A Study of Silica Gel Adsorption Desalination System

By

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Abstract

Rising water scarcity due to climate change and over-exploitation of traditional water resources is of increasing concern around the World, both because of its economic implications as well as the continued habitability of long-standing communities. One solution to this issue is desalination of saline or brackish water, which has long been used in regions that have traditionally faced water shortage such as the Middle East. There are several ways in which desalination is carried out, including multi-effect desalination, multi-stage flash desalination, and membrane-based reverse osmosis (RO), which are all widely exploited commercially. The high energy demands and large 'carbon footprint' of these various current commercial technologies have spurned interest in several potential alternative technologies.

One of these alternatives is adsorption-based desalination (AD). This approach uses low-grade heat such as waste heat from a process or solar energy to generate potable water and, depending on the cycle details, cooling as well. The low-grade heat is used to form water vapour from the saline or brackish source. The vapour is then passed through a bed of silica into which it adsorbs until the silica is saturated. Once saturated, the bed of silica is heated using further low-grade heat to drive off the now desalinated water before being re-condensed in a receiving vessel.

Adsorption-based desalination has a range of advantages, including: (1) it is driven by low-grade heat that is free and/or would otherwise go to waste; (2) it has few moving parts, leading to reduced maintenance costs; (3) fouling and corrosion is reduced due to the low operating temperatures and confinement of the saline/brackish water to a fraction of the total system; and (4) it offers the ability to treat/desalinate saline and brackish waters containing organic compounds. Besides these advantages, which may be shared in part with some conventional desalination methods, AD also offers two unique benefits: (1) it has the ability to co-generate cooling along with the potable water; and (2) it yields double distillate, minimizing the possibility of so-called '(bio) gen-contamination'.

Despite the many advantages of AD, it has received remarkably little attention by researchers. Given how established existing desalination technologies are, take-up of AD is unlikely until we have a far greater understanding of the effect of process parameters on the productivity of AD – the work therefore reported here addresses directly this need.

This thesis reports a detailed study of the impact of operational and design parameters such as operating heating and cooling water temperatures and cycle times on the nature of the thermodynamic cycles of AD and its performance in terms of, for example, system water productivity and specific energy consumptions. This aim is achieved by using a range of novel models validated by experimental data also obtained as part of the research. Key findings of this study include: 1) In AD, an optimum hot water temperature existing for the minimum energy consumption of per unit mass fresh water produced. The optimum temperature depends on the cooling water temperatures and other operating parameters of the system; 2) the performance of the AD cycles is bounded by the capacity of the adsorbent used, the optimal water production rate of the cycles increases directly with the capacity whilst the corresponding energy consumption rate per kg of water produced decreases at a diminishing rate; 3) the evaporator temperature relative to cooling water temperature can significantly impact on the nature of the AD cycles and the performance of the AD systems. At different evaporator temperature relative to the cooling water temperature, the thermodynamic cycles had been theoretically and experimentally identified to form three unique cycle categories when they are presented on the set of *P-T-X* relationship coordinates. Analysis of these cycles showed that the best performance is achieved when the temperature of the evaporator is greater than that of the water used to cool the silica-gel bed and condenser; 4) an optimum system cycle time existing for the maximum fresh water production over a specific period of time under the given operational conditions using validated dynamic model.

This thesis is presented in the form of a collection of published or submitted journal articles that are the results of research by the author. These five articles have been chosen

to best demonstrate the study of an AD system (both theoretical and experimental studies). Additional background information is provided in order to establish the context and significance of this work.

Declaration

This work contains no material which has been accepted for the award of any other degree or diploma in any University or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

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Jun Wei Wu

Date

Thesis by Publication

This thesis is submitted as a portfolio of publications either published or submitted for publication by peer-reviewed journals according to the 'Academic Program Rules' of the University of Adelaide. The international journals that these papers have been published in or submitted to are all closely related to the field of the research of this work.

The thesis is based on the following publications:

1. Wu J. W., Biggs M. J., Hu E. J. (2012) Dynamic Model for the Optimisation of Adsorption-based Desalination Processes. *Chemical Engineering Science,* under review.

2. Wu J. W., Biggs M. J., Pendleton P., Badalyan A., Hu E. J. (2012) Experimental Implementation and Validation of Thermodynamic Cycles of Adsorption-based Desalination. *Applied Energy*, 98, 190-197.

3. Wu J. W., Hu E. J., Biggs M. J. (2012) Thermodynamic Cycles of Adsorption Desalination system. *Applied Energy*, 90, 316-322.

4. Wu J. W., Hu E. J., Biggs M. J. (2011) Thermodynamic Analysis of an Adsorption-based Desalination Cycle (part II): Effect of Evaporator Temperature on Performance. *Chemical Engineering Research and Design*, 89, 2168-2175.

5. Wu J. W., Biggs M. J., Hu E. J. (2010) Thermodynamic Analysis of an Adsorption-based Desalination Cycle. *Chemical Engineering Research and Design*, 88, 1541-1547.

The Following conference papers are of close relevance to the present work and are included in the appendices:

1. Wu J. W., Biggs M. J., Hu E. J. (2010) Comparison of Adsorption-based Desalination Plant Performance Models. *Chemeca 2010: The 40th Australasian Chemical Engineering Conference*, Adelaide, September 26-29, ISBN: 978-085-825-9713.

2. Wu J. W., Biggs M. J., Hu E. J. (2010) Thermodynamic Analysis of Adsorption-based Desalination Cycles. *Chemeca 2010: The 40th Australasian Chemical Engineering Conference*, Adelaide, September 26-29, ISBN: 978-085-825-9713.

The following journal publication was completed as part of this research candidature, but not included as part of this thesis.

1. Wu J. W., Hu E. J., Biggs M. J. (2012) Low Energy Adsorption Desalination Technology. *Advanced Materials Research*, 347, 601-606.

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Finally, and most particularly, I would like to acknowledge my friends and family, especially my wife Mrs Yuanjia Lu and my parents Mr Guoqing Wu and Mrs Fengjuan Du, for their constant support and encouragement.

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CHAPTER 1: INTRODUCTION

1.1 Overview

The desalination of saline and brackish water to produce potable water is of increasing concern around the World (Omenn, 2006). There are several ways in which desalination is carried out, including multi-effect desalination (MED), multi-stage flash (MSF) desalination, and membrane-based reverse osmosis (RO) (Mosry et al., 1994, Wazzan and Al-Modaf, 2001, Bruggen and Vandecasteele, 2002b, Sayyaadi and Saffari, 2010), which are all widely exploited commercially. The high energy demands of these various current commercial technologies have prompted some to investigate means by which the ‘carbon footprint’ of desalination can be reduced. Examples include energy recovery measures (Chua et al., 2010), heat integrated distillation (Jana, 2010), waste-heat driven barometric flash-type desalination (Maidment et al., 2007), solar thermal assist synthetic energy desalination (Tchanche et al., 2010) and, of particular interest here, adsorption-based desalination (AD) (Wu et al., 2010, Thu et al., 2010, Wang et al., 2011), which is viewed by some as being potentially one of more sustainable alternatives (Ray, 2010a, Ng et al., 2008).

AD has its origins in adsorption chillers (Rezk and Al-Dadah, 2012, Al-Alili et al., 2010, Saha et al., 2007), which use fresh water as the refrigerant that circulates between an evaporator, adsorption/desorption beds and condenser. In AD, however, saline water replaces the fresh water and switches the system from the closed cycle (in an adsorption chiller) to an open cycle (in AD). In this method, instead of using recycled pure water (from the condenser), saline or brackish water is supplied to the evaporator from an external source. The vapour created in the evaporator using low-grade heat (*e.g.* from the sun or waste process heat) travels into a bed of silica gel where it is adsorbed until the silica is saturated. Once saturated, the bed of silica is heated using, once again, low-grade heat to drive off the now desalinated water before being re-condensed in a receiving vessel (i.e. the condenser).

Figure 1.1 shows a schematic of a two-bed adsorption-based desalinator, which is the most basic model of any practicable production system (*i.e.* one that is capable of producing fresh water on an essentially continuous manner). This system consists of three major components: a condenser, two silica gel beds, and an evaporator. The source saline water is first charged into the evaporator and a vacuum is applied to the entire system. Valve 1 is then opened to allow the source water to evaporate at temperature T_{evap} and travel as a vapour into Bed 1 where it adsorbs on the silica gel. The heat generated during adsorption is removed by cold water circulating at temperature T_{cw} in Bed 1. Once the silica in Bed 1 is saturated with water, Valve 1 is closed. The water circulating through Bed 1 is then switched to hot water at temperature T_{hw} to bring the bed pressure up to the condenser pressure. Valve 2 is then opened so as to allow the adsorbed water in Bed 1 to pass into the condenser to form, finally, pure water at a temperature T_{cond}. Once much if not all the water has been driven off the silica gel (the amount depends on the hot water temperature), this silica gel regeneration process stops. Valve 2 is then closed and cold water (at T_{cw}) is circulated through Bed 1 to reduce its pressure to the evaporator pressure. Valve 1 is then opened to start the next cycle. The time elapsed from the beginning of the process until now is so called cycle time. Pure water is produced, essentially, continuously by the system in Fig 1.1 by carrying out the above process alternately in Bed 1 and Bed 2. To improve energy efficiency, in practice systems with two or more beds (with even numbers) are normally used (Chua et al., 1999).

The performance of AD is normally expressed in terms of its water productivity (e.g. in litres per day) and specific energy consumption (e.g. in kJ per litre of water produced). Key operational and design parameters such as operating heating and cooling water temperatures (e.g. T_{hw} and T_{cw}) and the cycle time operated have major impact on the performance of AD. For example the evaporator temperature relative to the cooling water temperature (which controls the bed and condenser temperatures) affects the nature of the thermodynamic cycle of AD and consequently influences the AD performance (Wu et al., 2012b).

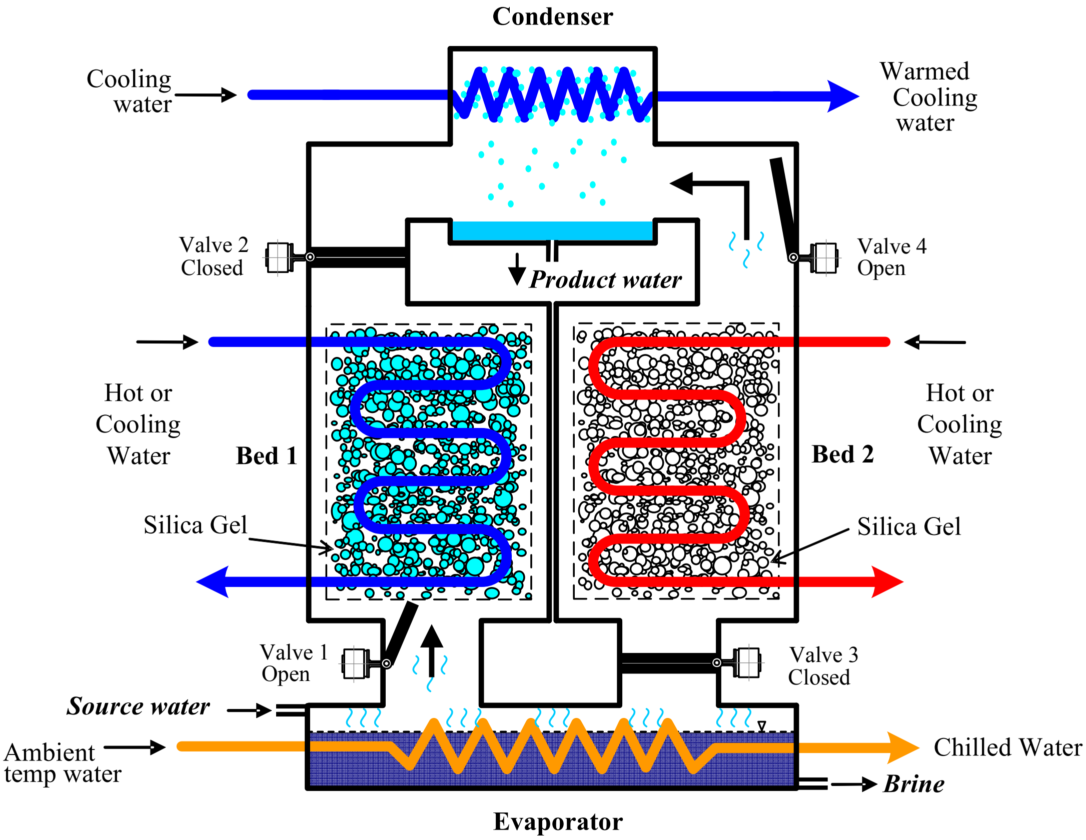

Fig. 1.1. Schematic of a two-bed adsorption desalination system. Refer to text for a description of its operation.

Despite many considerable advantages of Adsorption-based desalination as discussed in Abstract, it has received very little attention in the literature. Extensive studies (for both experimental and simulation studies) have only been carried out in the field of adsorption chilling, which can be viewed as the origins of AD. The modeling work of adsorption chilling can be classified into two main categories: lumped models where transport phenomena are ignored or, at the very least, not modelled explicitly, and models that include spatial gradients and transport processes that arise from these (Yong and Sumathy, 2002). The former (Passos et al., 1989, Cho and Kim, 1992, Chua et al., 1999, Wang et al., 2005, Wang and Chua, 2007) do not allow for non-isothermal beds, an omission that is questionable given the relatively low thermal conductivity of typical adsorbents as well as the non-uniform concentration profiles that will arise from such non-isothermality. An example of the second group of models is that due to Chua *et al.* (Chua et al., 2004), who modelled the adsorption chiller cycle using a simplified 3-D distributed-parameter approach. This model was validated against experimental data but the temperature distributions in the sorbent bed were not presented. Luo and Tondeur (2000) did present temperature profiles obtained using an experimentally-validated 1-D model, but did not consider continuous operation and, hence, the effect of cycle time on performance. A small number of groups (1987, Maggio et al., 2006, Niazmand and Dabzadeh, 2012) have used experimentally-validated 2-D models involving both heat and mass transfer to determine detailed temperature distributions in the sorbent bed but, once again, did not consider the effect of cycle time on performance. Amar *et al.* (1996) used a 2-D model to study the effect of cycle time on the coefficient of performance (COP), but their model was not experimentally validated; they also did not provide or discuss the temperature distribution in the beds despite solving the non-isothermal problem. Finally, Zhang (2000) has used an experimentally-validated 3-D model for an adsorption cycle; however only mean bed and outlet water temperatures were presented and discussed in the paper.

Although the working principle and operation scheme of adsorption chiller and AD plant are similar, the focus for these two field are very different: in the former, the system coefficient of performance (COP) and cooling load are the focus, whereas in AD the fresh water production rate and system energy consumption are the main parameters of interest. To date, for AD, only Ng and co-workers (Wang and Ng, 2005, Ng et al., 2006, Chakraborty et al., 2007, Ng et al., 2008, Thu et al., 2011, Chakraborty et al., 2012, Thu et al., 2013a, Ng et al., 2013) have investigated the performance of AD both experimentally and theoretically. However, their modelling work and performance analysis of AD are restricted to the cooling associated thermodynamic cycle only, and none of them offered up any insight into the underlying origins of the optimum cycle time with respect to the specific daily water production (SDWP). Therefore, given how established existing desalination technologies are, take-up of AD is unlikely until we have a far greater understanding of the effect of process parameters on the productivity of AD – the work reported here addresses directly this need. This thesis reports a detailed study of the impact of operational and design parameters such as operating heating and cooling water temperatures and cycle times on the nature of the thermodynamic cycles of AD and its performance in terms of, for example, system water productivity and specific energy consumptions. This aim is achieved by using a range of novel models validated by experimental data also obtained as part of the research.

1.2 Aim and Objectives

The aim of the research reported here was to investigate the impact of operational and design parameters on the performance of adsorption-based desalination (AD) and draw conclusions on its economic viability. This aim was achieved by meeting the following objectives:

1. develop a validated thermodynamic cycle model that allows rapid estimation of AD performance as a function of the process temperatures and silica gel material parameters;
2. develop a validated dynamic model that allows prediction of AD performance as a function of process conditions, including cycle times; and
3. use of the models developed above to elucidate the effect of process parameters on the performance of AD and draw conclusions on the range of conditions where AD is likely to be economically viable.

1.3 Details of the Publications

Up to now, the outcomes of the study have been reported in the form of 4 published and one submitted journal papers. In addition, 2 peer reviewed conference papers have also been published. In this section, the aims and objectives of each individual journal paper and how they link together with the global objectives of this thesis are described.

The current research is divided into four main stages: *1. Static model development and detailed thermodynamic analysis for the performance of AD* (for objectives 1 and 3), *2. Possible thermodynamic cycles of AD identification and comparison* (for objective 3), *3. Static model validation and possible AD cycles implementation* (for objectives 1 and 3), and *4. Dynamic model development and validation of AD* (for objectives 2 and 3). The papers included in this thesis (in publication format) have been chosen to best describe the progression of the research, which includes both static and dynamic model development of AD, experimental validations of the developed models and the elucidation of the effect of process parameters on the performance of AD using validated models. In addition, summaries of the aims and approach for each article are provided below.

1.3.1 Static model development and detailed thermodynamic analysis for the performance of AD (Ch. 3-4)

Ch.3 Thermodynamic analysis of an adsorption-based desalination cycle

(Published in *Chemical Engineering Research and Design-Official Journal of the European Federation of Chemical Engineering: Part A*, Vol. 88, pp. 1541-1547, 2010)

The aim of this paper was to study the factors that influence the performance of AD using a thermodynamic model. This aim was achieved by meeting the following objectives:

- to develop a thermodynamic model to estimate the fresh water productivity and specific energy consumption as a function of the silica gel characteristics and thermodynamic parameters of the AD cycle,
- to elucidate the effect of operational thermodynamic and silica gel material parameters on the performance of AD.

Ch.4 Thermodynamic analysis of an adsorption-based desalination cycle (part II): Effect of evaporator temperature on performance

(Published in *Chemical Engineering Research and Design-Official Journal of the European Federation of Chemical Engineering: Part A,* Vol. 89, pp. 2168-2175, 2011)

The aim of this paper was to investigate the effect of evaporator temperature (relative to cooling water temperature) on performance of AD in detail. This aim was achieved by meeting the following objectives:

- to investigate the significant effect of evaporator temperature (relative to cooling water temperature) on the nature of the cycles (and consequently on performance) of AD,
- to elucidate the impact of cooling water temperature on performance when evaporator temperature relative to the cooling water temperature is fixed,
- to investigate the relationship between adsorbent (silica gel) capacity, evaporator temperature, system water productivity and specific energy consumption.

1.3.2 Possible thermodynamic cycles of AD identification and comparison (Ch. 5)

Ch.5 Thermodynamic cycles of adsorption desalination system
(Published in *Applied Energy*, Vol. 90, pp. 316-322, 2012)

The aim of this paper was to enumerate all possible thermodynamic cycles of AD, analyse and compare their relative performance. This aim was achieved by meeting the following objectives:

- to enumerate all possible thermodynamic cycles of AD at various operational and design conditions and describe their operational processes in details,
- to determine and compare the relative performance of various types of AD cycles in terms of specific energy consumption and fresh water productivity using mathematical model.

1.3.3 Static model validation and possible AD cycles implementation (Ch. 6)

Ch.6 Experimental implementation and validation of thermodynamic cycles of adsorption-based desalination
(Published in *Applied Energy*, Vol. 98, pp. 190-197, 2012)

The aim of this paper was to experimentally validate the developed thermodynamic model and implement the proposed AD cycles. This aim was achieved by meeting the following objectives:

- to design the experiment and build the experimental rig,
- to experimentally validate the proposed thermodynamic/ static model of AD,
- to experimentally implement the proposed thermodynamic cycles of AD.

1.3.4 Dynamic model development and validation of AD (Ch. 7)

Ch.7 Dynamic Model for the Optimisation of Adsorption-based Desalination Processes
(Submitted to *Chemical Engineering Science*, 2012)

The aim of this paper was to develop a validated dynamic model that allows prediction of AD performance as a function of process conditions, including cycle times. This aim was achieved by meeting the following objectives:

- to develop a one-dimensional multi-cycled dynamic mathematical model, which incorporates transient mass and heat transfer processes in the stream-wise direction of the silica gel bed,
- to experimentally validate the dynamic model of AD,
- to determine the temperature distribution and water uptake profiles in the adsorbent bed through time using validated model,
- to determine the optimum cycle time (for achieving the maximum water production over a day) for the given AD system under the given operational conditions.

CHAPTER 2: BACKGROUND AND LITERATURE REVIEW

2.1 Introduction

The purpose of this chapter is to provide a general overview into issues relating to Adsorption desalination (AD) to identify the gaps in the knowledge. More detailed investigations into specific area of AD are contained in the introduction section of each of the journal publications and submitted articles that make up the subsequent chapters.

Firstly, this chapter gives brief descriptions on the working principle of other commercialized traditional desalination technologies, such as Multi- stage flash distillation (MSF), Multi-effect evaporation (MEE) and Reverse Osmosis (RO) desalination, followed by an energy cost comparison between adsorption desalination (AD) and these well established desalination technologies. This section is used to provide an overview of existing desalination technologies in the field and how AD can be taken up with its unique advantages.

Secondly, the current research status of AD is described, which listed what have been done in the field to locate the gaps in the knowledge. Also, the research focus and progress of related research groups in the world are introduced.

As adsorption plays important role in AD system, detailed understanding and studies on adsorption mechanism is needed. The next section in this chapter provides the fundamental and background overview of adsorption, including the essential sectors related to adsorption (i.e. adsorption isotherms and heat of adsorption), the history of adsorption science, and various types of adsorption models (e.g. surface adsorption models, micropore adsorption models). In addition, the selection procedures on the adsorbent and the adsorbent and adsorbate working pairs in AD are discussed in detail in this chapter.

Finally, as the transport process is the essence to describe the mass flow of the vapour in AD and it is closely related to the key operational parameter, e.g. AD operating cycle times, the mass transfer models in fixed adsorption bed, including the commonly employed LDF models are reviewed in this chapter.

2.2 Other desalination methods and their energy cost compared with AD

The innovation of desalination technology may bring the mechanical field forward to new engineering revolution since fresh water shortage is now become the second largest environmental problem in the world. In the past many desalination techniques have been researched with varying degrees of success, there are several ways in which desalination – which is defined as separation of excess salt and other minerals from water molecules – is carried out, including multi-effect, multi-stage flash and membrane-based reverse osmosis (RO) desalination, which are all exploited commercially (Bruggen and Vandecasteele, 2002a). Electro-dialysis (ED) or electro-dialysis reversal (EDR) is considered one of the most promising new in desalination techniques (Hummel, 2001). Being understood and comparing of similar/ existing technologies helps me further design the improved AD project, the following paragraphs in this chapter are going to discuss them in details. There are two main categories of water desalination methods commercially available, they are: thermal distillation and membrane process.

2.2.1 Multi-stage flash distillation (MSF)

Multi-stage flash distillation (MSF) is one of the thermal distillation processes that continues to play a major role in the desalination industry with a market share that has largely remained close to 60% (El-Dessouky et al., 1999) despite many alternative technologies being developed in recent years. MSF distils sea water by flashing it through different chambers in multiple stages, shown in Fig. 2.1. The cold seawater is delivered through a bank of tubes, which plays the role of cooling agent to extract the condensing heat from the steam. This pre-warmed seawater is then heated by other heating element (i.e. heating steam in Fig. 2.1) to the boiling temperature (i.e. 112 degrees). Then the heated water is injected to another container (stage) where the surrounding pressure is lower than that in the brine heater. This sudden drop in pressure leads to boiling (of flashing) of the brine. Since it is a factor that only a small amount of the water is converted into steam, the remaining brine will be needed to sent through a series of additional stages to distil the rest of water from it, and each of them processing a lower ambient pressure than the previous stage. Once the steam is generated, it is condensed on tubes of heat exchangers which are located at each stage with new charged cold seawater running through them. The collected droplets from the bank of tubes are distilled water, which will be removed from the tank continuously as the product of this system. Fig. 2.1 shows a completed cycle of the MSF process.

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Fig. 2.1. Multi-stage flash (MSF) distillation process schematic (Veolia, 2012); refer to text for a description of its operation.

The MSF system requires considerable high-quality energy input in the form of, typically, steam to bring the temperature of the source saline water to about 105-112°C (Kahraman and Cengel, 2005). This contrasts with other water desalination processes.

2.2.2 Multi-effect evaporation (MEE)

Multi-effect evaporation (MEE) desalination is also a thermal distillation type process, which uses the heat released from the steam to evaporate the source water (i.e. sea and brackish water). As Fig. 2.2 indicates, the whole system consists of numbers of evaporators, and the source water is boiled in these evaporators in a sequence. By heating up the first evaporator, the produced steam will then heat up the second evaporator while condensing. Since the boiling temperature of water decreases as pressure decreases, if the second evaporator held the lower pressure than the first one, it will also be boiled, which means the steam boiled off in one evaporator is able to be used to heat next. Therefore, numbers of evaporators can be heated and operated continuously with the heat input to the first evaporator. Evaporators may be built with an arbitrarily large number of stages to desalinate water. However, in practical, more than four stages are rarely used due to the relatively high maintenance costs.

Based on the different arrangement and types of the feed pre-heater, the MEE process can be separated into many configurations (Nafey et al., 2006). The purpose of having these different configurations is to reduce the energy consumption cost by increasing the steam heat transfer efficiency.

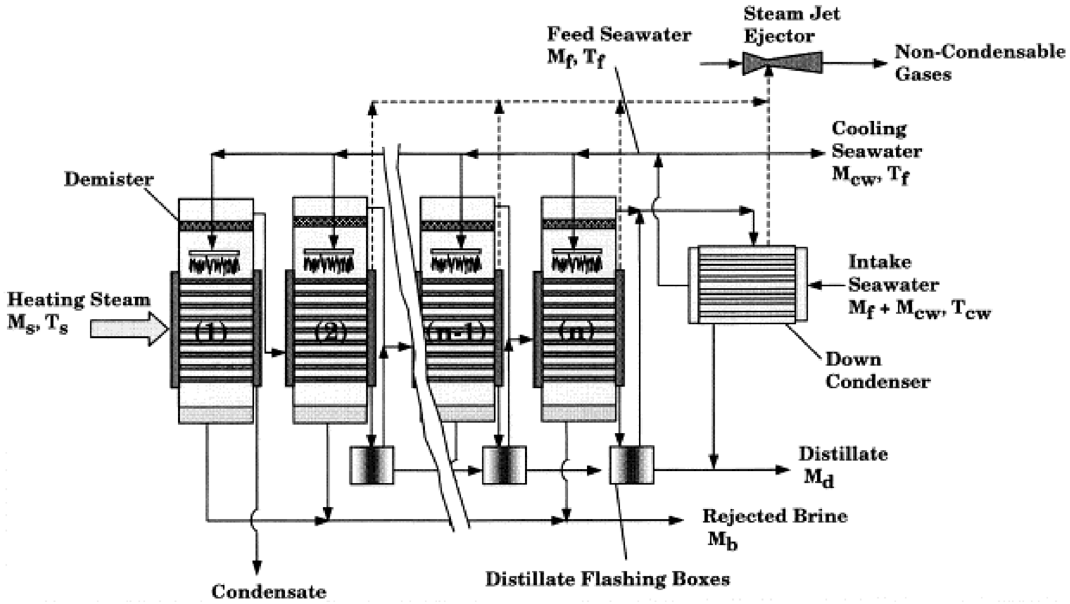


Fig. 2.2. Schematic of four- effects parallel feed multiple evaporation system (El-Dessouky et al., 2000); refer to text for a description of its operation.

Compared to Adsorption Desalination (AD) system and the Multi Stage Flash (MSF) system, MEE has similar lower energy consumption. However, MEE system has the disadvantage that the capacity is reduced if the boiling point rise is significant. Further more, this system also requires pre-heating of the source water to a relatively high boiling temperature with the specific pressure in order to process the rest of effects, which means a fraction of the heating steam does not accomplish any evaporation in the first effect (Smith, 2002). So that less vapour is generated in this effect (per unit mass of heating steam), which results a decreasing of the overall system performance ratio.

2.2.3 Reverse Osmosis (RO) desalination

Reverse Osmosis (RO) membrane desalination is a typical membrane type desalination process. RO technology has been developed for over 40 years now and its share of the world market has risen from 44% to 80% (Greenlee et al., 2009).

In the RO desalination process, water from a pressurized saline solution is separated from the dissolved salts by flowing through a water-permeable membrane with a hydraulic pressure, which means water flowing through the membrane is encouraged to flow through the membrane by the pressure differential created between the pressurized feed water and product water (Karagiannis and Soldatos, 2008). The remaining feed water continues through the pressurized side of the reactor as brine. No heating or phase change takes place, the major energy requirement coming from the initial pressurization of the feed water. For brackish water desalination, operating pressures range from 250 to 400 psi, and for seawater desalination from 800 to 1000 psi (Greenlee et al., 2009). The feed water is pumped into a closed tank against the membrane to pressurize it in practice. The remaining feed water and brine solution becomes more and more concentrated and this high concentrated water will be withdrawn from the container after the product water passes through the membrane several times. The concentration of dissolved salts in the feed water would continue to increase and requiring more energy inputs to produce the same amount of product water if there is no discharging process (Karagiannis and Soldatos, 2008).

A typical Reverse Osmosis system consists of four major processes. They are: pre-treatment, pressurization, membrane separation and post-treatment stabilization. Fig. 2.3 shows a completed process of a Reverse Osmosis desalination system.

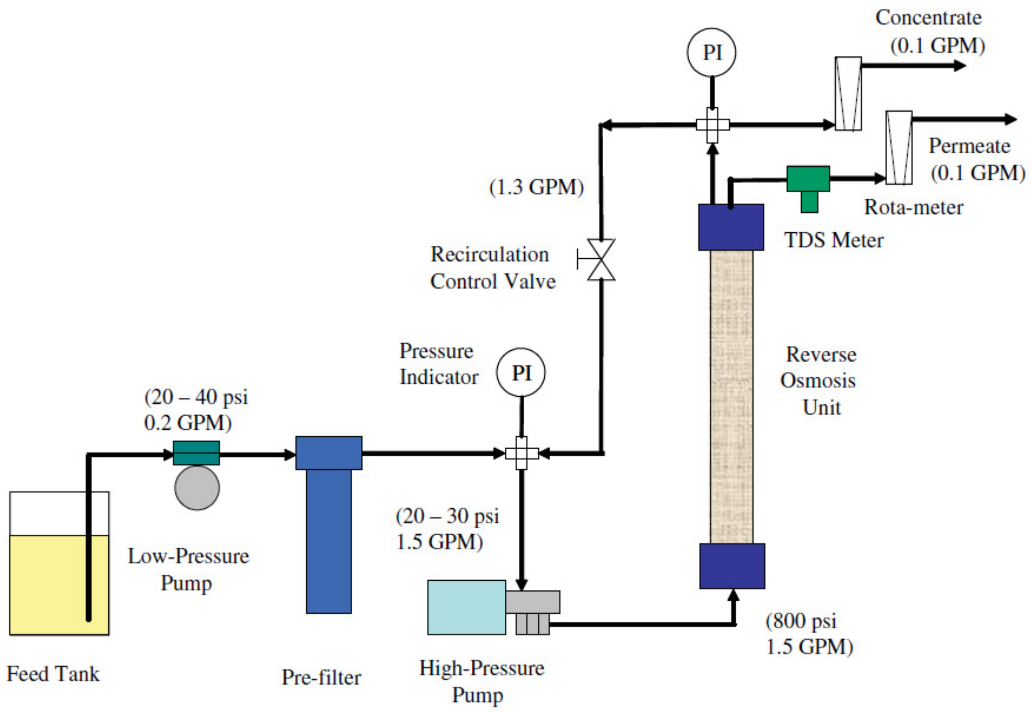


Fig. 2.3. A process schematic of RO system (Diltz et al., 2007)

Compare to other thermal desalination processes, although RO requires less energy to produce fresh water, it requires pre-treatment and post-treatment of the water to maintain its performance. Also, it cannot block bacteria or other particles smaller than the size of the pores (e.g. 0.2-1 nm) in the membrane (Kosutic and Kunst, 2003). For example, if the feed water contains organic compounds the RO membrane will not be able to process it, since the organic compounds pass through the membrane. This is the main reason for most of the applications it requires carbon filters, chemical or UV disinfection and additional micron filters to completely the desalination process.

2.2.4 Energy costs comparison for various methods of desalination

The energy cost of the specific water production has significant influence on the desalination system selection, which is a major factor for the feasibility of installing a new desalination system. Ng et al. (2008) have therefore carried out an energy cost analysis of adsorption desalination (AD) system. The advantage of the AD system becomes apparent while comparing the specific energy consumption, i.e. *SEC* (kWh/m^3), for various commercially available desalination methods, e.g. the multi-stage-flash (MSF), the multi-effect-distillation (MED) and the reverse osmosis (RO). Tab. 2.1 describes the energy cost of water production between the AD system and other conventional methods, such as MSF, MED and RO. According to Ng (2008), In spite of the smaller laboratory scale apparatus, the AD system is found to have the lowest specific energy consumption at about 1.5 KWh/m^3, which is equivalent to US$0.227 per m^3, while the highest production cost is from the MSF at US$0.647 (from Tab. 2.1). It is believed that, a full-scaled (or economy scale) AD plant, the specific energy consumption and energy cost of water of AD system will further be reduced.

Tab.2.1. Energy costs comparison for various desalination methods (Ng et al., 2008)

Method of desalination	Thermal energy consumption KWh/m^3 (A)	Electric energy consumption KWh/m^3 (B)	Primary fuel input KWh/m^3 $C = \left(A/\eta_b + B/\eta_c\right)$	Energy cost of water US\$/m^3. $= \overbrace{5*\left(C*3.6\right)/1055}^{GJ}$
Multi-stage flash (MSF)	19.4	5.2	37.9	0.647
Multi-effect distillation (MED)	16.4	3.8	30.5	0.520
Vapor compression (VC)	-	11.1	29.2	0.497
Reverse osmosis (RO)-single pass	-	8.2	21.5	0.366
Reverse osmosis (RO)-double pass	-	9.0	23.7	0.403
Adsorption desalination (AD)	Free energy from waste heat	1.5	3.9	0.067

The electricity conversion efficiency, η_c, of power plants is 38%, and the efficiency of boiler, η_b, is 80%.

2.3 The state of the art of AD

As it is discussed in the introduction, adsorption desalination method has a number of significant advantages compared with more traditional desalination techniques (Wang and Ng, 2005, El-Sharkawy et al., 2007, Wang et al., 2007), including fewer moving parts, reduced fouling and corrosion, ability to co-generate potable water and cooling, double distillation, low electricity usage, the reduction in global warming due to the utilization of low temperature renewable or waste heat and to treat/desalinate saline water containing organic compounds. Despite these considerable advantages, AD has received very little attention in the literature.

To date, for AD only Ng and co-workers (Wang and Ng, 2005, Wang et al., 2007, Ng et al., 2009, Ng et al., 2012) have investigated in detail the performance of a pilot scale adsorption-based desalination system (mainly in experiment) as a function of system configuration and operating parameters, including a study (Thu et al., 2011) based on an advanced AD cycle with internal heat recovery scheme. Modelling work (lumped model based) and performance analysis of AD are restricted to the cooling associated thermodynamic cycle only. Therefore, the potential thermodynamic cycles of running an AD system were not fully investigated. Further, Thu et al. (2009) have carried out a thermodynamic modelling and performance analysis of an AD cycle, operational parameters simulated including bed temperatures and pressures; optimum cycle time was not model or simulated, instead experimental investigation on the optimal cycle time (on performance - AD water productivity) was performed for a two-bed/four-bed AD system from 65-85 ^{o}C and the operating cycle time was varied between 1240 S and 1960 S. Although the results showed the optimal cycle times could be found in this time range, the feasibility of fully exploration on the optimal cycle times is still restricted by the experimental limitations. Therefore, a dynamic model (on performance - AD water productivity) which accounts for vapour transport process is needed to fully probe the optimal cycle times for an AD bed.

Above mentioned pilot scale AD system is a four-bed (can switch to two-bed operational mode for different applications) silica gel-water adsorption desalination plant located in the laboratory of the National University of Singapore (NUS). Fig. 2.4 shows a pictorial view of the four-bed adsorption desalination plant, which comprises two major facilities, namely (i) the water facility where saline or brackish water is desalinated as fresh water, and (ii) the rating facility that supplies energy to the system by controlling the temperatures of the heat source and cooling water. Fig. 2.5 presents a detailed flow diagram/ schematic of the AD plant. The main difference of the operation scheme between this plant and the four-bed adsorption chiller (Ng et al., 2003) is that the refringent (i.e. after condensed pure water) is removed by a 10 m high liquid filled tubing or a vacuum pump (Wang and Ng, 2005). Wang and Ng (2005) reported that the specific daily water production of the AD plant can be approximately about 4.7 kg/kg of silica gel operating at 12.5 ^{o}C chilled water temperature. El-Sharkawy et al. (2007) also reported that the AD cycle is able to achieve a production of 8.2 m^3 fresh water per tonne of silica gel used per day when the chilled water temperature approaches the ambient temperature. In most recent, Thu et al. (2009) reported that the maximum potable water production per tonne of silica gel per day is about 10 m^3 whilst the corresponding performance ratio is 0.61 with a longer cycle time. NUS has cooperated with Deakin University Australia on developing an AD demonstrator in order to explore and develop this new desalination technique and introduce it to Australia. A two-bed silica gel-water adsorption desalination demonstration plant has been built in later 2008. Fig. 2.6 shows a side view of the AD plant with the main components (i.e. evaporator, adsorber and condenser) showing from the left to the right hand side. Their research is currently in the early stages of development, i.e. the system operation.

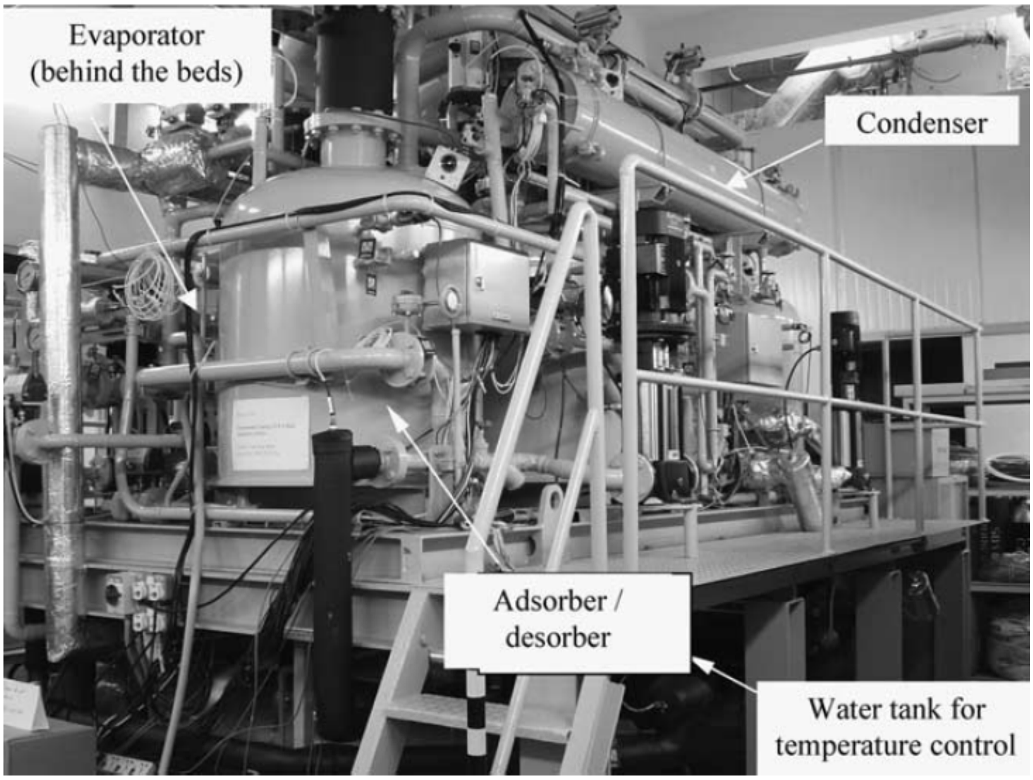


Fig. 2.4. A practical view of the NUS four-bed silica gel-water adsorption desalination plant (Wang and Ng, 2005).

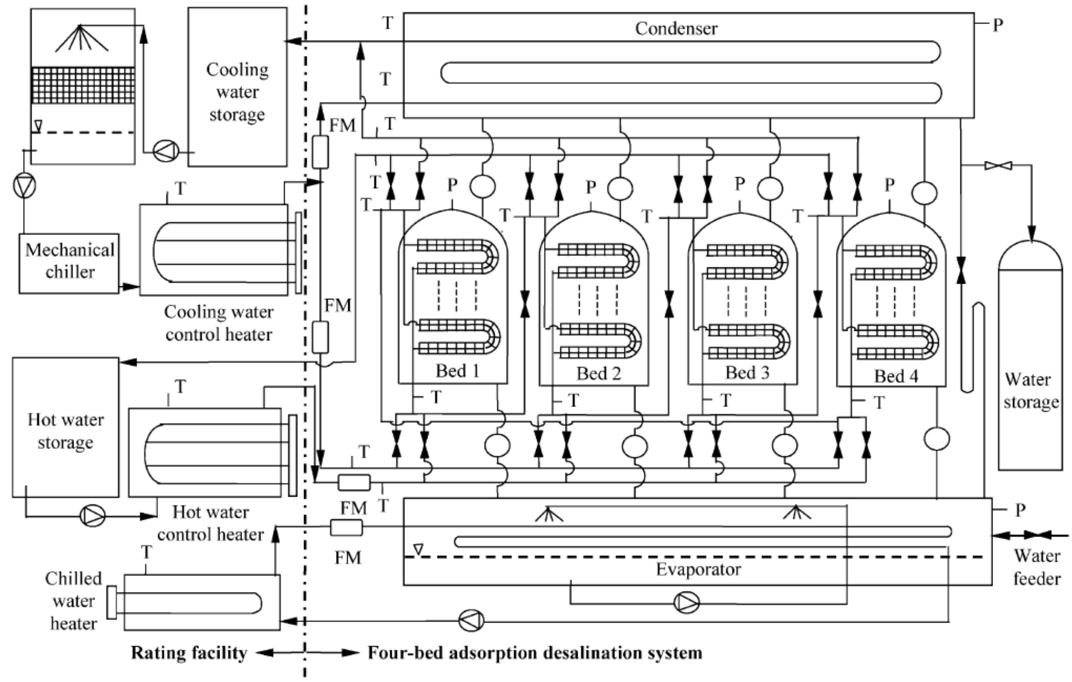


Fig. 2.5. Schematic of the NUS four-bed silica gel-water adsorption desalination plant (Wang and Ng, 2005).

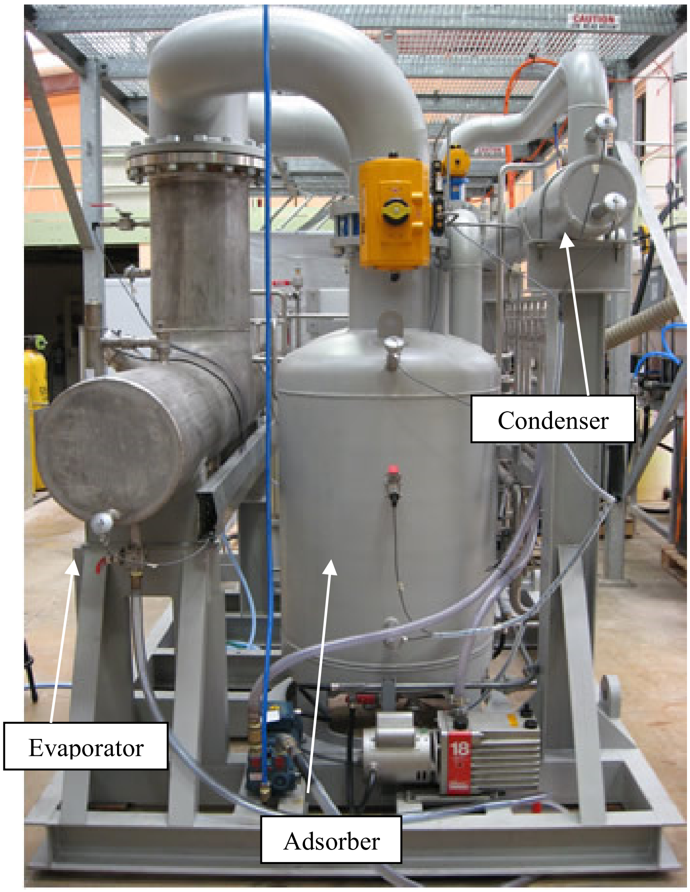


Fig. 2.6. A side view of Deakin University two-bed silica gel-water adsorption desalination demonstration plant.

2.4 Adsorption

In adsorption desalination (AD), instead of using recycled pure water (from the condenser), saline or brackish water is supplied to the evaporator from an external source. The vapour created in the evaporator using low-grade heat (e.g. from the sun or waste process heat) travels into a bed of silica gel where it is adsorbed until the silica is saturated. Once saturated, the bed of silica is heated using, once again, low-grade heat to drive off the now desalinated water before being re-condensed in a receiving vessel (i.e. the condenser). Silica gel in the bed as an adsorbent plays important role in the whole desalination process, which uses to balance the pressure between the evaporator and condenser under heating/cooling and hold up a large amount of water vapour together with its highly surface area. It is believed that the adsorption characteristics of the adsorbent has major effect on the performance of AD and a good understanding of adsorption mechanism is needed to better model the system, therefore an overview of adsorption is given in the following section.

The flow process of adsorption/desorption is illustrated in Fig. 2.7. The basic principle of adsorption is the accumulation of atoms or molecules (termed the adsorptive) on the surface of a material (termed the adsorbent). A film of the adsorbate is formed on the adsorbent's surface (but the pores are also filled at saturation in the adsorption process). This process (for most of the case) is exothermic reversible and it reversed (i.e. the desorption process) by heating (or drawing vacuum or use both).

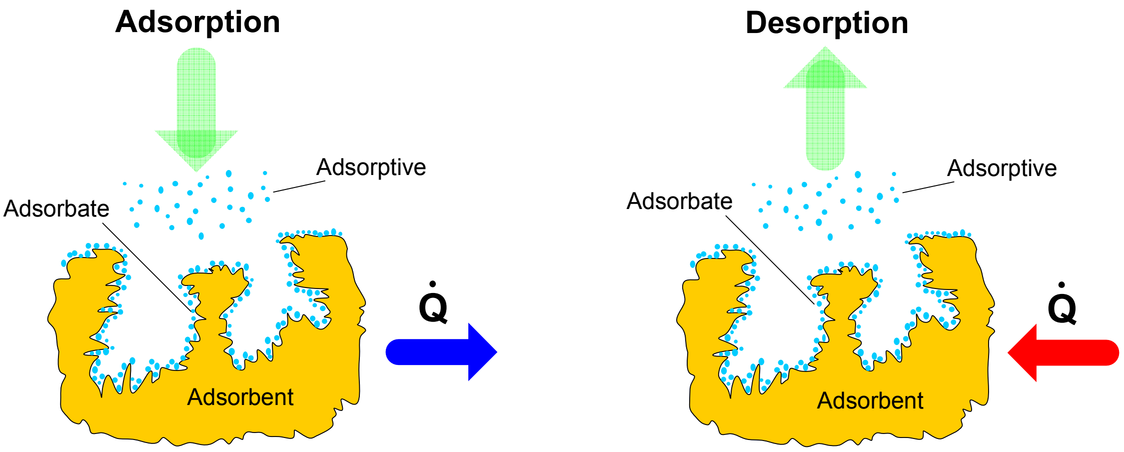


Fig. 2.7. The flow process of adsorption and desorption.

In practical applications, the adsorbent is typically required to have high thermal stability, high abrasion resistance and large surface area per unit volume for high adsorption capacity. Popular adsorbent materials include activated carbon, silica gel, zeolite and activated aluminium. Their surface areas are in the range of 300 to 1000 m^2 per gram and the typical pore size is between 0.5 to 1 nm. The typical shapes of the adsorbents include spherical pellets, rods, monoliths, powdered or granular with diameters 0.5 to 10 mm for different purposes.

The adsorption can be divided into two categories, i.e. physical adsorption and chemical adsorption depending on the nature of attractive forces between the adsorbate and adsorbent (Ruthven, 1984). In physical adsorption (physisorption), Van Der Waals forces (Srivastava and Eames, 1998) provide the linkage of binding adsorbate molecules to the surface of solid-state adsorbent. Since the attractive Van Der Waals forces are weak, the physisorption process can be easily reversed by heating or decreasing the pressure, called desorption. In chemical adsorption (chemisorption), the adsorbate is chemically bound to the adsorbant, leading to forces between the two that are 10-100 times greater than in physisorption (Ruthven, 1984). Such bonds leading to the adsorption, differs from the physical adsorption chemisorption process is normally irreversible, since the chemical properties of both adsorbate and adsorbent are changed during the adsorption process.

2.4.1 Adsorption isotherms

When a pair of adsorbent and adsorbate is getting contact under the certain condition (e.g. temperature and pressure) for a sufficiently long time, they reach equilibrium. The relation between amounts adsorbed, q, at temperature, T, is called the adsorption isotherm at T. Fig. 2.8 shows two typical Toth type adsorption isotherms at T_1 *and* T_2 (where $T_1 < T_2$) for the same adsorbent-adsorbate working pair (e.g. silica gel and water) when saturated (i.e. $q = q_0$ = adsorption capacity). Adsorption isotherms are described in many mathematical forms, some of them are based on physical principles of adsorption and desorption, while others are empirical and intended to correlate the experimental data in simple equations with two or three empirical parameters. More empirical parameters give better fit of the experimental data; however empirical equations only offer a compact way of representing experimental data, which have less practical significance (compared to equations which based on fundamental theories) since they unrelated to physical factors.

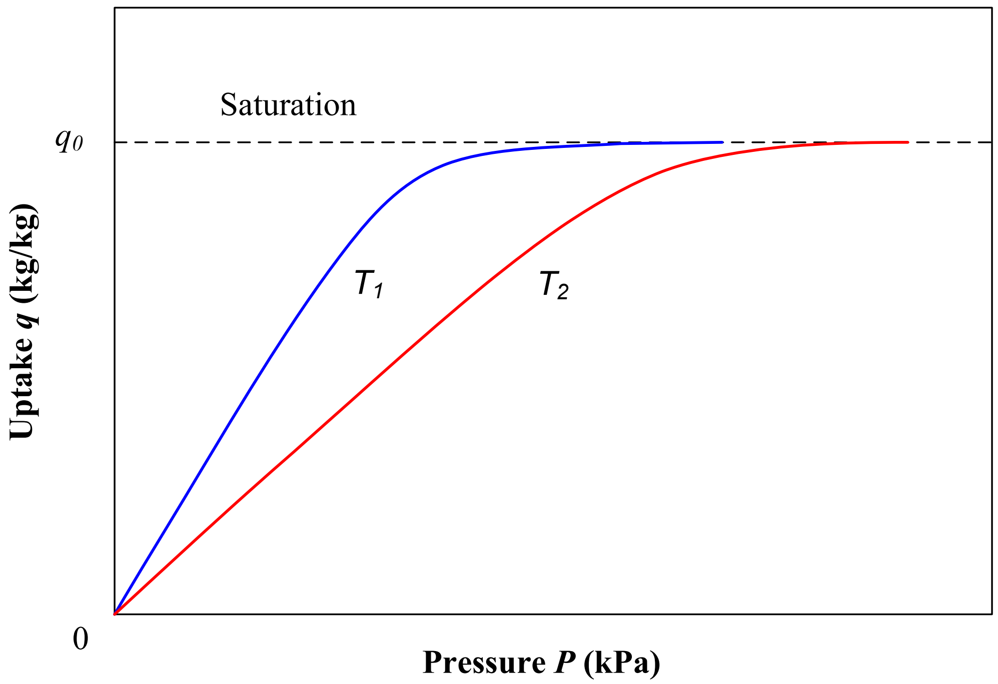


Fig. 2.8. Two typical Toth type adsorption isotherms at T_1 *and* T_2 (where $T_1 < T_2$)

2.4.2 Heat of Adsorption

According to Ross and Olivier (1964), phase change exists during the adsorption, thus it may involve mechanical work. Therefore, the amount of heat evolution by unit adsorption depends on the system adopted. From the engineering point of view, the heat of adsorption is normally defined as 'differential heat of adsorption' with 'isosteric heat of adsorption' (Suzuki, 1990).

Differential heat of adsorption, Q_{diff}, is the heat evolution when unit adsorption process happens in an isolated system, which can be measured directly by calorimeter. Isosteric heat of adsorption, Q_{st}, is defined from isotherms at different temperatures by van't Hoff equation as

$$Q_{st} = RT^2 \left(d \ln P / dT \right) \tag{2-1}$$

Q_{st} can be obtained by experimental isotherms at temperature T_1 and T_2, as

$$Q_{st} = R(\ln P_1 - \ln P_2)/\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{2-2}$$

It also can be expressed as

$$Q_{st} = Q_{diff} + RT \tag{2-3}$$

where R is the gas constant, T is temperature, P is partial pressure, RT is equivalent to the work (i.e. $PV = RT$). For Langmuir and Henry type equations, Q_{st} is related to the equilibrium constant, K, (Ng et al., 2001) as

$$Q_{st} = RT^2(d\ln K/dT) \tag{2-4}$$

where K_0 is the equilibrium constant, and

$$K = K_0 \exp(Q_{st}/RT) \tag{2-5}$$

The heat of adsorption is independent of the amount adsorbed, q, if the adsorption sites are energetically homogeneous and there is no interaction between adsorbed molecules (Suzuki, 1990). However, when interaction among adsorbed molecules cannot be neglected or there is surface coverage on the adsorbent, Q_{st} varies with the surface coverage (Ross and Olivier, 1964). In this case, the heat of adsorption can be described as a function of amount adsorbed q, $Q(q)$. The relationship between $Q(q)$ and the energy distribution, $f(Q)$ can be expressed as

$$f(Q) = q(Q/q_0) \tag{2-6}$$

where $Q(q)$ is converted so that the amount adsorbed, q, is written as an explicit function of Q, $q(Q)$.

2.4.3 History of adsorption science

Researches on the adsorption science have been experienced two main ages, i.e. the pioneering experimental age and the pioneering theoretical age. Before 1956, studies on the adsorption science were mostly experimental based, Fontana (1777) reported some gases adsorption/uptake experiments on charcoal and clays from various sources. De Saussure (1814) discussed systematic studies of adsorption of various gases by porous substances as sear-foam, charcoal, cork and asbestos and discovered the exothermic character of adsorption processes. Kayser (1881) introduced the terms 'adsorption', 'isotherm' and 'isotherm curve' and proposed some basic concepts of monomolecular adsorption theory. In 1903, Tswett used adsorption on silica to separate chlorophyll and other plant pigments from ethanol and, hence, in effect discovered the phenomenon of selective adsorption (Tsweet, 1990). The term of 'absorption' was initially introduced by McBain (1909), to describe a slower hydrogen uptake by carbon than adsorption. He also distinguished the difference between the term of 'sorption' for adsorption and absorption. Barrer and Breck invented the zeolite synthesis method in 1956 (Barrer, 1978). During the same year production of synthetic zeolites at a commercial scale was started by the North American Linde Company (Breck et al., 1956).

Isotherm equations of physical adsorption of gases and vapours provide important characteristics of sorbent, which express how much adsorbate is adsorbed as a function of pressure for a given temperature. Such isotherm equations are derived in closely with the assumptions concerning a physical model of the adsorption system. If this model or hypothesis is approved by repeated experiments, it develops into a theory (Dabrowski, 2001). However, there was no adsorption theory developed before 1914 although many independent adsorption experiments have been performed (Dabrowski, 2001). According to McBain (1932) the Freundlich equation was used; however it was not justified theoretically until 1888 van Bemmelen put it into an empirical equation. The so-called Freundlich adsorption was initially proposed by Boedecker, and is known in literature as the Freundlich's equation when Freundlich assigned great importance to it and popularised its use according to Dabowski (2001). Langmuir (1918) derived for the first time a clear concept of gas adsorption by monolayer, which led to the formulation of a general treatment of reaction kinetics on surfaces. According to Dabrowski (2001), Langmuir was awarded the Nobel Prize in chemistry for this discovery in the realm of surface chemistry in 1932. After six years, Brunauer, Emmett and Teller (BET) proposed the multilayer isotherm equation, which further developed the research of adsorption science (Brunauer et al., 1938). The BET isotherm describes a generalisation of the Langmuir isotherm to multiple layers (Dabrowski, 2001). Dubinin (1960) proposed the theory of volume filling of micropores (TVFM), assumed a distribution of Gaussian type for the characteristic curve and derived Dubinin-Radushkevich (DR) equation. Later this equation was generalized and improved by Dubinin and Astakhov (1970), so-called DA equation. In 1971, Toth modified the Langmuir isotherm by adding two parameters, and introduced the Toth's equation, which provided better fitting of the data on rough surface (Dabrowski, 2001). In conclusion, established isotherm equations in the history of adsorption science can be distinguished into three main categories: 1. the wholly empirical isotherms such as Freundlich isotherm; 2. those based in fundamental theories, e.g. Langmuir, BET and D-R isotherms; and 3. those in the basis of developing these fundamental theories (a mixture area of empirical and theatrical equations), such as Toth and D-A equations, they are commonly employed in today's adsorption research. However, they may have different accuracy when describing a given process.

Nowadays, fundamental studies of adsorption science move to the computer modelling and simulation decade, which relies on the powerful computational methods and complex equipment, e.g. X-ray and neutron diffraction (Goyal et al., 2000). Commercial simulation software with finite elements methods and analytical equations are now used to provide numerical solutions for a range of dynamic problems in sorption process. In addition, molecular Monte Carlo and molecular dynamics simulations create the possibilities to study the interactions between atoms in sorption process, which offers us to understand the adsorption principle from the atomistic level, and may consequently provide predictive guideline in the research of synthetic adsorptive materials.

2.4.4 Surface adsorption

Langmuir isotherm is the simplest model of adsorption on surface, in which localized adsorption takes place on an energetically uniform surface without any interaction between adsorbed molecules (Suzuki, 1990). The equilibration (Langmuir, 1918) of adsorption and desorption rate has the relation as

$$\theta = \frac{Kp}{1+Kp} \tag{2-7}$$

where $\theta(=q/q_0)$ is the surface coverage or fractional filling of the microspore, q (equivalent to X) is the fraction of amount adsorbate adsorbed by the adsorbent at equilibrium condition (kg /kg dry adsorbent), q_0 is the adsorption capacity. p is the partial pressure in the gas phase, and $K = k_a / k_b$ is called the adsorption equilibrium constant (k_a and k_b are the adsorption and desorption constant, respectively).

When the amount adsorbed, q, is far smaller compared with the adsorption capacity, q_0, Eq. (2-7) can be reduced to the Henry type equation as

$$\theta = Kp \tag{2-8}$$

Further, if the concentration is high enough, i.e. $p >> 1/K$, then Eq. (2-7) becomes

$$\theta = 1 \tag{2-9}$$

which means the adsorption sites are saturated.

Another typical adsorption isotherm frequently employed is Freundlich type equation (Freundlich, 1926), which can be expressed as

$$q = k_F C^{(1/nF)} \tag{2-10}$$

Freundlich type equation is normally considered as an empirical equation. It fits well with the experimental data for a limited range of concentrations; however the Freundlich equation does not satisfy the conditions given in Eqs. (2-8) and (2-9), since it provides no limit of adsorption capacity, which resulting the amount adsorbed go to infinity when concentration increase (Suzuki, 1990). Therefore, this equation is only applicable below the saturation concentration.

Another common used expression is the Toth equation (Toth, 1971), which also contains three parameters, and expressed as

$$\theta = q / q_0 = \left[1/(Kp)^t + 1\right]^{-1/t} \tag{2-11}$$

when the parameter, *t*, is unity, this equation is identical to the Langmuir equation. According to Suzuki (1990) the values of parameter, *t*, can be varying between 0-2, however Wang et al., (2004) reported that the values of parameter, *t*, can actually increase to 10. Besides, the Toth equation is useful for correlating isotherm data obtained in both high and low concentrations.

Based on the monolayer adsorption concept proposed by Langmuir, Brunauer, Emmett and Teller (1938) developed multilayer adsorption BET equation as an extension of the Langmuir equation as

$$q / q_m = K_B p_r / \left[(1 - p_r)(1 - p_r + K_B p_r)\right] \tag{2-12}$$

This multilayer adsorption equation is considered to be based on different attractive forces. Where p_r is the relative pressure (= p/p_0), p_0 is the saturation pressure and K_B is the BET constant and q_m is the amount adsorbed by monomolecular coverage on the surface. This equation assumes gas molecules physically adsorb on a solid in layers infinitely and there is no interaction between each adsorption layer, here the Langmuir equation can still be applied on each layer.

2.4.5 Micropore adsorption

Instead of no interaction between adsorbed molecules, the adsorption takes place by attractive force from the wall surrounding the micropores, and the adsorbate molecules fills the micropore volumetrically in micropore adsorption (Suzuki, 1990).

The adsorption equilibrium relation for Micropore adsorption in a given adsorbate-adsorbent combination can be expressed by adsorption potential (Suzuki, 1990) (independent of temperature) as

$$W = q / \rho = W(A) \tag{2-13}$$

where,

$$A = -RT \ln(p / p_0) \tag{2-14}$$

where W is the volume of micropore filled by the adsorbate, ρ is the density of the adsorbed phase and A is the adsorption potential, which is defined as the difference in free energy between the adsorbed phase and the saturated liquid. In which, R is the gas constant, T is the adsorbent temperature and p is the relative pressure.

The Dubinin-Radushkevich (D-R) equation proposed by Dubinin (1960) assumes a distribution of the Gaussian type for the characteristic curve and expressed as following

$$V = V_0 \exp\left[-B\left(\frac{T}{\beta} \ln\left(\frac{p_0}{p} \right) \right)^2 \right] \tag{2-15}$$

where V is the volume filled by adsorbate (m^3/kg adsorbent), V_0 is the limiting pore volume, T is the absolute temperature, B is a function of the microstructure of the adsorbent, β is the DR constant, p_0 is the saturated vapour pressure of adsorbate at temperature and p is the equilibrium pressure. This equation estimates the quantity of the adsorbate that can be adsorbed by the inner micropores of the adsorbent corresponding to the temperature and well separates the property characteristics of the adsorbate and adsorbent.

Later this equation was generalized by Dubinin and Astakhov (1970) to obtain a better fit to experimental data. The equation is expressed as

$$V = V_0 \exp\left[-D\left(\frac{T}{\beta}\ln\left(\frac{p_0}{p}\right)\right)^n \right] \tag{2-16}$$

The parameter *n* in D-A equation improves the fit but it does not necessarily have a direct physical significance, however it was initially considered to have interger value, where *n* = 1, 2 and 3 corresponds to adsorption on the surface, in micropores and ultramicropores (where adsorbed molecules lose one, two or three degrees of freedom) respectively (Suzuki, 1990).

Suzuki and Sakoda (1982) extended the D-A equation to include adsorbent which has apparent micropore size distribution. In this case, they assumed *d/D* is the ratio of molecule size to pore size, and *n* and *E* to be the functions of this ratio, the adsorption isotherm in integral form is expressed as

$$W = \int_0^{\infty} W_0 f(D) \exp\left[-\{A / E(d/D)\}^{n(d/D)}\right] \tag{2-17}$$

where *f(D)* is the density distribution function of micropore size, *n(d/D)* and *E(d/D)* are two functions of *d/D*, *A* is still the adsorption potential.

2.4.6 Selection of adsorption working pair

Adsorption working pairs (e.g. silica gel and water) are the critical component in the adsorption refrigeration system. Based on the working principle of the adsorption refrigeration system, the adsorbent should have large adsorption capacity, good adsorptive sensitivity (i.e. adsorptive capacity difference between ambient temperature and high temperature) on the temperature variation and good compatibility with the common adsorbate. As for the adsorbate/ refrigerant, it requires large latent hear per volume, good thermal stability, non toxicity and non-flammable and etc. Many commonly used physical adsorption working pairs can meet most of these requirements, such as zeolite-water, activated carbon-methanol, activated carbon-ammonia, silica gel-water, calcium-ammonia and composite adsorbent-ammonia. However, as for the purpose of desalination, the refrigerant must be water. Therefore, only the zeolite-water and silica gel-water working pairs will be taken into considerations for the adsorption desalination system.

Comparing zeolite-water and silica gel-water adsorption working pairs, silica gel has incompletely dehydrated polymeric structure of colloidal silicic acid with the pattern of $SiO_2.nH_2O$. The amorphous material consists of spherical particles 2-20 nm in size and sticking together to form the adsorbent silica gel (Unger, 1979). Silica gel exhibits an excellent capacity for adsorption of water up to 35-40% of its dry mass at the chiller operation conditions and have the advantages of exploiting low-temperature heating sources of between $50^{o}C$ and $90^{o}C$ (Ng et al., 2001). However, zeolites are as the synthetic crystalline aluminosilicate which only release water at high temperature, which means higher grade of energy is required to operate the adsorption system compared with silica gel-water working pair. Therefore, silica gel-water working pair is chosen for this study.

2.4.7 Selection of silica gel

As the silica gel is chosen for the adsorbent of the adsorption desalination (AD) system, however there are many different types of silica gel commercially available, and not all of them are good for the AD purpose. For example, silica gel with average pore diameter between 2.0 and 3.0 mm is good as a desiccant packed in a vapour-permeable plastic to control local humidity in order to avoid spoilage or degradation of some goods, but certain pore size silica gel particle is not suitable for the AD purpose. AD system requires the adsorbent silica gel has large adsorption capacity, good thermal conductivity, fast regeneration time and low regeneration temperature. According to Wang et al. (2004), the average pore diameter between 2.0 and 4.0 nm will be suitable for AD purpose as an adsorbent. Therefore, Fuji Davison Type A, Type 3A and Type RD silica gel are short-listed for the selection in this study.

Table 2.2 shows the thermophysical properties of these types of silica gel. As we can see, Type A and Type RD silica gel have many physical similarities, which result in their similar desorption characteristics at different regeneration temperatures. In addition, Type RD silica gel has the highest thermal conductivity, which is one of the advantages while selecting adsorbent for AD purpose.

Tab. 2.2 Thermophysical properties of silica gel (Ng et al., 2001).

	Type A	Type 3A	Type RD
Specific surface area (m^2/g)	650	606	650
Porous volume (ml/g)	0.36	0.45	0.35
Average pore diameter (nm)	2.2	3.0	2.1
Apparent density (kg/ m^3)	730	770	800
pH value	5.0	3.9	4.0
Water content (wt. %)	< 2.0	0.87	-
Specific heat capacity (kJ/kg K)	0.921	0.921	0.921
Thermal conductivity (W/m K)	0.174	0.174	0.198
Mesh size	10-40	60-200	10-20

In terms of the rates of desorption (i.e. drive the water vapour out of the adsorbent), the behaviour is both time and temperature dependent. Ng et al. (2001) performed the silica gel-water adsorption isotherm characteristics experiments incorporated the moisture balance technique with a control-volume-variable-pressure (CVVP) apparatus. Fig. 2.9 shows the percentage desorption achieved at various regeneration temperatures and the percentage desorption achieved with respect to time for Fuji Davison Type A, Type 3A and Type RD silica gel. The results indicate that a 90°C temperature heat source is sufficient to achieve 95% regeneration. As observed in Fig. 2.9(b) for all three types of silica gel. For a regeneration heat source of 140°C, Type 3A silica gel would take 2.5 mins to desorb 95% of its original mass of adsorbate, whilst Type RD and Type A silica gel would take 4 mins and 5 mins, respectively. Here, Type 3A silica gel has the fastest response time, which may due to the larger porous volume.

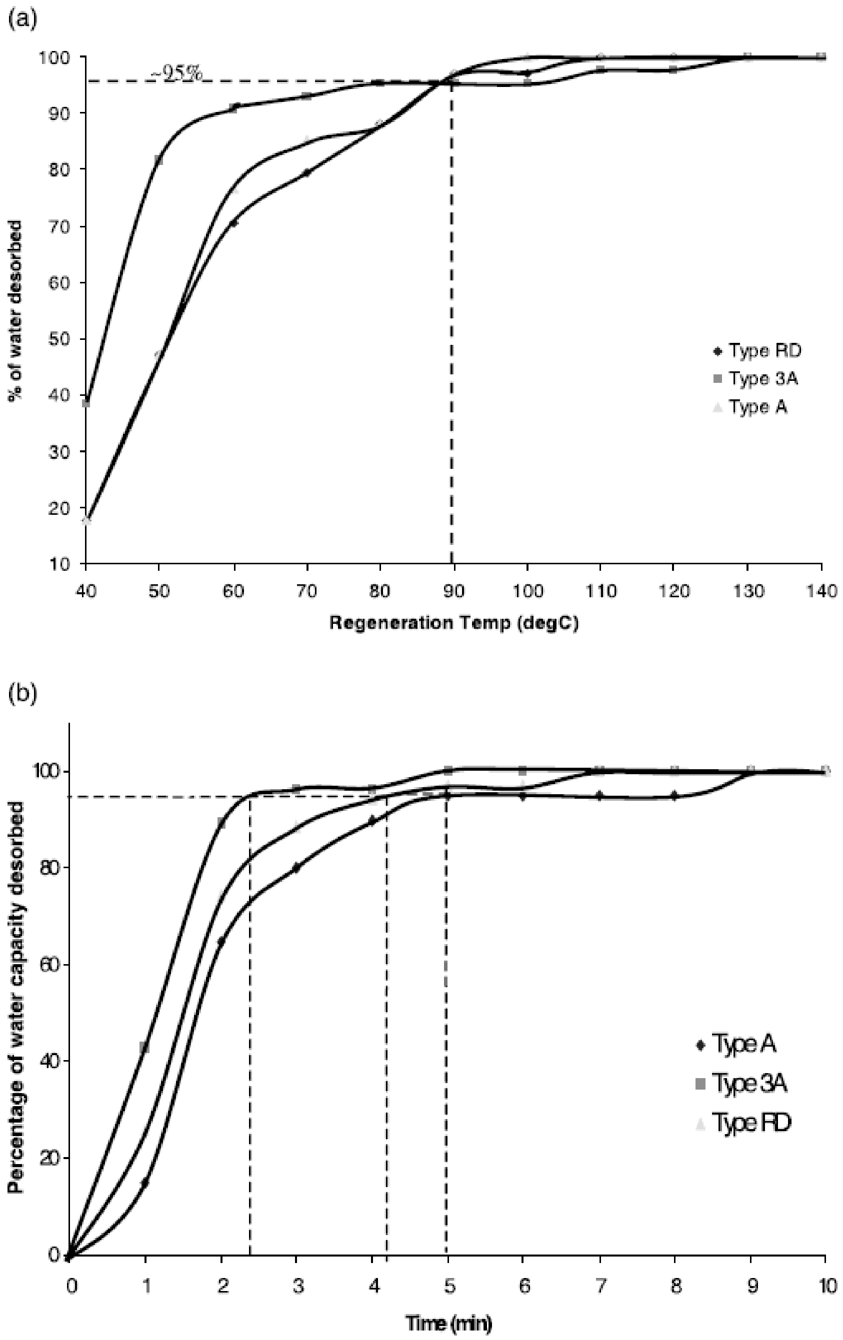
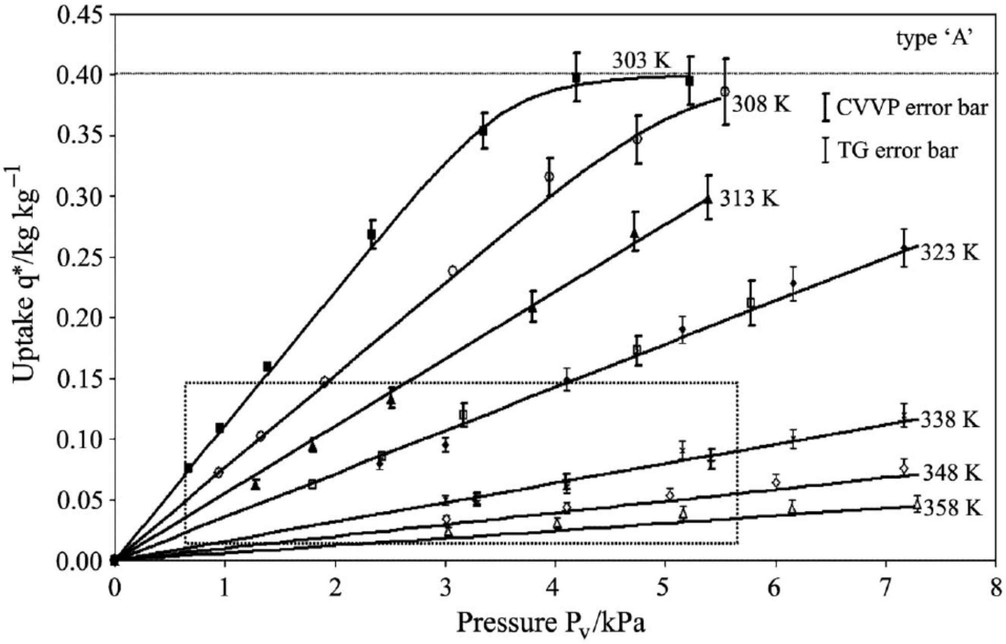


Fig. 2.9. (a) Plot of the percentage desorption achieved at various regeneration temperatures. (b) The plot of the percentage desorption achieved with respect to time. (Ng et al., 2001)

The last adsorbent selection criteria is the water vapour capacity (i.e. uptake), higher water vapour capacity gives higher water productivity in the AD thermodynamic cycle. Wang et al. (2004) measured the adsorption isotherm of water vapour for Type A and Type RD silica gel under a variety of conditions all referring to chiller operation cycles (or AD cycle), i.e. temperatures from 303 to 358 K and pressures from 500 to 7000 Pa, however the isotherm data of Type 3A silica is not available, therefore it is not used for further comparison and abnegated. Fig. 2.10 shows the adsorption isotherm for both Type A and Type RD silica gel, where water vapours capacity (i.e. uptake), q^*, are 0.40 kg/kg and 0.45 kg/kg, respectively. It means that the Type RD silica gel adsorb/desorb more water than Type A silica gel in a thermodynamic cycle as an adsorbent in silica gel + water system.

Therefore, Fuji Type RD silica gel is chosen as the adsorbent for this study, due to the good thermo conductivity, fast response time for the desorption, low regeneration temperature, and large water vapour capacity.



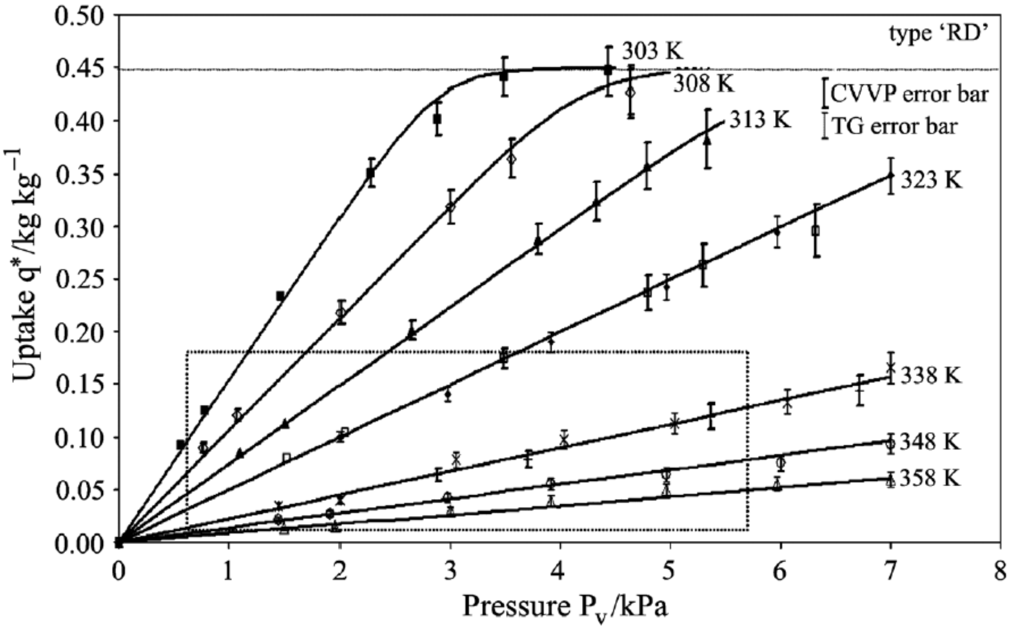


Fig. 2.10. Isotherm data for Type A and Type RD silica gel + water system (Wang et al., 2004).

2.5 Transport process in AD

As discussed in previous chapter, adsorption desalination (AD) is one of the thermal distillation methods, in which the vapour created in the evaporator using low-grade heat travels into a bed of silica gel where it is adsorbed until the silica is saturated. Once saturated, the bed of silica is heated using, once again, low-grade heat to drive off the now desalinated water before being re-condensed in a receiving vessel (i.e. the condenser). The mass transport in the packed adsorption bed plays important role in the whole flow process of AD, where the vapour transfer rate directly links to the water productivity of the system. Therefore, closely looking into the mass transport process of AD is needed to better understand and model the system performance, especially when determining the optimal cycle times of the operation (where the dynamic behaviour of the system needs to be taken into account). This section discuss the mass transfer models which closely related to the AD bed, including a commonly employed LDF (linear driving force) equation, which is believed having relative high accuracy while describing mass transfer process in fixed bed.

2.5.1 Mass transfer models in fixed adsorption bed

Porous solids are widely used in mass transfer operation in fixed adsorption-based bed to allow a large surface area per unit volume for transfer. Figure 2.11 shows a typical fixed bed with its detailed composition (a spherical adsorbent pellet and some cages of the zeolite particle), in which (c) represents zeolite crystals; (d) macro pore; (e) boundary layer and (f) micro pore. To theoretically describe the dynamic mass transfer process in a packed adsorption bed, all models must include following (Weber and Chakravorti, 1974): 1. A mass balance in a fixed bed adsorber; 2. A description of intra-particle (pellet) diffusion process of a single adsorbent to account for the mass transfer resistance within the particle; 3. A coupling equation to describe the mass transfer resistance of the film between the bulk of the fluid and the fluid at the surface of the adsorbent particle (boundary layer). Following equations describe the mass transfer resistance in three difference levels (e.g. external voids, boundary layer and intra-particle) of mass transfer processes as:

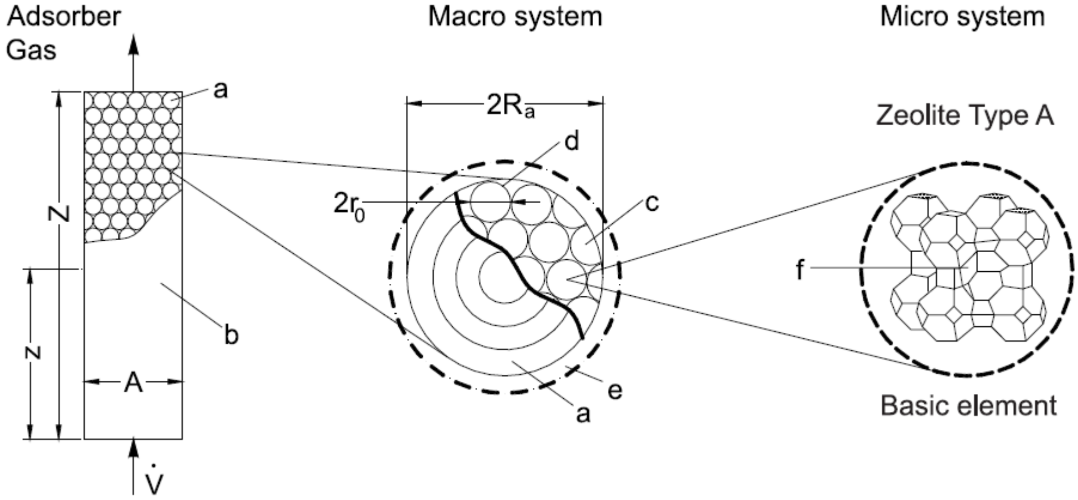


Fig. 2.11. A typical porous catalyst particle (Zeolite) in a fixed bed (*left*: fixed bed, *center*: pellet, *right*: zeolite crystal with some cages) (Mersmann et al., 2011)

1) Mass balance in a fixed bed adsorber (assumed in axial dispersion) (Mersmann et al., 2011):

$$\frac{\partial c}{\partial t}+\frac{1-\psi}{\psi}\rho_p\frac{\partial X}{\partial t}=-\frac{\dot{v}}{\psi}\frac{\partial c}{\partial z}+D_{ax}\frac{\partial^2 c}{\partial z^2} \tag{2-18}$$

2) Mass balance within a pellet using pore diffusion model (Lee and Weber, 1961):

$$\frac{\partial c}{\partial t}+\frac{\rho_p}{\varepsilon}\frac{\partial X}{\partial t}=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{D_m}{\mu_p}\frac{\partial c}{\partial r}\right)+\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\rho_p D_s}{\varepsilon}\frac{\partial X}{\partial r}\right) \tag{2-19}$$

3) Coupling equation between the fluid and the particle surface (boundary layer) (Rosen, 1952):

$$D_s\frac{\partial X}{\partial r}=h(c-q_s/K) \tag{2-20}$$

where c as concentration in the fluid phase and X as the mass loading of the dry adsorbent; ψ denotes the external void fraction; $\dot{v}$ as the fluid velocity; q_s represents the concentration of adsorbate at the surface of a pellet; ε denotes the internal void fraction; r represents the particle radius; D_{ax}, D_s and D_m denote the mass diffusion coefficient in axial direction, at the surface of a pellet and in the pellet, respectively. Integration of these differential equations leads to the description of the concentration profile in the fixed bed and in the pellets.

2.5.2 The LDF model

Use above mentioned particle diffusion models can accurately describe the mass transfer processes in fixed bed (Carta, 1993). However it takes complicated numerical iteration to solve, linear driving force (LDF) model (Gluekauf, 1955) is often used in practice due to its simplicity in solving the model. In LDF model, regardless of the exact nature of the mass diffusion process, mass transfer rates are calculated with an equivalent film resistance model, with an effective rate coefficient determined experimentally to provide an accurate description of the mass diffusion process (Ruthven, 1984, Carta, 1993, Yang, 1987). It should be noted, following assumptions (Mersmann et al., 2011) are made in LFD model as:

- No axial dispersion in a fixed bed ($D_{ax} = 0$).
- The adsorbent pellets are spheres and the local porosities differences in the bed are small.
- Ideal gas law applies.
- The particle diffusion coefficient D_m and tortuosity factor μ are not a function of the pellet radius R.

Based on these assumptions, a very simple linear driving force equation was justified by Glueckauf (1955) to describe the adsorption rate as

$$\frac{\partial X}{\partial t} = \frac{15 D_{eff}}{{R_p}^2}\left(X^* - X\right) \tag{2-21}$$

where R_p as the average particle radius of the silica gel. X^* the mass fraction of water uptake of an adsorbent at equilibrium for a given temperature and bulk phase pressure, X^* (T, P) can expressed by an adsorption isotherm (e.g. Langmuir, D-A or Toth isotherms). D_{eff} is a so-called effective diffusion coefficient, it can be expressed as

$$D_{eff} = \frac{(D_m / \mu_p)}{\left(1 + \frac{\rho_p}{\varepsilon} \frac{\partial X}{\partial c}\right)} \tag{2-22}$$

It should be noted that, this coefficient is not a real diffusion coefficient which related to a characteristic path length of the diffusion units (ions, atoms, molecules and etc.) or to a characteristic velocity (Mersmann et al., 2011). It is an expression comes from the mathematical interoperation based on the Eqs. (2-18) to (2-20) and the assumptions made above.

Depends on the dominant resistance in mass transfer process, LDF model can be further divided into two categories, i.e. LDFC and LDFQ models (Suzuki, 1990). LDFC and LDFQ refer to linear driving force model based on concentration difference and on particle phase concentration difference, respectively. Their mathematical expressions are as

$$\rho_b \frac{\partial X}{\partial t} = K_F a_v \left(C - C^*\right) \tag{2-23}$$

$$\rho_b \frac{\partial X}{\partial t} = K_s a_v \left(X^* - X\right) \tag{2-24}$$

where C^* is an equilibrium concentration with X; Ka refers to overall mass transfer coefficient. Eq. (2-23) is suitable cases where fluid-to-particle mass transfer is a dominant mass transfer resistance, and Eq.(2-24) gives better approximation when intra-particle diffusion plays a major role in mass transfer process (Suzuki, 1990). LDFC and LDFQ models become identical when the adsorption isotherm is linear ($X = KC$, by setting $K_s a_v = K_F a_v / K$).

In LDFQ model, when intra-particle diffusion is the only rate controlling step of mass transfer, $K_s a_v$ can be replaced by particle phase mass transfer coefficient, $k_s a_v$. Depends on the dominant mechanism of intra-particle diffusion, $k_s a_v$ can be expressed in two difference forms (Suzuki, 1990) as

$$k_F a_v = \rho_b 15\phi_s D_s / R^2 \tag{2-25}$$

$$k_F a_v = \frac{\rho_b 15\phi_s D_p / R^2}{X_0 / C_0} \tag{2-26}$$

where Eq. (2-25) should be used when surface diffusion kinetics are controlling; Eq. (2-26) is for the case when pore diffusion kinetics are controlling.

2.6 Summary of gaps

This section provides a summary of research gaps of Adsorption Desalination (AD) that have been identified through the literature.

Despite the many advantages of AD, it has received remarkably little attention by researchers. As discussed in chapter 2.3, to date, only a few papers have been published on adsorption-based desalination. Much of this is by the group of KC Ng at the National University of Singapore (NUS), who have investigated AD experimentally off the back of their long-standing interest in adsorption chillers. Only a few researches which specifically focused on the silica gel AD and most of models/plants are initially designed for chilling purpose only. Although the heat and mass transfer phenomenon in fixed bed has been extensively studied, there is hardly any the modelling work related to AD system, which limits the capacity to thoroughly explore the operational envelope of the process of AD, and this makes AD is unlikely to be taken (given how established existing desalination technologies are) until we have a far greater understanding of the effect of process parameters on the productivity of AD – the work therefore reported here addresses directly this need and the research gaps are summarized as follows:

1. Existing modelling work (lumped model based) and performance analysis of AD are restricted to the cooling associated thermodynamic cycle only. The detailed design and operational processes of AD regarding to all possible thermodynamic cycles are not clear, which results in an insufficient understanding on the operational envelop of the process of AD and an under-prediction on the AD performance (i.e. system water productivity and specific energy consumptions).

2. The parametric analysis (such as operating heating and cooling water temperatures and cycle times) on the performance of AD is lack, which can be fully probed by developing experimentally validated static and dynamic simulation models of AD.

3. The optimum cycle times of AD were only determined experimentally, i.e. no modelling work was performed, which limits the feasibility of fully exploration on the AD performance. A dynamic model (on performance - AD water productivity) which accounts for dynamic vapour transport process is needed to fully probe the optimal cycle times for an AD bed.

CHAPTER 3: THERMODYNAMIC ANALYSIS OF AN ADSORPTION-BASED DESALINATION CYCLE

Statement of Authorship

Thermodynamic Analysis of an Adsorption-based Desalination Cycle.

Published in *Chemical Engineering Research and Design (Official Journal of the European Federation of Chemical Engineering: Part A),* Vol. 88, pp. 1541-1547, 2010.

Wu, J. W. (Candidate)

Developed mathematical models, performed all analysis, interpreted data, and wrote manuscript.

Signed Date 12/10/2012

Biggs, M. J. (Supervisor)

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Signed Date 12/10/2012.

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Supervised development of work, participated in discussion of work, manuscript review and evaluation. Act as corresponding author.

Signed Date 12/10/2012

Wu, J.W., Biggs, M.J. & Hu, E.J. (2010) Thermodynamic analysis of an adsorption-based desalination cycle.
Chemical Engineering Research and Design, v. 88, pp. 1541-1547

CHAPTER 4: THERMODYNAMIC ANALYSIS OF AN ADSORPTION-BASED DESALINATION CYCLE (PART II): EFFECT OF EVAPORATOR TEMPERATURE ON PERFORMANCE

Statement of Authorship

Thermodynamic Analysis of an Adsorption-based Desalination Cycle (part II): Effect of Evaporator Temperature on Performance.

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Wu, J.W., Hu, E.J. & Biggs, M.J. (2011) Thermodynamic analysis of an adsorption-based desalination cycle (part II): Effect of evaporator temperature on performance.
Chemical Engineering Research and Design, v. 89, pp. 2168-2175

CHAPTER 5: THERMODYNAMIC CYCLES OF ADSORPTION DESALINATION SYSTEM

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CHAPTER 6: EXPERIMENTAL IMPLEMENTATION AND VALIDATION OF THERMODYNAMIC CYCLES OF ADSORPTION-BASED DESALINATION

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Wu, J.W., Biggs, M.J., Pendleton, P., Badalyan, A. & Hu, E.J. (2012) Experimental implementation and validation of thermodynamic cycles of adsorption-based desalination.
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CHAPTER 7: DYNAMIC MODEL FOR THE OPTIMISATION OF ADSORPTION-BASED DESALINATION PROCESSES

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Signed Date 12/10/12.

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Dynamic Model for the Optimisation of Adsorption-based Desalination Processes

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Abstract

Climate change is leading to an increasing interest in desalination, particularly methods such as adsorption-based desalination (AD), which uses waste heat to co-generate cooling and fresh water from saline water. In this paper, a one-dimensional dynamic mathematical model of an AD system that incorporates transient mass and heat transfer processes in the stream-wise direction of the adsorbent bed is developed, validated and then demonstrated. The model compares well with both adsorbent temperature distributions and water production profiles obtained experimentally by the authors, with small deviations being linked to a number of assumptions including the omission of sorption hysteresis and multi-dimensional transport effects. The validated model was used to show that the water production rate for a finite operation period varies in a complex monotonic way. It was also demonstrated how the model may be used to identify the optimal cycle time for a finite period of operation, showing that the model provides a good basis for optimising AD-based technology and processes.

Keywords: Desalination; Silica gel; Temperature swing adsorption; Process optimization.

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1. INTRODUCTION

The desalination of saline and brackish water to produce potable water is of increasing concern around the World (Wu et al., 2010). Presently available desalination methods include reverse osmosis (RO), multi-effect distillation (MED), multi-stage flashing (MSF), vapour compression (VC) and electrodialysis (ED) amongst others, where RO and MSF account for over 80% of the large-scale desalination market in the world (Thu et al., 2013a). The considerable energy demands of these various commercial technologies have prompted some to investigate means by which the 'carbon footprint' of desalination can be reduced (Ray, 2010b). Examples include energy recovery measures (Chua et al., 2010, Ammar et al., 2012), waste-heat driven barometric flash-type desalination (Maidment et al., 2007), solar thermal assist membrane distillation (Chen et al., 2012), heat integrated distillation (Jana, 2010) and, of particular interest here, adsorption-based desalination (AD) (Thu et al., 2010, Wu et al., 2010, Wang et al., 2011, Wu et al., 2012b, Wu et al., 2012a, Thu et al., 2013b), which is viewed by some as being potentially one of competitive alternatives from an energy perspective (Ray, 2010a, Ng et al., 2008). For example, a pilot scale four-bed AD system has been demonstrated by Ng and co-workers (Ng et al., 2008, Thu et al., 2009, Ng et al., 2013) to consume around 1.5 kWh/m^3 of water, a figure that is likely to be improved on for larger systems and which is competitive with, for example, typical RO systems which consume 3.7 – 6.7 kWh/m^3 of water, depends on the conditions (Avlonitis et al., 2003). The reason for such low energy consumption of AD is due to the low-grade heat (*e.g.* from the ambient or waste process heat) is used to form water vapour from the saline source, which is considered to be non-payable energy with no cost. The vapour is then passed through a bed of silica into which it adsorbs until the silica is saturated. Once saturated, the bed of silica is heated using further low-grade heat to drive off the now desalinated water before being re-condensed in a receiving vessel. AD has its origins in adsorption chillers (Choudhury et al., 2013, Myat et al., 2013, Al-Alili et al., 2012), which use fresh water as the refrigerant that circulates between an evaporator, sorption beds and condenser. In AD, however, saline water replaces the fresh water and the system switches from a closed cycle to an open cycle in that the saline/brackish water enters the system and the fresh water is recovered.

Adsorption-based desalination has six significant advantages over many of the traditional desalination techniques and other potential alternatives (Wang and Ng, 2005, Ng et al., 2013, Thu et al., 2011, Ng et al., 2006, Chakraborty et al., 2007, Ng et al., 2008, Chakraborty et al., 2012, Thu et al., 2013a): (1) it is driven by low-grade heat; (2) it has far fewer moving parts, leading to reduced maintenance costs; (3) it experiences reduced fouling and corrosion due to the low operating temperatures and confinement of the saline/brackish water to a fraction of the total system; (4) it offers the ability to co-generate cooling along with the potable water; (5) it yields double distillate, minimizing the possibility of so-called '(bio) gen-contamination'; and (6) it offers the ability to treat/desalinate saline and brackish waters containing organic compounds.

Fig. 1 shows a schematic of a two-bed adsorption-based desalinator, which is the most basic model of any practicable production system (*i.e.* one that is capable of producing fresh water on an essentially continuous manner). This system consists of three major components: a condenser, two silica gel beds, and an evaporator. The source saline water is first charged into the evaporator and a vacuum is applied to the entire system. Valve 1 is then opened to allow the source water to evaporate at temperature T_{evap} and travel as a vapour into Bed 1 where it adsorbs on the silica gel. The heat generated during adsorption is removed by cold water circulating at temperature T_{cw} in Bed 1. Once the silica in Bed 1 is saturated with water, Valve 1 is closed. The water circulating through Bed 1 is then switched to hot water at temperature T_{hw} to bring the bed pressure up to the condenser pressure. Valve 2 is then opened whilst circulation of hot water through Bed 1 is continued so as to drive the adsorbed water off the silica (*i.e.* the silica is regenerated) where upon it passes into the condenser to form, finally, pure water at a temperature T_{cond} . Once much if not all the water has been driven off the silica gel, depending on the hot water temperature the silica gel regeneration process stops. Valve 2 is then closed and cold water (at T_{cw}) is circulated through Bed 1 to reduce the bed pressure back to the evaporator pressure. Valve 1 is then opened and the next cycle is ready to start. Pure water is produced, essentially, continuously by the system in Fig 1 by carrying out the above process alternately in Bed 1 and Bed 2.

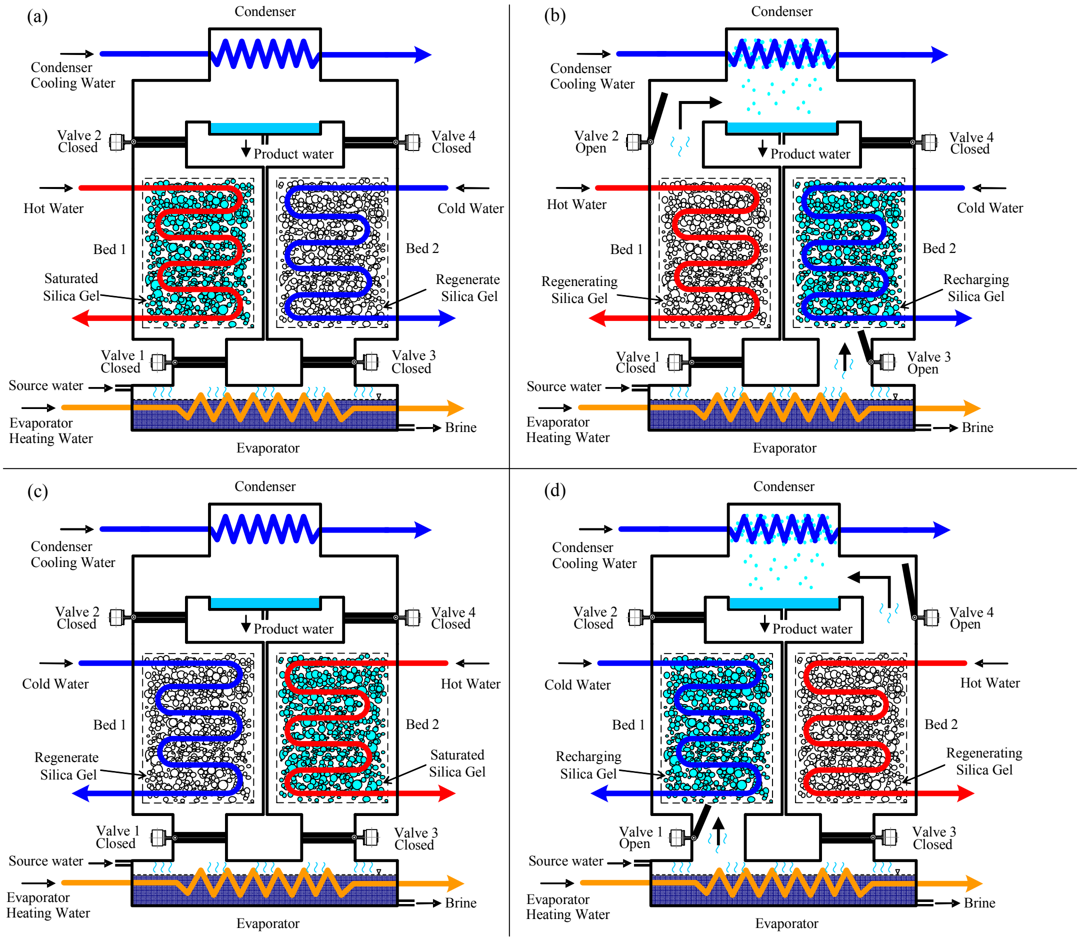

Fig. 1. Schematic of a two-bed adsorption desalination system. (a): Bed 1- Process 1→2 (isosteric heating); Bed 2- Process 3→4 (isosteric cooling); (b): Bed 1- Process 2→3 (isobaric heating/ desorption); Bed 2- Process 4→1 (isobaric cooling/ adsorption); (c): Bed 1- Process 3→4 (isosteric cooling); Bed 2- Process 1→2 (isosteric heating); (d): Bed 1: Process 4→1 (isobaric cooling/ adsorption); Bed 2: Process 2→3 (isobaric heating/ desorption).

Clearly modelling of the AD process such as that described above is of interest. As AD can, at least in part, be viewed akin to adsorption-based chilling, the various models of the latter that have appeared in the literature are relevant here. They can be classified into two main categories: lumped models where transport phenomena are ignored or, at the very least, not modelled explicitly, and models that include spatial gradients and transport processes that arise from these (Yong and Sumathy, 2002). The former (Passos et al., 1989, Cho and Kim, 1992, Chua et al., 1999, Wang et al., 2005, Wang and Chua, 2007) do not allow for non-isothermal beds, an omission that is questionable given the relatively low thermal conductivity of typical adsorbents as well as the non-uniform concentration profiles that will arise from such non-isothermality. An example of the second group of models is that due to Chua *et al.* (Chua et al., 2004), who modelled the adsorption chiller cycle using a simplified 3-D distributed-parameter approach. This model was validated against experimental data but the temperature distributions in the sorbent bed were not presented. Luo and Tondeur (2000) did present temperature profiles obtained using an experimentally-validated 1-D model, but did not consider continuous operation and, hence, the effect of cycle time on performance. A small number of groups (1987, Maggio et al., 2006, Niazmand and Dabzadeh, 2012) have used experimentally-validated 2-D models involving both heat and mass transfer to determine detailed temperature distributions in the sorbent bed but, once again, did not consider the effect of cycle time on performance. Amar *et al.* (Amar et al., 1996) used a 2-D model to study the effect of cycle time on the coefficient of performance (COP), but their model was not experimentally validated; they also did not provide or discuss the temperature distribution in the beds despite solving the non-isothermal problem. Finally, Zhang (Zhang, 2000) has used an experimentally-validated 3-D model for an adsorption cycle; however only mean bed and outlet water temperatures were presented and discussed in the paper.

Although the working principle and operation scheme of adsorption chiller and AD plant are similar, the focus for these two field are very different: in the former, the system coefficient of performance (COP) and cooling load are the focus, whereas in AD the fresh water production rate and system energy consumption are the main parameters of interest. The authors have recently (Wu et al., 2010, Wu et al., 2011) undertaken a detailed study of the performance of AD using an *equilibrium thermodynamic* model. The equilibrium assumption in this model permits rapid calculation and, therefore, consideration of many combinations of system parameters with modest resource. It is recognised, however, that this assumption is a significant one: it prevents consideration of the dynamic behaviour of AD systems, including the effect of cycle time, a key operational parameter, on performance as well as spatial gradients within the system. A number of prior studies (Wang and Ng, 2005, Ng et al., 2013, Thu et al., 2011, Ng et al., 2006, Chakraborty et al., 2007, Ng et al., 2008, Chakraborty et al., 2012, Thu et al., 2013a) have investigated the performance of AD both experimentally and theoretically. Of these, four (Thu et al., 2009, Thu et al., 2011, Thu et al., 2013a, Ng et al., 2013) specifically considered the effect of cycle time on performance of AD to a greater or lesser extent. None, however, offered up any insight into the underlying origins of the optimum cycle time with respect to the specific daily water production (SDWP). In the study reported here, we have addressed this issue through the use of an experimentally-validated dynamic mathematical model of AD that incorporates stream-wise mass and heat transfer within the bed.

2. MODEL DETAILS

2.1 Prototypical AD system considered

The prototypical single-bed AD system illustrated in Fig. 2 is modelled in this paper. The adsorbent bed sits within a cylindrical annulus defined by a thin outer stainless-steel tube of radius R_o and a thin highly perforated stainless steel inner tube of radius R_i that is connected to the evaporator and condenser by Valve 1 and Valve 2 respectively; the inner tube is assumed here to be of negligible thickness and offer no resistance to heat and mass transfer. Mass flow is assumed to occur in the radial direction only (*i.e.* resistance to flow through the bed is assumed much greater than along the inner tube of the annulus). The adsorbent bed is heated and cooled by a water jacket around the outside of the bed.

The ends of the annulus are well insulated so as heat transfer also only occurs in the radial (i.e. streamwise) direction; heat transfer in the circumferential and axial directions are assumed negligible.

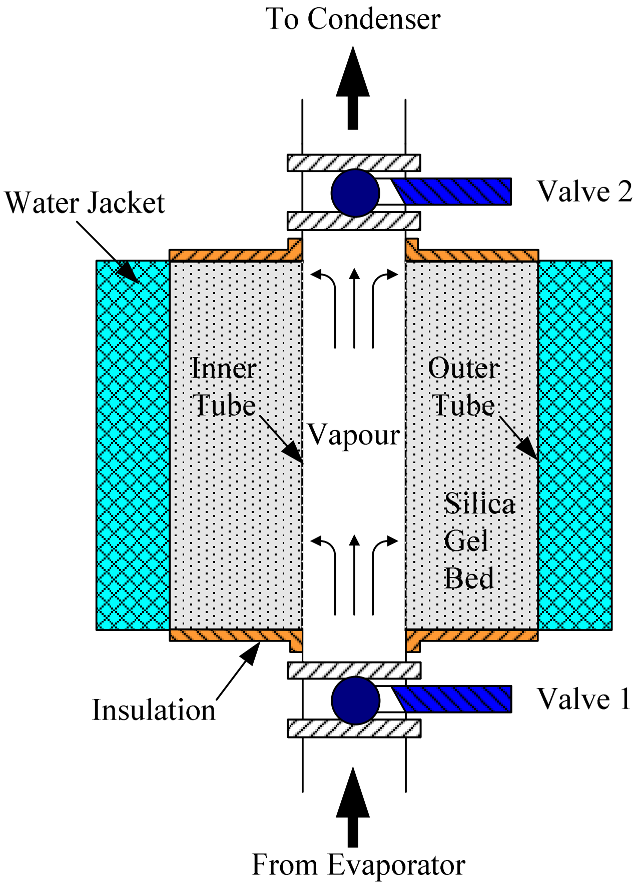

Fig. 2(a). The prototypical single-bed adsorption-based desalination system considered here.

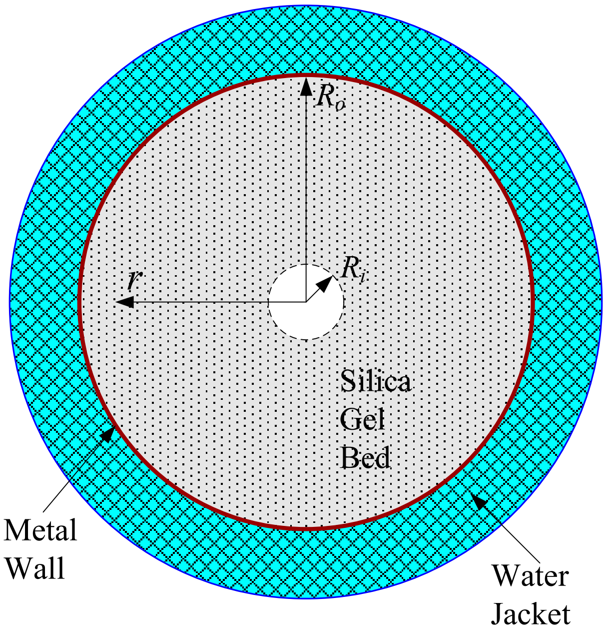

Fig. 2(b). Schematic showing the cross-section of adsorbent bed.

2.2 Operation of the AD system considered

The idealized adsorption-based desalination cycle for a system consisting of the Silica Gel Bed only is shown in Fig. 3. The cycle typically consists of two isosteric processes, 1 → 2 and 3 → 4, and the two isobaric processes, 2 → 3 and 4 → 1. Heating occurs through the process 1 → 2→ 3, whilst cooling occurs over process 3 → 4→ 1.

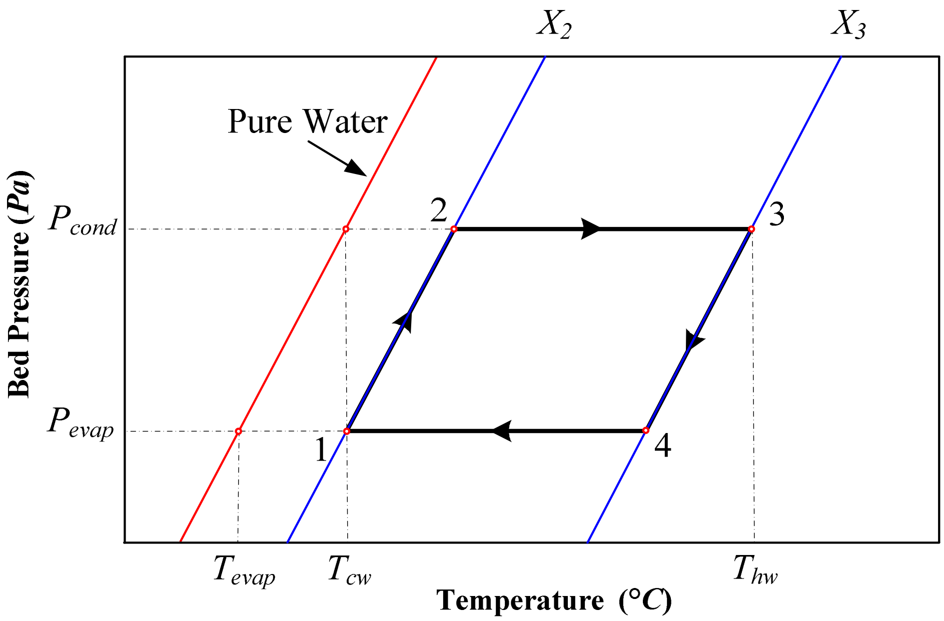

Fig. 3. Idealized working principle diagram of an AD cycle (Wu et al., 2010).

After the source saline water is charged into the Evaporator and a vacuum applied to the system, Valve 1 is opened and the source water evaporates (*e.g.* at $T_{evap} = 7^{\circ}$C) and travels from the Evaporator into the Silica Gel Bed where it is adsorbed (*i.e.* process 4 → 1). The heat liberated during the adsorption process is removed by the cooling water circulating through the Water Jacket. Once the Bed is saturated with water vapour, Valve 1 is closed and Valve 2 is opened after hot water circulating in the Water Jacket heats the bed up to a desired temperature in process 1 → 2. The heat transferred from the hot water drives off the water previously adsorbed on the silica gel where upon it passes out into the Condenser in process 2 → 3 to obtain the pure water as desired. Once the temperature of the Bed peaks, the silica gel regeneration process (i.e. process 2 → 3) ceases and Valve 2 is closed. After cooling water circulating in the Water Jacket reduces the bed temperature and consequently reduces the Bed pressure to that of the evaporator (i.e. process 3 → 4), the cycle is ready to re-start.

2.3 Model assumptions

The following assumptions have been adopted in the model here, which are broadly consistent with the experimental situation used to validate the model here:

a) The vapour phase is an ideal gas.

b) Mass and heat transfer in the axial and circumferential directions of the Bed is negligible; mass transfer only occurs in the radial direction.

c) Intra-particle diffusion dominants over particle boundary layer mass transfer (Suzuki, 1990), with mass transfer from the vapour phase into the particle being described by a linear driving force model.

d) The heat transfer between the vapour phase and the adsorbent particles is rapid (Mahle et al., 1996), allowing both to be assigned a single local temperature (i.e. $T_v=T_{sg}$).

e) The heat transfer between the Water Jacket and the metal wall is rapid (i.e. $T_f=T_m$).

f) All heat transfer from the system other than that into the Water Jacket is negligible.

g) The Water Jacket temperature is constant in the bed heating and cooling processes.

h) Adsorption and desorption of water on the silica gel are identical (i.e. no adsorption hysteresis).

i) The properties of all materials are temperature independent.

2.4 Model

2.4.1 Mass transfer

The overall mass transfer equation in the silica gel bed is described by (Mahle et al., 1996)

$$\varepsilon_t \frac{\partial \rho_v}{\partial t} + (1-\varepsilon_t)\rho_{sg} \frac{\partial X}{\partial t} = -\frac{1}{r}\frac{\partial (r\rho_v u)}{\partial r} \tag{1}$$

where $\varepsilon_t = \varepsilon_{bed} + (1 - \varepsilon_{bed}) \cdot \varepsilon_{pa}$ is the total porosity of the adsorbent bed (ε_{bed} and ε_{pa} are the porosity of the bed voidage and silica, respectively), and ρ_v the density of the vapour, which can be evaluated using the Ideal Gas Law, $\rho_v = \frac{M}{RT_v} P$. The vapour velocity in the packed bed, *u,* is given by Darcy's Law (Taqvi et al., 1997)

$$u = -\frac{K}{\mu} \frac{\partial P}{\partial r} \tag{2}$$

where μ is the vapour viscosity, *P* the pressure, and *K* the permeability of bed of silica gel particles of diameter d_{pa}, which is modelled using the Blake-Kozeny equation (Bird et al., 1960)

$$K = \frac{\varepsilon_t^{\ 3} d_{pa}^{\ \ 2}}{150(1 - \varepsilon_t)^2} \tag{3}$$

So as to reduce the computational cost, intraparticle mass diffusion is not resolved explicitly but, rather, captured *via* adoption of a linear driving force (LDF) model (Gluekauf, 1955). In a LDF model, regardless of the exact nature of the mass diffusion process, mass transfer rates are calculated with an equivalent film resistance model, with an effective rate coefficient determined experimentally to provide an accurate description of the mass diffusion process (Ruthven, 1984, Carta, 1993, Yang, 1987). The LDFQ model of Nakao and Suzuki (Nakao and Suzuki, 1983), which assumes surface diffusion dominates intraparticle mass transport, has been used previously to successfully model mass transport within silica gel and is, therefore, used here. In this model, the rate of water uptake is modelled by (Sakoda and Suzuki, 1984, Suzuki, 1990)

$$\frac{\partial X}{\partial t} = \frac{15 D_{so}}{\left(\frac{1}{2} d_{pa}\right)^2} \exp\left(\frac{-E_a}{RT}\right)\left(X^* - X\right) \tag{4}$$

where D_{so} is the pre-exponent constant, E_a the activation energy of diffusion, and X^* (*T*, *P*) the mass fraction of adsorbed water at equilibrium for a given temperature and bulk phase pressure, which is assumed here to be described by a linear adsorption isotherm (2007, Ng et al., 2001) of the form

$$X^{*} = PK_{0}^{I} \exp\left(\frac{Q_{st}}{RT}\right) \tag{5}$$

where $K_0^{I}=K_0X_0$ with X_0 being the amount of water adsorbed at saturation, and Q_{st} the isosteric heat of adsorption.

2.4.2 Heat transfer

As significant thermal energy is released during water vapour adsorption on silica gel and is also required for regeneration of the gel, its transport through the silica gel bed must also be accounted for. Under the assumptions used here, the expression for heat transfer in the radial direction through the bed is given by

$$(\rho C)_{eq} \frac{\partial T}{\partial t} = k_{eq} \frac{\partial^2 T}{\partial r^2} + \frac{k_{eq}}{r} \cdot \frac{\partial T}{\partial r} + \dot{q} \tag{6}$$

where k_{eq} is the effective thermal conductivity of the bed assembly, $(\rho C)_{eq}$ the effective heat capacity of the bed, and $\dot{q}$ the rate of heat generation due to sorption. The latter can be evaluated by (Chua et al., 2004)

$$\dot{q} = (1-\varepsilon_t) \frac{\partial X}{\partial t} \rho_{sg} Q_{st} \tag{7}$$

The effective total heat capacity on the control volume of the silica gel is equal to mass-weighted average of the heat capacities of the individual components of the bed (e.g. silica gel, adsorbed water and vapour) (Chua et al., 2004)

$$(\rho C)_{eq} = (1-\varepsilon_t)\rho_{sg} C_{sg} + (1-\varepsilon_t) X \rho_{sg} C_w + \varepsilon_t \rho_v C_v \tag{8}$$

2.4.3 Initial and boundary conditions

For the AD process starting at point 1 in Fig. 3, the initial conditions are

$$T\left(t=0,r\right)=T_{cw} \tag{9}$$

$$P(t=0,r)=P_0 \tag{10}$$

$$X\left(t=0,r\right)=X^* \tag{11}$$

The boundary conditions are

$$\left.\frac{\partial P}{\partial r}\right|_{r=R_o}=0 \tag{12}$$

$$P\left(t,r=R_i\right)=P_{cond} \quad \text{when connected to condenser (process 2 → 3)} \tag{13}$$

$$P(t,r=R_i)=P_{evap} \quad \text{when connected to evaporator (process 4 → 1)} \tag{14}$$

$$\left.\frac{\partial T_{sg}}{\partial r}\right|_{r=R_i}=0 \tag{15}$$

$$-k_{sg}\left.\frac{\partial T_{sg}}{\partial r}\right|_{r=R_0}=h_{m,sg}(T_m-T_{sg}) \tag{16}$$

$$T_f=T_{hw} \text{ during the heating phase (process 1 → 2 → 3 in Fig. 3)} \tag{17}$$

$$T_f=T_{cw} \text{ during the cooling phase (process 3 → 4 → 1 in Fig. 3)} \tag{18}$$

2.5 Model solution methodology

The model outlined above was numerically solved using MATLAB. Finite differences were used to solve the differential equation system defined by the coupled equations of (1), (4) and (6). The time derivatives and boundary conditions were discretised using second-order forward difference schemes. The spatial derivatives were discretised using second-order central differences. The Newton-Raphson method associated with a Predictor-Corrector technique (Sagara and Fukushima, 1986, Houwen et al., 1995, Weber and Kuhn, 2007) were then employed to solve the converted set of linear equations.

3. EXPERIMENT

The model described in the previous section was compared against experimental results obtained in the laboratory of the authors. The apparatus and procedure used to obtain the results for validation purposes are described in the following.

3.1 Experiment facility

The AD apparatus used here, which is a modified version of that of Zhao et al. (Zhao et al., 2011), is shown schematically and pictorially in Fig. 4. The main components of the AD apparatus are the adsorbent (silica) bed, condenser and evaporator. Movement of vapour or condensate between them is *via* a stainless steel-316 pipe of internal diameter 15.80 mm and wall thickness 2.77 mm. To prevent excessive condensation in the pipes, a heating element and insulation were applied to the external surfaces of all pipes where possible. Valves V1 and V2 are used to control the flow of the vapour and condensate during the process as described below. To keep the experimental apparatus as simple as possible, it differs from the schematic shown in our previous papers (Wu et al., 2010) in that the condenser lies between the evaporator and adsorbent bed. This means that the functions of the ‘condenser’ and ‘evaporator’ vessels vary depending on the process within the cycle. In particular, when the bed is adsorbing the vaporised water coming out of the evaporator, the ‘condenser’ vessel is simply part of the ‘pipe work’ between the two. Equally, when the fresh water is being recovered in the condenser after being desorbed from the bed, the graduated flask used for the ‘evaporator’ vessel simply acts as a receiver that allows the measurement of the quantity of condensate (i.e. it should be considered as part of the condenser and will be at the same temperature and pressure as the condenser).

The adsorbent bed and condenser are made from corrosion-resistant stainless steel-316 whilst the evaporator consists of a 1000 ml (±0.5% full scale accuracy) graduated glass measuring cylinder (MBL, England). To simplify the system and mass measurements, the evaporator vessel is used to receive under gravity-driven flow the condensate from the condenser during the recovery phase. The temperatures of the evaporator, condenser and adsorbent bed are controlled by pumping water from one of two (A or B) temperature-controlled water baths through jackets that encase each. The flow of the water through these jackets is controlled by the valves WV1-7. The temperatures of the condenser and evaporator are measured using Type-T thermocouples (±0.5°C) attached to the vessel. The pressure in the system tanks is measured with a heat resistant Edwards D395-57 pressure transducer (USA) whose operational temperature ranges is −20 to 125°C with ±0.2% full scale accuracy. A two-stage rotary vane vacuum pump (Edwards RV3, USA) is used for evacuation of the system. The adsorbent bed is composed of 2124.4±0.1 g of dry silica gel (see below for details) packed into the annulus formed by the external surface of the bed (which is in contact with the water jacket used to control its temperature) and a stainless steel-316 mesh tube of 0.16 mm aperture and 20.0 mm diameter; the silica was dried at 140°C for 16 hours prior to use. The temperature in the adsorbent bed is measured at five separate equally spaced radial points using T-type thermocouples placed in contact with the silica gel. A calibrated data logger (DT80 DataTaker; Australia) with 18-bit resolution (0.02% accuracy) is used to record these and other temperatures of the system. In the present experiment facility, the major measurement bottleneck lied in the measurement of the water production, as the human reading error might be involved in reading the glass measuring cylinder.

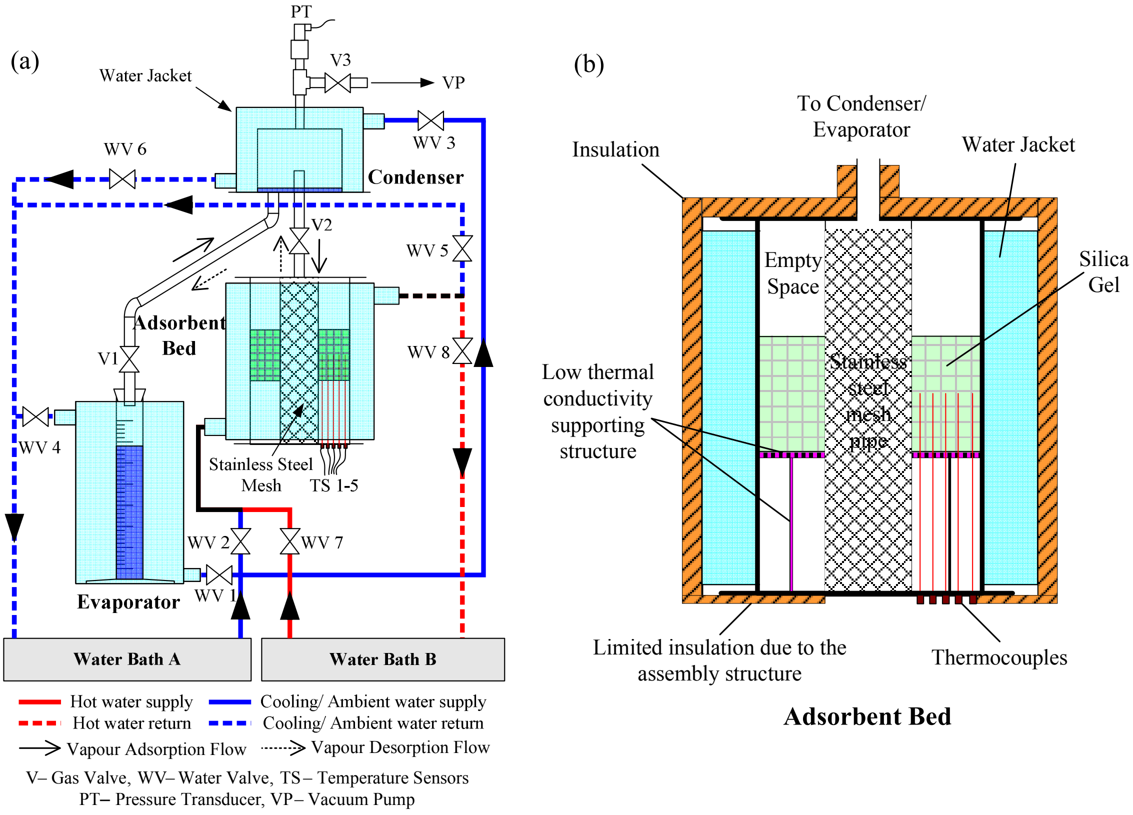

Fig. 4. (a) Schematic of the adsorption-based desalination system used in the work reported here. (b) Close-up view of the adsorbent bed to show better it’s construction.

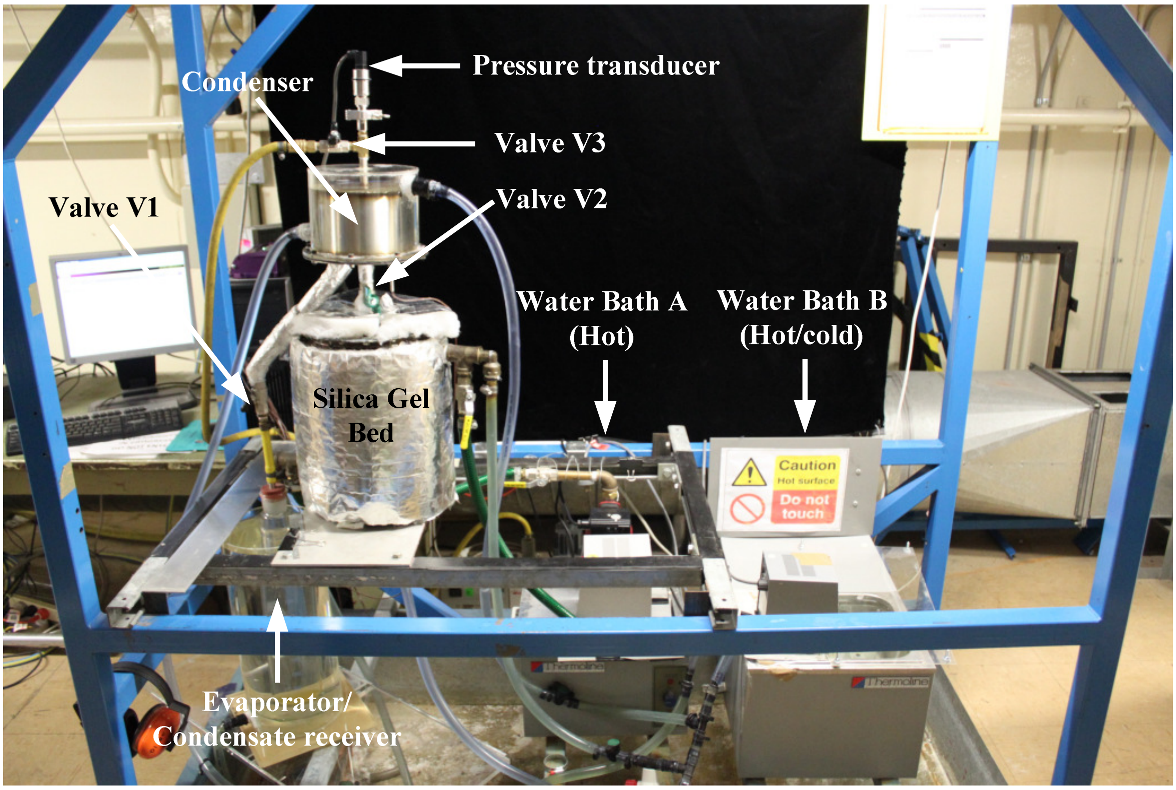

Fig. 4.(c). Photo of the experimental AD apparatus illustrated in Figures 4.(a) and (b).

3.2 Experimental procedures

Prior to the experiments reported here, the whole system was checked for vacuum tightness by ensuring that the system pressure remained constant over 7 days after evacuation. The silica gel sample (2124.4±0. 1 g) was then filled into the adsorbent bed.

Since the fresh water is produced in the isobaric desorption process as described in section 2.2 above, only the heating process (processes 1 → 2→ 3 in Fig. 3 in text) of the AD cycle was considered experimentally here. The detailed procedure for this is:

1. MilliQ deionized water was charged into the evaporator vessel. Valve V2 was closed, and valves V1 and V3 were opened. The water in the evaporator vessel

was degassed by applying a vacuum of 3166 Pa (the saturation vapour pressure at the 25°C room temperature) for at least three hours, allowing some water to boil off to ensure no dissolved air remained in the water. Valves V1 and V3 were then closed and the water level in the evaporator was measured and recorded.

2. The adsorbent bed was dried by opening Valves V2 and V3 and applying a vacuum for 12 hours whilst circulating 90°C hot water through the water jacket around the adsorbent bed. Valves V2 and V3 are were closed at the conclusion of this drying process.

3. Valves V1 and V2 were opened to establish a connection between the adsorbent bed and the evaporator vessel and water was supplied from the water baths to both for 24 hours to ensure their temperature was steady at the desired value (T_{evap} = 13°C and T_{cw} = 20°C here) and the silica gel was fully saturated (i.e. which was established as when the water level in the evaporator ceased to change). This corresponds to point 1 on the cycle diagram shown in Fig. 3.

4. Valve V2 was closed to isolate the silica bed and hot water (at T_{hw} = 80°C) was circulated around the bed, leading to the increase of the pressure in the bed to P_{cond} (i.e. 2337 Pa, the saturated water vapour pressure at 20°C). As the evaporator and condenser are at this point in effect the condensing system, their temperatures also increased to 20°C. This procedure represents the *isosteric process in the heating step*, which leads to point 2 on Fig 3.

5. After $P_{bed} = P_{cond}$, Valve V2 was opened to connect the silica bed to the condenser vessel, whose temperature was maintained at $T_{cond} = T_{cw}$ = 20°C by controlling the surrounding cooling water jacket temperature and flow rate to minimize the pressure fluctuations occurred in condenser vessel (to match the constant pressure assumption). Meanwhile, the silica bed was maintained at T_{hw} = 80°C in order to initiate water desorption. The temperature and pressure in the adsorbent bed and the water level of the evaporator were recorded every 5 seconds and every hour,

respectively during the desorption process. This procedure represents an *isobaric desorption process* at the saturation vapour pressure for 20°C, and it continued until the average temperature of the adsorbent reached 76°C (i.e. 95% of the heat source temperature (80°C), which is typical of that used by others for regeneration of silica gel (Ng et al., 2001)), which corresponds to point 3 on Fig. 3.

4. RESULTS AND DISCUSSIONS

The model parameters used in the study reported here, are listed in Table 1.

Table 1. Model parameters

Property	Symbol	Value	Ref.
Numerical model parameters			
Time step	Δt	0.01 s	-
Number of radial subdivisions (layers)	n	200	-
Thermophysical properties			
Metal wall density	ρ_m	8000 kg/ m^3	-
Water vapour density	ρ_v	0.15 kg/ m^3	-
Silica gel bulk density	ρ_{sg}	2027 kg/ m^3	(Fuji)
Mass of the silica gel	m_{sg}	2.1244 kg	-
Water vapour specific heat	C_v	1.92 kJ/(kg K)	-
Water specific heat	C_w	4.1855 kJ/(kg K)	-
Silica gel specific heat	C_{sg}	0.92 kJ/(kg K)	(Chua et al., 2004)
Effective bed thermal conductivity	k_{eq}	0.175 W/(m K)	(Zhao et al., 2011)
Heat transfer coefficient (metal to silica gel)	$h_{m,sg}$	36 W/(m^2 K)	(Chua et al., 2004)

Silica gel + water system adsorption constant	K_0^I	7.3×10^{-10} Pa^{-1}	(Ng et al., 2001)
Silica gel + water system heat of adsorption	ΔH	2370 kJ/kg	(Ng et al., 2001)
Pre-exponent constant	D_{so}	2.5×10^{-4} m^2/s	(Chua et al., 2004)
Activation energy of diffusion	E_a	4.2×10^{4} J/mol	(Chua et al., 2004)
Adsorber geometry and silica gel bed structural characteristics			
Silica gel inner radius	R_i	0.01 m	-
Silica gel outer radius	R_o	0.11 m	-
Average silica gel particle diameter	d_{pa}	0.5 mm	(Fuji)
Silica gel particle porosity	ε_{pa}	0.43	(Chua et al., 2004)
Bed porosity	ε_{bed}	0.37	(Chua et al., 2004)
Equivalent bed total porosity	ε_t	0.64	(Chua et al., 2004)
Operating conditions			
Metal wall initial temperature	$T_{m,0}$	20 ^{o}C	-
Silica gel initial temperature	T_0	20 ^{o}C	-
Hot water temperature	T_{hw}	80 ^{o}C	-
Cooling water temperature	T_{cw}	20 ^{o}C	-
Adsorber initial pressure	P_0	1000 Pa	-
Evaporator pressure	P_{evap}	1000 Pa	-
Condenser pressure	P_{cond}	2337 Pa	-
Cycle time	T_{cycle}	4000-10^5 s	-

4.1 Model validation

Fig. 5 shows the dynamic temperature distributions of the adsorber during the heating processes 1 → 2 → 3 in Fig. 3, the second part being where the silica gel undergoes drying. The temperatures at three radial locations in the bed are presented: the innermost ‘layer’ of silica gel (*R*=10mm), middle of the bed (*R*=50mm) and the outermost ‘layer’ of silica gel (*R*=100mm). This figure shows that the experimentally observed thermal behaviour of the bed is matched quite well (within 5%) except at early times, where there is some over-prediction at the outer periphery of the bed and some under-prediction elsewhere as better shown in the insert to Fig. 5. The under-prediction seen at short times for R = 10 mm and R = 50 mm is due to the omission of axial heat transfer from the model, which will have occurred to some extent in the experiment from the Water Jacket through the steel ends of the bed and thereafter axially through the packing and, in particular, the perforated steel inner tube of the bed. The slow oscillation in the experimentally observed temperature of the packing adjacent to the perforated steel inner tube of the bed (i.e. at *R*=10 mm) arises from the slow variation of the ambient temperature, which is most felt by the system *via* the bottom end of this tube (see Fig. 4b) over the 3-4 days of the experiment.

The transition from region A to region B in Fig. 5 represents the point where the valve between the previously isolated bed and the condenser is opened. This event sees the water vapour desorbed up to that point leaving the bed in a rush, taking with it significant enthalpy that leads to a lower rate of temperature increase in the bed around this point compared to that predicted by the model, which does not incorporate this effect.

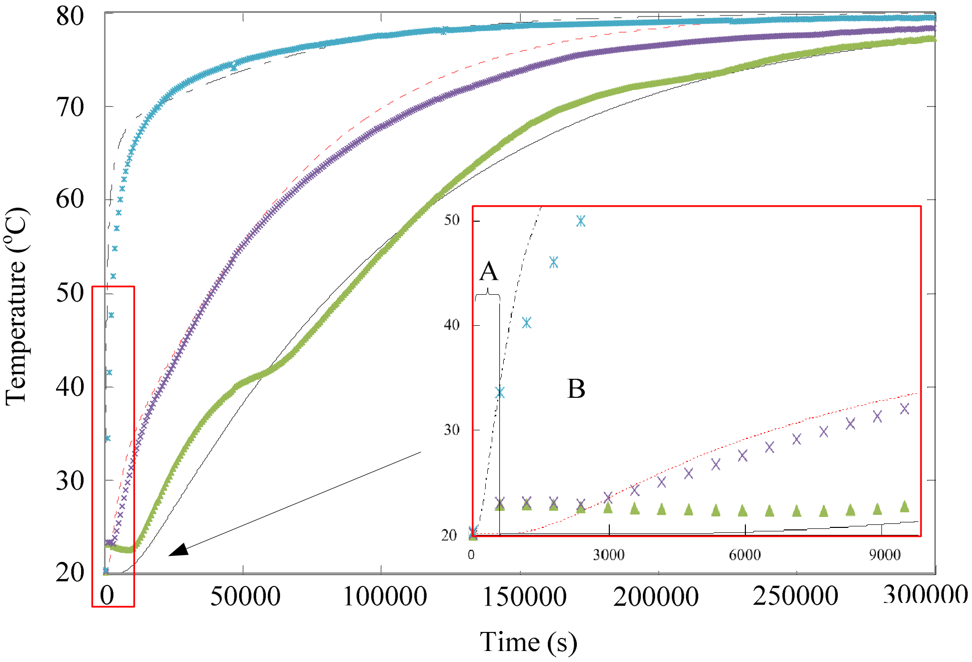

Fig. 5. Variation of bed temperature during the heating stage of the cycle (i.e. processes1 → 2→ 3 in Fig. 3) as obtained from experiment (points) and the model (line): (∗ and —·—) R = 100 mm, (× and ---) R = 50 mm and (▲ and —) R = 10 mm. The insert shows the short-time behaviour. The region A corresponds to the isosteric heating processes, 1 → 2 in Fig. 3, whilst region B corresponds to the isobaric processes, 2 → 3 in the same figure.

The fresh water production in a given time period is a key element in describing the performance of a desalination system. This quantity is defined by

$$m_{wp} = \sum_{j=1}^{N} m_{sg} \cdot \Delta\overline{X}_j \tag{21}$$

where $\Delta\overline{X}_j$ represents the difference of average water uptake of the silica gel within a cycle, and N is the number of the cycles the system performs in the time period. Fig. 6 shows the water production profiles of the system during the heating process considered in Fig. 5 (i.e. processes 1→2→ 3 in Fig. 3). The model predicts reasonably well the experimental observed water production behaviour (within 7%). At the intermediate period of the experiment (region I in Fig. 6), however, a not insignificant (15-20%) over-prediction by the model is seen that diminishes to around 5% at longer times (region L). This over-prediction is in part due to some of the water condensing on the inside walls of the glass measuring cylinder (*i.e.* the condenser) in the experiments, which is not measured. It is, however, also due to our omission of adsorption hysteresis, which is known to occur in reality for water on silica gel.(Tompsett et al., 2005) Such hysteresis leads in practise to more water being retained by the gel during the desorption process.

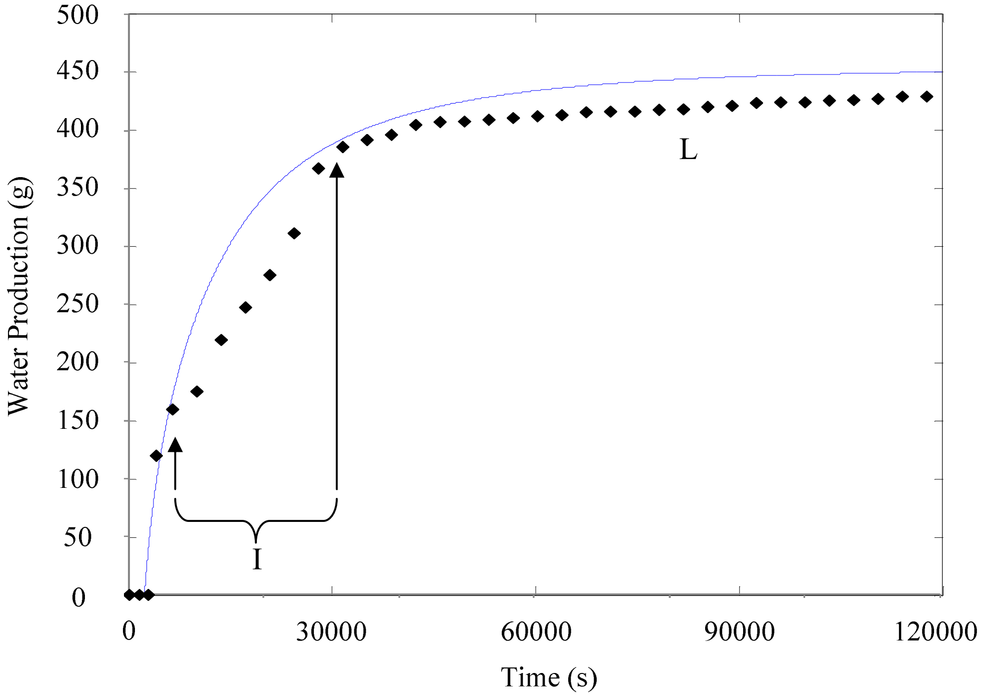

Fig. 6. Water production during the heating stage of the cycle (i.e. processes 1→2→ 3 in Fig. 3) as obtained from experiment (points) and the model (line).

4.2 Cyclic performance

We now consider the cyclic performance as predicted by the validated model. Fig. 7 illustrates the time variation of the water production and the corresponding adsorbent average concentration for four cycles of 25×10^3 seconds each. This shows that whilst the water production/accumulation increases in a semi-continuous manner as expected, the increase *per* cycle diminishes from the first to the fourth cycle where it appears to take on a steady value (see Fig. 7b). The average concentration of water retained in the bed similarly oscillates about a steadily decreasing average that plateaus after around four cycles.

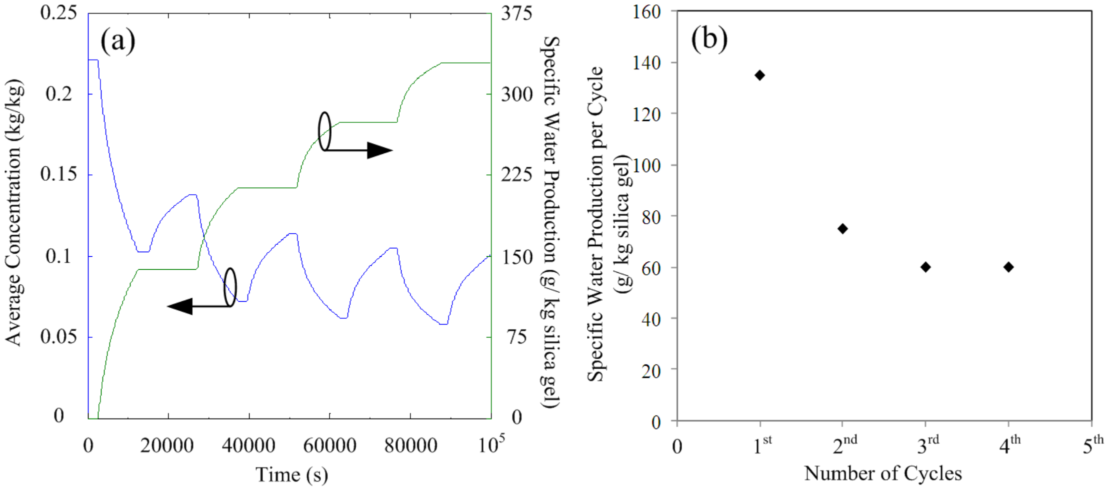

Fig. 7. (a) Adsorbent average concentration profiles and its corresponding specific water production for 10^5 seconds operation when the cycle time is 25×10^3 seconds, and (b) the specific water production for the four initial cycles

Fig. 8 shows a comparison of the water production over a 10^5 second period for three different cycle times: 10^5 seconds (one cycle), 25×10^3 seconds (four cycles) and 10^4 seconds (ten cycles). This figure clearly illustrates that the water production rate does not vary with cycle time in a straightforward manner. The best of the three cycle times considered in this figure balances the number of cycles in the fixed period with the degree of recovery from the silica gel. In the case of the longer cycle time, on the other hand, the bed is completely dried (at around 50×10^3 s), leading to half the cycle time being effectively wasted. The shortest cycle time in this figure leads to a lower production rate despite their being more cycles than in the other two cases because the bed is only ever partially dried (i.e. only part of the porosity in the silica gel is ever used).

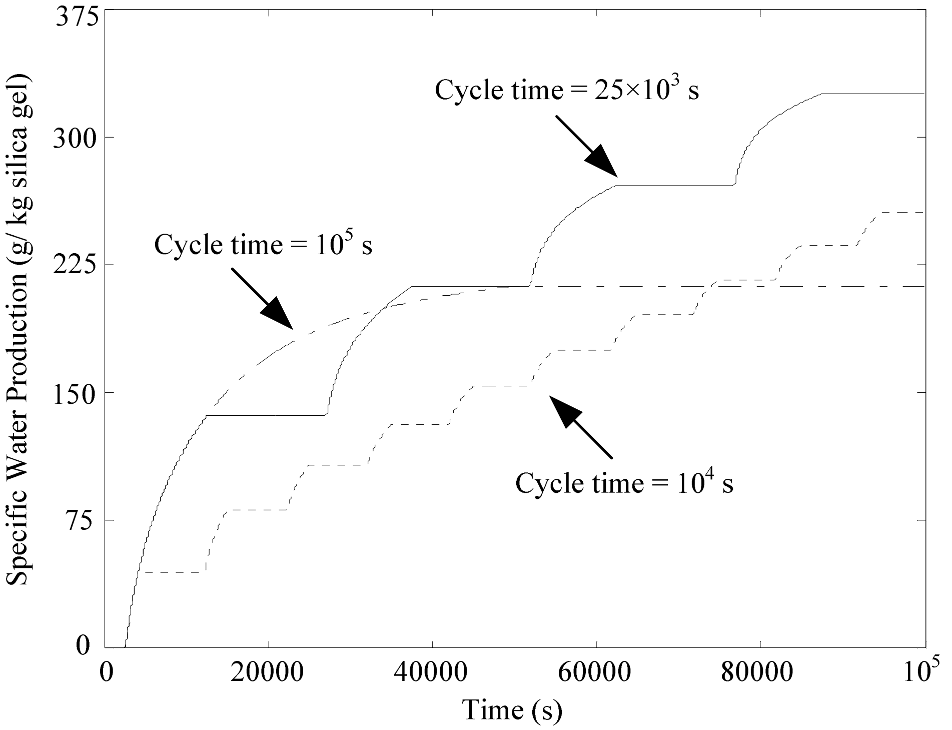

Fig. 8. A specific water production comparison of three different cycle times (i.e. 10^4, 25×10^3 and 10^5 seconds) for 10^5 seconds.

4.3 Identification of the optimal cycle time

Fig. 9 presents the evaluated specific water production rate as a function of the cycle time for our model system over a fixed period. This figure indicates there is a complex non-monotonic variation of the water production rate with cycle time, the reasons for which were outlined in the previous section. Fig. 9 reveals that the cycle time that yields the maximal production in the designated period (i.e. long-term average production rate) for the system investigated here (see Table 1) is 24×10^3 s. Further analysis reveals rather interestingly that this cycle time is less than 10% of the time it takes for the moisture content of the gel to reach its equilibrium value (i.e. the gel over a cycle only sees around a 10% change in its water content), indicating that optimal operation for the system considered here is driven more by quantity of cycles rather than effective utilisation of the gel. This balance may well change with the process parameters, something the model presented here would allow us to investigate in detail.

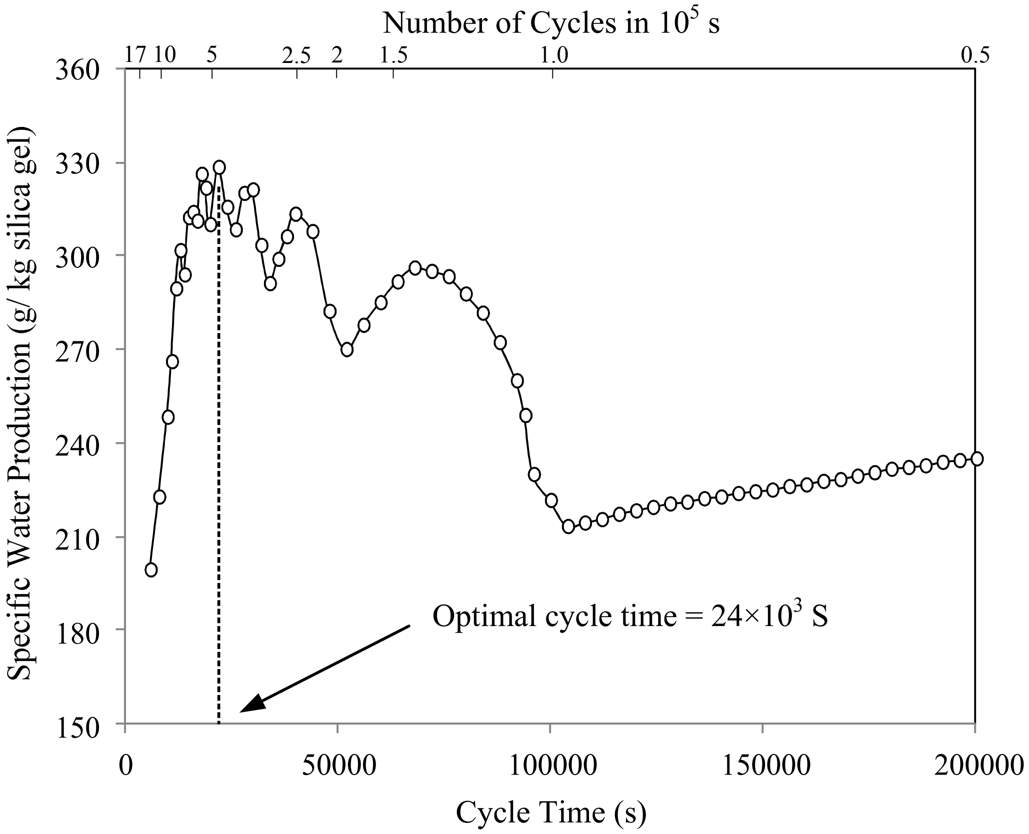

Fig. 9. The effect of the cycle time on the system water production rate for 1.0 kg of dry silica gel in 10^5 seconds.

5. CONCLUSIONS

A one-dimensional, multi-cycle dynamic mathematical model of an adsorption-based desalination (AD) system, which incorporates transient mass and heat transfer processes in the stream-wise direction of the silica gel bed, has been developed in this paper. The model has been found to compare well with both adsorbent temperature distributions and water production profiles obtained experimentally by the authors. The validated model was used to elucidate the effect of cycle time on water production rate and it was demonstrated how it can be used to identify the optimal cycle time. The deviations of the model from experiment, which were modest, can be linked to a number of assumptions that will be addressed by us in coming reports, including the omission of sorption hysteresis and multi-dimensional transport effects.

Nomenclature

Symbols

- C specific heat capacity (kJ/kg K)
- d diameter (mm)
- D diffusion coefficient (m^2/s)
- D_{so} Pre-exponent constant (m^2/s)
- ε porosity
- E_a activation energy of diffusion (kg/kg)
- h enthalpy (J/kg)
- h heat transfer coefficient
- K effective diffusion coefficient (m^2/sec)
- K_0^{I} adsorption equilibrium constant of the isotherm equation (dimensionless)
- k thermal conductivity
- M Molar mass of the adsorbate
- m mass (kg)
- $\dot{m}$ mass flow rate (kg/sec)
- P pressure (Pa)
- R gas constant (kJ/kg K)
- ρ density
- X^* fraction of amount adsorbate adsorbed by the adsorbent at equilibrium condition (kg /kg dry adsorbent)
- $\dot{q}$ rate of sorption heat generation
- Q heat of desorption for water on silica gel (kJ/kg)
- Q_{st} isosteric heat of adsorption for water on silica gel (kJ/kg)
- R_g gas constant (kJ/ kg K)
- r radius (mm)
- T temperature (^{o}C)

- μ dynamic viscosity (kg/m s)
- u gaseous velocity (m/s)
- V volume (m^3)

Superscripts/ subscripts

- ads adsorption
- bed adsorption or desorption bed
- $cond$ condenser
- cw cooling water
- $cycle$ cycle
- des desorption
- eq effective
- $evap$ evaporator
- f water jacket fluid
- hw hot water
- i inner
- m metal
- o outer
- pa particle
- sg silica gel
- t total
- v vapor
- w water
- wp water production
- $1 \rightarrow 2$ state 1 to state 2
- $2 \rightarrow 3$ state 2 to state 3
- $3 \rightarrow 4$ state 3 to state 4
- $4 \rightarrow 1$ state 4 to state 1

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CHAPTER 8: GENERAL DISCUSSION AND CONCLUSIONS

The aim of this research was to develop the knowledge base for the impact of operational and design parameters on Adsorption Desalination (AD) performance by developing mathematical models under various conditions and validating them with designed experiments. The detailed objectives of this thesis were to:

- develop a validated thermodynamic cycle model that allows rapid estimation of AD performance as a function of the process temperatures and silica gel material parameters;
- develop a validated dynamic model that allows prediction of AD performance as a function of process conditions, including cycle times; and
- use of the models developed above to elucidate the effect of process parameters on the performance of AD and draw conclusions on the range of conditions where AD is likely to be economically viable.

8.1 Research findings

These objectives were achieved and the principle findings of the research were reported through 6 papers listed in Chapters 3-7, which can be summarised as:

8.1.1 Static model development and detailed thermodynamic analysis for the performance of AD (Ch. 3-4, or papers 1&2)

- In paper 1 (Chapter 3) working principle and thermodynamic cycle of adsorption desalinator were described and its performance evaluated under equilibrium conditions. The analysis showed that there is an optimum hot water temperature existing for the minimum energy consumption of per unit mass fresh water produced. The optimum temperature depends on the cooling water temperatures and other operating parameters of the system. The temperature of the cooling water entering the bed during the adsorption process has significant impact on the both water productivity and energy consumption: the lower the better. Therefore any effort to improve the system performance and reduce costs should be put into the cooling water entering the bed (e.g. recycle the cooling effect from the evaporator). These results also indicated an air cooled condenser may be suitable for the cooling water entering the condenser. The results also showed that silica gel adsorption equilibrium constant (K_0^{I}) and the fresh water productivity are linearly related. K_0^{I} has little impact on the energy consumption.

- Paper 2, i.e. Chapter 4 revealed that the evaporator temperature can significantly impact on the nature of the cycles and the performance of the AD systems; when the evaporator temperature relative to the cooling water temperature is fixed, the cooling water temperature has little impact on performance of the AD cycles; the performance of the cycles is bounded by the capacity of the adsorbent used; the minimum evaporator temperature at which the performance becomes bounded increases at a diminishing rate with adsorbent capacity; and the optimal water production rate increases directly with the capacity whilst the corresponding energy consumption rate per kg of water produced decreases at a diminishing rate.

8.1.2 Possible thermodynamic cycles of AD identification and comparison (paper 3 or Ch. 5)

- At different evaporator temperature relative to the cooling water temperature, the thermodynamic cycles had been identified for the first time, to form three unique shapes (i.e. Cases 1, 2 and 3 cycles in Chapter 5) when they are presented on the set of *P-T-X* relationship coordinates –under the conditions of no energy recovery measures and negligible sensible heats of the bed and evaporator materials.
- Analysis of these cycles showed that the best performance in terms of maximum water production and minimum energy consumption is achieved when the

temperature of the evaporator is greater than that of the water used to cool the silica-gel bed and condenser (i.e. Case 3 cycles in Chapter 5).

8.1.3 Static model validation and possible AD cycles implementation (paper 4 or Ch. 6)

- In Chapter 6, the adsorptive properties test of the employed silica gel- water pair indicated that the Toth isotherm has the best fit (by the least square regression method) with experimental data (compared to Henry's and DA isotherms) under the current operation conditions. However, it does not capture the sigmoidal nature of the adsorption isotherm at low pressures and hence under-predicts the actual isotherm by up to 19% for water vapour pressures below approximately 500 Pa.
- The experimental results obtained in Chapter 6 also indicated that the theoretical thermodynamic cycles (outlined in Chapter 5) for AD system have been successfully implemented. Differences between the observed experimental performance and that predicted by the models could be attributed to some water condensation in the pipework of the system that could not be measured, and the fact that the hysteresis exhibited by the silica under desorption was not modelled.

8.1.4 Dynamic model development and validation of AD (paper 5 or Ch. 7)

- In Chapter 7, it showed the predicted temperature profiles of the adsorbent in the bed generally agrees with the experimental data, although difference were observed at the beginning of the desorption. The deviations of the model from experiment, which were modest, can be linked to a number of assumptions that will be re-visited in future efforts by us, including the omission of sorption hysteresis, and multi-dimensional transport effects.
- Use of the validated model to identify the optimal cycle time has been demonstrated. It shows the optimal cycle time is relatively short compared to the time takes for the moisture content of the gel to reach its equilibrium value.

8.2 Principle significance of the findings

The significances of above findings in this study on Adsorption Desalination (AD) can be summarised as follows:

- The performed sensitivity/ parametric analysis using developed thermodynamic model of AD helped us to identify one of the most important parameters–the evaporator water temperature relative to the cooling water temperature, which has the significant impact on the nature of the thermodynamic cycle of AD and consequent affect the system performance.
- With this finding we enumerated all possible thermodynamic cycles of AD, described their operational processes in detail and validated these theoretical cycles in the experiment, for the first time ever.
- The use of the equilibrium thermodynamic model allows rapid calculation and, therefore, consideration of many combinations of system parameters with modest resource. It is, however, recognised that the equilibrium assumption means the results here can only be used as a guide. The model also does not give any information about the dynamic behaviour of AD systems. Both these issues were be overcome by developing a 1-D dynamic model, which incorporates transient mass and heat transfer processes in the stream-wise direction of the silica gel bed and calculates multi-cycled operation of the system. The validation of the model in the laboratory and encouraging comparison demonstrate that the model assists the better understanding of the relationship between the performance of AD and the operational parameters (e.g. the cycle time in the dynamic situation).
- With the results we have obtained from the validated models, we could draw conclusion that, AD is likely to be economically viable, since: 1. the optimum hot water temperature under the design condition is relatively low (e.g. 65°C), which is typically considered as wasted heat; 2. The optimum operating cycle time is relatively short, and the water can be produced in a continuous manner with two or more beds; 3. When AD system running in case 3 cycles (i.e. the evaporator

temperature is greater than the cooling water temperature), it has the great potential to both improve the fresh water productivity and reduce specific energy consumption, depends on the capacity of the silica gel used; 4. Previous research also shows that the cost of AD to produce water is about US$0.227 per m^3, (while the highest production cost is from the MSF at US$0.647 (from Tab. 2.1)). It is believed that, a full-scaled (or economy scale) AD plant, the specific energy consumption and energy cost of water of AD system will further be reduced.

8.3 Recommendations for future research

Several general recommendations for areas of further research are:

- A second key performance parameter (besides the water productivity) for AD is the (thermal) energy required per unit mass of water produced. We have derived this quantity for the various thermodynamic cycles implemented in this study. Future experimental study may focus on this aspect.
- Higher-dimensional dynamic models (2-D or 3-D) that allow bed geometry to be included are still needed to fully probe the transient mass and heat transfer processes in the adsorbent bed, especially when the bed diameter and height are small.
- Current AD models use same adsorption isotherm equations for both adsorption and desorption processes calculations, which is not very accurate due to the existing desorption hysteresis kinetics as we briefly discussed in early section. Developing new AD models with both adsorption and desorption isotherms included may overcome this problem.
- The long term performance of AD is not clear (e.g. silica gel aging problems), further study can be carried out to investigate whether there is a salt migration problem occurs between the source water (sea water) and silica gel during the process after long term usage, therefore affects the performance of the AD system.

- Dynamic simulation for the operation of multi-bed systems with energy recovery scheme would be of great use in making the AD technology stronger for supplanting more traditional desalination technologies in practice.

APPENDIX A:

COMPARISON OF ADSORPTION-BASED DESALINATION PLANT PERFORMANCE MODELS

Wu J. W., Biggs M. J., Hu E. J. (2010) Comparison of Adsorption-based Desalination Plant Performance Models. *Chemeca 2010: The 40th Australasian Chemical Engineering Conference*, Adelaide, September 26-29, ISBN: 978-085-825-9713.

COMPARISON OF ADSORPTION-BASED DESALINATION PLANT PERFORMANCE MODELS

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ABSTRACT

Adsorption-based desalination (AD) is attracting increasing attention because of its ability to use low-grade thermal energy to co-generate fresh water and cooling. Various levels of model ranging from the simplest thermodynamic model through to the most sophisticated three-dimensional multiphysics models can be deployed to predict the performance of AD plants. Whilst the simplest of these models are unlikely to predict the performance as reliably as the more complex, their low computational cost means they are ideal for scoping analysis. Comparison of these simpler models against experiment and more complex models is, therefore, warranted. In this paper, we compare a thermodynamic model developed by the authors with an experimentally-validated lumped (i.e. zero-dimensional, or 0D) kinetic model developed by Thu *et al.* (2009). The predicted values of the specific daily water production (SDWP) and performance ratio (*PR*) at various heat source temperatures of a two-bed silica gel AD system from two models are compared. Good agreement between the two models is found for the SDWP when the heat source (i.e. hot water inlet temperature) is lower and the operation cycle time is longer. It was found, however, that the thermodynamic model predicts more than double the SDWP of the 0D kinetic model at the shortest cycle times investigated here. Further comparison indicates that whilst the thermodynamic model over-predicts the PR, the differences are modest.

Keywords: Adsorption Desalination; Model Comparison; Silica gel-water; Thermodynamic cycles

INTRODUCTION

Adsorption-based desalination (AD) uses low temperature waste heat to inexpensively desalinate saline and brackish water to produce potable water for both industrial and residential applications (Wang and Ng, 2005). This desalination method has a number of significant advantages compared with more traditional desalination techniques (Wang and Ng, 2005; El Sharkawy et al., 2007 and Wang et al., 2007), including fewer moving parts, reduced fouling and corrosion, ability to co-generate potable water and cooling, double distillation and to treat/desalinate saline water containing organic compounds. Despite its considerable advantages, AD has received very little attention in the literature. Ng and co-workers (Wang and Ng, 2005; Wang et al., 2007; and Ng et al., 2009) have investigated in detail the performance of a pilot scale adsorption-based desalination system as a function of system configuration and operating parameters. This group (Chua et al., 1999; Chua et al., 2004) and others (Wang et al., 2005; Wang and Chua, 2007) have also developed and used a lumped (i.e. 0D) kinetic model of an adsorption chiller (same working principle with AD system) to study the dynamic behaviour of adsorption refrigeration systems as a function of operating parameters such as the cycle time.

In order to more fully probe the effect that thermal parameters and adsorbent properties have on the performance of AD system, we have developed and used a thermodynamic model of an AD cycle based on a silica-gel adsorbent (Wu et al., *Chem. Eng. Res. Des.*, in press). Also very recently, a lumped kinetic model has been used to study the performance of an AD system in two-bed and four-bed operational modes (Thu et al., 2009). This group compare their models with experimental data for an AD system in terms of key performance parameters, namely: (i) specific daily water production (SDWP), (ii) cycle time, and (iii) performance ratio (PR). We compare here our thermodynamic model with this 0D kinetic model and experimental data in order to determine the validity of the equilibrium model, which has the advantage that it can be used to undertake extensive parametric studies of AD system performance because of its low computational cost.

The paper first outlines in detail the thermodynamic model along with details of the adsorbent and other conditions used in the study here. Results obtained from the model under the equilibrium assumption are then compared with the experimental results and the 0D kinetic model, including the SDWP at different cycle times and the PR at various hot water inlet temperatures for a two-bed AD system.

WORKING PRINCIPLE

Fig. 1 shows a schematic of a two-bed adsorption-based desalinator, which is the most basic form of such a system. This system consists of three major components: the condenser, the (silica gel) beds, and the evaporator. After the whole system is degassed and the saline/source water is charged into the evaporator, with Valve 1 open, the source water evaporates and travels from the evaporator into Bed 1 where it is adsorbed by the silica gel as the heat liberated by the adsorption is removed by the cooling water circulating in the manifold of Bed 1. Once Bed 1 is saturated with water vapour, Valve 1 is closed and Valve 2 is opened. At the same time, the circulating water in Bed 1 is switched to hot water. The hot water drives off the water adsorbed on (i.e. regenerates) the silica gel to the condenser where it is finally condensed and harvested as pure water. Once the temperature of Bed 1 peaks, the silica gel regeneration process ceases and the cycle for the bed is ready to re-start. Beds 1 and 2 are operated alternatively in this way to produce fresh water (and cooling capacity from the evaporator) in a continuous manner.

It should be noted that the fresh water is distilled twice (i.e. double-distilled). At the same time, a cooling effect is created by the evaporator, which can be used for air conditioning purposes as in a normal adsorption chiller, or be fed back to the bed or condenser. In other words, the adsorption desalination system has the ability to perform as a chiller and double-distilling desalinator simultaneously. Silica gel is a popular adsorbent because it is able to take-up significant levels of water (up to 40% by mass) (Ng at al., 2001) without significant structural or volume change and readily release it under mild heating (Chakraborty et al., 2009). To improve energy efficiency, in practice systems with two or more beds are used (Chua et al., 1999). However, in this study, consideration will be restricted to a single-bed system for simplicity sake.

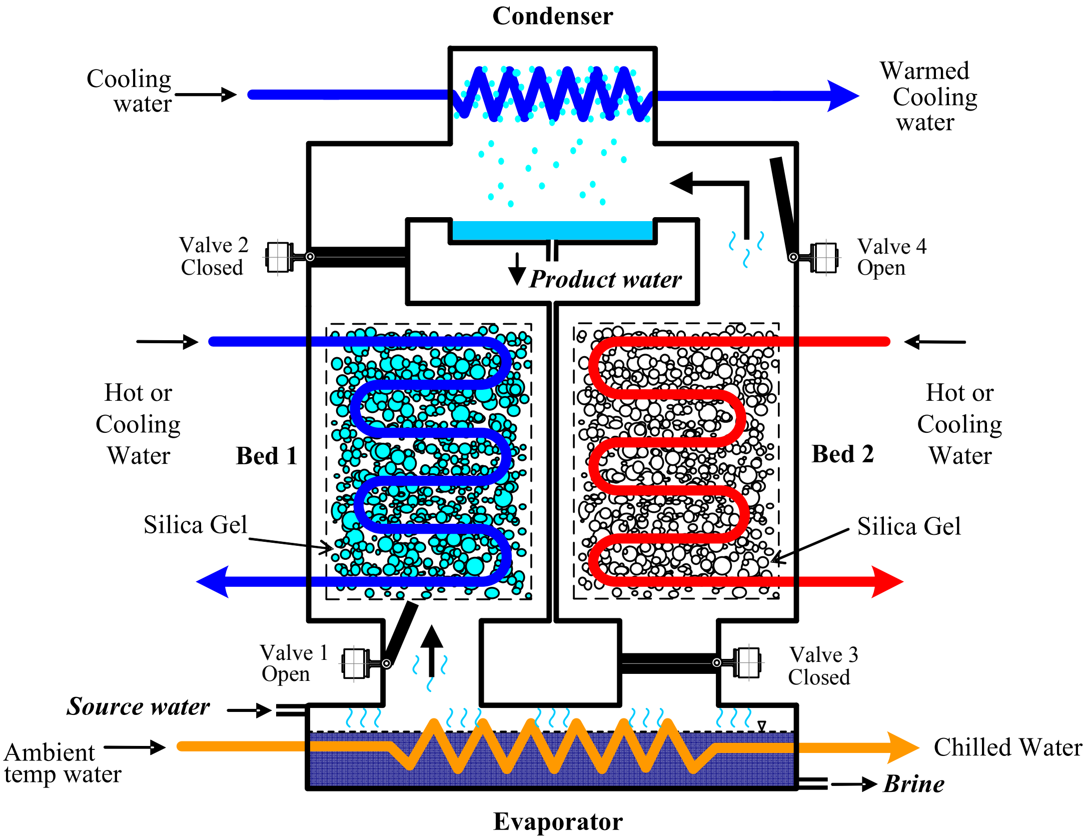

Fig. 1. Schematic of a two-bed adsorption desalination system. Refer to text for a description of its operation.

MODELLING

Adsorption isotherms, kinetics and energy balances form the basis for performance modelling of AD systems. The water adsorption has been described here by the Toth isotherm as it appears to describe well the experimental adsorption isotherms across the applicable pressure range (Suzuki, 1990).

The physical properties of the Type RD-silica gel employed here are listed in Tab. 1. The equilibrium water vapour uptake of the silica gel can be calculated by the Toth equation (Chua et al., 2002)

$$X = \frac{K_0 \cdot \exp\left[\Delta H_{ads} / \left(R \cdot T\right)\right] \cdot P}{\left\{1 + \left[\frac{K_0}{X_{\max}} \cdot \exp\left(\Delta H_{ads} / \left(R \cdot T\right)\right) \cdot P\right]^t\right\}^{\frac{1}{t}}} \tag{1}$$

where X is the amount of adsorbate at equilibrium in *kg* of adsorbate per *kg* of adsorbent, P and T the bed partial pressure and temperature respectively, X_{max} the monolayer capacity, R the gas constant, ΔH_{ads} the isosteric enthalpy of adsorption, K_0 the pre-exponential constant, and t the dimensionless Toth constant. The physical property parameters used in the calculation are listed in Tab. 2.

Tab. 1 Properties of type-RD silica gel (Thu et al., 2009).

Property	**Value**
Pore diameter	0.8-7.5 nm
Average pore diameter	2.2 nm
Pore volume	0.37 cm^3/g
Pore surface area	720m^2/g
Apparent density	700 kg/m^3
pH	4.0
Specific heat capacity	0.921 kJ/ (kg K)
Thermal conductivity	0.198 W/ (m K)

Tab. 2 Physical property parameters used in the calculation.

Property	**Value**
c_w	4.1855 kJ/(kg K)
c_{sg}	0.92 kJ/(kg K)
K_o	7.3×10^{-10} Pa^{-1*}
ΔH_{ads}	2510 kJ/kg*
R	0.4619 kJ/ (kg K)
t	12 (-)*
X_{max}	0.45 (kg/kg)
$\Delta H_{fg}^{T_{evap}}$	2475.72 kJ/kg
$\Delta H_{fg}^{T_{cond}}$	2448.53kJ/kg

*(Chua et al., 2002)

The *P-T-X* diagram on *lnP vs. -1/T* coordinates is a convenient way to describe and model the thermodynamic cycle of an AD system. Theoretically the cycle consists of two isosters and two isobars, as shown in Fig 2.

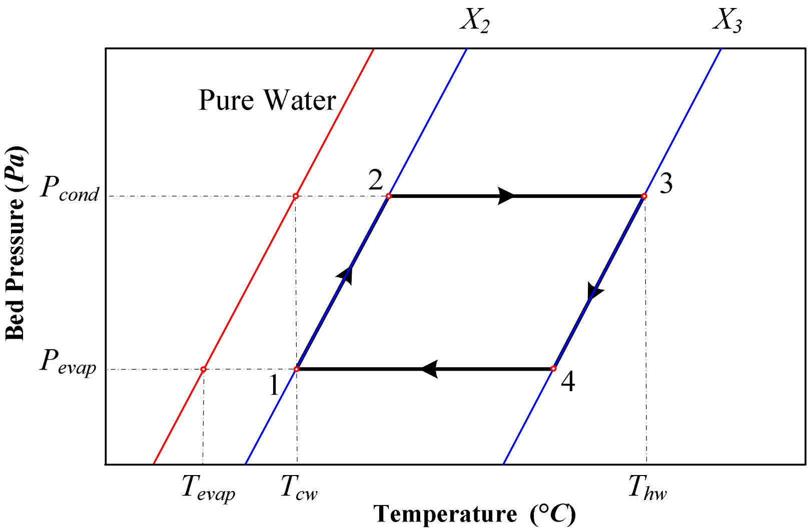

Fig. 2. P-T-X diagram of the cyclic-steady-state condition of the bed cycle. Detailed description of each process has been reported by (Wu et al., *Chem. Eng. Res. Des.*, in press).

Based on the cycle diagram shown in Fig. 2, the mass of fresh water produced in a single cycle from one bed (i.e. water productivity) can be expressed as

$$m_{water} = \Delta m_{2\rightarrow 3} = m_2 - m_3 = X_2 \cdot m_{sg} - X_3 \cdot m_{sg} \tag{2}$$

where m_{sg} is the mass of the silica gel in one bed, $\Delta m_{2\rightarrow 3}$ is the mass change of the water adsorbed in the silica gel between state 2 and state 3, X_2 and X_3 are the adsorbed phase concentration at equilibrium for state 2 and 3, which can be calculated by using Eq. (1). Here, the water productivity is of key interest as it is used to calculate the specific daily water production (SPWP). The expression of SPWP given below

$$SDWP = \frac{N \cdot m_{water}}{\rho_{water}} \tag{3}$$

where N is the number of cycles the system could perform per day and ρ_{water} is the density of the water. Here the SDWP is expressed as m^3 of potable water per tonne of silica gel can be produced per day.

The energy required to drive out water vapours from silica gel during the desorption process can be calculated by the heating input ($Q_{heating,bed}$) to the process $1 \rightarrow 2$ and process $2 \rightarrow 3$, and this is given by

$$\begin{aligned} Q_{heating,bed} &= (X_1 m_{sg} C_{water} + m_{sg} C_{sg}) \cdot (T_2 - T_1) \\ &+ [m_{sg} C_{sg} + (\frac{X_2 + X_3}{2}) m_{sg} C_{water}] \cdot (T_3 - T_2) + (X_2 - X_3) \cdot m_{sg} Q_{des} \end{aligned} \tag{4}$$

where T_1, T_2 and T_3 are the corresponding temperatures at each state, C_{water} is the specific heat of water, C_{sg} is the average specific heat of silica gel, and Q_{des} is the amount of heat required for desorbing 1 *kg* of water.

The condensation energy rejected at the condenser is given by

$$Q_{cond} = m_{sg} \cdot \Delta H_{fg}^{T_{cond}} \cdot \left(X_1 - X_4 \right) \tag{5}$$

where $\Delta H_{fg}^{T_{cond}}$ is the isosteric enthalpies at condenser temperature.

Another key parameter which describes the performance of the AD system is the performance ratio (*PR*), and it is defined by

$$PR = \frac{Q_{cond}}{Q_{heating,bed}} \tag{6}$$

The following assumptions are used in the study:

1. temperature difference for heat transfer is 5°C,
2. structure mass is ignored; and
3. $Q_{ads} = Q_{des} = \Delta H_{ads}$ for all X_s

RESULTS AND DISCUSSION

Using equations 1-6, the specific daily water production (SDWP) and performance ratio (*PR*) have been evaluated for the operating temperatures shown in Tab. 3. The 5 degrees Celsius is assumed to be necessary for the heat transfer during the heating and cooling process here. These results are compared below with the experimental validated 0D kinetic model reported by Thu et al. (2009).

Tab. 3 Operating water temperatures.

Temperature of …	**Proposed (^{o}C)**	**Evaluated at (^{o}C)**
hot water inlet (desorbing bed)	65-85	60-80
cooling water inlet (adsorbing bed)	29.5	34.5
cooling water inlet (condenser)	30	35
chilled water inlet (evaporator)	30	25

The specific daily water production (SDWP)

Fig. 3 shows the specific daily water production (SDWP) at different cycle times with various heat source temperatures for a two-bed AD system. This figure shows that the SDWP predicted by the thermodynamic model decreases with increasing cycle time for all heat source temperatures (i.e. $T_{hw} = 65^{o}$C, 75^{o}C and 85^{o}C). For all heat source temperatures, the SDWP of the thermodynamic model approaches that of the 0D model when the cycle times are large (840 s, 930 s and 960 s for the three T_{hw} in ascending order), in line with the expectation that the real system will tend to approach the thermodynamic limit at sufficiently large cycle times. The differences between the thermodynamic and 0D kinetic model increase with decreasing cycle time and increasing hot water temperature. In particular, the thermodynamic model over-estimates the performance by approximately 100% at the lowest cycle times considered here.

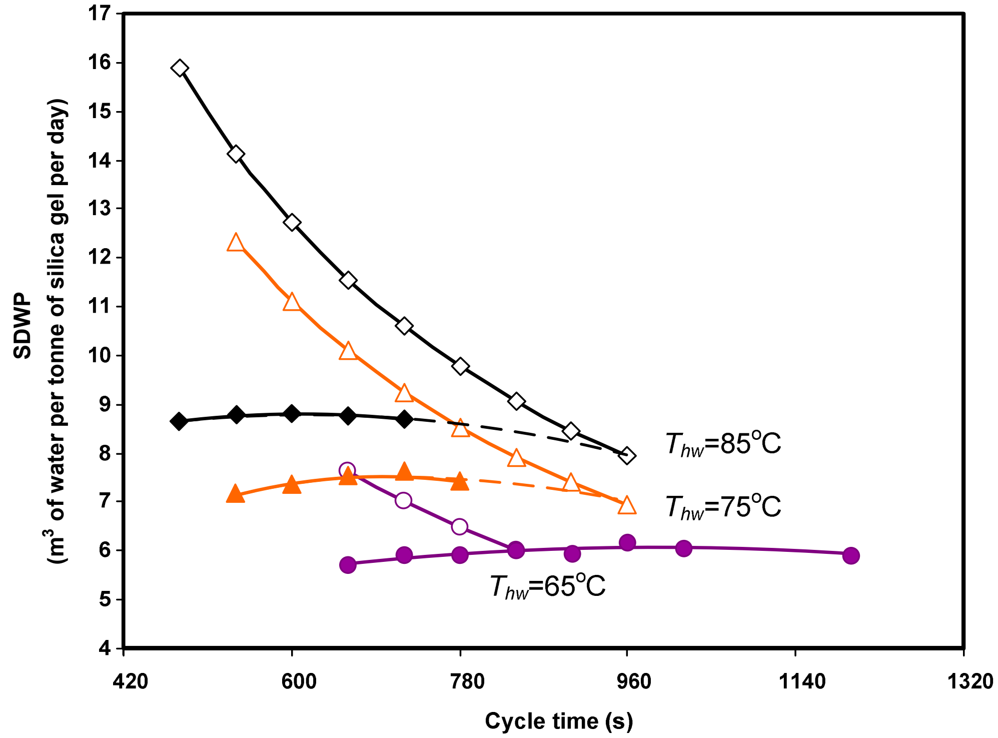

Fig. 3. Comparison of SDWP predicted by the thermodynamic model (◊, Δ, ○) with that predicted by the experimentally-validated 0-D kinetic model (♦, ▲, ●) of Thu et al. (2009) for a two-bed AD system. The dashed lines for the model of Thu et al. (2009) represent extrapolation of their results to cycle times greater than they considered.

The comparison of performance ratio (*PR*)

Fig. 4 shows the comparison of the system performance ratio (*PR*) predicted by the two models for various hot water inlet temperatures (i.e. heat source temperatures) for a two-bed AD system when an adsorbent (silica gel) mass of 1000 kilograms is used. In which, the 0D model used the optimal cycle times in respective hot water inlet temperature for each bed to evaluated *PR* results (i.e. T_{hw} = 65°C--t_{cycle}=980 s, T_{hw} = 75°C--t_{cycle}=740 s and T_{hw} = 85°C--t_{cycle}=620 s). This figure shows that the thermodynamic model over-predicts the performance by between 7% at T_{hw} = 65°C to 17% at T_{hw} = 85°C. This difference originates from the definition of the heating input to the bed for two different models, where our model defines $Q_{heating,\,bed}$ as an effective heat (shown in Eq. 4), which is ignoring the heat transfer to the bed structures and the heat loss. On the other hand, the 0D model defines the $Q_{heating,\,bed}$ as a total heating input, which includes the heat loss and the heat transferring to the structural mass, and can be written as

$$Q_{heating,bed} = \dot{m}_{hw} \cdot C_{water(T_{des})} \cdot (T_{hw,in} - T_{hw,out}) \tag{7}$$

where $\dot{m}_{hw}$ is the hot water inlet mass flow rate, $C_{water(T_{des})}$ defines the specifics heat capacity of heating water in desorption temperature, $T_{hw,in}$ (or T_{hw}) and $T_{hw,out}$ describes the hot water inlet and hot water outlet temperatures respectively.

The decrease in difference between the *PR* of the two models with decreasing hot water temperature is supported by the results in Fig. 3 *viz.* the equilibration time decreases with the heat source temperature.

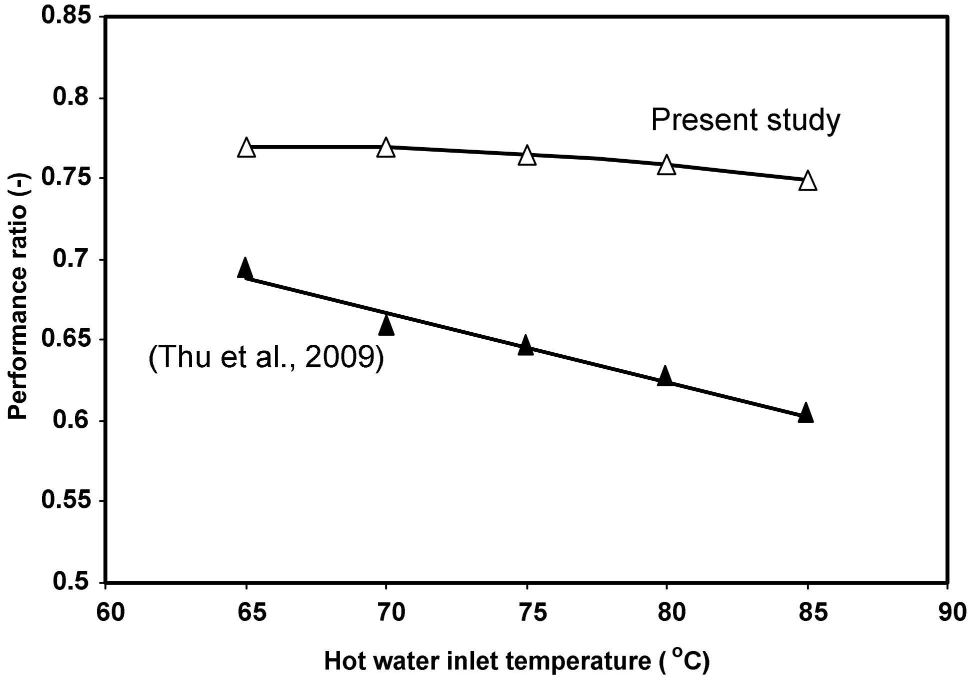

Fig. 4. Comparison of the performance ratio predicted by the thermodynamic model (Δ) with that predicted by the experimentally-validated 0-D kinetic model (▲) for different hot water inlet temperatures in a two-bed AD system.

CONCLUSION

The working principle and an equilibrium thermodynamic model of an adsorption-based desalination (AD) system have been presented and its results have been compared with the experimentally-validated zero-dimensional (0D) kinetic model of Thu *et al.* (2009). This comparison shows that the daily water production predicted by the thermodynamic model is double that of the kinetic model for the lowest cycle times investigate, but the difference disappears once cycle times increase sufficiently (800-1000 s) to make the thermodynamic assumption valid. The thermodynamic model also over-predicts the performance ratio by between 7-17% as the hot water inlet temperature is increased from 65-85°C.

The analysis here clearly shows that the equilibrium assumption that underpins the thermodynamic model can lead to significant over-predictions in performance. However, by better understanding the scale of the over-predictions, we hope that this will enable use of the thermodynamic model in the scoping analysis context where its low computational cost is particularly desirable.

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APPENDIX B:
THERMODYNAMIC ANALYSIS OF ADSORPTION-BASED DESALINATION CYCLES

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THERMODYNAMIC ANALYSIS OF ADSORPTION-BASED DESALINATION CYCLES

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ABSTRACT

Adsorption-based desalination (AD) is attracting increasing attention because of its ability to use low-grade thermal energy to co-generate fresh water and cooling. In this paper, a thermodynamic model has been developed in order to study the factors that influence the fresh water production rate (FWPR) and energy consumption of silica gel based AD system. Water adsorption on the silica gel is modelled using a Langmuir isotherm and the factors studied are the silica gel adsorption equilibrium constant, and the heating and cooling water temperatures, which supply and remove heat from the silica gel respectively. The result shows that in terms of the energy consumption, a heating water temperature of 65°C is optimal for the conditions studied here. The cooling water temperature has far more significant impact on the both water productivity and energy consumption compared to the heating water temperature. The results also show that silica gel adsorption equilibrium constant, whilst related to the FWPR in a linear manner, has little impact on the energy consumption. The paper also discusses the impact of evaporator temperature on the thermodynamic cycle when the system is operated in desalination mode only.

Keywords: Adsorption Desalination; Cooling; Silica gel-water; Thermodynamic cycles

INTRODUCTION

Adsorption-based desalination (AD) uses low temperature waste heat to inexpensively desalinate saline and brackish water to produce potable water for both industrial and residential applications (Wang and Ng, 2005). There are five significant advantages of the AD compared with more traditional desalination techniques (Wang and Ng, 2005; El Sharkawy et al., 2007 Wang et al., 2007): (1) fewer moving parts, which reduces maintenance costs, (2) reduced fouling and corrosion due to the low operating temperature and confinement of the saline/brackish solution to a fraction of the total system, (3) ability to co-generate potable water and cooling; (4) double distillation – the desalination process minimizes the possibility of so-called '(bio) gen-contamination'; and (5) ability to treat/desalinate saline water containing organic compounds.

Adsorption-based desalination has received very little attention in the literature despite its considerable advantages. Ng and co-workers (Wang and Ng, 2005; Wang et al., 2007; Thu et al., 2009 and Ng et al., 2009) have investigated in detail the performance of a pilot scale adsorption-based desalination system as a function of system configuration and operating parameters. This group (Chua et al., 1999; Chua et al., 2004) and others (Wang et al., 2005; Wang and Chua, 2007) have also developed and used a lumped dynamic model of adsorption desalination to study the dynamic behaviour of adsorption desalination systems as a function of operating parameters such as the cycle time. In order to more fully probe the effect that thermal parameters and adsorbent properties have on the performance of adsorption-based desalination, we have undertaken a comprehensive thermodynamic analysis of an AD cycle based on a silica-gel adsorbent.

The paper first outlines in detail the thermodynamic model along with details of the adsorbent and other conditions used in the study. Results obtained from the model are then presented, including the effect the silica gel adsorption equilibrium constant and the evaporator temperature, and the heating and cooling water temperatures have on the fresh water production rate (FWPR) and energy consumption of AD under.

Working principle

Fig. 1 shows a schematic of a two-bed adsorption-based desalinator, which is the most basic form of such a system. This system consists of three major components: the condenser, the (silica gel) beds, and the evaporator. After the whole system is degassed and the saline/source water is charged into the evaporator, with valve 1 open, the source water evaporates and travels from the evaporator into bed 1 where it is adsorbed by the silica gel as the heat liberated by the adsorption is removed by the cooling water circulating in the manifold of bed 1. Once bed 1 is saturated with water vapour, valve 1 is closed and valve 2 is opened. At the same time, the circulating water in bed 1 is switched to hot water. The hot water drives off the water adsorbed on (i.e. regenerates) the silica gel to the condenser where it is finally condensed and harvested as pure water. Once the temperature of bed 1 peaks, the silica gel regeneration process ceases and the cycle for the bed is ready to re-start. Beds 1 and 2 are operated alternatively in this way to produce fresh water (and cooling capacity from the evaporator) in a continuous manner.

It should be noted that the fresh water is distilled twice (i.e. double-distilled). At the same time, a cooling effect is created by the evaporator, which can be used for air conditioning purposes as in a normal adsorption chiller, or be fed back to the bed or condenser. In other words, the adsorption desalination system has the ability to perform as a chiller and double-distilling desalinator simultaneously. Silica gel is a popular adsorbent because it is able to take-up significant levels of water (up to 40% by mass) (Ng at al., 2001) without significant structural or volume change and readily release it under mild heating (Chakraborty et al., 2009). To improve energy efficiency, in practice systems with two or more beds are used (Chua et al., 1999). However, in this study, consideration will be restricted to a single-bed system for simplicity sake.

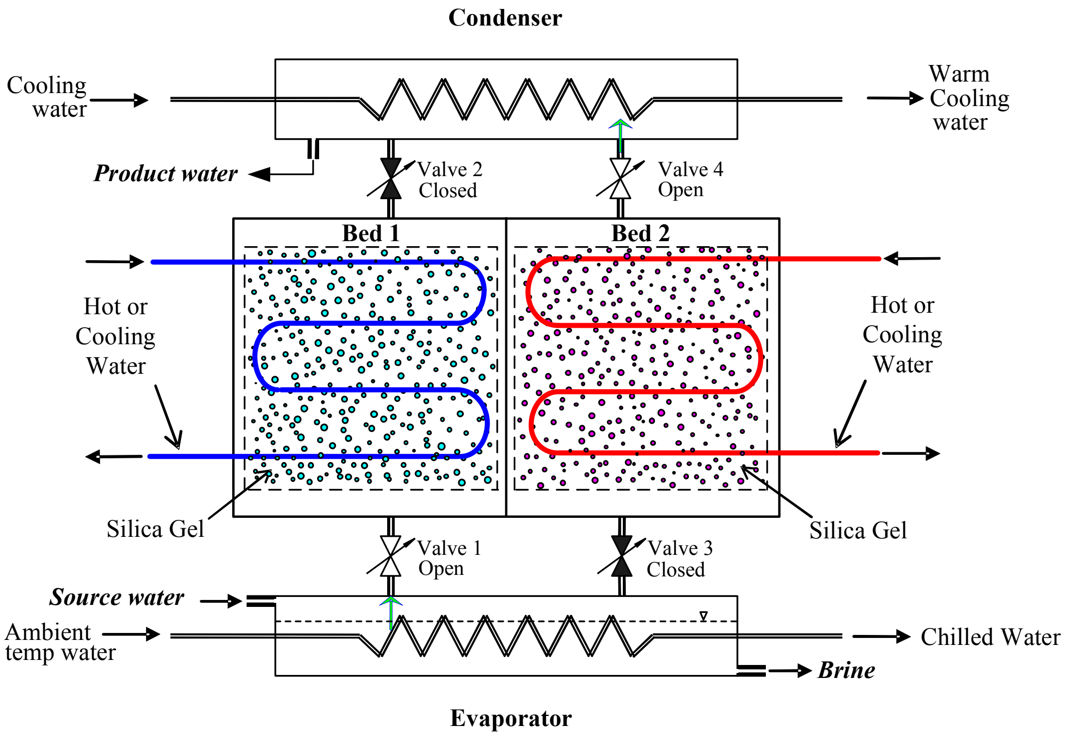

Fig. 1. Schematic of a two-bed adsorption desalination system. Refer to text for a description of its operation.

MODELLING

A modified Langmuir equation derivate by Henry Law and van't Hoff equation is used to model the AD system. The practical form of the working equation (Ng et al., 2001) is expressed as:

$$X = PK_0^I \exp(\frac{Q_{st}}{RT}) \qquad (1)$$

K_0^I ($=K_0X_0$) is the adsorption constant. X_0 is the theoretical water vapour capacity of the absorbent. Once the Q_{st} and K_0^I are known for a particular adsorptive -adsorbent pair (e.g. from experiment), then the P-T-X relationship is known and the analysis of the AD cycle can be undertaken.

The mass of fresh water produced in a single cycle from one bed (i.e. water productivity) can be expressed as

$$m_{water} = X_{\max} \cdot m_{sg} - X_{\min} \cdot m_{sg} \tag{2}$$

where X_{max} and X_{min} are the highest and the lowest water vapour concentration within a cycle respectively, m_{sg} is the mass of the silica gel in one bed, the water productivity is the mass change of the water adsorbed in the silica gel between the highest and the lowest adsorbed phase concentration at equilibrium for two specific states. The water vapour concentration can be calculated by using Eq. (1).

The total heating input ($Q_{heating,bed}$) to the system of the whole cycle is given by

$$\begin{aligned} Q_{heating,bed} &= (X_{\max} m_{sg} C_{water} + m_{sg} C_{sg}) \cdot \Delta T_{isoster} \\ &+ [m_{sg} C_{sg} + (\frac{X_{\max} + X_{\min}}{2}) m_{sg} C_{water}] \cdot \Delta T_{isobar} + (X_{\max} - X_{\min}) \cdot m_{sg} Q_{des} \end{aligned} \tag{3}$$

where $\Delta T_{isoster}$ is the temperature change during the isosteric process, ΔT_{isobar} is the temperature change during the isobaric process, C_{water} is the specific heat of water, C_{sg} is the average specific heat of silica gel, and Q_{des} is the amount of heat required for desorbing 1 *kg* of water.

In order to have a clear view of energy consumption of the system per cycle, the energy required per kilogram of water produced, *EC*, is required. This may be evaluated using

$$EC = \frac{Q_{heating(bed)}}{m_{water}} \tag{4}$$

The following assumptions are used in the study:

1. temperature difference for heat transfer is 5 °C,
2. structure mass is ignored; and

3. Unless otherwise stated, the porous properties of Type RD Fuji Davison silica gel-water system are used, where $K_0^I = 5.5 \times 10^{-12} Pa^{-1}$, Q_{st} = 2370 kJ/kg and X_{max} = 0.45 (Ng et al., 2001).
4. $Q_{ads} = Q_{des} = Q_{st}$ for all X_s

RESULTS AND DISCUSSIONS

Effects of heating water temperature

Fig. 2 shows the water productivity and energy consumption versus the heat source temperature when the cooling water is fixed at T_{cw} = 20°C or 30°C and the evaporator temperature is maintained at 13°C (i.e. P_{evap}=1.5kPa according to the saturated steam pressure). For 20°C cooling water, the system uses the lowest energy to produce a unit mass of fresh water when the heating water temperature is around 65°C. The energy cost increases if higher grade energy is used, although the quantity of silica gel required per unit mass of water produced would decrease, thus reducing the costs associated with the adsorbent.

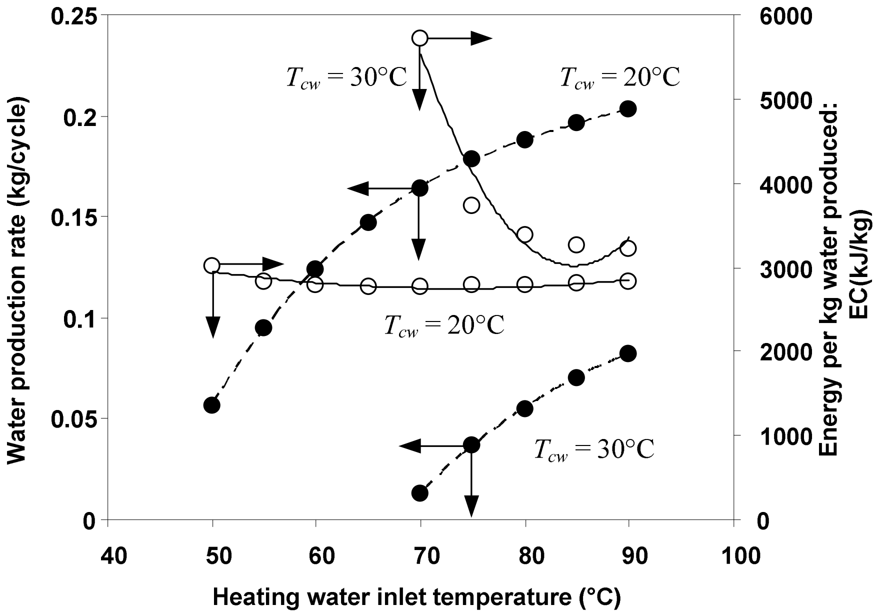

Fig. 2 The effect of varying heating water temperature on the fresh water production rate and energy requirement per kilogram water produced for two different cooling water temperatures at 20^{o}C and 30^{o}C.

Effects of cooling water temperature

There are two cooling water streams: one that cools the silica gel beds and a second for the condenser. Figs. 3-5 show the effect of varying the temperatures of these two streams on the fresh water production rate and energy consumption per kilogram of water produced. Fig. 3 shows the impact of varying simultaneously the temperatures of the cooling water entering the bed and the condenser on the water productivity and energy consumption for two different heating water temperatures, $T_{hw} = 75°C$ and $T_{hw} = 90°C$, when the evaporator temperature is maintained at 13°C (i.e. P_{evap}=1.5kPa according to the saturated steam pressure). It can be seen from Fig. 3 that the change of heating water temperature from 75^{o}C to 90^{o}C does not have a major impact on either the water productivity or energy consumption. Also, contrary to the trend for the heating water temperature (Fig. 2), the lower the cooling water temperature, the better the performance (i.e. higher fresh water production rate and lower energy consumption rate). Additionally, changing the cooling water temperature has a greater impact on the water productivity and energy consumption. For example, reduction of the cooling water temperature by 20^{o}C (from 25^{o}C to 5^{o}C) would lead to a water productivity and energy consumption increase and decrease of 314% and 10.5% respectively, while increasing the heating water temperature by the same amount (from 65^{o}C to 85^{o}C) would lead to a productivity increase of just 33.3 % along with a small (1.5%) increase in the energy consumption rate.

Figs. 4 and 5 show the impact when just one stream of cooling water temperature changes. The latter figure suggests the temperature of the cooling water entering the condenser has little impact on water productivity. Fig. 4 shows the temperature of cooling water entering the bed has, on the other hand, a more significant impact on the system performance. These results also indicate an air cooled condenser may be suitable.

The results in Figs. 3-5 also suggest that any energy recovery effort (to improve energy efficiency of the system) should be on the cooling water side, especially the stream of the cooling water entering the bed rather than the one entering the condenser. For example, the effort should be put into recovering extra cooling generated (in the evaporator) to cool down further the cooling water entering the bed if no external cooling demand (e.g. air conditioning) is required. This would be more effective than recycling the cooling to the stream entering the bed.

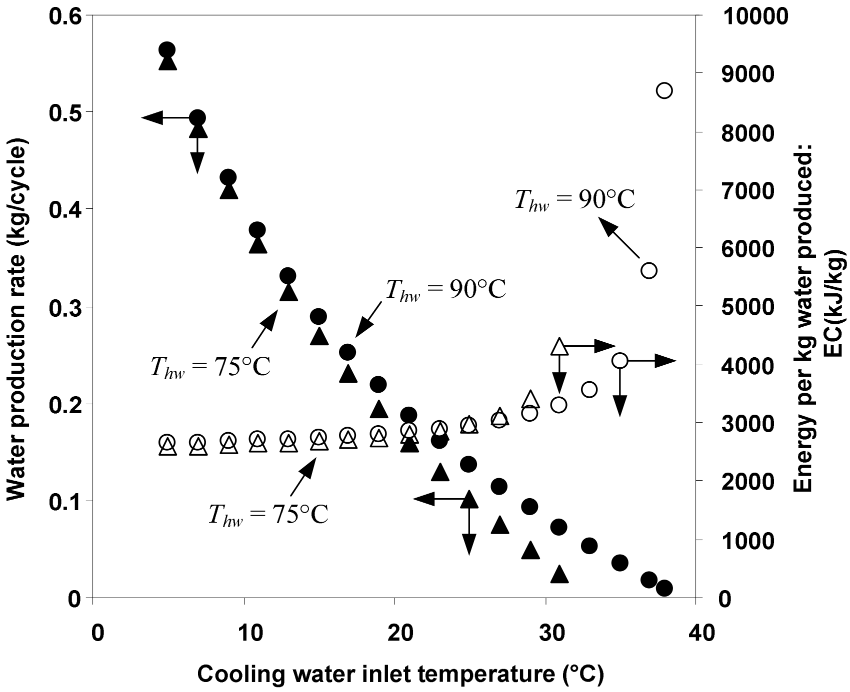

Fig. 3 The effect of varying temperature of the cooling water entering both the bed and condenser on the fresh water production rate and energy consumption per kilogram water produced for two different heat source temperature at 75^{o}C and 90^{o}C,

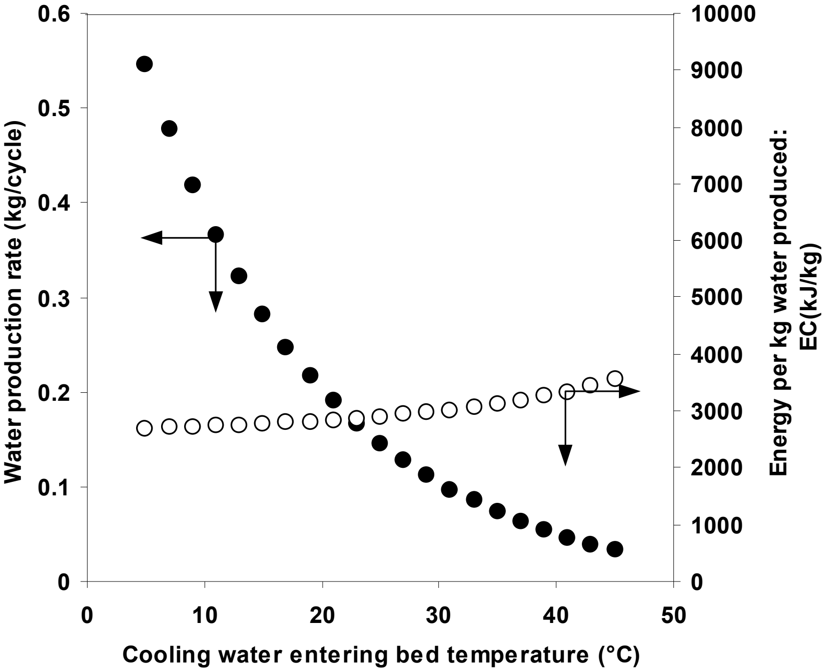

Fig. 4 The change of water production rate and system energy consumption on different cooling source temperatures entering the bed, while the cooling water entering condenser temperature is fixed at 20°C.

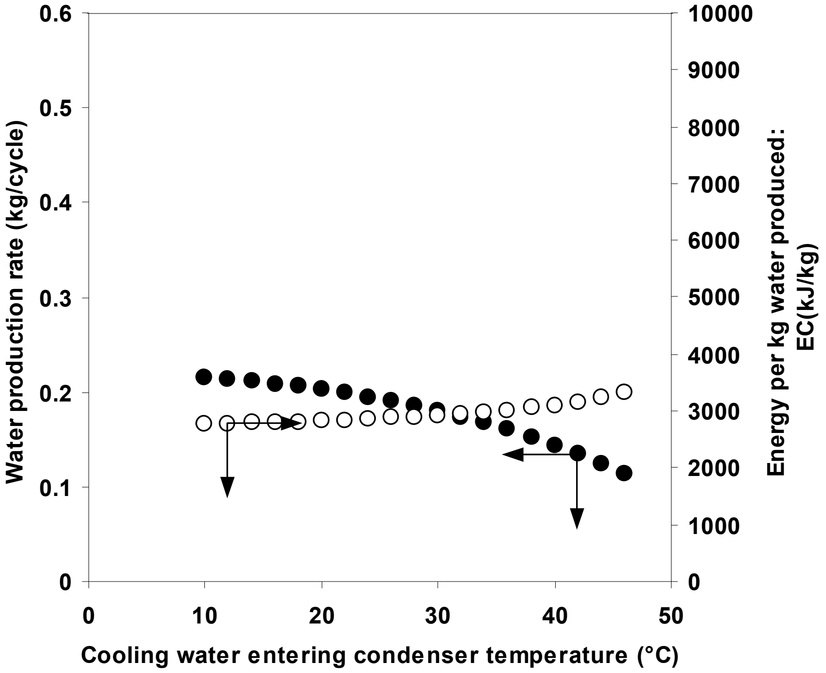

Fig. 5 The change of water production rate and system energy consumption on different cooling water temperatures entering condenser, while the cooling water entering bed temperature is fixed at 20°C.

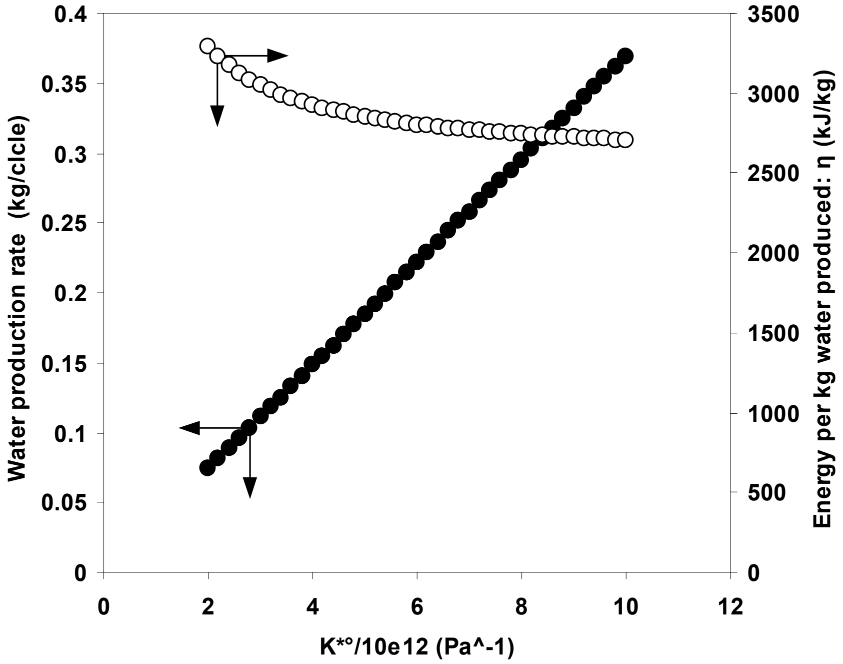

Fig. 6 The change of fresh water production rate and desalination process energy consumption on different levels of K_0^I value, when the typical input water temperatures $T_{cw} = 20°C$, $T_{hw} = 90°C$ and T_{evap}=13°C (i.e. evaporator operating at 1.5kPa) are fixed.

Effects of silica gel adsorption equilibrium constant

Some surface treatment technologies can improve the K_0^I for silica gel (Ng et al., 2001; Wang and Chua, 2007). Fig. 6 shows the effect of modifying K_0^I on the fresh water productivity and energy consumption rate. The determination of K_0^I range for the study is based on the consideration that the value of K_0^I is typically less than $23.7 \times 10^{-12} Pa^{-1}$, which is calculated from the model with the limit of X (i.e. $X \leq 1$). There is a linear increase of the fresh water production rate with K_0^I. In other words, the bigger K_0^I the better the performance (i.e. increase in water production and decrease in energy consumption). As the water productivity increases with K_0^I, the quantity of silica gel required per unit mass of water produced is reduced and, hence, the sensible energy part of the total energy consumption also decreases. However, as the sensible heat component of the energy accounts for just a small fraction (about 17%) of the total energy consumption, K_0^I only marginally affects the energy consumption as shown in Fig. 6.

Effects of evaporator temperature

In all of the above, we considered $T_{evap}<T_{cw}$ only. There are, however, three possibilities in this regard: $T_{evap}<T_{cw}$ (Case I), $T_{evap}=T_{cw}$ (Case II) and $T_{evap}>T_{cw}$ (Case III). Fig. 7 shows the effect of T_{evap} on both water productivity and energy consumptions when the heating water inlet temperature to the bed is 90°C and the cooling water inlet temperature to the bed and condenser are at 20°C; T_{evap}-T_{cw} is used to clearly show the demarcation between the three different cases. This figure shows that the water productivity of the system is capped at 0.432kg/cycle and the energy consumption can go no lower than 2677.37kJ per kg water produced. These limits are reached at T_{evap}=17.9°C, which corresponds here to $T_{evap} - T_{cw} = -2.1$°C.

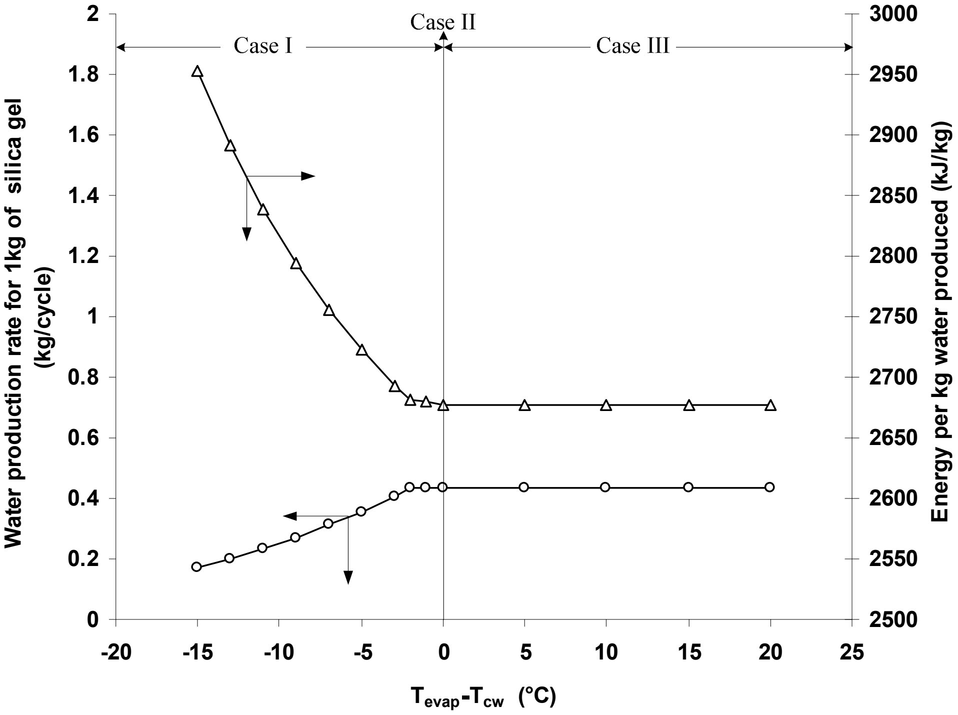

Fig. 7. Effect of T_{evap} on the water production rate for 1 kg of silica gel and energy consumption (for X_{max}=0.45; T_{cw}= 20°C and T_{hw}= 90°C).

CONCLUSION

In this study, the working principle and thermodynamic cycle of AD system has been described and its performance evaluated under equilibrium conditions. The analysis shows that an optimum heating water temperature exists for the minimum energy consumption per unit mass fresh water produced. The optimum temperature depends on the cooling water temperatures and other operating parameters of the system. The temperature of the cooling water entering the bed during the adsorption process has significant impact on the both water productivity and energy consumption: the lower the better. Therefore any effort to improve the system performance and reduce costs should be put into the cooling water entering the bed (e.g. recycle the cooling effect from the evaporator). These results also indicate an air cooled condenser may be suitable for the cooling water entering the condenser. The results also show that whilst the silica gel adsorption equilibrium constant and the fresh water productivity are linearly related, the former has little impact on the energy consumption. Finally, the evaporator temperature can significantly impact on the nature of the cycles and the performance of the AD systems with the impact depending on the capacity of the adsorbent used.

The use of the equilibrium thermodynamic model here allows rapid calculation and, therefore, consideration of many combinations of system parameters with modest resource. It is, however, recognised that the equilibrium assumption means the results here can only be used as a guide. The model also does not give any information about the dynamic behaviour of AD systems. Both these issues may be overcome by adopting lumped dynamic models such as done by some (Chua et al., 1999; Chua et al., 2004; Wang et al., 2005; Wang and Chua, 2007) or even one- or higher-dimensional dynamic models that allow adsorptive dispersion and bed geometry to be included – such models are currently under development by the authors and will be reported on elsewhere.

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