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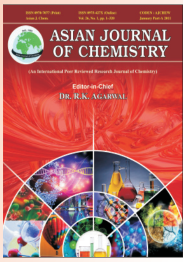

Adsorption Equilibrium and Kinetics of Anisole/Water Mixture on Molecular Sieve 4A

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In this study, the adsorption equilibrium and kinetics of anisole/water mixture on molecular sieve 4A were investigated experimentally and theoretically. The Langmuir isotherm equation and pseudo-second-order model interpreted the observed experimental data of adsorption equilibrium and kinetics properly. Adsorption mechanism was also indicated by the plot of [-0.4977-ln(1-F)] against time *t*. The adsorption process was indicated to be thermodynamically favorable, spontaneous and endothermic in nature. The feasibility of dehydrating anisole by adsorbing water on molecular sieve 4A was demonstrated by fixed-bed breakthrough curves.

Keywords: Anisole/water, Adsorption, Equilibrium, Mechanism, Molecular sieve 4A.

INTRODUCTION

Because of the special properties of boron-10 and boron-11, the enriched boron and boron compounds are used as neutron absorbers in nuclear industry, a relatively selective radiation dose delivery to the tumour tissue (BNCT), additions to steel and so on[1-5]. There is and will be an increasing demand for separated boron isotopes. The process of chemical fractionation with anisole as donor is the most appropriate now. But serious side-reactions and corrosion caused by the trace water in anisole have a very bad influence on the production and stability of the boron isotopes separation system[6]. The water content should be controlled under 30 ppm to ensure the boron isotopes separation system running normally. So the dehydration of anisole is necessary for this process. By contrast with the distillation or stripping process, adsorptive dehydration is one of the most energy-efficient methods for this purpose[7,8].

Adsorption is a versatile treatment technique used widely in fine chemical and process industries for waste water and gas treatment. The usefulness of the adsorption process lies in the simple operation and reuse of adsorbents during long term applications[9]. In consideration of the kinetic diameters of adsorbates, molecular sieve 4A was selected.

Adsorption equilibrium and kinetics data are important in the design and simulation of the adsorption processes. In this paper, the adsorption isotherm, kinetics, thermodynamics and mechanism involved in the sorption process of the anisole-water mixture on molecular sieves were studied. Then the parameters were used in Aspen Adsorption. The breakthrough curves (BTC) of simulation and experiment result were made to verify the validity of the study.

EXPERIMENTAL

Molecular sieves were obtained from Guangfu Fine Chemical Research Institute(Tianjin, China). Table-1 shows the properties of molecular sieves. The molecular sieves were preconditioned by thermal activation in an electronic furnace at 350 °C for 12 h and then kept in a vacuum desiccator for use.

Anisole was obtained from Guangfu Fine Chemical Research Institute. It was a reagent grade chemical with purity higher than 99.5 % and was used without further purification. A series of solutions were prepared using distilled water. Water content was measured with a Coulometric KF titrator C20 (METTLER TOLEDO).

An electrical balance with a standard uncertainty of 0.1 mg was used and the standard uncertainty of the timer was 0.1 s. In this work, the relative uncertainty of the concentration measurement was less than 0.6 %.

Equilibrium: The equilibrium isotherm was determined at a range of temperatures from 288.15 to 303.15 K over a range of water concentrations in the fluid phase from 80 to 2600 ppm (the mass fraction). The 0.5 g molecular sieves and 150 g liquid mixtures were put in conical flasks. The conical flasks were put in a thermostatted shaker at a pre-settled temperature with a standard uncertainty of ± 0.01 K under 200 rpm. The final concentrations were measured after 12 h.

Kinetic: Kinetic studies were carried out at 288.15, 293.15, 298.15, 303.15 K with an initial water concentration

TABLE-1
CHARACTERISTICS OF MOLECULAR SIEVES ADSORBENT

Parameters	Molecular sieve 4A
Form	Sphere
Real density (g cm^{-3})	2.698
Porosity (ε)	0.63
Bed void fraction ε_b	0.4
Diameter (mm)	2-3
BET surface area (m^2 g^{-1})	27.29

of 320 ppm the same as the equilibrium studies. But the samples of solution were withdrawn from the bulk solution at specified time intervals until the constant concentration at equilibrium was achieved.

Fixed-bed breakthrough curves experiments and simulation: Breakthrough experiments were carried out in jacketed glass columns (3.33 cm diameter × 30 cm height) packed with preconditioned molecular sieves. The column was maintained at 298.15 K and the feed, an anisole-water mixture containing about 320 ppm water, was introduced at the bottom. The operating flow rate was 5 mL/min. Samples of the product were collected at suitable time intervals and analyzed to establish the breakthrough curves. The parameters obtained from equilibrium and kinetic experiments were input into Aspen Adsorption[10]. Then the simulation and experiment breakthrough curves were compared. The uncertainties or relative uncertainties of varibles were also same as the equilibrium studies.

RESULTS AND DISCUSSION

Equilibrium isotherm: Equilibrium is established in adsorption for the distribution of the adsorbate between the fluid and the solid adsorbent. The various equilibrium isotherms and their applications are clearly reviewed in the literature[11]. Langmuir and Freundlich isotherms were applied to the experimental data in this study. The mathematical form of each model is as follows:

$$\text{Langmuir: } q = \frac{q_m kC}{1+kC} \tag{1}$$

$$\text{Freundlich: } q = aC^b \tag{2}$$

In eqn. (1), C, q_m and k are the concentration of water (the mass fraction), the adsorption capacity and the Langmuir constant, respectively. While a and b are the Freundlich constants in eqn. (2).

The equilibrium amount of water adsorbed on the adsorbent q was calculated by mass balance according to the following equation:

$$q = \frac{m\left(C_0 - C\right)}{W} \tag{3}$$

where C_0, m and W are the initial liquid-phase concentration of water, the amount of the solution and the amount of the adsorbent.

To model the adsorption equilibrium results at different temperatures, the variation of the constants k and a are included in eqn. 4 and 5:

$$k = k_0 \exp(-\frac{\Delta H_1}{RT}) \tag{4}$$

$$a = a_0 \exp(-\frac{\Delta H_2}{RT}) \tag{5}$$

where k_0 and a_0 are the pre-exponential factor and ΔH_1 and ΔH_2 are the adsorption enthalpy.

The equilibrium isotherms are shown in Fig. 1. The isotherm parameters and the correlation factor are shown in Table-2. The positive value of ΔH for the adsorption of water on the molecular sieve 4A indicates that the adsorption capacity is favored at lower temperatures.

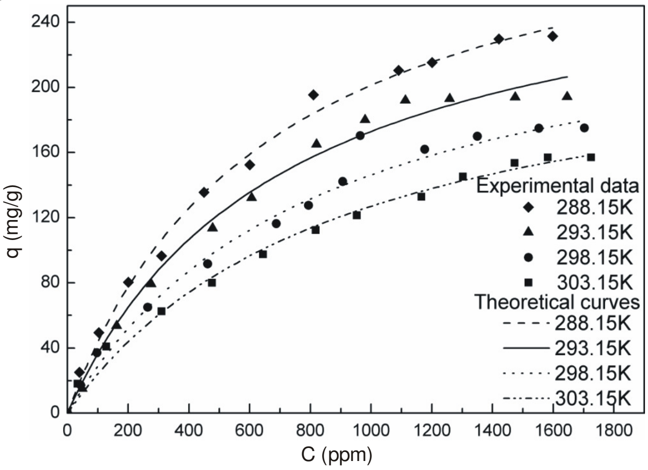

Fig. 1. Adsorption isotherms of anisole-water on molecular sieve 4A

Adsorption kinetics: From the result of the adsorption mechanism studies, it is obvious that film diffusion plays an extremely important role for internal diffusion. A number of studies on film diffusion have been carried out to elucidate the mechanism of film diffusion and to estimate film diffusion coefficient. In this study, the pseudo-second-order model was chosen, as the correlation coefficients of pseudo-second-order model are approximate to unity in the similar studies[9, 12-15].

The equation for the pseudo-second-order model and initial conditions are as follows:

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \tag{6}$$

$$t = 0 \text{ for } \Gamma = k_s q_e^2 \tag{7}$$

TABLE-2
PARAMETERS OF LANGMUIR AND FREUNDLICH ISOTHERMS OF ANISOLE-WATER ON MOLECULAR SIEVE 4A

T (K)	Langmuir					Freundlich				
	q_m (mg g^{-1})	10^3 k	r^2	10^6 k_0	ΔH (kJ mol^{-1})	a (mg g^{-1})	b	r^2	105 a_0 (mg g^{-1})	ΔH (kJ mol^{-1})
288.15	334.73	1.508	0.9947	2.292	6.768	5.169	0.5249	0.9767	5.837	11.850
293.15	295.25	1.413	0.9901			4.319	0.5289	0.9499		
298.15	266.69	1.215	0.9934			3.371	0.5403	0.9845		
303.15	241.55	1.109	0.9909			3.003	0.5370	0.9955		

where k_s is the pseudo-second-order model rate coefficient, Γ is the initial sorption rate.

If eqn. 6 is integrated at the initial condition, a linear equation is obtained. This equation is shown as follows:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^{\ 2}} + \frac{1}{q_e} t \tag{8}$$

The values of k_s, q_e and Γ are calculated from the slope and intercept of the plot t/q_t *versus* t. The plots are shown in Fig. 2. And the values of k_s, q_e and Γ are shown inTable-3.

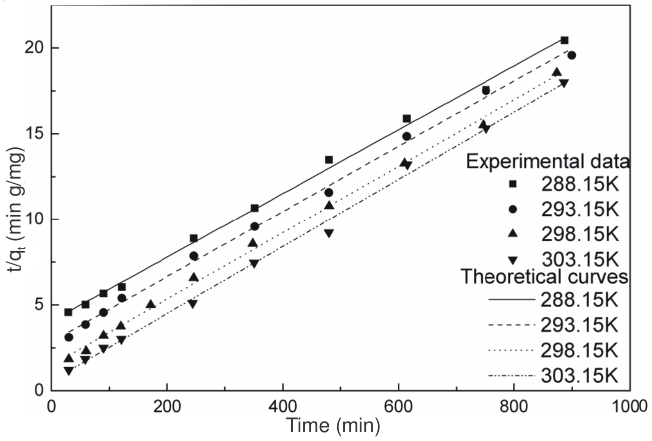

Fig. 2. Plots of t/q_t *versus* t for the adsorption of water on molecular sieve 4A

The influence of the initial concentration of water on the adsorption kinetics was shown in Fig. 3. The adsorption was very fast in the first 100 min. With further increase of time, the sorption kinetics decreased progressively and the adsorption approached to equilibrium finally. The reason for the fast adsorption at the initial stage is probably the great concentration gradient between the adsorbate in solution and adsorbate in adsorbent, as there must be large number of vacant sites available in the beginning. The initial increase in adsorption and consequently the attainment of adsorption equilibrium probably due to limited mass transfer of the water molecules from the bulk anisole to the external surface of molecular sieve 4A, initially and subsequently by slower internal mass transfer within the molecular sieve 4A particles[9].

Thermodynamic parameters[12]: The activation energy of the water adsorption on the molecular sieve 4A was calculated using the Arrhenius equation:

$$k_s = k_{s0} \exp(-\frac{E_a}{RT}) \tag{9}$$

where E_a, R and k_s denote the activation energy of adsorption, universal gas constant and the rate constants corresponding to temperatures T, respectively. From eqn. 9, the activation energy E_a of adsorption was found to be 124.64 kJ mol^{-1}.

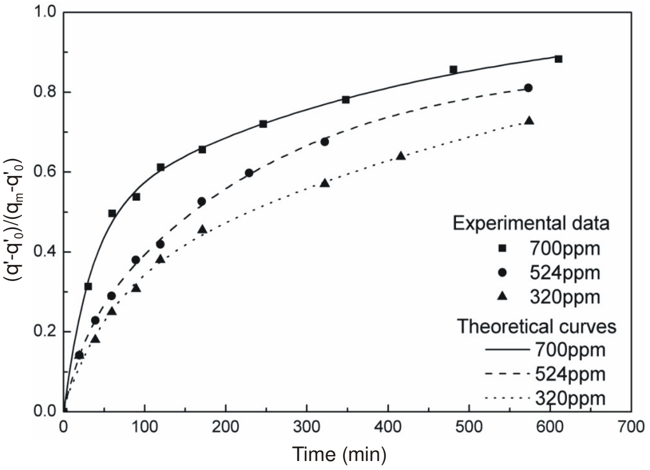

Fig. 3. Influence of the initial concentration of adsorbate on the adsorption kinetics

The thermodynamic parameters for the adsorption process, ΔH^0, ΔS^0 and ΔG^0, were calculated using the van't Hoff equation:

$$\log K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \tag{10}$$

$$\Delta G^0 = RT \ln K_c \tag{11}$$

where ΔS^0 is the entropy of adsorption and ΔH^0 is the enthalpy of adsorption, ΔG^0 is the Gibbs energy of adsorption and T is the absolute temperature.

The values of log K_c were defined as follows:

$$\log K_C = \frac{X_e}{1 - X_e} \tag{12}$$

where X_e is the fraction of water adsorbated at equilibrium.

The calculated thermodynamic parameters such as E_a, ΔH^0, ΔS^0 and ΔG^0 are given in Table-4. The negative value of ΔG^0 at all temperatures indicates that water adsorption onto molecular sieve 4A is spontaneous. The fact that ΔG^0 decreases with increase in temperature manifests that process is favored at higher temperatures. But the adsorption at ambient temperature is fast enough, so there is no need of extra energy. The positive value of ΔH^0 for the adsorption of water on the molecular sieve 4A indicates that the adsorption process is endothermic. During the adsorption of water on the molecular sieve 4A, the increased randomness at the solid/solution interface is manifested from the positive value of ΔS^0.

Adsorption mechanism: It is important to predict the rate-limiting step in an adsorption process. The steps of adsorption mechanism are as follows:

(1) Film diffusion, which involves the transport of adsorbate from the bulk of the solution towards the adsorbent external surface.

TABLE-3
PARAMETERS OF THE PSEUDO-SECOND-ORDER MODEL FOR THE ADSORPTION OF WATER ON MOLECULAR SIEVE 4A

T (K)	10^4 k_s (g mg^{-1} min^{-1})	q_e (mg g^{-1})	Γ (mg g^{-1} min^{-1})	r^2
288.15	0.8497	53.76	0.2456	0.9972
293.15	1.266	52.63	0.3507	0.9974
298.15	2.549	51.55	0.6774	0.9981
303.15	6.593	51.02	1.716	0.9969

TABLE-4
THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF WATER ON MOLECULAR SIEVE 4A

Water	E_a (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	ΔG^0 (kJ mol^{-1})			
				288.15 K	293.15 K	298.15 K	303.15 K
	124.64	11.68	73.37	-9.429	-9.848	10.241	10.518

(2) Particle diffusion, which refers to that the adsorbate molecules diffuse in the interior of the adsorbent particles.

(3) Adsorption, where the adsorbate molecules adsorb on the interior of the porous adsorbent.

Of the three steps, the third step is assumed to be so rapid that it can be neglected. For the purposes of design, the slowest step should be identified between film diffusion and particle diffusion. Then Boyd kinetic equation was applied, which is represented as[13]:

$$F = 1 - \frac{6}{\pi^2}\exp(-Bt) \quad (13)$$

$$F = \frac{q}{q_e} \quad (14)$$

where q_e is the amount of water adsorbed at equilibrium and q represents the amount of water adsorbed at any time *t* and Bt is a mathematical function of F.

Eqn. (13) can be rearranged by taking the natural logarithm to obtain the equation:

$$Bt = -0.4977 - \ln(1 - F) \quad (15)$$

The plot of [-0.4977-ln(1-F)] against time *t* can be employed to test the linearity of the experimental data[14].

If the plots are linear and pass through origin, then the rate controlling step is the internal diffusion and *vice versa*. In Fig. 4, the plots were linear but did not pass though the origin. It suggests that the adsorption process was controlled by film diffusion. The calculated B values were used to calculate the effective diffusion coefficient D_i using the equation:

$$B = \frac{\pi^2 D_i}{r^2} \quad (16)$$

where D_i is the effective diffusion coefficient of solute in the adsorbent phase and r is the radius of the adsorbent particles. The D_i values are given in Table-5 .

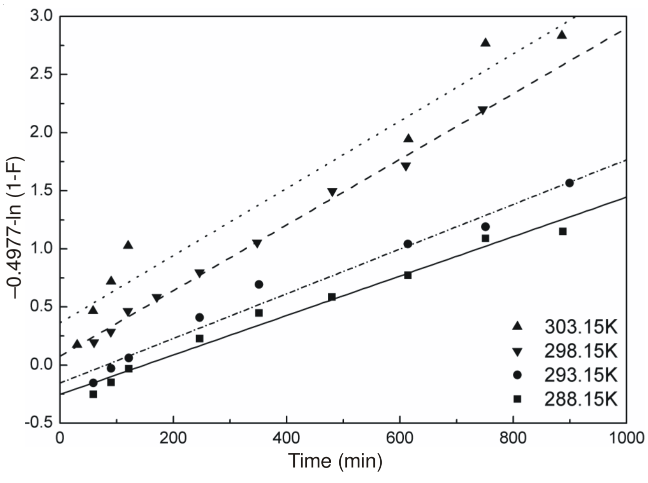

Fig. 4. Boyd plot for the adsorption of water on molecular sieve 4A

TABLE-5
EFFECTIVE DIFFUSION COEFFICIENT
OF WATER IN MOLECULAR SIEVE 4A

T (K)	10^{11} D_i (m^2 s^{-1})	r^2
288.15	1.797	0.9797
293.15	2.007	0.9800
288.15	2.958	0.9949
303.15	3.063	0.9597

Fixed-bed breakthrough curves: Once the kinetic and thermodynamic aspects of adsorption of water from anisole with molecular sieve 4A were known, an adsorption study with a fixed bed column was carried out. The semicontinuous adsorption system is widely used in industry. Two or three fixed bed columns are used: one of them is operated in adsorption mode whereas the others are in regeneration mode. The simulation and experiment breakthrough curves were shown in Fig. 5. The breakthrough curves exhibit a steep increase in the relative concentration of water at the breakthrough point. It is evident that the simulation curves give a good prediction of the experimentally observed behaviour[7,15,16].

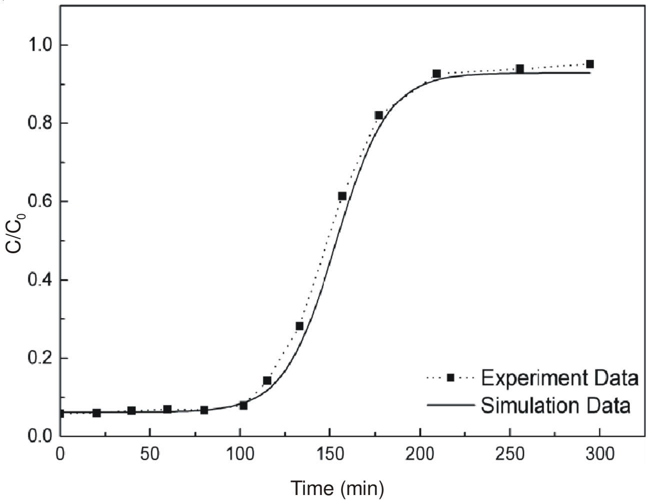

Fig. 5. Simulation and experiment breakthrough curves

Conclusion

In this study, the adsorption of water on molecular sieve 4A is investigated. The feasibility of dehydrating anisole by adsorbing water on molecular sieve 4A has been demonstrated. The adsorption isotherm is fitted using Langmuir equation and the adsorption kinetics data is fitted by the pseudo-second-order model. The results show that adsorption process is controlled by film diffusion. The increase of the initial water concentration and temperature are both positive effects on adsorption. The values of thermodynamic parameters (ΔH_0, ΔS_0 and ΔG_0) indicate that the adsorption process is thermodynamically favorable, spontaneous and endothermic in nature.

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