Desalination 344 (2014) 350–356

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Adsorption characteristics of water vapor on ferroaluminophosphate for desalination cycle

Young-Deuk Kim [a,b,*], Kyaw Thu [c], Kim Choon Ng [b,c]

[a] Department of Mechanical Engineering, Hanyang University, 55 Hanyangdaehak-ro, Sangnok-gu, Ansan, Gyeonggi-do 426-791, Republic of Korea
[b] Water Desalination and Reuse Center, 4700 King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia
[c] Department of Mechanical Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 117576, Singapore

HIGHLIGHTS

- Adsorption isotherms of water vapor on ferroaluminophosphate for desalination cycle.
- Thermophysical properties and surface characteristics of ferroaluminophosphate.
- Development of hybrid isotherm model comprising the Henry and the Sips isotherms.
- Comparison of water vapor adsorption between ferroaluminophosphate and silica gels.

ARTICLE INFO

Article history:
Received 14 March 2014
Received in revised form 5 April 2014
Accepted 7 April 2014
Available online 3 May 2014

Keywords:
Adsorption
Ferroaluminophosphate
Adsorption isotherm
Hybrid isotherm
Desalination

ABSTRACT

The adsorption characteristics of microporous ferroaluminophosphate adsorbent (FAM-Z01, Mitsubishi Plastics) are evaluated for possible application in adsorption desalination and cooling (AD) cycles. A particular interest is its water vapor uptake behavior at assorted adsorption temperatures and pressures whilst comparing them to the commercial silica gels of AD plants. The surface characteristics are first carried out using N_2 gas adsorption followed by the water vapor uptake analysis for temperature ranging from 20 °C to 80 °C. We propose a hybrid isotherm model, composing of the Henry and the Sips isotherms, which can be integrated to satisfactorily fit the experimental data of water adsorption on the FAM-Z01. The hybrid model is selected to fit the unusual isotherm shapes, that is, a low adsorption in the initial section and followed by a rapid vapor uptake leading to a likely micropore volume filling by hydrogen bonding and cooperative interaction in micropores. It is shown that the equilibrium adsorption capacity of FAM-Z01 can be up to 5 folds higher than that of conventional silica gels. Owing to the quantum increase in the adsorbate uptake, the FAM-Z01 has the potential to significantly reduce the footprint of an existing AD plant for the same output capacity.

1. Introduction

Since solid–vapor adsorption refrigeration was first revealed by Faraday in 1848, the adsorption processes have been extensively used for heating, cooling, humidity control, sea or brackish water desalination and waste water treatment systems [1–14]. As environmental and energy issues such as global warming and climate change have been intensified, environmentally benign cycles such as adsorption cooling system have been vigorously studied as an alternative to conventional vapor compression cooling. Some salient features of the adsorption cycles are energy efficient and environment friendly, which (i) can be operated by low-temperature waste heat or solar heat, (ii) has almost no moving parts rendering less maintenance and (iii) does not require ozone depleting refrigerants. Lately, the application of adsorption process in sea or brackish water desalination has received great attention because this system can employ a low-temperature heat source for producing two useful effects, such as cooling and desalting [1–6]. The cooling energy is produced from the first phase (evaporation–adsorption) while the fresh water is collected from the second batch process, i.e., desorption–condensation. The operation of the adsorption desalination (AD) cycle is a batch-operated, therefore, concomitant with the adsorption-initiated-evaporation and the desorption-assisted-condensation processes utilizing the sorption characteristics of highly porous hydrophilic adsorbent.

It is well known that the performance of AD cycle depends on how the adsorbents behave in both equilibrium adsorption isotherms and kinetics. In order to attain these prerequisites, the adsorbents should have (i) a fairly high surface area or micropore volume and (ii) a relatively large pore network for the molecules transport to the interior of adsorbents [6]. For these prerequisites the adsorbent must have small pore

* Corresponding author at: Department of Mechanical Engineering, Hanyang University, 55 Hanyangdaehak-ro, Sangnok-gu, Ansan, Gyeonggi-do 426-791, Republic of Korea. Tel.: +82 31 400 5254; fax: +82 31 436 8146.
E-mail address: youngdeuk@hanyang.ac.kr (Y.-D. Kim).

http://dx.doi.org/10.1016/j.desal.2014.04.009
0011-9164/

size with a reasonable porosity, e.g., a combination of micropores (pore width <2 nm) to mesopores (pore width in the range 2–50 nm) [6]. In this regard, a considerable amount of study has been conducted on a number of adsorbent–adsorbate pairs like silica gel–water [7,8], activated carbon–methanol/ethanol/ammonia [9–11] and zeolite–water [12–14] for air conditioning and refrigeration systems, while silica gel–water or zeolite–water for seawater/brackish water desalination and waste water treatment systems [1–6]. Among the pairs, silica gel–water has been considered as an ideal adsorbent–adsorbate pair for the utilization of waste heat or solar energy in the cooling or desalination system due to its low regenerating temperature less than 85 °C, whilst zeolite and activated carbon have been used where the waste heat is higher than 100 °C. However, the output cooling power or fresh water production per unit volume of such system is relatively small, resulting in bulky and space-demanding system, which is one of the reasons why such system is not as widespread. Furthermore, the adaptation of the adsorption cycles for both cooling and desalination applications is hindered by the limitation in the temperature of the intermediate thermal reservoir to reject the heat of adsorption. For instance, the major concern to apply the AD cycles in the Middle Eastern region is the high ambient temperature where the cycle has to reject the isosteric heat to the temperature as high as 45 °C. Thus, the development of novel adsorbent material having a higher water vapor uptake and heat exchanger with a higher heat and mass transfer characteristic are indispensable.

As noted above, mesoporous solids having a pore diameter of 2 to 10 nm like silica gel [15] have gained much attention for their potential use in various applications, e.g., adsorbents and catalysts. In addition, the large surface area and pore size uniformity of mesoporous solids can enhance their application feasibility for removal and separation operations. A huge amount of water vapor can be also adsorbed on the mesoporous solids since their mesopores are well-suited for capillary condensation at moderate pressure [16]. This kind of adsorption isotherms of water vapor is also observed in microporous aluminophosphate molecular sieves [17]. In this respect, a microporous ferroaluminophosphate molecular sieve, functional adsorbent material zeolite 01 (FAM-Z01, developed by Mitsubishi Plastics), was studied for adsorption heat pump or desiccant air conditioning system that can bring about both the compact system and the utilization of low regeneration temperatures ranging from 50 to 80 °C [18,19]. It is expected that FAM-Z01 possesses the essential characteristics for sorption cycles such as high affinity for water vapor uptake, lower regeneration temperature (less than 85 °C) and the ability to sustain uptake process at relatively higher adsorption temperature. Therefore, FAM-Z01 may contribute to reduce the footprints of adsorption plants and increase the chances for commercial success of AD cycle for desalination application in the Middle Eastern region.

In this study, the adsorption equilibrium isotherms of water vapor on a ferroaluminophosphate are investigated for its applicability as a suitable adsorbent in the AD cycle. The adsorption isotherms of water vapor on FAM-Z01 are then investigated using a hybrid isotherm composing of the Henry isotherm at low pressure and the Sips isotherm at moderate pressure. This work also takes into account the thermophysical properties and surface characteristics evaluation of FAM-Z01 using nitrogen adsorption isotherm at 77 K using static volumetric method. The water vapor uptake capacity of FAM-Z01 is finally compared against the commercial silica gels, namely, (i) Type-A5BW (KD Corporation), (ii) Type-RD 2560 (Fuji Silysia Chemical) and (iii) Type-A^{++} (Mayekawa), at the specific operating conditions of AD cycle.

2. Experimental section

2.1. Materials

FAM-Z01 with iron content of 2–8 mol% is an AFI-type structure ferroaluminophosphate (FAPO-5), which has isotypic framework structure with AlPO-5. AlPO-5, a member of the aluminophosphate molecular sieves ($AlPO_4$'s) family, possesses a structure comprising of alternating tetrahedral of Al and P linked together to build a microporous structure with unidimensional 4-, 6- and 12-membered ring channels [20,21]. In contradiction to zeolites, AlPO-5 possesses a neutral framework with a mild hydrophilicity [21]. FAM-Z01 has a unidimensional structure with 0.73 nm windows and its framework comprises AlO_4, PO_4 and FeO_4 tetrahedrons, where a part of Al and P atoms are substituted with Fe atoms as the heteroatom for improving the hydrophilicity of adsorbent. FAM-Z01 is synthesized from iron-containing aluminophosphate gels in the presence of organic amines under hydrothermal condition [18,19]. The thermophysical properties of FAM-Z01 are shown in Table 1 [18].

Table 1
Thermophysical properties of FAM-Z01.

Bulk density (kg/dm^3)	0.6–0.7
Typical particle size (μm)	100–2000
Thermal conductivity (W/mK)	0.113 (303 K)
	0.123 (343 K)
Differential heat of adsorption (H_2O, 298 K) (kJ/mol)	56
Specific heat (kJ/kgK)	0.805 (303 K)
	0.896 (343 K)

2.2. Apparatus and procedure

The microstructure and morphology of FAM-Z01 are systematically characterized using analytical and spectroscopic techniques. The crystalline phase is identified with powder X-ray diffraction (XRD) (D8 Advance, Bruker) using Ni-filtered Cu-Kα radiation ($\lambda = 1.5418$ Å) and a step size of 0.02° over the range $3° < 2\theta < 50°$. Morphologies and structure analysis are undertaken using scanning electron microscopy (SEM) (Quanta 600 FEG, FEI).

Nitrogen adsorption and desorption isotherms on FAM-Z01 are measured at 77 K using static volumetric method (Autosorb-1, Quantachrome) to measure the physical properties such as total surface area, micropore surface area, external surface area, micropore volume, micropore and mesopore size distributions of FAM-Z01. Before the measurements, the adsorbent sample of 0.028 g is evacuated at 140 °C for 12 h under vacuum. Based on the adsorption isotherms of nitrogen, the aforementioned physical properties are determined from standard multi-point Brunauer–Emmett–Teller (BET), t-plot, Dubinin–Radushkevich (D–R), Dubinin–Astakhov (D–A) and non-local density functional theory (NLDFT) methods.

The equilibrium adsorption of water vapor on FAM-Z01 is then measured using static volumetric method (Hydrosorb-1000, Quantachrome Ins.) at the temperature range of 20–80 °C. Prior to the experiments, adsorbent samples of 0.045 g are degassed to vacuum for 5 h at 200 °C. The water vapor adsorption isotherms for commercial silica gels such as Type-A5BW, Type-RD 2560 and Type-A^{++} are also measured using static volumetric method at the temperature range of 25–80 °C. All the silica gel samples are degassed at 120 °C under vacuum for 6 h prior to the experiments.

3. Results and discussion

3.1. Characteristics of FAM-Z01

The SEM pictures and XRD patterns of FAM-Z01 are shown in Fig. 1. According to the XRD pattern FAM-Z01 is well crystallized and shows the typical feature of the AFI structure.

The adsorption and desorption isotherms of nitrogen on microporous FAM-Z01 at 77 K are shown in Fig. 2. Although $AlPO_4$'s are known to exhibit type-I isotherms with nitrogen and other nonpolar adsorbates [20,22], adsorption isotherms of FAM-Z01 present features which can be described as type-IV according to IUPAC classification