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Adsorption of ethanol onto phenol resin based adsorbents for developing next generation cooling systems

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ABSTRACT

Adsorption characteristics of ethanol onto two promising adsorbents have been investigated for developing high performance adsorption chillers. These new adsorbents are based on spherical phenol resin treated with different mass ratios of KOH named as KOH4-PR and KOH6-PR. Experimental adsorption isotherm measurements show that the adsorption capacity of KOH4-PR/ethanol is as high as 1.43 kg kg^{-1} whilst one kg of KOH6-PR able to adsorb nearly about 2 kg of ethanol. To the best of our knowledge, the studied adsorbents possess the highest ethanol uptake. Moreover, it is found that the KOH4-PR/ethanol pair has notably high adsorption kinetics at the lower range of adsorption temperatures. Experimental measurements of adsorption uptake and adsorption uptake rate of the studied pairs have been analyzed and isosteric heats of adsorption have also been extracted.

1. Introduction

According to International Institute of Refrigeration (IIR), approximately 15% of electricity produced in the world has been utilized for refrigeration and air-conditioning applications [1,2]. The intensive use of air conditioning during summer periods, especially in hot climate regions, increases the peak of electricity demand. Adsorption cooling systems could be an effective option in reducing the peak electrical demand as they can be driven by solar energy or low-grade waste heat typically below 100 °C. Moreover, these systems are environmental friendly since they use natural refrigerants or alcohols such as water, ethanol and methanol. However, the main hindrance for spreading this technology is the poor system performance and bulkiness due to the limitation of sorption capacity of adsorbent material and the low heat transfer rate inside adsorber/desorber reactors. Therefore, characterization of innovative and promising pairs that possess high adsorption uptake and/or fast kinetics becomes a hot research topic for developing high performance adsorption cooling systems. The working pairs can be classified as pairs working at partial sub-atmospheric pressure which dominated mainly by silica gel/water, zeolite/water, activated carbon (AC)/methanol, activated carbon/ethanol and activated carbon fibers (ACFs) + ethanol or methanol. Pairs working at pressurized conditions such as AC/ammonia, AC/butane, AC/R134a and others. Adsorption characteristics of water onto two types of silica gel namely A and RD have been experimentally investigated using volumetric method [3]. The measurements have been conducted within a temperature ranges from 298 to 338 K and pressure ranges from 500 to 700 Pa. Adsorption isotherm data have been correlated using Tóth equation and isosteric heat of adsorption has been evaluated. Aristov et al. [4] measured the water sorption equilibrium and specific heat of water onto a family of composite materials called selective water sorbents. These materials consist of a porous host matrix with open pores and a hygroscopic substance impregnated into its pores. Authors reported that composites based on $CaCl_2$ and LiBr as impregnated salts and different micro- and mesoporous silica gels as host matrices have adsorption capacity as high as 0.75 kg kg^{-1}. Solmuş et al. [5] measured adsorption isotherms of natural zeolite/water pair for adsorption cooling applications. The Dubinin–Astakhov adsorption isotherm model has been used to fit the experimental data. They

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Nomenclature

D	diffusivity ($m^2\ s^{-1}$)	R_g	gas constant ($kJ\ kg^{-1}\ K^{-1}$)
D_{so}	pre-exponential constant ($m^2\ s^{-1}$)	R_p	adsorbent particle radius (μm)
E	adsorption characteristics parameter ($kJ\ kg^{-1}$)	T	temperature (K)
E_a	activation energy ($kJ\ kg^{-1}$)	t	time (s)
F	fractional uptake (–)	W	equilibrium adsorption uptake ($kg\ kg^{-1}$)
P	equilibrium pressure (kPa)	w	instantaneous adsorption uptake ($kg\ kg^{-1}$)
P_s	saturated pressure (kPa)	w_{in}	initial uptake ($kg\ kg^{-1}$)
q_{st}	isosteric heat of adsorption ($kJ\ kg^{-1}$)	W_o	maximum adsorption capacity ($kg\ kg^{-1}$)

reported that the maximum adsorption capacity of natural zeolite is about 0.12 $kg\ kg^{-1}$ for adsorption temperature ranges from 40 to 150 °C and evaporation pressure from 0.87 to 7.38 kPa. El-Sharkawy et al. [6] measured adsorption uptake of ethanol onto two types of activated carbon fibers namely ACF (A-20) and ACF (A-15). It is reported that one kg of ACF (A-20) has the ability to adsorb about 0.797 kg of ethanol whilst ACF (A-15) has adsorption capacity of about 0.57 $kg\ kg^{-1}$. The study also addressed the effect of packing density of adsorbent on adsorption rate. El-Sharkawy et al. [7] studied the adsorption characteristics of ethanol onto parent and surface treated activated carbon powder. Adsorption isotherms and kinetics of ethanol onto three adsorbents namely, parent Maxsorb III, KOH-H_2 treated Maxsorb III, and H_2 treated Maxsorb III have been measured gravimetrically. It is found that the maximum adsorption uptakes of ethanol onto H_2 treated Maxsorb III, parent Maxsorb III and KOH-H_2 treated Maxsorb III are 1.23, 1.20 and 1.01 $kg\ kg^{-1}$, respectively. However, adsorption kinetics of KOH–H_2 treated Maxsorb III/ethanol pair is faster than other two studied pairs. Gordeeva and Aristov [8] presented the dynamic characteristics of methanol adsorption onto activated carbon ACM-35.4 for enhancing the specific cooling power of the adsorption chillers. The study addressed the effects of adsorbent grain size, bed thickness and adsorption/desorption temperatures under conditions close to real adsorption chiller operations. Tamainot-Telto et al. [9] studied the adsorption characteristics of ammonia onto 26 different activated carbons. They used a thermodynamic cycle model coupled with adsorption isotherm equations to select the optimum pair based on the cooling/heating production and/or coefficient of performance. Adsorption characteristics of other pairs could be found elsewhere [10–19].

This study presents an experimental investigation of ethanol adsorption onto two newly developed phenol resin based adsorbents namely KOH4-PR and KOH6-PR. Adsorption isotherms and kinetics of the studied pairs have been measured gravimetrically using magnetic suspension adsorption measurement unit. Experimental data have been analyzed and correlated with popular adsorption isotherm and kinetic models. Adsorption uptakes of ethanol onto the studied adsorbents are found to be very promising which may lead to the design and development of high performance adsorption chillers.

2. Adsorbents

Spherical phenol resin samples, as provided BEAPS® series (Asahi Organic Chemicals Industry Co., Ltd.), have been used as a raw material. The BEAPS® which is a registered trademark of Asahi Organic Chemicals Industry Co., Ltd. has been carbonized at 600 °C for an hour in a flow of N_2 using a vertical electric furnace. For the preparation of activated carbons, potassium hydroxide (purity > 85.0%, Wako Pure Chemical Industries, Ltd.) is used as an activating agent. Weight ratio of KOH/carbonized BEAPS has set to 4 or 6. The mixture of KOH and the carbonized BEAPS® has been put in a nickel container, and then the nickel container is located in a stainless steel container. After that, the stainless steel container is placed in an electric furnace vertically. The mixture is heat-treated up to 900 °C at a heating rate of 5 °C/min and maintained at 900 °C for one hour under N_2 flow. After the activation, the remaining KOH and salts formed during the heat treatment are removed by the washing with HCl solution for three times and deionized water once to adjust pH to be about 7. After washing, the collected samples are dried at 100 °C for 3 h in an air oven and dried again at 150 °C for 12 h in a vacuum oven. Fig. 1 shows the SEM pictures of both KOH4-PR and KOH6-PR samples whilst their porosity and elemental composition are furnished in Table 1.

Laser Diffraction Particle Size Analyzer, SALD-2300, supplied by Shimadzu Corporation, Japan is used to measure the particle size distribution of adsorbent. Figs. 2a and 2b show the particle size distributions for KOH4-PR and KOH6-PR samples. It can be seen from Figs. 2a and 2b that both adsorbent samples have narrow particle size distributions and the normalized particle amount reaches 50% at particle diameters of 26 and 23 μm for KOH4-PR and KOH6-PR, respectively.

3. Experiments

Magnetic suspension adsorption measurement unit of type (MSB-VG-S2) supplied by BEL Japan, Inc. is used to measure adsorption isotherms and kinetics of the studied pairs. For each adsorption isotherm, the sample temperature is kept constant whilst evaporator temperature increases stepwise until reaches a relative pressure of about 0.9 or above. Experiments have been conducted at adsorption temperatures of 30, 40, 50, 60 and 70 °C. For the experimental isotherm and kinetics measurement of both studied samples, a 47 mg of dry sample has been used. Ethanol of 99.5% purity supplied by Osaka Kishida Chemical Co., Ltd., Japan is used as adsorbate. Experimental procedure has been described in detail by El-Sharkawy et al. [7].

4. Results and discussion

4.1. Adsorption isotherms

Figs. 3a and 3b show adsorption isotherms of KOH4-PR/ethanol and KOH6-PR/ethanol pairs. It can be seen that one kg of KOH4-PR type adsorbent can adsorb 1.43 kg of ethanol whilst KOH6-PR has an adsorption capacity as high as about 2 $kg\ kg^{-1}$. Repeatability of the experimental adsorption isotherm data is also confirmed. To the best of our knowledge, adsorption uptakes of ethanol onto the two studied spherical phenol resin based adsorbents are significantly higher than adsorption capacity of ethanol onto any other adsorbent. It is worthy to mention that, adsorption capacity of KOH6-PR/ethanol pair is about 40% higher than that of KOH4-PR/ethanol pair. This is might be due to the difference between the micropore volumes of both adsorbents since KOH6-PR possesses micropore volume of 2.37 $cm^3\ g^{-1}$ whilst KOH4-PR has 1.85 $cm^3\ g^{-1}$.