of the organic mixture was preferentially transported through the membrane with a reasonably high flux and selectivity. Transport and selective parameters were dependent on the preparation conditions of the membrane.

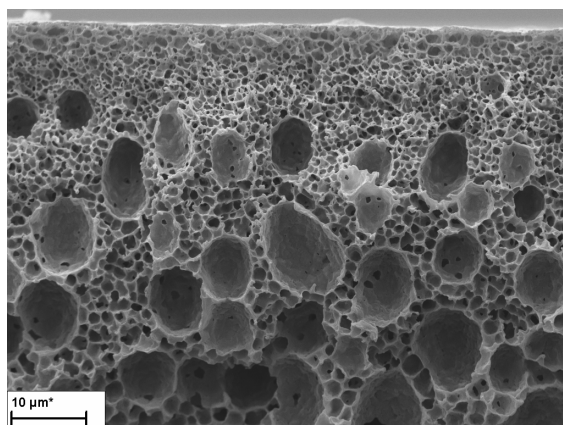


Fig. 1. SEM of the cross-section of PA-6 ultrafiltration membrane

PERMEABILITY OF DIVALENT CATIONS ACROSS ANION-EXCHANGE MEMBRANES IN THE PRESENCE OF SULFURIC ACID. PART 1: ELECTRODIALYSIS OF MgSO_4 AND H_2SO_4 MIXTURE

Monika Kultys, Stanisław Koter

*Nicolaus Copernicus University, Faculty of Chemistry, 7 Gagarina St., PL-87100
Toruń, Poland
e-mail: mkultys@chem.umk.pl*

Taking into account economical and environmental aspects, crucial issue in the present industrial technologies is the raw materials recovering and reusing. The metal plating and finishing industry consumes large amount of inorganic acids used for etching in metal preparatory processes. One of the well known method of acid recovery and its separation from metal ions is electrodialysis (ED) - widely used in many industrial branches (1,2). In this method the cation-exchange membranes and the anion-exchange membranes are used. A weak point of ED is anion-exchange membrane which should be selective in wide range of acid concentration.

In this work, the experimental results of electrodialytic separation of H_2SO_4 and MgSO_4 in the module with the Neosepta ACM and Selemion AAV membranes are presented. The permeability of magnesium cations across anion-exchange membranes (strong and weak base) during ED is shown. The influence of current density and concentration of H_2SO_4 on the membrane permeability of Mg^{2+} is described. The current efficiency of acid removal from the cathodic compartment is determined.

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PERMEABILITY OF DIVALENT CATIONS ACROSS ANION-EXCHANGE MEMBRANES IN THE PRESENCE OF SULFURIC ACID. PART 2: ELECTRODIALYSIS OF $ZnSO_4$ AND H_2SO_4 MIXTURE

Monika Kultys, Stanisław Koter

*Nicolaus Copernicus University, Faculty of Chemistry, 7 Gagarina St., PL-87100
Toruń, Poland
e-mail: mkultys@chem.umk.pl*

The electrodialysis (ED) is one of commonly used membrane techniques. ED modules are applied in many different areas of people activity, like water desalination, ions separation, deacidification in food industry etc. (1-3). Important application of ED is substance recovering from wastewater and its purification. In the metal plating and finishing industry one of group of wastewater is acidic/alkaline sewage. Depending on used technology effluents after etching contain inorganic acids as H_2SO_4 , HCl , H_3PO_4 and metals (Fe, Ni, Zn, Al). To reduce cost production and minimize harmful influence on environment the ED can be used to recover and purify acids.

The excess of zinc in water is strongly hazardous. Zinc pollution of water is highly poisonous to aqueous organisms and the result of soil pollution by zinc is limitation of proper plants growth. From economic point of view, the recovery of metal salt is strongly desirable - purified water can be reused for rinsing bath.

The experimental results of electrodialytic separation of H_2SO_4 and $ZnSO_4$ in module with ACM and AAV are presented. The permeability of zinc cations across anion-exchange membranes (strong and weak base) during ED is shown. The influence of current density and concentration of H_2SO_4 on the permeability of Zn^{2+} is described. The current efficiency of acid removal from the cathodic compartment is determined.

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APPLICATION OF TETRAPHENYL AND ETHYLTRIPHENYLPHOSPHONIUM SALTS FOR REMOVAL OF ANIONIC DYES PROCION RED MX-5B AND REACTIVE BLACK 5 FROM AQUEOUS SOLUTIONS

Jana Martinková, Tomáš Weidlich

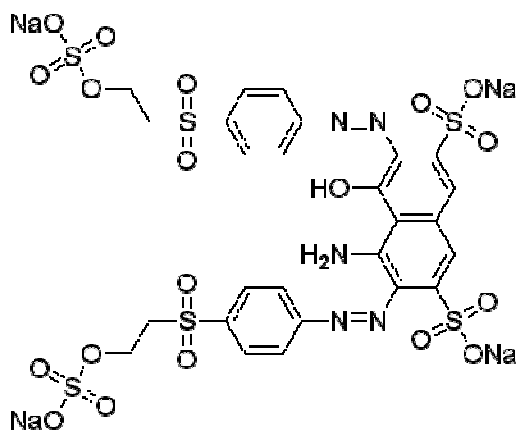
University of Pardubice, Institute of Environmental and Chemical Engineering,
Faculty of Chemical Technology, Studentská 95, Pardubice 53210, Czech
Republic
e-mail: jana.martinkova1@student.upce.cz

In this poster attention is focused on studying efficiency of the removal of azo-dyes containing sulfonic groups of model waste waters using cationic tensides.

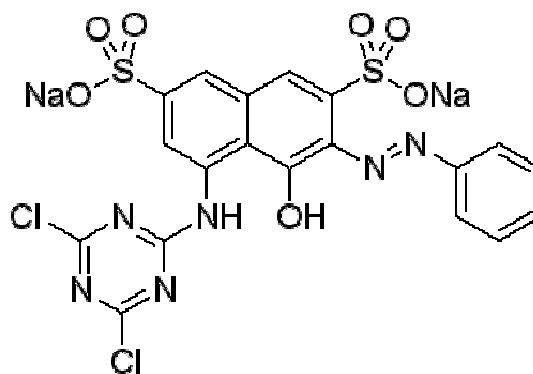
During each experiment there was used azo-dyes solutions, namely Procion Red MX-5B and Reactive Black 5. Azo-dyes were coagulated by cationic tensides (phosphonium salts), as tetraphenylphosphonium bromide and ethyltriphenylphosphonium bromide.

During all experiments analysis of efficiency of azo-dyes removal by UV-visible recording spectrophotometer UV-160A was made.

As a result of the work it was found that both of cationic tensides are very efficient in the removal of azo-dye, especially in the removal of Procion Red MX-5B. There were the best results (near 100% efficiency).



Structure Reactive Black 5



Structure Procion Red MX-5B

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DESALINATION OF GLYCERINE BY ION EXCLUSION

Ireneusz Miesiac, Krzysztof Alejski

Poznań University of Technology, Inst. Chem. Technol. & Eng.
pl. Skłodowskiej-Curie 2, 60-965 Poznań, Poland
e-mail: ireneusz.miesiac@put.poznan.pl

The main source of glycerol is nowadays the glycerine fraction coming as a side product from alkaline transesterification of fats and oils. After treating with mineral acid to neutralize the alkaline catalyst and soaps the raw glycerine is often characterized by important content of salts in the range of 2-6%. One of the excellent and simple method of salt removing is the ion exclusion using cation exchange resin.

For the investigation the diluted glycerine fraction containing 48% of glycerol, 2.1% of NaCl and some dyestuff (absorbance 1.6 at 410nm, 1cm) was used. Amberjet 1200 (Rohm&Haas) monodisperse (0.62mm) in sodium form was used as a cation exchange resin, placed in a jacketed glass column (1000x23mm) heated to 70°C. The column was feed with the glycerine fraction in the amount of 0.2-0.5V_B (V_B = 400mL) then rinsed with water at the flow rate 1-4h⁻¹. Exemplary results of the obtained separations are shown in Fig. 1.

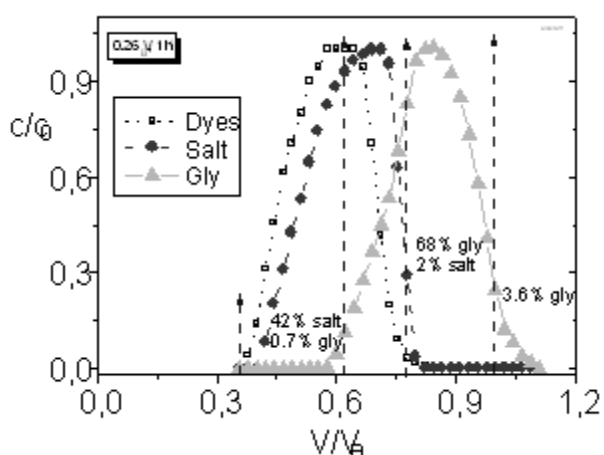


Fig. 1. Isoplane diagram for separation of dyes, salt and glycerol on Amberjet 1200Na cation exchanger (feed 0.26V_B, flow rate 1h⁻¹)

The eluate from ion exclusion process can be divided into three fractions: waste salt containing 42% of initial salt content and only 0,7% of glycerol lost, main product with (68+3,6)% of glycerol content and only 2% of initial salt content. The rest in the middle forms a mixture of unseparated components and has to be recycled. As a result, about 40% of salt can be continuously removed as a waste stream together with the dyes and in the main stream it is possible to obtain about 70% of glycerol with desalination degree as high as 97%. The ion exclusion process can be incessantly repeated every 20-40 min without any regeneration of cation exchange resin.

Acknowledgements: This work was supported by Polish grant DS 32/267/2011.

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SEPARATION OF SUCCINIC ACID AND GLYCEROL

I. Miesiac, K. Alejski, A. Rogaliński, M. Przewoźna

*Poznań University of Technology, Inst. Chem. Technol. & Eng.
pl. Skłodowskiej-Curie 2, 60-965 Poznań, Poland
e-mail: ireneusz.miesiac@put.poznan.pl*

Fermentation of low-cost carbohydrates or of waste glycerol from biodiesel production is a potential source of low-cost succinic acid. The acid is present in the fermentation broth at the concentration of 30-60g/L. Several possible alternatives exist for the preliminary recovery of succinic acid or its salt from the fermentation broth such as electrodialysis, reactive extraction with tertiary amines, sorption on anion exchange bed. The classical method for recovery of di- or tricarboxylic acids has been addition of $\text{Ca}(\text{OH})_2$ to precipitate calcium salts, followed by addition of sulfuric acid to regenerate the acid. However, this approach incurs costs for chemical consumption and the environmental problem of waste CaSO_4 .

An excellent and simple method to separate succinic acid and glycerol seems to be the sorption on the anion exchange column. Two alternative methods are possible to achieve a separation effect:

- a reversible sorption of succinic acid on strong anion exchanger in chloride form using water as a regenerative reagent,
- a sorption of succinic acid on weak anion exchanger in its hydroxyl form followed by the regeneration with dilute alkaline solution.

In Fig. 1 the sorption of glycerol and succinic acid (each 5%) on strong base Lewatit VPOC 1071 in chloride form (Bayer) is shown. Both the components are sorbed in the exchanger particles but in different manner. The sorption of glycerol is of physical principle and can be used for separation of salts in so-called ion exclusion process. The sorption of succinic acid exhibits some anion exchange mechanism like acid retardation process, well known in the purification of mineral acids.

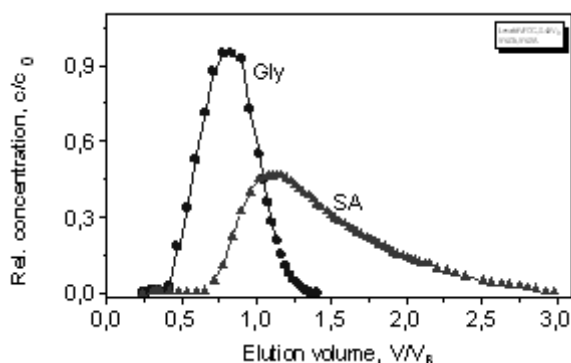


Fig. 1. Separation of aqueous solution of glycerol and succinic acid (each 5%) on Lewatit VPOC 1071 (feed $0.45 V_B$, flowrate 2h^{-1})

Acknowledgements: This work was supported by EU grant POIG 01.01.02-00-074/09.

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ELECTRODIALYTIC SATURATION OF CHLOR-ALKALI DEPLETED BRINE

Marian Turek, Krzysztof Mitko, Marzena Chorażewska

Faculty of Chemistry, Silesian University of Technology, ul. B. Krzywoustego 6,
44-100 Gliwice, Poland
e-mail: krzysztof.mitko@polsl.pl

The environmental problems of RO brine disposal can be mitigated by the reduction of wastewater volume. One of the possibilities is the RO retentate concentration, which can give industrially-usable saturated brine, or be followed by evaporative salt obtaining. An integrated seawater desalination system developed by the authors consisting of ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), a thermal process (MED/MSF), and salt crystallization offers low unit desalination cost (\$0.5 at ca. 50,000 m³/d capacity) and very high water recovery (78.2%) (1). A concept was proposed to use the RO brine from mentioned system as the salt source for membrane chlor-alkali electrolysis.

The proposed solution was to use the electro dialyzer (ED) equipped with univalent permselective membranes. The chlor-alkali depleted brine would work as ED concentrate and the saturated brine with low contents of calcium, magnesium and sulfate ions (see table for preliminary results) would be produced. The RO retentate – ED diluate – would simultaneously be desalinated down to the level similar to the seawater fed to the earlier mentioned integrated system.

A possibility of the membrane electrolysis feed saturation was investigated first by a batch mode electro dialysis with the membrane effective area of 4.5 cm² and 0.26 mm spacers. Next, the single pass mode electro dialysis was investigated using the electro dialyzer of effective length 42 cm, equipped with 0.26 mm spacers. The electro dialyzer was constructed to have short mean residence time and narrow residence time distribution, which, if used in industrial scale, should prevent from the blockage of the membranes by the crystallization of the sparingly soluble salts present in the RO retentate. The energy consumption of such preconcentration was calculated.

Processes streams compositions

Component	UF permeate, g/L	NF permeate, g/L	RO retentate, g/L	Electrolysis depleted brine, g/L	ED concentrate, g/L	ED diluate, g/L
Calcium	0.41	0.20	0.58	0.00	0.07	0.56
Magnesium	1.31	0.49	1.22	0.00	0.14	1.17
Chloride	19.70	16.91	50.8*	133.4**	182.3***	20.2
Sulfate	2.74	0.26	0.75	5.00	5.03	0.76

*) – ca. 84 g/L as NaCl

***) – ca. 220 g/L as NaCl

****) – ca. 300 g/L as NaCl

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ADSORPTION OF TETRAALKYLAMMONIUM HYDROXIDE WITH MESOPOROUS SILICA

Syouhei Nishihama, Akane Kawasaki and Kazuharu Yoshizuka

*Department of Chemical Engineering, The University of Kitakyushu,
Hibikino 1-1, Kitakyushu 808-0135, Japan
e-mail: Nishihama@env.kitakyu-u.ac.jp*

Tetraalkylammonium hydroxides (TAAH) are widely used as organic alkali in the semiconductor and liquid crystal display manufactures. The treatment of the waste solution containing TAAH becomes important issue due to their high toxicity. In a previous work, zeolitic adsorbent was prepared for the selective recovery of tetramethylammonium hydroxide (TMAH) (1). The adsorption amount of TMAH with zeolitic adsorbent is however low due to its small pore diameter. In the present work, therefore, mesoporous silica (MCM-41 and MCM-48) was prepared and adsorption properties of several TAAHs having different alkyl chains of methyl (TMAH), ethyl (TEAH), propyl (TPAH), and butyl (TBAH) were investigated.

Effect of pH on the adsorption of TAAHs with MCM-41 is shown in Figure 1. The adsorption amount increases with increasing pH until pH of ca. 9, and then dramatically decreases due to the dissolution of MCM-41. The behaviours in the case of MCM-48 are almost the same as of MCM-41. The adsorption isotherms of TAAHs with MCM-41 and MCM-48 at equilibrium pH of ca. 9.9 are progressed with Langmuir mechanism. The relationship between maximum adsorption amounts and the molecular diameters of TAAH shown in Figure 2 was obtained to be linear (2). These results indicate the adsorption amounts of TAAH with mesoporous silica are determined by the relationship between pore and molecular diameters.

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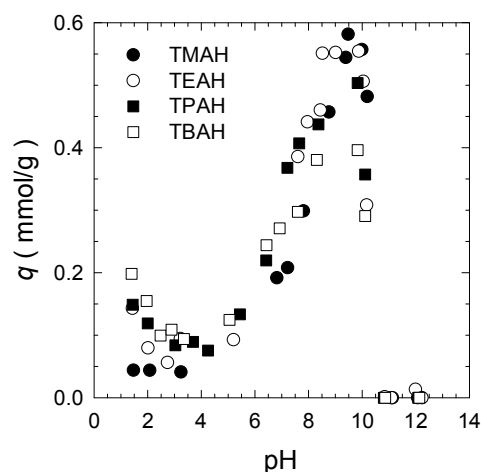


Figure 1. Effect of pH on adsorption amount of TAAHs with MCM-41

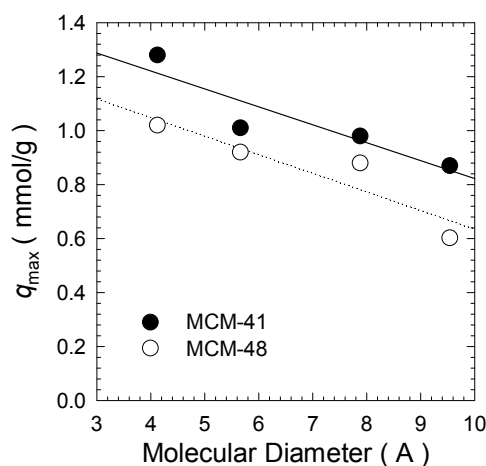


Figure 2. Effect of molecular diameter of TAAH on maximum adsorption amounts

TRANSFER OF ZINC(II) AND IRON(III) IONS THROUGH POLYMER INCLUSION MEMBRANES CONTAINING PHOSPHONIUM CHLORIDE

Łukasz Nowak, Magdalena Regel-Rosocka, Maciej Wiśniewski

*Poznań University of Technology, Institute of Chemical Engineering and
Technology, pl. M. Skłodowskiej-Curie 2,
60-965 Poznań, Poland
e-mail: lukasznowak-poczta@wp.pl*

Protection of the natural environment is one of the most important issues of the contemporary world. Although the zero charge and harmless technologies are the ideal solution, in some industrial fields they are not achievable. Then, the only solution is to reduce waste streams dumped into the environment and recycle or recover the chemicals.

Construction industry is nowadays based on the use of steel elements that are threatened with corrosion. There are a few methods developed to protect steel from corrosion, one of them is hot-dip galvanizing. This method is applied on industrial scale because the hot-dip galvanized elements are very resistant and well protected from the unfavorable atmospheric conditions. Pickling is one of the steps of preparation of the steel surface for galvanizing. Waste streams generated after pickling contain mainly zinc and iron (5 – 150 g/dm³) and must be recycled or utilized.

Zinc(II) content in the waste streams should not exceed 2 mg/dm³ (1). Rising zinc prices on world markets have increased an interest in alternative sources of zinc. Therefore, the treatment of spent pickling solutions is a key issue in hot-dip galvanizing plants.

The work aims to study zinc(II) and iron(III) transport through PIM containing trihexyl(tetradecyl)phosphonium chloride (QPCI) from chloride solutions.

Liquid-liquid extraction is one of the methods applied for treatment of spent pickling solutions (2). However, it must be applied in solution with toluene or another organic solvent to overcome problems with high viscosity of the phosphonium chloride itself. To eliminate the diluent the authors carried out studies in polymer inclusion membranes containing QPCI as a carrier. PIM enables simultaneous extraction-stripping process in small module. Flow rates of the feed and stripping solution were equal to 0.25 cm³/s. QPCI concentration in the membrane amounted 20%.

Acknowledgements: The work was supported by the 32/067/2011-DS.

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SELECTIVE TRANSPORT OF Ag^+ AND Cu^{2+} ACROSS PLASTICIZER MEMBRANES WITH CALIX[4]PYRROLE

Anna Nowik-Zajac¹, Cezary Kozłowski¹, Andrzej Trochimczuk²

¹Institute of Chemistry, Environment Protection and Biotechnology, Jan Długosz University of Częstochowa, 42-201 Częstochowa, Armii Krajowej 13, Poland

²Institute of Organic and Polymer Technology, Wrocław University of Technology, 50-370 Wrocław, Wybrzeże Wyspiańskiego 27, Poland
e-mail: a.zajac@ajd.czyst.pl

Calix[4]pyrroles belong to the family of heterocalixarenes, in which four pyrrole hydrogen bond donors are ideally pre-organized for anions and ion pair binding (1). Thus calixpyrrole derivatives exhibit many novel properties and applications, when compared with the classical calixarenes (2). A hybrid calixpyrroles chelating resin has been used for sorption studies of some noble metals like Au(III), Ag(I), Pt(IV), Pd(II) and other metal cations including Cu(II), Pb(II) and Cd(II) (3). Functionalized calix[4]pyrroles are outstanding as solid supports for the separation of anionic substrates (4). Zhou and co-workers showed selective separation and preconcentration of Ag^+ by liquid extraction(5).

The polymer inclusion cellulose triacetate membrane with plasticizer (*o*-nitrophenyl octyl ether) (PIM) was prepared by physical immobilization of calixpyrrole (Fig. 1). Transport experiments were carried out in permeation cell in which the membrane was tightly clamped between two compartments. The application of PIM with macrocyclic carriers for selective transport of Ag(I) and Cu(II) is increasingly attracting attention. We found that the transport of Ag(I) and Cu(II) across PIM with **1** via carrier mediated mechanism depends on pH. The competitive transport of Ag(I) and Cu(II) from aqueous phases across PIM is an effective method for silver(I) separation. Fig. 2 shows the possibility the high separation of Ag(I) over Cu(II) with **1**. The maximal metal flux for silver and copper ions were equal 1.05 and 0.005 $\mu\text{mol}/\text{m}^2\text{s}$, respectively.

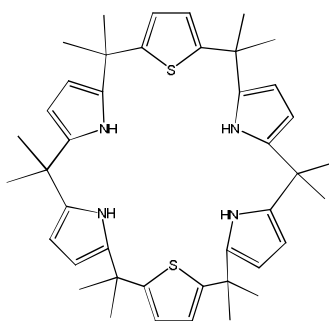


Fig. 1. Structures of calixpyrrole **1**

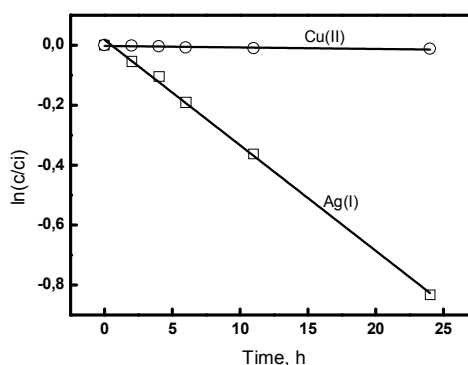


Fig. 2. Kinetics curves of Ag(I) and Cu(II) transport with 0.05 M **1**; the aqueous source phase: 0.0010 M AgNO_3 and $\text{Cu}(\text{NO}_3)_2$; the aqueous receiving phase: 0.010 M EDTA

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SPECIFIC METAL EXTRACTION WITH CALIX[4]ARENE CARBOXYLIC ACIDS CAUSED BY SODIUM ADDITION

**Keisuke Ohto, Hirotohi Sadamatsu, Shigemasa Kuwata,
Tomoaki Yoneyama, Hideaki Ishibashi, Hidetaka Kawakita**

*Department of Chemistry and Applied Chemistry, Saga University
1-Honjo, Saga 840-8502, Japan
e-mail: ohtok@cc.saga-u.ac.jp*

In our previous work, two sodium ions was found to be self-coextracted with a single molecule of *p*-*t*-octylcalix[4]arene tetraacetic acid, that is, the first sodium is specifically complexed by surrounding with phenoxy, carbonyl and carboxyl oxygens, and the second one is just ion-exchanged with a carboxyl group shown in Fig. 1 (1,2). It is attributed to size-fitting with the first sodium ion and the enhancement of the dissociation of the second carboxyl group caused by the first sodium complexation. Consequently, the first sodium ion act as a trigger of the extractive enhancement. When other multivalent metal ions with higher affinity to the second sodium ion coexist, they are easily substituted by the second sodium ion. (3,4) It is typical allosteric effect caused by addition of sodium ion as an effector. It causes not only enhancement of the extraction efficiency, but also change of the metal selectivity due to structural change based on complexation with the first sodium ion.

In the present work, extraction mechanism of calix[4]arene tetraacetic acid is further elucidated and various specific extraction behaviour supporting allosteric effect by using calix[4]arene carboxylic acid derivatives with different spacer length shown in Fig. 2 is introduced.

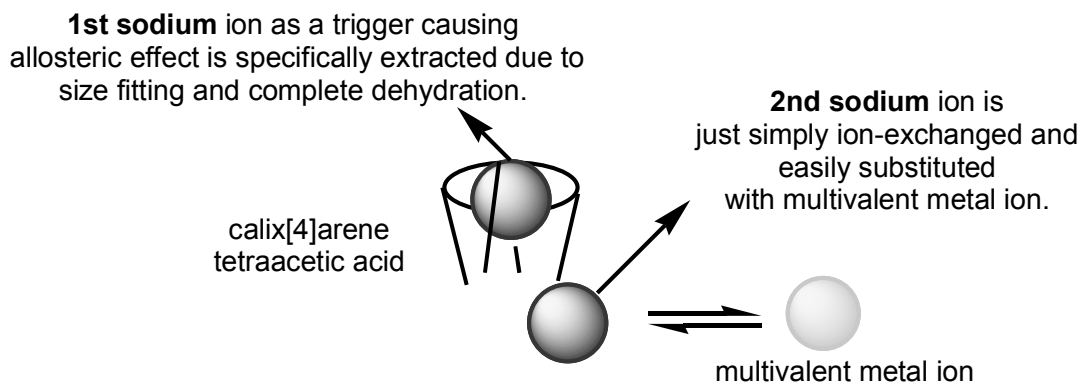


Fig.1. Different mechanism of two sodiums with calix[4]arene acetic acid

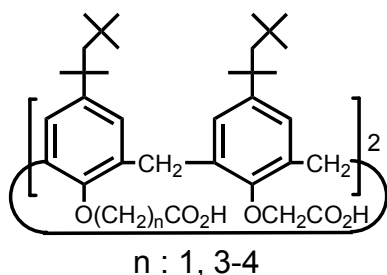


Fig. 2. Structures of the extractants with different spacer length

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ESSENTIAL STRUCTURAL FACTOR OF BIS-1,2-DIOL IN POLYOL MOLECULES FOR CAPTURING BORON

Tadashi Okobira¹, Naoko Matsuoka², Hiroaki Fujino², Naomi Tajiri²
and Kazuya Uezu²

¹Fukuoka Industry, Science & Technology Fundation (Fukuoka IST), Acros Fukuoka Nishi Office 9F, 1-1-1, Tenjin, Chuo-ku, Fukuoka-shi 810-0001, Japan

²Department of Chemical Engineering, The University of Kitakyushu, Hibikino 1-1, Kitakyushu 808-0135, Japan
e-mail: okobira@env.kitakyu-u.ac.jp

Small amount of boron in washing water sometimes causes serious problem for the semiconductor industry. The method to remove the boron from the solution is coaggregation method using alumina sulfate and calcium hydroxide, solvent extraction using polyol, and adsorption using *N*-methyl-D-glucamine resin. However, no adsorbents showed the sufficient capturing capability for boron in the very low concentration, and it is difficult to detect boron contained in ultrapure water. It is well known that *N*-methyl-D-glucamine (NMG) captures boron selectively. The binding mechanism and essential structural factor are still unclear. Then, the binding mechanism between boron and polyol molecules was investigated by using Nuclear Magnetic Resonance (¹¹B-NMR), Electrospray Ionization Time-of-Flight Mass Spectrometry (ESI-TOF-MS) and computational chemistry (1).

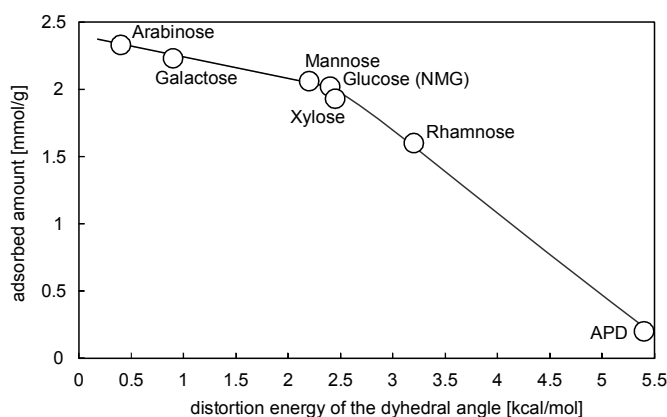


Figure 1. Relationship between the amount of boron adsorption by each mono-saccharide and the distortion energy of the dihedral angle

of each monosaccharide-containing resins and the distortion energy of bis-1,2-diol of the monosaccharides. The boron adsorption capacity was strongly associated with the distortion energy of the dihedral angles and was significantly decreased when the distortion energy of the dihedral angle was more than 2.5kcal/mol.

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We compared the most stable dihedral angles and heats of formations between the structures of stand-alone mono-saccharides and the geometry-optimized structure of the mono-saccharide-boron complexes. These dihedral angles of binding moiety with boron were investigated. The boron adsorbed amounts of these monosaccharide-containing resins were already reported (2,3). Figure 1 shows the relationship of the boron adsorption capacity

SEMI-INTERPENETRATED IONIC HYDROGELS BASED ON CHITOSAN AND POLYACRYLAMIDE

Maria Marinela Perju, Maria Valentina Dinu, Ecaterina Stela Dragan

*“Petru Poni” Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A,
700487 Iasi, Romania
e-mail: sdragan@icmpp.ro*

Hydrogels have a high affinity for water but are prevented from dissolving due to their physical (hydrogen bonding, van der Waals interaction, hydrophobic interaction, chain entanglements, or ionic complexation) or chemically cross-linked network (1). The swelling behavior of hydrogels may dramatically change in response to the external environment, such as pH, ionic strength, temperature, or electromagnetic radiation. Because of their high water content, hydrogels are similar to a variety of natural living tissues, having widespread applications as biomaterials. To control the diffusion of solutes in hydrogels, multicomponent networks as semi- or interpenetrated polymer networks (IPN) have been designed (1-4). Semi-IPNs (s-IPN) hydrogels are typically produced in a “single step” by synthesizing a hydrophilic polymer matrix around the preexisting water soluble polymer chains considered the trapped polymer (5,6).

Numerous water soluble polymers, either neutral or polyelectrolytes, have been used as trapped polymer in the synthesis of s-IPN hydrogels. Chitosan (CS), due to its outstanding properties such as biocompatibility, biodegradability and antimicrobial behavior, has been used in the preparation of various composite hydrogels (7,8). In our investigations, CS has been used as trapped polymer in the synthesis of some poly(acrylamide) (PAAm)/CS s-IPN hydrogels following the influence of the crosslinking ratio, the concentration of CS, and the CS molar mass on the gel fraction yield and the fraction of CS trapped in the s-IPN hydrogels. Finding the optimum synthesis conditions to ensure the highest stability of CS in the s-IPN gels constituted the main objective of the study. The s-IPN hydrogels have been structural and morphological characterized by FT-IR and SEM, respectively. The swelling ratio and the interaction of the composite gels with some anionic dyes have been also followed.

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SORPTION PROPERTIES OF NATURAL ZEOLITES FOR REMOVAL OF HAZARDOUS ELEMENTS FROM INDUSTRIAL EFFLUENTS

L.F. Petrik¹, G. Ndayambaje¹, O.O. Fatoba¹, R. Akinyeye¹, N.T. Van der Walt²

¹*Environmental and NanoSciences Group, Chemistry Department, University of the Western Cape, Private Bag X17, Bellville 7535, South Africa.*

²*Department of Chemistry, Cape Peninsula University of Technology, Cape Town, South Africa.*

e-mail: lpetrik@uwc.ac.za

Clinoptilolite is a type of natural zeolite which is a crystalline aluminosilicate of group one and two elements. It is mostly composed of SiO₄ and AlO₄ tetrahedral joined into three-dimensional frameworks with extra-framework cations such as: Na⁺, K⁺, Mg²⁺ and Ca²⁺. The pretreatment of natural clinoptilolite can enhance its ion exchange capacity. The aim of this study was to characterize natural clinoptilolite mined in South Africa, activate it in order to enhance its cation exchange capacity and then use it to remove ammonia from synthetic solutions and wastewater using adsorption method. Natural South African clinoptilolite supplied by Pratley Polymers (Pty) mined in Kwazulu Natal Province was milled and then sieved into <125 µm particle size. Solutions of 0.02M, 0.1M and 1.0M HCl were used to pre-treat the natural clinoptilolite. This was done by adding 150 mL of the acid solutions to the natural clinoptilolite and stirred for 4 h at 250 rpm and at 25°C. This process was repeated severally with the different concentrations of the acid solutions in order to determine the optimum acid concentration for the activation process (1,2). Cation exchange capacity (CEC) was determined by extracting 0.5 g of clinoptilolite using ammonium acetate solution at pH 8.2. Zeolite morphology was characterized by HRTEM and SEM. X-ray diffraction was used to identify and quantify the mineral phases present and XRF for the determination of chemical compositions. Major exchangeable cations were analyzed using ICP-OES method. The 0.02 M HCl solution was found to be the optimum. HCl concentration for acid treatment of clinoptilolite showing a lower dealumination of clinoptilolite after 23 extractions at 4 h each and at 25°C compare to 0.1M and 1.0M HCl. Natural South African clinoptilolite showed the maximum cation exchange capacity (CEC) of 3.2 meq/g clinoptilolite at 25°C using ammonium acetate method. Major exchangeable cations in clinoptilolite before the pre-treatment were found to be Na⁺(13764 ppm), K⁺(24074 ppm), Ca²⁺(8827 ppm) and Mg²⁺(10164 ppm) using ICP-MS method. XRF data showed the chemical compositions of natural clinoptilolite with Si/Al ratio of 4.4 and the sample was found to be 81.4% pure clinoptilolite using XRD. Further work is being done on the adsorption of ammonia from synthetic solutions and waste water considering the pH, concentration, reaction time, sorbent mass and particle size for kinetics study of ammonia on treated and untreated clinoptilolite (3).

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SEPARATION OF WATER-ETHANOL MIXTURE BY MEANS OF PERVAPORATION

Karol J. Pokomeda, Anna Witek-Krowiak

*Faculty of Chemistry, Wrocław University of Technology
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
e-mail: karol.pokomeda@gmail.com*

Separation of water-ethanol mixture is one of the oldest problem in chemical engineering. It is mostly connected with production of spirits. Although this subject is much wider and consist production of pure ethanol as a substrate for synthesis, solvent or component of biofuel. Moreover, in last 20 years new market of dealcoholized beverages has grown. This huge part of industry induced studies for new methods of separation. One of relatively new and promising methods is pervaporation.

Different solutions of ethanol in water were used as subject of studies. Water and ethanol mass transport through hydrophobic membrane was examined as a function of temperature and feed composition. Both, stream and selectivity increased with temperature. Meyer-Blumenroth model was used to describe mass transfer process through the membrane. In both cases, water and ethanol transport through the membrane, mass transfer resistance through porous layer was irrelevant in comparison with mass transfer resistance through solid layer. This led to simplification of the Meyer-Blumenroth model, by omitting mass transfer through porous layer. Diffusion coefficients for active layer for both mixture components grow as a function of temperature, according to Arrhenius' equation. It has been proven that pervaporation can be used both, to produce spirits and dealcoholize low alcoholic beverages, like wine or beer.

SEPARATION OF SILVER(I) AND COPPER(II) FROM AQUEOUS SOLUTIONS BY TRANSPORT THROUGH POLYMER INCLUSION MEMBRANES WITH CYANEX 471X

Beata Pośpiech

*Department of Chemistry, Częstochowa University of Technology,
42-200 Częstochowa, Armii Krajowej 19, Poland
e-mail: bak@wip.pcz.pl*

In this work the separation of silver(I) from aqueous nitrate(V) solutions containing copper(II) ions using transport through polymer inclusion membranes (PIMs) has been studied. Cyanex 471X (triisobutylphosphine sulphide) has been applied as the ion carrier in this process.

The liquid membranes containing an ion carrier have been used for the concentration and separation of silver ions. The application of liquid surfactant membranes (LSMs) for Ag(I)/Cu(II) separation from electronic wastes was investigated by Ennassef et al (1). The membrane phase was composed of the carrier (Cyanex 471X) with the surfactant (Span 80) and the diluent dodecane. The best chemical and operating conditions for separation of Ag(I) ions have been determined in this work. Cyanex 302 (di(2,4,4-trimethylpentyl) monothiophosphinic acid) was examined as ion carrier in emulsion liquid membrane for separation of silver from liquid photographic waste containing various ions such as silver, iron, sodium and potassium by Othman et al. (2). The results showed that the mobile carrier Cyanex 302 is selective towards silver compared to the other metals. The use of polymer inclusion membranes containing new pyridino- and bipyridino-podands has been reported by Lamb et al (3). Using PIMs system, Ag(I) ion could be selectively removed from a complex mixture containing high concentration of Cd(II), Zn(II), Co(II), Ni(II), Pb(II) and Cu(II).

This paper will present the results for the selective transport of Ag(I) and Cu(II) from aqueous nitrate(V) source phase through PIM containing cellulose triacetate (CTA) as the support, *o*-nitrophenyl octyl ether (ONPOE) as the plasticizer and Cyanex 471X as the ion carrier. The effect of ion carrier concentration on the silver(I) ions transport has been studied. The concentration of Cyanex 471X was varied between 1.0– 3.0 M. The recovery factor of Ag(I) increases with the ion carrier concentration increase in the membrane. The highest fluxes of Ag(I) was obtained by using PIM containing 3.0 M Cyanex 471X. Cu(II) was not detected in the receiving phase.

The effect of kind of the receiving phase on the transport of Ag(I) and Cu(II) has been also investigated. The deionized water and 0.1 M HNO₃ have been applied as the receiving phase. The initial flux of Ag(I) ions depend strongly on the kind of the receiving phase. Ag(I) ions can be effectively separated from aqueous solutions containing Cu(II) ions in hydrometallurgical processes of transport across polymer inclusion membranes with Cyanex 471X.

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SIMULTANEOUS REMOVAL OF ANILINE AND NITRATE BY MICELLAR ENHANCED ULTRAFILTRATION

Ryszard Pożniak, Gryzelda Pożniak

*Faculty of Chemistry, Wrocław University of Technology
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
e-mail: ryszard.pozniak@pwr.wroc.pl*

The simultaneous removal of organic and inorganic contaminants from aqueous media is a great problem. New membrane separation technique - micellar enhanced ultrafiltration (MEUF) is a promising technology that allows to solve this problem. MEUF constitutes a combination of two phenomena: solubilizing of organic and inorganic solutes by surfactant micelles (large amphiphilic aggregates at a concentration higher than critical micelle concentration, cmc) and ultrafiltration.

Polysulfone (PSU) is frequently used as membrane material, but this polymer possess hydrophobic, non-polar surface. Hydrophobicity of the PSU porous membranes can be counterbalanced by introduction of ionic functional groups to the polymer chain. The porous ion exchange membranes form a new category of the polymeric filtration media (1-4).

The aim of this work was to examine simultaneous rejection of aniline and nitrate in the presence of hexadecylpyridinium chloride, CPC, as a cationic surfactant, using membrane made from aminated polysulfone (APSU).

Polysulfone (PSU), UDEL P-1700, Amoco, was chloromethylated using a mixture of methyl chloromethyl ether with SnCl_4 (0.5 mole/mole PSU) and 1,2-dichloroethane (10 wt.-%). The porous asymmetric membrane was formed directly from chloromethylated derivative by phase-inversion method: 15 wt.-% solution in DMF and methanol as a coagulant. Aminolysis of chloromethylated membrane was carried out in 50 vol.-% solution of N,N-dimethylaminoethanol. The Amicon 8200 dead-end cell was used. The pressure was equal to 0.1 MPa.

To reduce tendency of cationic surfactant deposition on the membrane surface, APSU membrane was selected (the same charge on both bodies: membrane and surfactant). The nitrate anions are located at the surface of micelles due to electrostatic interactions and aniline is solubilized in the hydrophobic interior of micelles. Rejection of nitrate was equal to 95% and aniline only 75% at 5 cmc concentration of CPC. Higher rejection of nitrate than aniline indicates that strong ionic interactions are more desired than hydrophobic ones in micellar enhanced ultrafiltration of substances. The significant dependency between simultaneous rejection of nitrate and aniline in regard to their single separation effects are not observed.

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NICKEL(II) AND COBALT(II) EXTRACTION FROM CHLORIDE SOLUTIONS WITH QUATERNARY PHOSPHONIUM SALTS

Magdalena Regel-Rosocka, Kamila Kicińska, Maciej Wiśniewski

*Poznań University of Technology, Institute of Chemical Engineering and Technology, Pl. M. Skłodowskiej-Curie 2, 60-965 Poznań
e-mail: magdalena.regel-rosocka@put.poznan.pl*

Phosphonium ionic liquids (phosphonium ILs): trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101), trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104) supplied by Cytec Industries Inc. (USA) are used as extractants dissolved in toluene. Ni(II) and Co(II) extraction with the quaternary phosphonium salts presented in this abstract has not been described up to now.

At first, extraction from individual metal ion solutions was investigated. Cyphos IL 104, which is a derivative of the well known acidic extractant Cyanex 272, is an effective extractant of Co(II). However, with increasing metal ion concentration, percentage extraction decreases from 99 to 35%. While Ni(II) extraction is also high and amounts to 60–80%. Cyphos IL 101 transports up to 70% Co(II) to the organic phase, while Ni(II) is almost completely retained in the aqueous phase when extracted with Cyphos IL 101.

Selectivity has been studied for a mixture containing near 5 g/dm³ of each Co(II) and Ni(II), various HCl concentration and constant chloride concentration equal to 1 M (adjusted with NaCl). Selectivity factors of cobalt(II) over nickel(II) confirm extraction results mentioned above.

Stripping of Ni(II) and Co(II) has been carried out only from Cyphos IL 104, because its selectivity of Co(II) extraction is very high and seems to be prospective. Five solutions such as: deionised water, 0.25 and 2 M sulphuric acid, and 0.5; 4 M hydrochloric acid has been used as stripping phases. Type and concentration of a stripping phase are the most significant issues, and they affect the process. The most efficient stripping phase for Co(II) is 2 M sulphuric acid and 0.5 M hydrochloric acid.

It can be concluded that quaternary phosphonium salts such as Cyphos IL 101 and Cyphos IL 104 are very effective extractants of metal ions from chloride solutions. Successful separation of Co(II) over Ni(II) can be achieved with Cyphos IL 104 at particular HCl concentrations. Additionally, efficiency of Co(II) stripping from Cyphos IL 104 decreases in the following order of the stripping phases: 2 M H₂SO₄ (97%) > 0.5 M HCl (96%) > 0.25 M H₂SO₄ (84%) > 4 M HCl (61%) > H₂O (39%), and for Ni(II): 2 M H₂SO₄ (65%) > 0.25 M H₂SO₄ (55%) > deionised water (39%).

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DIBENZOTHIOPHENE UPTAKE FROM FUELS BY THE POLYMER-DERIVED CARBON MATERIALS

Sylwia Ronka, Andrzej W. Trochimczuk

*Faculty of Chemistry, Wrocław University of Technology,
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland,
e-mail: sylwia.ronka@pwr.wroc.pl*

The problem of deep removal of sulfur has become more serious due to the lower and lower limit of sulfur content in finished gasoline and diesel fuel products by regulatory specifications, and the higher and higher sulfur contents in the crude oils. Currently the sulfur level in gasoline and diesel fuel must be reduced to 30 and 10 ppm, respectively. Using adsorbents to remove the sulfur compounds in liquid hydrocarbon fuels is one of the promising approaches (1,2). As it is well known, the liquid hydrocarbon fuels contain not only sulfur compound but also a large number of aromatic compounds that have aromatic skeleton structure similar to the coexisting sulfur compounds. This inherent problem makes a great challenge in the development of an effective adsorbent with high adsorptive selectivity for the sulfur compounds.

In this work we present the dibenzothiophene sorption abilities of polymer-derived carbon materials. The synthetic carbons prepared from polymers are expected to have reproducible characteristics and controlled pore size, as well as good mechanical and thermal properties (3). So, phosphorus-containing carbon materials have been prepared by the carbonization (850°C, Ar) and following CO₂ activation ($U^{\text{daf}} = 10\%$) of Cu²⁺, Co²⁺ and Fe³⁺ form of phosphorylated S/DVB copolymers. Sorption experiments have been carried out using obtained carbon materials and dibenzothiophene (DBT) solution prepared in isoctane (50 mg S/dm³). For selectivity studies, a mixture of DBT and naphthalene (1:1) was used. The amounts of adsorbates were analyzed using a Varian GC equipped with a capillary column.

The investigations indicate that the transition metal-based carbon materials obtained by carbonization of styrene-divinylbenzene copolymers have favorable features for the removal of sulfur compounds from fuels. The structure of the carbon adsorbents has the effect upon their sorption ability towards DBT. The good selectivity results probably from the interaction between the heteroatom in the adsorbate and the metal introduced into the carbon surface. The results will be presented during the conference.

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INFLUENCE OF THE MAGNETIC POWDER TYPE AND GRANULATION ON THE AIR SEPARATION PROCESS BY MAGNETIC MEMBRANES

Aleksandra Rybak, Gabriela Dudek, Anna Strzelewicz, Monika Krasowska, Zbigniew J. Grzywna

*Silesian University of Technology, Faculty of Chemistry, Department of Physical Chemistry and Technology of Polymers, Strzody 9, Gliwice, Poland
e-mail: Aleksandra.Rybak@polsl.pl*

Currently, the production of high purity gases or enriched gas mixtures is of a great importance, especially in industry, medicine and in everyday life (1,2). In last years membrane processes have become competitive to another air separation methods (3). This paper is a continuation of the work on polymer membranes filled with neodymium or ferrite powder and magnetized ("magnetic membranes") used for an air enrichment (4–6). Membranes of various polymer matrix (EC, PPO) with different types (ferrite and neodymium powders) and granulation (20-32 μm and 32-50 μm) of dispersed magnetic powder were casted in an external magnetic field of a specially designed coil (magnetic induction up to 0,04 T). For final magnetization a strong field magnet of about 2,5 T, was used. All these membranes were examined for nitrogen, oxygen and air permeability in experimental setup with a gas chromatograph HP 5890A. Data analysis was carried out using Time Lag method and D1-D8 system analysis. During our studies we have analysed the influence of magnetic powder type, granulation, polymer matrix and magnetic field on separation process by magnetic membranes. We have found that granulation and amount of added magnetic neodymium powder remarkably influence the oxygen content in permeate. During our research we have obtained almost 62% of oxygen enrichment in one permeation run through PPO "magnetic membranes" with dispersed neodymium magnetic powder with 20-32 μm granulation (magnetic induction of membrane in magnetic diffusive chamber was 2,70 mT).

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GRAFTING OF POLYACRYLAMIDE ONTO CLAY FOR SELECTIVE REMOVAL OF Hg²⁺ ION FROM WATER

Gamze Barim¹, Erdem Yavuz², M. Sabri Celik³, B. Filiz Senkal²

¹*Department of Chemistry, Adiyaman University, Adiyaman, TURKEY*

²*Department of Chemistry, Istanbul Technical University, Maslak-Istanbul 34469, Turkey*

³*Department of Mining Engineering, Istanbul Technical University, Maslak-Istanbul 34469, Turkey
e-mail: bsenkal@itu.edu.tr*

In order to monitor and prevent Hg²⁺ pollution, a number of different technologies, such as precipitation (1,2), biosorption (3), membrane filtration (4), ionic exchange (5) and solvent extraction (6), have been used for removal of Hg²⁺ from wastewater. Removal of mercury and other toxic metals require more efficient sorbents. Specially designed chelating polymers show excellent metal-uptake capabilities and these have been discussed in many articles and reviews (7,8). Crosslinked polyacrylamide was extremely powerful sorbent for mercury uptake (9).

In this study, polyacrylamide grafted onto clay by using redox polymerization method in the presence of Ce(IV) salt is presented. Obtained sorbent has been demonstrated to be a very efficient selective sorbent for removal of mercuric ions from aqueous solutions.

The mercury-uptake capacity of the sorbent is as high as 1.65 mmol/g and sorption is also reasonably fast. The Hg(II) sorption is selective and no interferences have been observed in the presence of Pb(II), Cd(II), Fe(III) ions in 0.1 M concentrations. Regeneration of the mercury loaded sorbent without losing its original activity can be achieved using hot acetic acid.

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REMOVAL OF ARSENIC FROM GROUND WATER WITH TITANIUM DIOXIDE

Kanako Shibata, Syouhei Nishihama, and Kazuharu Yoshizuka

*Department of Chemical Engineering, The University of Kitakyushu,
Hibikino 1-1, Kitakyushu 808-0135, Japan
e-mail: m11a0601@hibikino.ne.jp*

Arsenic (As) contamination of groundwater spreads in all over the world. As is one of the most toxic compounds in groundwater, existing as arsenite (As(III)) and arsenate (As(V)), and toxicity of As(III) is 25 – 60 times higher than that of As(V) (1,2). Removal of As from ground water is therefore presently an active issue, and adsorption is a main technique for As removal. Recently, detoxiation of As by oxidizing As(III) to As(V) followed by adsorption of As using titanium dioxide (TiO_2) has been reported (2). The adsorption amount on the TiO_2 (P25 Degussa) was relatively low (As(III): 0.347 mmol/g at pH = 8, As(V): 0.347 mmol/g at pH = 4). In the present work, TiO_2 adsorbent having higher adsorption amount is developed to investigate the adsorption behavior of As.

TiO_2 was synthesized as follows. Ammonia solution is added to TiCl_4 solution until pH becomes 7 to produce $\text{Ti}(\text{OH})_4$, and hydrogen peroxide is then added to the suspended solution of $\text{Ti}(\text{OH})_4$. The mixture was hydrothermally synthesized at 120°C for 5 h to produce anatase-type TiO_2 . Granulation of powdery TiO_2 was conducted with alumina-based binder.

The powdery and granulated TiO_2 were applied for batch adsorption of As (Fig.1). The adsorption amount of As(III) shows maximum value in pH 8 - 9, while that of As(V) was decreased with pH value. Adsorption isotherms of As(III) and As(V) with powdery TiO_2 at pH = 8 is of Langmuir mechanism, and the maximum adsorption amount is 1.29 mmol/g for As(III) and 0.414 mmol/g for As(V). Comparing with the reported data (2), the present TiO_2 obviously possesses high adsorption ability for As, especially for As(III), to be applied for As removal in groundwater. The granulated TiO_2 still possesses adsorption ability for As in spite of slight decrease of adsorption amount. The granulated TiO_2 is applied to the chromatographic removal of As by using column operation.

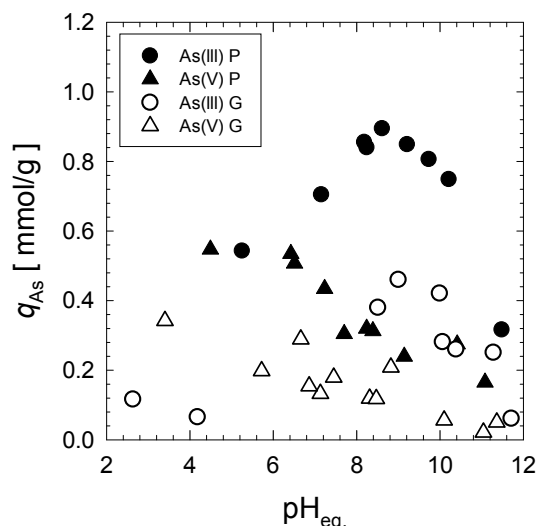


Fig. 1. Effect of pH on adsorption of As(III) and As(V) with powdery (P) and Granulated (G) TiO_2 adsorbents

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SORPTION OF METALS BY COMPOSITE SORBENTS BASED ON IRON OXIDE

Petra Šlapáková, Helena Parschová

*Department of Power Engineering, Institute of Chemical Technology,
Technická 5, Prague 166 28, Czech Republic
e-mail: petra.slapakova@vscht.cz*

Sorbents based on hydrated ferric hydroxide are primarily used for arsenic removal from aqueous solutions. ArsenXnp, Lewatit FO 36 and GEH were chosen.

Sorption of metals (Cu, Zn, Be, Ni) was observed and their impacts on sorption of As. We also studied the effectiveness of the regeneration of the composite sorbents. Regeneration was performed in three steps by 2% NaOH, 2% NaCl, demineralized water and carbonated demineralized water.

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THE WEIGHT DISTRIBUTION COEFFICIENTS OF Zr(IV), Hf(IV), Ti(IV), Th(IV), Fe(III), Al(III), Cr(III), Y(III), La(III), Cu(II), AND Zn(II) ON DIPHONIX® RESIN IN 0.5 M H₂SO₄ SOLUTION

M. Smolik¹, Z. Hubicki², A. Jakóbk-Kolon¹, T. Korolewicz¹, Ł. Siepietowski¹

¹Faculty of Chemistry, Silesian University of Technology,
Bolesława Krzywoustego 6, 44-100 Gliwice, Poland

²Faculty of Chemistry, Maria Curie-Skłodowska University
Pl. M. Curie-Skłodowskiej 5, 20-031 Lublin, Poland
e-mail: marek.smolik@polsl.pl

Zirconium and hafnium due to their similar chemical properties occur together in many minerals. These minerals are the sole source of hafnium. On the other hand zirconium used in nuclear industry should contain less than 100 ppm Hf. Therefore, the separation of both elements is desirable. However, this separation belongs to the most difficult problems of this kind in chemistry. The most effective methods of Zr and Hf separation are ion exchange ones. Using one of these methods employing chelating cation exchange resin Diphonix® it was possible to obtain good effects of their separation (1,2).

Zirconium salts contain many other impurities, which may influence the efficiency of Zr and Hf separation. Analysis of available zirconium raw materials revealed the presence of numerous impurities such as: Ti, Th, Y, La, Cr, Fe, Al, Cu and Zn (3). Hence, it was important to examine their impact on the process of Zr and Hf separation in established (for the separation of zirconium from hafnium) optimal conditions. The first stage of this study was to determine the affinity of the ions of these elements to the Diphonix® resin in this conditions by determination of their weight distribution coefficients λ , defined as the quotient of the numbers of moles of ions per g of dry resin and per cm³ of solution at equilibrium. It is the purpose of this presentation.

The weight distribution coefficients λ of the examined ions have been determined on Diphonix® resin in 0.5 M H₂SO₄ solutions. Concentrations of ions of mentioned above impurities in these solutions before and after equilibration within 48h has been determined by ICP-AES or ICP-MS.

Obtained weight distribution coefficients are very diverse ranging from 21 (λ_{Zn}) to 1830 (λ_{Ti}) and indicate, that only Ti(IV), Th(IV) and Fe(III), due to their high λ values, may influence the separation zirconium from hafnium in established optimal conditions. Their impact on this separation by dynamic methods will be further investigated.

Acknowledgements: This work was financed by Polish Ministry of Science and Higher Education grant No. N N209 231838.

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SORPTION OF NOBLE METAL IONS ON HEXAMETHYLENEIMINE VBC/DVB DERIVED RESIN

Michał Sowa, Dorota Jermakowicz-Bartkowiak

*Department of Polymer and Carbonaceous Materials,
Wrocław University of Technology,
50-370 Wrocław, Wybrzeże Wyspiańskiego 27, Poland
e-mail: michal.sowa@pwr.wroc.pl*

Extraction of noble metal ions (i.e. Au(III), Pd(II), Pt(IV), Re(VII)) from acidic media was examined. Sorptions were carried out using a hexamethyleneimine derived VBC/DVB copolymer, modified under microwave irradiation (Fig. 1).

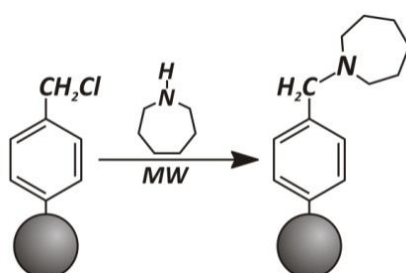


Fig. 1. Chelating resin synthesis

Single-component extractions were performed using diluted solutions of Au(III), Pd(II), Pt(IV) and Re(VII) in 0.1M HCl. Selectivity was determined using a diluted multi-component solution containing Au(III), Pd(II), Pt(IV) and Re(VII) ions in 0.1M HCl.

Table 1. Sorption values for single- and multi-component solutions

Metal ion	Single-component solution Sorption [%]	Multi-component solution Sorption [%]
Au (III)	100.0	95.8
Pd (II)	98.1	76.4
Pt (IV)	100.0	98.9
Re (VII)	64.6	12.8

Sorption isotherms were obtained from single-component Re(VII) solutions in 0.1 M HCl, 1 M H₂SO₄ and 3 M H₂SO₄. Isotherm of 0.1 M HCl Re(VII) solution best fits the Langmuir model, whereas 1 M and 3 M H₂SO₄ can be most accurately fitted to Freundlich model.

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COMPUTATIONAL FLUID DYNAMICS (CFD) MODELING OF POROUS MEMBRANES

Katarzyna Staszak, Maciej Staszak

*Institute of Technology and Chemical Engineering, Poznań University of Technology, pl. M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland
e-mail: Katarzyna.Staszak@put.poznan.pl*

The membrane filtration processes have played important role in the industrial separation process. Although these processes are known for about twenty years, there are still many studies focused on the testing of new membranes' materials, determination of conditions for optimal selectivity i.e. the optimum transmembrane pressure or permeate flux to minimize fouling (1). Computational fluid dynamics techniques may provide lot of interesting information for the development of the membrane processes.

In the membrane filtration processes both free and porous flow occurs. In the model proposed the flows were described by Navier–Stokes equations (2):

$$\rho \frac{\partial v_j}{\partial t} + \rho v_{j,i} v_i + p_j - \tau_{ij,i} - \rho F_j = 0$$

where indices i and j correspond to cartesian space directions, ρ – density, v – velocity, p – pressure, F – body forces, τ – viscous stress tensor. Additionally, the flow in porous media was described by the Darcy's equation. Assuming isotropy of a membrane the total pressure gradient across it is given by:

$$\nabla p = -\frac{\eta}{\alpha} v$$

where α is the permeability and η is the viscosity of the media. The calculations were performed using Ansys/Fluent software.

The laboratory-scale ultrafiltration systems (SPIRALB from TAMI Industries) were used to validate the proposed model. In these experiments ceramic disc membrane from TAMI Industries with a diameter 90 mm was used.

Acknowledgements: The work described in this paper was supported by DS – 32/067/2011 and DS – 32/267/2011.

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APPLICATION OF CALIX[6]ARENE FOR EXTRACTION OF URANIUM(VI) FROM WATER SOLUTION

Łukasz Steczek, Katarzyna Kiegiel, Grażyna Zakrzewska-Trznadel

*Institute of Nuclear Chemistry and Technology, Dorodna 16,
03-195 Warsaw, Poland
e-mail: l.steczek@ichtj.waw.pl*

Production of uranium from uranium ores involves many separation steps and different processes leading to recovery of this element to obtain fertile material for nuclear fuel fabrication – the "yellow cake" U_3O_8 .

The most common methods of uranium production rely on liquid-liquid extraction, which is effective, however may create an environmental and health hazards due to large amount of secondary wastes produced in hydrometallurgical process. Development of novel extractants that are effective and environment-friendly is a very important task for the perspective of liquid-liquid extraction application at different stages of nuclear cycle. The high cost of such emerging extractants is a reason for searching new separation techniques that involve small inventory of these materials, e.g. liquid membrane separation (LM).

In the present work the authors based on the literature (1-8) design synthesis route for novel modified calix[6]arenes that can be used for extraction of Uranium(VI) in aqueous solutions. Calix[6]arenes are a class of compounds whose three-dimensional cavity can host cations, anions or neutral molecules. Research works reported in the literature show that the organo-phosphorus functionalized calix[6]arenes possess high chelating ability towards actinides. The design of synthesis pathway of modified calix[6]arenes with organo-phosphorous substituents will bring practical sense to produce novel selective uranophilic compounds, which can be used in extraction of Uranium(VI) from water solution.

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KINETIC MODEL FOR p-NITROPHENOL TRANSPORT THROUGH AN AGITATED BULK LIQUID MEMBRANE

P. Szczepański¹, I. Diaconu², D. A. Radu²

¹*Nicolaus Copernicus University, Faculty of Chemistry,
Gagarina Str. 7, 87-100 Toruń, Poland*

²*University Politehnica Bucharest, Faculty of Applied Chemistry and Materials,
Science, 1-5 Polizu Street, Bucharest, Romania
e-mail: piotrs@chem.uni.torun.pl*

The pertraction of p-nitrophenol (PNP) through an agitated bulk liquid membrane (ABLM) was studied. The influence of the feed phase (PNP), stripping phase (NaOH), carrier (tri-n-octylphosphine oxide, TOPO) concentration and type of an organic solvent (benzene, toluene, p-xylene) on the transport efficiency were investigated.

The experiments were carried out in an H type glass transport cell. The volume of the feed and stripping solution was 200 cm³ while the volume of the liquid membrane was 50 cm³. All the phases were stirred. The concentration of the PNP was determined using a UV-Vis spectrophotometer (UV-2101PC Shimadzu). The absorbances of the feed and stripping solution were measured at wavelength $\lambda=317$ nm and at $\lambda=404$ nm, respectively.

In order to describe the pertraction kinetics we applied simple mathematical model formally identical to the consecutive irreversible first order chemical reaction model. According to Danesi et al. (1), we used a simple conversion of kinetic constants, k_1 and k_2 , in order to derive the apparent mass transfer coefficients independent of the volume of the phases and the interface contact area. The experimental results demonstrate that maximum fluxes decrease in the series:

benzene > toluene > p-xylene

These results cannot be interpreted according to the Stokes-Einstein equation (2) which indicates that the main factor influencing the transport rate is the distribution ratio of PNP. An application of the carrier (TOPO) significantly increases the fluxes of PNP. It was also found that a simple kinetic model can be applied for description of the feed, liquid membrane, and stripping phase concentration vs. time dependences. The overall mass transfer coefficient calculated from the maximum flux vs. feed phase concentration dependence is equal to $3.564(\pm 0.047)\times 10^{-4}$ cm/s and is of the same magnitude as the one obtained by Tompkins et. al. (3) for the membrane-supported solvent extraction of PNP in the system with octanol as the organic phase.

The work has been funded by the Sectorial Operational Programme Human Resources Development 2007-2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/6/1.5/S/19.

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NETWORK MODEL FOR DESCRIPTION OF THE BENZOIC ACID PERTRACTION IN AN AGITATED BULK LIQUID MEMBRANE SYSTEM

P. Szczepański, R. Wódzki

*Nicolaus Copernicus University, Faculty of Chemistry,
Gagarina Str. 7, 87-100 Toruń, Poland
e-mail: piotrs@chem.uni.torun.pl*

The network thermodynamic analysis (NTA) was recognized as the advanced method for dynamic systems description including the membrane ones (1-3). Therefore, a bond-graph method was applied here to the formulation of a mathematical model for description of liquid membrane transport (pertraction). The verification of the model was carried out using the experimental results of benzoic acid pertraction through an agitated bulk liquid membrane (ABLM). An H-type transport cell was applied in the experiments (feed phase: 190 cm³ of benzoic acid aqueous solution; stripping phase: 190 cm³ distilled water at t = 0; the liquid membrane: 50 cm³ heptane, octane or dodecane). The time dependent acid concentrations in the feed and stripping solutions were analyzed conductometrically.

Typical experimental results corresponding to the ABLM system (dodecane as the liquid membrane, 0.016 M solution of benzoic acid as the feed phase) are presented in Fig. 1. and compared with the results of calculations.

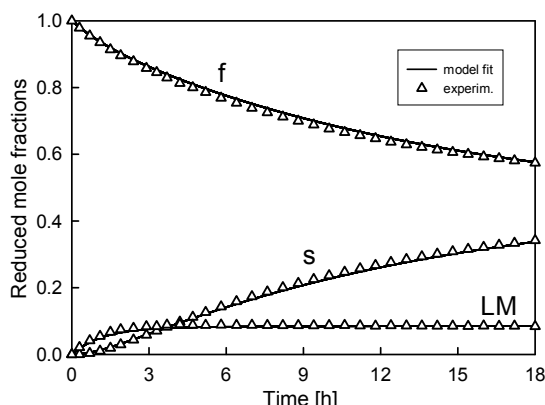


Fig. 1. Experimental (points) and modeling (lines) results for benzoic acid pertraction: f-feed, s-stripping, LM-liquid membrane phases

The results demonstrated that NTA network model can be used for quantitative description and prediction of the pertraction kinetics as dependent on the various operation conditions and physicochemical characteristics of the system.

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SEPARATION AND RECOVERY OF Zn(II) FROM ELECTROPLATING PLANT WATER BY HYBRID ROTATING PERTRACTOR

P. Szczepański, A. Raszowska-Kaczor, R. Wódzki

Nicolaus Copernicus University, Faculty of Chemistry, Gagarina 11 Str.,
87-100 Toruń, Poland
e-mail: piotrs@chem.uni.torun.pl

The hybrid rotating pertractor (1) was constructed and used for the separation and recovery of Zn (II) from rising water produced by an electroplating plant (Zelan, Nakło, Poland). This wastewater of the following composition: K(I) (2.1×10^{-4}); Ca(II) (2.0×10^{-3}), Na(I) (2.1×10^{-2}), Mg(II) (3.3×10^{-4}), Zn(II) (2.0×10^{-4}), Cu(II) (2.1×10^{-6} , mol/dm³) was used as the feed solution and the 1 mol/dm³ H₂SO₄ solution was applied as the stripping solution. The bulk liquid membrane was prepared of di(2-ethylhexyl) phosphoric acid (Chemical Co. Alfa Aesar, purity 95%) or di(2,4,4-trimethylpentyl)thiophosphinic acid (CYANEX 302, Fluka, purity 85%) dissolved in kerosene (b.p.= 204°C, viscosity $\eta^{25}=1,7851$ mm²/s, density $d = 0,7872$ g/cm³) to the concentration of 0.1 mol/dm³. The experiments were carried out using the pertractor with discs (diameter 19 cm) made of cation-exchange polymer (Nafion-117) rotating with 5 rpm.

The main results, i.e. separation coefficients of cations in time of pertraction, are presented in Fig. 1 a, b for D2EHPA and CYANEX 302, respectively:

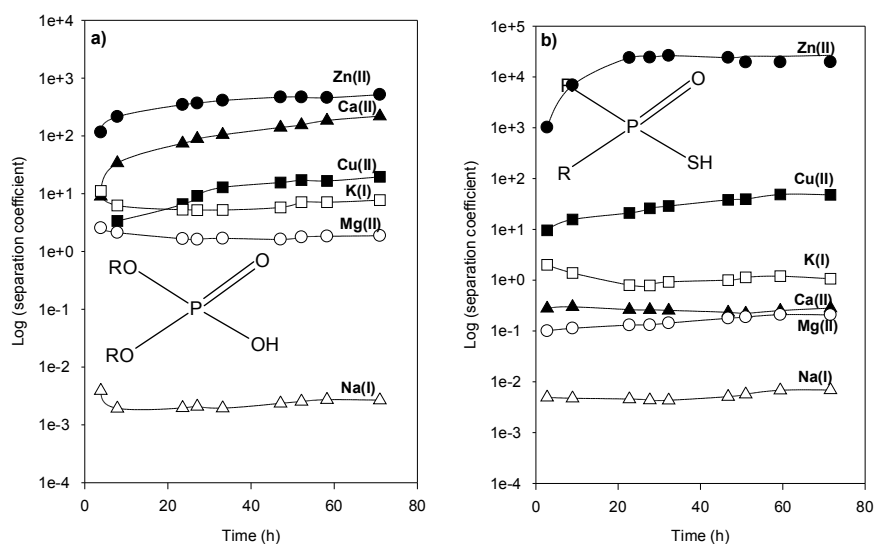


Fig. 1. Separation of cations from electroplating rinse water

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SUPPORTED AND POLYMER MEMBRANES PERTRACTION OF COPPER(II) FROM LIQUID SOLUTIONS BY 1-HEXYL-2-METHYLIMIDAZOLE

Małgorzata Ulewicz¹, Elżbieta Radzymińska-Lenarcik²

¹*Department of Metal Extraction and Recirculation, Czestochowa University of Technology, 42-200 Częstochowa, Armii Krajowej 19,*

²*Department of Inorganic Chemistry, University of Technology and Life Sciences, Seminaryjna 3, 85-326 Bydgoszcz
e-mail: ulewicz@mim.pcz.czest.pl*

Liquid membrane techniques are slowly but continuously becoming a very important and promising alternative to the liquid extraction for metal ions recovery and separation from aqueous solutions. The wider use of liquid membranes in practice is considerably limited by their low durability and instability of operation, resulting mainly from their structure and composition. Previously the authors shown, that 1-alkylimidazoles can be used for separation of the Cu(II) ions from an equimolar mixture of the Cu(II), Zn(II), Co(II) and Ni(II) ions in the transport process across polymer inclusion membrane (PIM). With elongation of the chain length of substituent -R in the imidazole ring, the initial flux of the ions increases, but the separation coefficients decrease. It was also proved that an increase in chloride ion concentration in the source phase resulted in the increase in the permeability coefficients which attained their top values at 1.0 M concentration of the chloride ions (1). In this work, the authors present results of their investigation of the competitive transportation of Cu²⁺ from different equimolar mixture of transition metal ions as Cu²⁺, Zn²⁺, Cd²⁺, Co²⁺ and Ni²⁺ ions across supported (Celgard 2500) and inclusion membranes containing 1-hexyl-2-methylimidazole from dilute chloride and nitrate solutions. The studied SLM and PIM membrane exhibit good stability described using the Danesi's thermodynamic model. The transport selectivity coefficient and orders for metal ions transport across the SLM and PIM doped with 1-hexyl-2-methylimidazole was obtained. More details will be presented on poster. The stability of SLM and PIM with imidazole derivatives was confirmed in replicate experiments. It was found that the transport of investigated ions across supported membranes, taking into consideration membrane morphology (normalized flux), was higher than polymer, whereas polymer membranes has higher stability than supported ones.

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NEW INORGANIC ION-EXCHANGERS FOR TREATMENT OF NUCLEAR WASTEWATERS CONTAINING ^{137}Cs , ^{90}Sr

S. L. Vasilyuk¹, V. N. Belyakov¹, A. V. Palchik¹, G. N. Bondarenko²

¹*Vernadsky Institute of general and inorganic chemistry NAS Ukraine
Palladin av. 32/34, Kiev 03142, Ukraine*

²*Institute for Environmental Geochemistry NAS Ukraine
Palladin av. 34, Kiev 03142, Ukraine
e-mail: vasilyuk@gmail.com*

It is well known that water plays major role in the existing ecological system. Any external impact on the water composition as a result of natural or industrial disasters as well as possible direct influence by humans (e.g. terrorism), may spell the death sentence for both the ecological system and mankind. Worldwide, 442 nuclear power plants generate electricity in 33 countries, 195 reactors are closed in Europe.

Ukraine is well known in the world after Chernobyl catastrophe. This was example when society had no chance to solve one common problem. Radiation leaks from Tokyo Electric Power Co.'s earthquake-stricken reactors in northeastern Japan represent the worst nuclear power accident since the meltdown at Chernobyl. For this purpose, we need safe, effective and technologically accessible production engineering solutions.

We developed new materials for treatment processes of radioactive liquid media - ion-exchange materials and membranes, for selective removal of radioactive metal ions from water and soil. New sorbents with high ion-exchange capacity, thermal and radiation stability and high sorption selectivity were produced and studied. There were inorganic materials based on hydroxides of Al(III), Zr(IV), Ti(IV), Sn(IV) and Mn(IV). It was shown that such materials have high sorption capacity towards radionuclides for its selective removal from liquid media.

Table 1. Main properties of new inorganic IEX oxides for removal of ^{137}Cs and ^{90}Sr ions

Oxide	Absorbed degree ^{137}Cs , %	K_d	Absorbed degree ^{90}Sr , %	K_d
MnO_2	89,4	844	99,58	23530
$\text{TiO}_2 \cdot \text{MnO}_2$	50,6	102	93,42	1420
$\text{ZrO}_2 \cdot \text{MnO}_2$	92,6	1245	99,89	95028
$\text{Al}_2\text{O}_3 \cdot \text{MnO}_2$	86,1	621	98,05	5039
$\text{SnO}_2 \cdot \text{MnO}_2$	91,1	1027	99,86	71246

$[\text{Cs}^+] - 16000 \text{ Bq/ml}$; $[\text{Sr}^{2+}] - 371 \text{ Bq/ml}$

Proposed technology is highly effective for removal of long-lived isotopes: ^{137}Cs , ^{90}Sr , which usually appear in the cooling system of nuclear reactors as a side products.

INDIRECT ELECTROCHEMICAL OXIDIZING DECOLORIZATION OF WASTEWATER FROM THE PRODUCTION OF AMINOANTRAQUINONE DYES

Barbora Vystrčilová, Libor Dušek, Ladislav Novotný

*University of Pardubice, Institute of Environmental and Chemical Engineering,
Faculty of Chemical Technology, Studentská 95, Pardubice 53210,
Czech Republic
e-mail: barbora.vystrcilova@student.upce.cz*

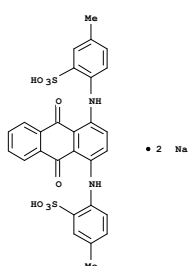
This poster is focused on the evaluation of possibilities of bleaching effluents containing five aminoantraquinone dyes selected by indirect electrochemical oxidation of single-chamber laboratory electrolyzers.

To evaluate the effectiveness of model solution decolorized wastewater containing Acid Green 25, Acid Green 27, Acid Blue 62, Acid Blue 129 and Acid Blue 80 UV-VIS spectroscopy method is chosen as suitable. During electrochemical oxidation of aminoantraquinone dyes velocity changes bleaches model solution were measured depending on the amount of auxiliary electrolyte, which was sodium chloride.

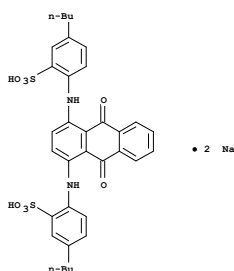
Furthermore, decolorization rate was observed depending on the voltage electrodes, which was constant during measurement. The results showed that the decolorization rate decreases under similar conditions in the order of Acid Blue 80 > Acid Green 25 > Acid Blue 62 > Acid Green 27 >> Acid Blue 129. The effectiveness of electrochemical oxidation of the dyes decreased in the same order.

Structures of aminoantraquinone dyes:

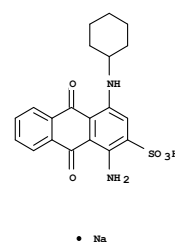
Acid Green 25



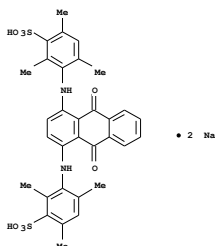
Acid Green 27



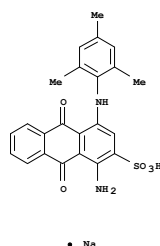
Acid Blue 62



Acid Blue 80



Acid Blue 129



Acknowledgements: Research works are funded by project (SGFChT 05/2011).

APPLICATION OF TETRAPHENYL- AND ETHYLTRIPHENYL-PHOSPHONIUM SALTS FOR THE SEPARATION OF REACTIVE BLACK 39, REACTIVE RED 45:1 AND H-ACID FROM AQUEOUS SOLUTIONS

Tomáš Weidlich, Jana Martínková

*University of Pardubice, Institute of Environmental and Chemical Engineering,
Faculty of Chemical Technology, Studentská 573, 532 10 Pardubice,
Czech Republic
e-mail: tomas.weidlich@upce.cz*

An attempt has been made to remove color from wastewater containing reactive anionic dyes substituted with sulfonic groups Reactive Black 39 and Reactive Red 45:1 and dyestuff intermediate H-acid (see Figures 1-3) from the model wastewater by the addition of two quaternary phosphonium salts, tetraphenylphosphonium bromide or ethyltriphenylphosphonium bromide. The effects of the concentration of both dye and phosphonium salt, pH and salt concentration on the removal efficiency have been studied. An optimum set of surfactant concentration, pH and salt concentration are obtained for removal of mentioned aromatic sulfonic acids.

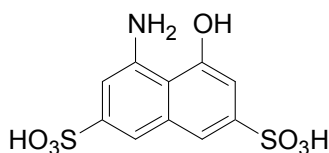


Fig. 1. Structure dyestuff intermediate H-acid

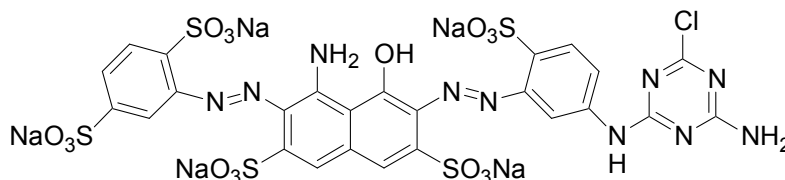


Fig. 2. Structure of textile anionic dye Reactive Black 39

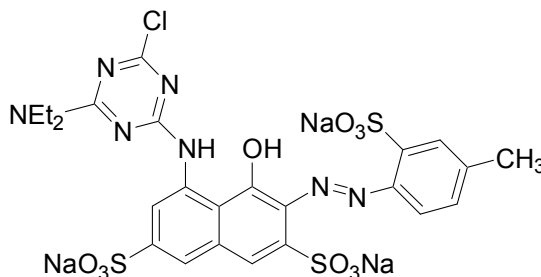


Fig. 3. Structure of textile anionic dye Reactive Red 45:1

Acknowledgements: Authors thank the Technology Agency of the Czech Republic (Grant No. TA01010606) and Ministry of Education, Youth and Sports of the Czech Republic (project No. MSM 0021627502) for financial support.

SORPTION OF PHTHALATES BY MOLECULARLY IMPRINTED POLYMERS

Joanna Wolska, Marek Bryjak

*Faculty of Chemistry, Division of Polymer and Carbonaceous Materials,
Wrocław University of Technology, Wyb. Wyspiańskiego 27,
50-370 Wrocław, Poland
e-mail: joanna.wolska@pwr.wroc.pl*

The industrial use of phthalate esters (PE) has resulted in ubiquitous presence of these xenobiotic compounds in the environment (1). Since the 1930s, phthalates have been used as plasticisers to improve plastics flexibility and in production of paints, glues, lubricants, pharmaceuticals, cosmetics and pesticides (1,2). Because PE are mostly not chemically bound to the products, they may escape into the environment during manufacturing and product use (1). The most commonly used phthalates in Europe are: dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), bis(2-ethylhexyl) phthalate (DEHP). Some of these phthalates can show prenatal and developmental toxicity, estrogenic effect and in induction of asthma (3). For this reason we have are developing studies on the use of molecularly imprinted polymer sorbents for removal of DMP from aqueous solutions.

In our work we have synthesized series of molecularly imprinted polymers (MIPs) with template of dimethyl phthalate. The MIPs were obtained by bulk polymerization of styrene (S) and divinylbenzene (DVB). In all cases octane or hexane was used as solvent and azoisobutyronitrile as initiator. To keep the template-monomer adduct organization the reaction was carried out at 60 °C for 24 h. Various amounts of DVB and DMP were used. As the references the samples without template were synthesized.

Characterization of prepared materials as specific sorbents towards DMP was investigated. Dimethyl phthalate sorption on polymer materials varied depending on the evaluated samples. The imprinted sorbents showed higher sorption capacity towards DMP than their analogues obtained without templates. The worst sorption properties showed polymers with the lower amount of crosslinker. In addition it was found that MIPs obtained with hexane showed better properties for DMP removal than materials synthesized with octane.

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SMART MEMBRANE OBTAIN BY PLASMA MODIFICATION

Bryjak Marek, Smolińska Katarzyna, Wolska Joanna

*Faculty of Chemistry, Division of Polymer and Carbonaceous Materials,
Wrocław University of Technology, Wyb. Wyspiańskiego 27,
50-370 Wrocław, Poland
e-mail: joanna.wolska@pwr.wroc.pl*

Stimuli-sensitive polymers belong to important class of modern materials. They have been used in biotechnology (e.g. enzyme immobilization) (1), medicine (e.g. drug delivery) (2) and engineering (e.g. separation) (3). Smart polymers alter their structure in response to small change in the environment conditions, e.g. polymers chain grafted on surface swells or collapses when external parameter is changed. Thermosensitive poly(N-isopropylacrylamide), PNIPAM shows such behavior. Its low critical solution temperature is 32°C. When temperature increases above LCST the chains of PNIPAM swelled and the membranes are permeability (4,5).

Surface grafting is technique that can provide polymer with a new, stable surface. The most versatile technique seems to be dielectric barrier discharge plasma. This kind of plasma works under the normal pressure. Its application for treatment of polymer surfaces has grown rapidly in the last years. A great contribution to this phenomenon gives a fact that plasma are fast, clean and environmentally friendly technique (4,5).

In this work two kind of polymer membranes were treated by plasma and subjected to grafting of poly(N-isopropylacrylamide). These membranes are: porous aromatic polycarbonate and aliphatic polypropylene with pores size of 0.2µm. Properties of the modified membranes were evaluated and compared. It was shown that polypropylene support was more effectively grafted than aromatic polycarbonate.

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MONODISPERSIVE MICROSORBENTS FOR REMOVAL OF SELECTED SPECIES FROM WATER

Joanna Wolska, Marek Bryjak

*Faculty of Chemistry, Division of Polymer and Carbonaceous Materials,
Wrocław University of Technology, Wyb. Wyspiańskiego 27,
50-370 Wrocław, Poland
e-mail: joanna.wolska@pwr.wroc.pl*

Due to increasing concentration of contaminations such as boron or arsenic in surface waters and the need for its removal from RO permeate, the research is focused on development of efficient technology to reduce its concentration. One of interesting method seems to be hybrid process, where resin beads have small diameter and are almost monodisperse. The loaded resins can be separated either by membrane or in magnetic field. Hence, the particles with 10-30 micrometer size are useful in such hybrids. However, that materials are not available on the market yet, thus there is a need to find technology for their preparation (1). There are several methods for obtaining polymeric microspheres. The choice of method depends on the size of the particles to be obtained and the chemical structure of the spheres. Recently, the most popular is a two-step method that was applied in this work also (2,3).

The paper presents the process for preparation of polymeric microspheres with and without magnetite that can be used to remove boron or arsenic from aqueous solutions. Four types of polymeric microspheres of vinylbenzyl chloride-styrene-divinylbenzene (VBC/S/DVB) with and without magnetite were prepared. VBC/S/DVB spheres with gel structure, containing 6 wt. % DVB, and VBC:S ratio 7:3, were obtained by means of membrane emulsification followed by suspension polymerization or conventional suspension polymerization. Obtained microspheres were modified with N-methyl-D-glucamine and were used in process of boron removal from water solutions. Some amount of materials was subjected to further modification – the process of quaternization in order to obtain a material capable for removal of arsenic from aqueous solutions. It was noted that resins obtained in two-steps process showed better sorption properties than these synthesized by conventional polymerization. Two stage process gives fine microspheres, with and without magnetite, with diameter about 25 – 30 μm . Using typical suspension polymerization the polymer particles were 10 times larger. All synthesized polymers were successfully modified with NMDG. The degree of substitution of chlorine by NMDG is comparable for respective pairs of polymers. Resins obtained using two-stage process and microwave modification shown the best properties towards boron and arsenic. Addition of magnetite generally not affected the sorption properties of obtained materials.

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ANION EXCHANGE RESINS AS EFFECTIVE SORBENTS FOR EGACID ORANGE II DYE REMOVAL FROM AQUEOUS SOLUTIONS AND WASTEWATERS

M. Wawrzekiewicz, Z. Hubicki, A. Wołowicz

*Maria Curie-Skłodowska University, Faculty of Chemistry, Department of Inorganic Chemistry, M. Skłodowska-Curie Sq. 2, 20-031 Lublin, Poland
e-mail: annamyrta@poczta.onet.pl*

The presence of dyes in water is a serious problem in many areas of industry, particularly in the production of dyes, textiles and paper. Even small amounts of dyes (of the order of a few ppm) are undesirable as they colourize water, make it look non esthetic and disturb life processes in it. Purification of sewage waters containing dyes becomes more and more important and aims at avoiding potential threat for the environment and increasing legal consequences.

Three anion exchange resins: weakly (Lewatit MonoPlus MP 62), intermediate (Lewatit MonoPlus MP 64) and strongly (Lewatit MonoPlus MP 500) basic were applied for Egacid Orange II dye (EO II) removal from the aqueous solutions and wastewater. The most effective anion exchanger in wastewater purification was Lewatit MonoPlus MP 500, total decolourization was achieved after 150 min. EO II sorption was not affected by the presence of Na_2SO_4 and CH_3COOH even at relatively high concentrations. The dye retentions were almost unchanged in the presence of non-ionic and anionic surfactants. EO II sorption by Lewatit MonoPlus MP 62, MP 64 and MP 500 sharply decreases when the cationic surfactant is present in the solution. The monolayer adsorption capacity (Q_0) for MP 62 was found to be 79.9 mg/g at 25°C. At 45°C this value was almost ten times higher (769.5 mg/g). The increase of Q_0 values from 568.5 to 896.8 mg/g for MP 64 and from 979.0 to 1004.4 mg/g for MP 500 was observed with the temperature rise. The optimal desorption conditions were found as follows: 1 M KSCN in 80-90% methanol for MP 62 (95-100% desorption) and MP 64 (~88% desorption) as well as 1 M HCl in 90% methanol for MP 500 (87% desorption).

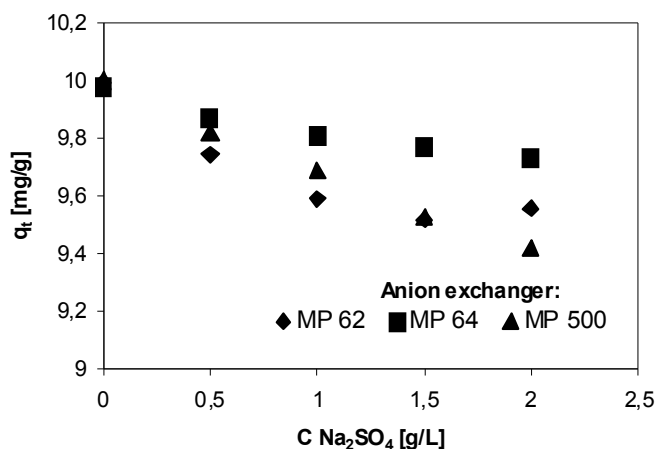


Fig. 1. Influence of Na_2SO_4 addition on EO II uptake by the weakly, intermediate and strongly basic anion exchangers in the solution containing 100 g/L of dye

APPLICATION OF WEAKLY BASIC ANION EXCHANGE RESINS FOR REMAZOL BLACK B REMOVAL FROM AQUEOUS SOLUTIONS AND WASTEWATER

M. Wawrzekiewicz, Z. Hubicki, M. Greluk, A. Wołowicz

*Maria Curie-Skłodowska University, Faculty of Chemistry, Department of Inorganic Chemistry, M. Skłodowska-Curie Sq. 2, 20-031 Lublin, Poland
e-mail: annamyrt@poczta.onet.pl*

As reactive dyes are available in a wide range of colors and owing to simple applicative methods as well as good resistant properties of decolorization, they have become common in cellulose dyeing. The disadvantage of these dyes is the fact that during application in the basic medium some amount of dye reacts with water (undergoes hydrolysis) and the hydrolyzed form of the dyes is incapable of forming a covalent bond with cellulose. Under typical dyeing conditions, up to 50% of the initial dye remains in the spent dye bath in its hydrolyzed form. Thus, after dyeing wastewaters, are characterized by intensive and difficult for removal color. Moreover, due to small affinity for fibres, they require application of a greater amount of electrolytes thus causing wastewater salination and resulting in increasing hazard for the environment. For example, reactive dyeing of 1 kg of cotton requires about 150 L of water, 0.6-0.8 kg of NaCl and about 40 g of reactive dye (1). More than 80,000 tons of reactive dyes are produced and consumed every year (1). The textile industry releases more than 0.2 million tons of salts in the environment each year according to EIPPCB (European Integrated Pollution Prevention and Control Bureau) estimations (2). One can easily imagine the total amount of pollution generated.

In this study, the use of the weakly basic anion exchange resins of phenolformaldehyde (Amberlyst A 23), polyacrylate (Amberlite IRA 67) and polystyrene (Lewatit MonoPlus MP 62) matrices for removal of reactive dye Remazol Black B (RBB) from aqueous solution and wastewater was investigated. RBB sorption on the anion exchangers was a time dependent process, 75.2, 33.9 and 25.1 % color reduction was found after 216 h of phase contact time for Lewatit MonoPlus MP 62, Amberlyst A 23 and Amberlite IRA 67, respectively. RBB uptake by the anion exchangers was influenced by inorganic salts and anionic surfactant addition. The amounts of dye retained by the anion exchangers increased with temperature rise and pH decrease. The maximum sorption capacities calculated from the Langmuir model were 66.4, 282.1 and 796.1 mg/g for Amberlite IRA 67, Amberlyst A 23 and Lewatit MonoPlus MP 62, respectively. Regeneration of phenolformaldehyde and polystyrene resins was possible using 1 M NaOH, 2 M KSCN, 1M KSCN in 20-60 % methanol as well as 1 M HCl in 80% methanol.

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COLUMN AND BATCH STUDIES OF Pd(II) IONS SORPTION ON ACRYLIC, GEL TYPE WEAKLY BASIC ANION EXCHANGE RESIN FROM CHLORIDE-NITRATE(V) SOLUTIONS

A. Wołowicz, Z. Hubicki, M. Greluk, M. Wawrzkievicz

*Maria Curie-Skłodowska University, Faculty of Chemistry, Department of Inorganic Chemistry, Maria Curie-Skłodowska Square 2, 20-031 Lublin, Poland
email: annamyrta@poczta.onet.pl*

Palladium is one of the most expensive metals. However, due to its specific properties, it is widely used in many branches of industry. The low concentration of palladium in the terrestrial crust and its low availability account for the fact that many processes have been investigated and developed to recover it in complex solutions, or aimed at palladium recovery from scrap materials (1-3). Ion-exchange processes applying anion exchangers of different basicity of their functional groups have been investigated for palladium recovery from systems of various compositions (4-6).

The main goal of this paper was the removal of palladium(II) ions from the chloride-nitrate(V) solutions using the weakly basic anion exchange (WBA) resin Amberlyst A-24. This work was mainly focused on the following aspects: characterization of sorption properties of Amberlyst A-24 towards Pd(II) ions, study of the phases contact time on sorption process, kinetic studies and column studies.

The phases contact time studies performed indicate that most of the sorption occurs in the first 30 min for all systems. A pseudo-second order kinetics was followed in all examined systems (0.1-0.9 M HCl – 0.9-0.1 M HNO₃ – 100 mg/dm³).

The Amberlyst A-24 column capacity was low and equal to 0.001-0.003 g/cm³. Column capacity increases with the hydrochloric acid concentrations increase in the system. The selectivity series of Amberlyst A-24 and other WBA resins can be presented as follows: for solutions 0.9 M HCl – 0.1 M HNO₃ – 100 mg/dm³ Pd(II): Amberlite IRA-92 (0.038 g/cm³) > Dowex 66 (0.0347 g/cm³) > Varion ADAM (0.0310 g/cm³) > Amberlyst A-23 (0.0295 g/cm³) ≈ Dowex WGR-2 (0.0292 g/cm³) > Amberlite IRA-96 (0.0205 g/cm³) >> Amberlyst A-24 (0.0030 g/cm³).

Structure type (gel or macroporous) can play a significant role in sorption behavior of WBA resins toward Pd(II) ions.

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REMOVAL OF REACTIVE DYES FROM AQUEOUS SOLUTIONS USING GEL ANION EXCHANGER

Magdalena Greluk, Zbigniew Hubicki, Anna Wołowicz, Monika Wawrzekiewicz

*Maria Curie-Skłodowska University, Faculty of Chemistry, Department of Inorganic Chemistry, M. Curie-Skłodowska Sq. 2, 20-031 Lublin, Poland
e-mail: magdalena.greluk@gmail.com*

In recent years the treatment of highly colored aqueous effluent streams from textile dye house industries has attracted the attention of environmentalists and entrepreneurs due to its socio-economic and political dimensions. In particular, the effluents from reactive dye baths are of great priority due to their highly colored streams, which contain unutilized, hydrolyzed dyes, as well as salts and auxiliary chemicals, etc (1). There are several methods for reactive dyes removal such as biological treatment, coagulation/flocculation, ozone treatment, chemical oxidation and photocatalytic processes, membrane processes and adsorption. Among these methods, adsorption is often considered as a simple and efficient technique due to its ability to remove reactive dyes, produce highly quality treated water and ease operation (2,3). A number of inorganic and organic adsorbents are used for the removal of reactive dyes. This includes the use of the synthetic clays, chitosan, calcined alunite, activated carbon, and so forth. A number of biosorbents are applied for this purpose with various success for color removal (4). Also anion exchange resins found to be very effective adsorbents for reactive dyes removal (5-7).

The characteristics of the dye adsorption behavior are mainly understood in terms of the equilibrium isotherms, kinetic models and effects of pH and ionic strength from adsorption batch experiments. In this study, the commercial anion exchange resin, strong base Amberlite IRA-458, was evaluated for the removal of anionic reactive dyes, C.I. Reactive Red 2 and C.I. Reactive Red 120, from the water. The Langmuir model was used to describe adsorption isotherms. The pseudo second-order model was used to describe the kinetic process. The factors such as the initial dye concentration, phase contact time, pH of solution and ionic strength were discussed.

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MEMBRANE SEPARATION OF DICARBOXYLIC ACID PRODUCED BY BIOSYNTHESIS

**Marta Woźniak, Katarzyna Staszak,
Magdalena Sottek, Krystyna Prochaska**

*Poznań University of Technology, Institute of Chemical Technology
and Engineering, Pl. M. Skłodowskiej-Curie 2, 60- 965 Poznań, Poland
e-mail: marta.l.wozniak@doctorate.put.poznan.pl*

Nowadays, one of the most interesting method of production of low-molecular weight organic acids is microbial fermentation. The success of this process is also affected by the purification step, because often monovalent organic acid salts like sodium acetate and/or sodium chloride are produced as by-products (1-3). For the isolation and concentration of organic acids many unit operations such as precipitation, crystallization, liquid-liquid extraction, electro dialysis and pressure-driven membrane techniques can be used (2,3).

In the presented study the usefulness of nanofiltration process was considered. A laboratory-scale nanofiltration system (SEPA CF, OSMONICS, USA) equipped with ceramic membranes with cut-off 1 kDa and 5 kDa was used. The rejection of organic acid at transmembrane pressure equal to 0.4 MPa was tested. In preliminary experiments model aqueous solution of fumaric acid and sodium fumarate at different concentration (2.5 to 5 mM/L) and various pH were investigated.

It was found that the rejection of fumaric salt increased strongly with increasing pH of feed solution (depending on the degree of dissociation), while the degree of fumaric acid rejection was lower than 5% irrespective of the initial concentration of filtrated solution. Taking into account the literature reports (1-5) the observed increase of fumaric salts rejection can be probably explained by increase of the electrostatic repulsion between dissociated form of organic acids and membrane material. The polarographic and chromatographic methods were used for qualitative and quantitative determination of the composition of the substrates and products.

The obtained results of preliminary investigations showed that NF is a process, which can be considered as one of the purification steps in the process of recovery of organic acid from fermentation broth.

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RECOVERY OF GOLD(III) IONS FROM CHLORIDE SOLUTIONS ON THE CARBON ADSORBENT LEWATIT AF5

Grzegorz Wójcik, Zbigniew Hubicki, Magdalena Górka

University of Maria Curie-Skłodowska, Faculty of Chemistry, Department of Inorganic Chemistry, Pl. M. Curie-Skłodowskiej 2, 20-031 Lublin, Poland, e-mail: grzegorzwojcikumcs@wp.pl

Precious metals such as gold have been known for ages with regard to their specific chemical and physical properties, which can be exploited in many fields. The increasing demand for precious metals, besides their small resources and high costs of their production, force to look for new sources (1).

A major use of activated carbons in the metallurgical industries is the extraction of gold and silver from low-grade ores (2). The high selectivity of carbons for gold and silver in the presence of large concentrations of base metals such as copper, iron, nickel, cobalt, and antimony and their availability in abundance, in several different grades having different surface characteristics, is going to play a significant role in the recovery of gold and silver in the future (3).

Gold can be recovered by using the ion exchange and extraction methods. For the selective recovery of gold (III) from chloride solutions the carbon adsorbent was used. There were carried out laboratory studies of selective removal of gold(III) microquantities from 0.1-6 M hydrochloric acid solutions and pH 3 on Lewatit AF5, which is a carbon based, spherical, microporous adsorbent with a large surface area and well defined pore distribution.

In these experiments % R of gold (III) depending on time was obtained. The kinetic parameters were calculated on the basis of static results. In these experiments the equilibrium isotherms of gold (III) sorption were obtained. The samples of carbon adsorbent with the appropriate solution were mechanically shaken for 24 hours. Afterwards the solution with carbon adsorbent was filtrated. The gold concentration was determined by the AAS method. The thermodynamic parameters of gold (III) sorption process on Lewatit AF5 were calculated based on the Langmuir and Freundlich isotherms.

The described method using Lewatit AF5 for recovery of ions gold (III) can be applied in preconcentration of gold (III) ions from the hydrochloric solutions. The sorption of gold (III) ions on the carbon adsorbent Lewatit AF5 can be best described by the pseudo-second order kinetic model. The Langmuir and Freundlich equations, which are commonly used for description of sorption equilibrium, were applied in the analysis of the obtained results. The experimental data was well fit by the Freundlich isotherm model.

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MODIFICATION OF CLAY WITH N-METYL-D-GLUCAMINE CONTAINING POLYMER FOR REMOVAL OF BORON

Gamze Barim¹, Yesim Gurse², Erdem Yavuz², B. Filiz Senkal²,
M. Sabri Celik³

¹Department of Chemistry, Adiyaman University, Adiyaman, Turkey

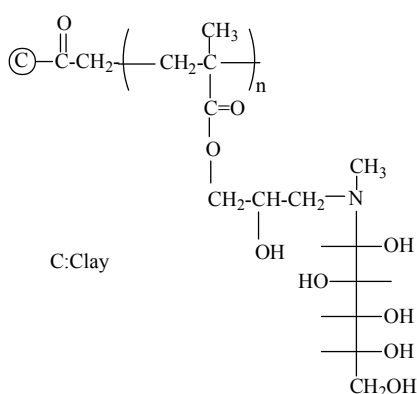
²Department of Chemistry, Istanbul Technical University, Maslak-Istanbul
34469, Turkey

³Department of Mining Engineering, Istanbul Technical University, Maslak-Istanbul 34469, Turkey

e-mail: yavuzerd@itu.edu.tr

Boron removal is of special importance due to its plant stunning effect. Presence of boric acid at concentration higher than 4 mg per liter have been reported to accelerate decay of fruit trees. Citrus plantations are especially susceptible to excessive boron concentration in the irrigation water (1). Numerous works have been done for boron removal from wastewaters. Amberlite IRA 743, a boron specific resin, was used in boron removal from drinking waters, boron containing wastewaters or geothermal waste waters (2,3). *N*-Glucamine-type chelating resins such as Diaion CRB 01, Diaion CRB 02, Purolite S 108(1) and Purolite S 108(2) were used in boron removal from wastewaters of geothermal plants (4).

In this study, clay was modified with poly (glycidyl methacrylate) shells by ATRP method. The epoxy group on the clay was modified with *N*-methyl-*D*-glucamine (NMG) by ring opening. This sorbent was used to remove boron from aqueous water and boron uptake capacity was found as about 2 mmol·g⁻¹ of sorbent.



Scheme 1. Clay with NMG containing polymer

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PREPARATION OF HYDRAZINE CONTAINING CORE-SHELL TYPE RESIN FOR REMOVAL OF ALDEHYDES

Erdem Yavuz¹, B. Filiz Şenkal¹, Gülay Bayramoğlu², M. Yakup Arıca²

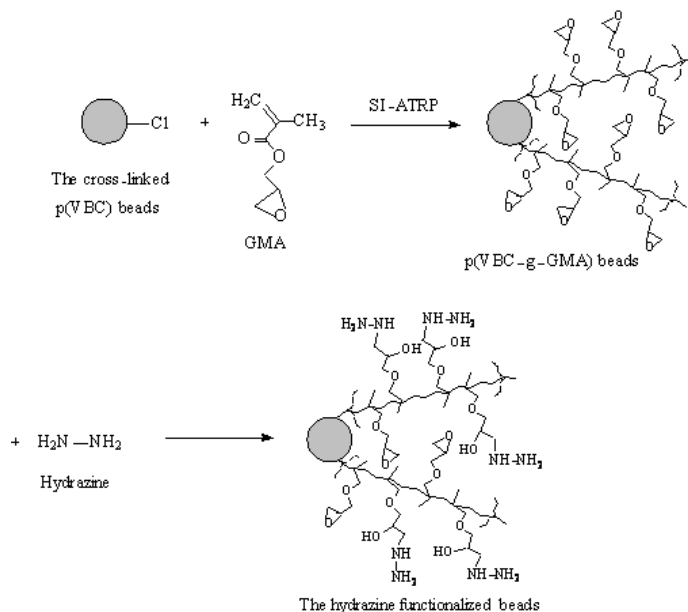
¹*Department of Chemistry, Istanbul Technical University, 34469 Maslak-
Istanbul, Turkey.*

²*Biochemical Processing and Biomaterial Research Laboratory, Faculty of Arts
and Sciences, Gazi University, 06500 Ankara,
e-mail: yavuzerd@itu.edu.tr*

Polymer-supported semicarbazide was demonstrated to be efficient for removal of small quantities of aldehydes by means of involvement of hydrazide groups (1). In a successful study, crosslinked polystyrene with diol residues was used to isolate aldehydes and ketones in benzene solutions by reversible acetal or ketal formation (2). 1,2-Diaminoethane-containing epoxy resins and Polymer-Supported Oligo(ethyleneimines) were used for removal of aldehydes (3,4).

In this study, poly(glycidyl methacrylate), poly(GMA) was grafted on the poly(VBC) beads via SI-ATRP and 75-150 µm size of fraction was used the presented study. Poly(GMA) grafted sorbent was reacted with excess of hydrazine to obtain hydrazine modified beads.

Obtained resin was used to remove aldehydes. Benzaldehyde loading capacity of the resin was found as 0.45 mmol.g⁻¹ resin.



Scheme 1. Preparation of hydrazine modified resin

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ION EXCHANGE OF Cd²⁺, Zn²⁺ and Pb²⁺ FROM AQUEOUS SOLUTION BY AMBERLITE IR 120

Iwona Zawierucha

*Institute of Chemistry, Environment Protection and Biotechnology, Jan Długosz University of Częstochowa, 42-201 Częstochowa, Armii Krajowej 13, Poland
e-mail: i.zawierucha@ajd.czyst.pl*

Many toxic heavy metals have been discharged into the environment as industrial wastes, causing serious soil and water pollution (1). The stricter environmental regulation on the discharge of heavy metals makes it necessary to develop various technologies for the removal (2). Ion exchange is one of the more popular methods for the removal of heavy metals from aqueous solution. Selective ion-exchangers can be used for purification of process liquids for re-use and for the treatment of final wastewaters (3). In the present study, the removal of Cd²⁺, Zn²⁺ and Pb²⁺ ions from aqueous solution was investigated. Experimental tests were undertaken using Amberlite IR 120 (strong cation exchange resin). Batch experiments were performed in order to examine the effect of pH, amount of resin and contact time on the metal ions removal process. It was observed that more than 99% removal efficiency was achieved under optimal conditions. The best parameters of process were found to be: a pH of 6, contact time of 60 min and 0.5 g of resin. The experimental equilibrium data were described by the Langmuir and Freundlich isotherms. The high values of correlation coefficients indicate good agreement with sorption models, i.e. Langmuir and Freundlich; the following order to fit isotherms for all metals was: Langmuir > Freundlich. Furthermore, pseudo-first and second order kinetic models were used for describing kinetic parameters. It was determined that removal of investigated metal ions was well-fitted for second order kinetic studies.

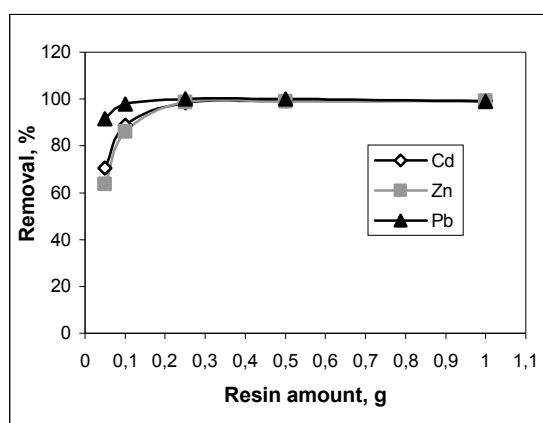


Fig. 1. Effect of resin amount on removal of metal ions (pH=6, 25 mg/L, 60 min)

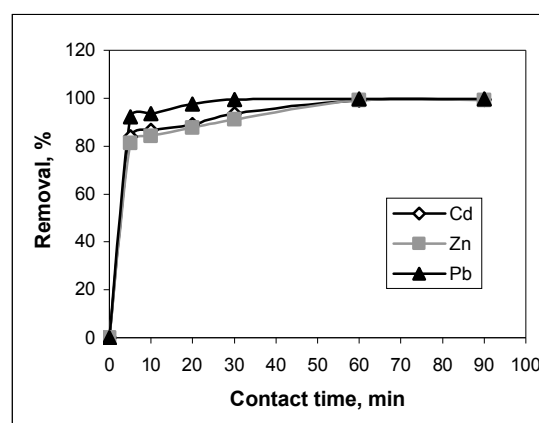


Fig. 2. Effect of contact time on removal of metal ions (pH=6, 25 mg/L, 0.5 g)

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EFFECT OF SURFACE DIFFUSION ON THE ASYMMETRY OF GAS TRANSPORT AND MIXTURE SEPARATION IN COMPOSITE MEMBRANES

Vladimir M. Zhdanov¹, Vjacheslav I. Roldughin², Elena E. Sherysheva²

¹*National Research Nuclear University "MEPhI", Kashirskoe shosse, 31
115409, Moscow, Russia*

²*Frumkin Institute of Physical Chemistry and Electrochemistry, Russian
Academy of Sciences, Leninsky prospect, 31, 119991, Moscow, Russia
e-mail: VMZhdanov@mail.ru*

Recently, it was experimentally established that composite membranes have asymmetric permeability at different flow directions of both gases and electrolyte solutions. This effect was observed for flows of gases and gaseous mixtures through tapered pores of track membranes and in multilayer ceramic membranes composed of layers with nano-sized and micro-sized pores (1). We discuss the effect of surface diffusion on the transport asymmetry in bilayer membranes.

We analyze the permeability of the bilayer porous membrane consisting of a finely disperse separating layer and a coarse substrate. Let the average pore sizes in the layers and the pressures at the input and the output of the membrane ensure the Knudsen and viscous (Poiseuille) regimes of the gas flow in the separating layer and the substrate, respectively.

In our consideration we take into account the gas transport in the pore bulk as well as in the adsorption layer. The gas transport in the pore bulk is described in terms of Knudsen diffusion. For diffusion transport in the adsorption layer we take into account the dependence of the surface diffusion coefficient on surface coverage θ . This dependence can be approximated by the equation

$$D = D_0/(1 - \theta),$$

where D_0 is the self-diffusion coefficient of gas molecule on the surface free of adsorbate. The adsorption of gas molecules on the pore surface is described by the Langmuir isotherm

$$\theta = p/(\alpha + p),$$

where p is the gas pressure and α is the parameter of the isotherm.

We calculated the asymmetry coefficients for parameters typical for CO₂ and CH₄ transport in Silicalite-1 membrane as separating layer and the coarse supporting layer with pore radius of 6 μm . The results of calculations shown the significant asymmetry effect related to the surface diffusion.

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AUTHORS INDEX

A

Abdulsalam W. 153
 Akinyeye R. 183
 Alejski K. 174, 175
 Alexandratos S.D. 18
 Ahmed A. 152
 Amerkhanova Sh.K. 131
 Apopei D.F. 149
 Apostoluk W. 67, 85, 132
 Arica M.Y. 214
 Avcı A.Ö. 136

B

Barim G. 190, 213
 Bastrzyk A. 134
 Bayramoğlu G. 214
 Beker Ü. 77, 135, 136,
 137
 Bekkulina F.Zh. 131
 Belyakov V.N. 63, 71, 201
 Bendová H. 139
 Bergmann H. 128
 Bernard J. 52
 Biernacki R. 140
 Birčák T. 41
 Bogacki M.B. 101, 105, 154
 Bohr T. 166
 Bondarenko G.N. 201
 Borisevich V.D. 129
 Borowiak-Resterna A. 140
 Borrull F. 93
 Branger C. 52
 Bratkowska D. 93
 Bryjak M. 142, 204, 205,
 206
 Bunia I. 58
 Butewicz A. 143, 147

C

Cekli S. 144
 Celik M.S. 190, 213
 Cherny M.L. 160
 Chmielewski T. 28, 85
 Chorążewska M. 145, 176
 Cierpiszewski R. 146
 Cormack P.A.G. 93

Cuciureanu A. 165
 Czulak J. 147

D

Davies A. 93
 Deska M. 164, 168
 Diaconu I. 197
 Dinu M.V. 21, 48, 148,
 182
 Drăgan E.S. 21, 48, 148,
 149, 182
 Dudek G. 150, 169, 189
 Duraj I. 142
 Duranoğlu D. 77, 135, 136,
 137
 Dušek L. 202
 Dydo P. 145, 151
 Dziak J. 152, 153
 Dzyazko Y. 63

F

Fatoba O.O. 183
 Fontanals N. 93
 Fujimoto R. 44
 Fujino H. 181

G

Gajda B. 154
 Gajewski P. 101
 Gęca M. 162
 Gęga J. 54, 110
 Górská M. 212
 Greluk M. 208, 209, 210
 Grzywna Z.J. 150, 169, 189
 Gurse Y. 213

H

Harada A. 25
 Hendry B.A. 126
 Hubicki Z. 81, 162, 193,
 207, 208, 209,
 210, 212

I

Ishibashi H. 180

J

Jakóbiak-Kolon A. 155, 193
 Jakubiak-Marcinkowska A. 147, 156
 Jaroszek H. 155
 Jelínek L. 41, 157
 Jermakowicz-Bartkowiak D. 158, 194
 Jyo A. 44, 59

K

Kapłon J. 152, 153
 Kawakita H. 96, 180
 Kawasaki A. 177
 Kaya Í.G.B. 137
 Kica M. 159
 Kicińska K. 187
 Kiegiel K. 196
 Kirillov E.V. 160
 Kitagaki M. 44
 Kohata K. 161
 Kołodyńska D. 162
 Konopczyńska B. 163
 Kończyk J. 164
 Korolewicz T. 193
 Koter S. 120, 165, 166,
 171, 172
 Kowalik A. 167
 Kozłowska J. 164, 168
 Kozłowski C. 164, 179
 Krasowska M. 150, 169, 189
 Królikowski L. 153
 Krupa M. 89
 Kunitake T. 36
 Kůc P. 41
 Kucukkaya I. 75
 Kujawski P. 105
 Kujawski W. 118, 170
 Kultys M. 165, 171, 172
 Kuwata S. 180

L

Laatikainen K. 109
 Laatikainen M. 109
 Linkov V.M. 71

M

Marcé R.M. 93
 Margaillan A. 52
 Martinková J. 173, 203

Matsuoka N. 181
 Matsuura H. 44, 59
 Mączka K. 167
 Michałek J. 165
 Mientka A. 122
 Miesiąc I. 174, 175
 Mištová E. 157
 Mitko K. 176
 Mól A. 146

N

Nakaatari H. 44
 Ndayambaje G. 183
 Neagu V. 58
 Nishihama S. 25, 161, 177,
 191
 Nowak Ł. 178
 Nowik-Zajac A. 179
 Novotný L. 202

O

Ochromowicz K. 85, 132
 Ohto K. 96, 180
 Okobira T. 181
 Olszanowski A. 89
 Otremska P. 54

P

Palatý Z. 139
 Palchik A.V. 201
 Parschová H. 157, 192
 Perju M.M. 21, 48, 182
 Petrik L.F. 183
 Piłśniak-Rabiega M. 147
 Pokomeda K.J. 184
 Polowczyk I. 134
 Ponomarova L.N. 63
 Pośpiech B. 185
 Poźniak G. 186
 Poźniak R. 186
 Prochaska K. 146, 163, 211
 Przewoźna M. 175

R

Radu D.A. 197
 Radzymińska-Lenarcik E. 200
 Raszkowska-Kaczor A. 199
 Regel-Rosocka M. 100, 178, 187

Rogaliński A. 175
 Roldughin V.I. 104, 216
 Ronka S. 147, 159, 188
 Rybak A. 150, 169, 189
 Rychkov V.N. 160

S

Sadowski Z. 134
 Sadamatsu H. 180
 Sainio T. 109
 Seko N. 44, 59
 Senkal B.F. 75, 137, 144,
 190, 213, 214
 Sherrington D.C. 93
 Sherysheva E.E. 216
 Shibata K. 191
 Shlyapov R.M. 131
 Siepietowski Ł. 193
 Şimşek E.B. 135
 Siren H. 109
 Smirnov A.Yu. 119
 Smolik M. 155, 167, 193
 Smolińska K. 205
 Sosenkin V.E. 63
 Sottek M. 211
 Sowa M. 194
 Staszak K. 163, 195, 211
 Staszak M. 195
 Steczek Ł. 196
 Strzelewicz A. 150, 169, 189
 Sulaberidze G.A. 109, 129
 Szczepański P. 197, 198, 199
 Szternel D.M. 100
 Šlapáková P. 192

Ś

Świerkowska E. 163

T

Tajiri N. 181
 Tamada M. 44, 59
 Tanaka S. 25
 Tepliakov V.V. 34
 Tomaszewska M. 122
 Trochimczuk A.W. 77, 143, 147,
 156, 179, 188
 Turczyn R. 150
 Turek M. 145, 151, 176

U

Ueki Y. 59
 Uezu K. 181
 Ulewicz M. 200

V

Van der Walt N.T. 183
 Vasilyuk S.L. 71, 201
 Volkovich Y.M. 63
 Vonková K. 41
 Vystrčilová B. 202

W

Walkowiak W. 164
 Wawrzekiewicz M. 207, 208, 209,
 210
 Weidlich T. 173, 203
 Wieczorek P.P. 32
 Wieszczycka K. 89
 Wionczyk B. 67, 146
 Wiśniewski M. 100, 178, 187
 Witek-Krowiak A. 184
 Wolska J. 142, 204, 205,
 206
 Wołowicz A. 81, 207, 208,
 209, 210
 Woźniak B. 85
 Woźniak M. 211
 Wódzki R. 198, 199
 Wójcik G. 58, 212

Y

Yamaguma R. 96
 Yang Y. 18
 Yavuz E. 75, 144, 190,
 213, 214
 Yonekawa H. 59
 Yoneyama T. 180
 Yoshizuka K. 25, 161, 177,
 191
 Yurchuk T. 128

Z

Zakrzewska-Trznadel G. 196
 Zawierucha I. 168, 215
 Zeng S. 129
 Zhdanov V.M. 114, 216
 Zhu X. 18