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Adsorption of Tetrahydrofuran + Water Solution Mixtures by Zeolite 4A in a Fixed Bed

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The adsorption of a tetrahydrofuran + water mixture on zeolite 4A was carried out using a fixed bed. The equilibrium behavior was shown to fit the Langmuir isotherm. A homogeneous surface diffusion model (HSDM) was proposed to predict the adsorption breakthrough curves in the fixed bed with respect to different temperatures, initial concentrations, and feed flow rates. The experimental results on the adsorption of the tetrahydrofuran + water mixture on zeolite 4A columns proved that the HSDM can predict the column performance satisfactorily and, therefore, can be used in the design of a fixed bed.

Introduction

Tetrahydrofuran (THF) is a good organic solvent, an important organic raw material, and the precursor of polymers. Due to its proton-accepting nature, it is used as a solvent in many chemical industries. It is fully miscible with water. Many chemical and pharmaceutical industries encounter problems in separating THF from aqueous waste streams since their mixtures form azeotropes at lower compositions of water (mass fraction of 5.8 % at 337.15 K).

Adsorption is an efficient and economically feasible process for separation and purification. It plays an important role in a number of natural and industrial systems. The performance of any adsorption-based process greatly depends on the effectiveness of its design and operating conditions. In order to properly design and operate fixed bed adsorption processes, the adsorption isotherm and the fixed bed dynamics, that is the breakthrough curves, must be known. This paper presents the adsorption equilibrium and adsorption kinetics of tetrahydrofuran + water solution mixtures by zeolite 4A in a fixed bed.

Experimental Section

Materials and Analytical Method. Zeolite 4A was obtained from the ShangHai Chemical Reagent Plant (Shanghai, China). Table 1 shows the properties of zeolite 4A. Prior to its use, the molecular sieve was crushed and screened to a series of particle sizes and then washed thoroughly in distilled water to remove fines. Before the measurement, the adsorbent was activated at 623.15 K in an electric furnace for 8 h, and it was kept under vacuum until use.

Tetrahydrofuran was obtained from the Shuanglin Chemical Reagent Plant (Hangzhou, China), was a reagent grade chemical with purity higher than 99 %, and was used without further purification. A series of solutions were prepared using distilled water. Their concentrations were analyzed by gas chromatography.

Table 1. Characteristics of Zeolite 4A Adsorbent

adsorbent	zeolite 4A
form	sphere
average pellet size/mm	0.8 to 2.0
pellet density/g·cm^{-3}	0.66
average pore radius/Å	4
heat of adsorption/ kJ·kg^{-1} (H_2O)	4200
BET surface area/m^2·g^{-1} (N_2)	28.09

Equilibrium. The equilibrium adsorption of the THF + water solution mixture at 298.15 K was performed as follows: A set of solutions of consecutively increasing concentration were prepared and brought into contact with known masses of zeolite in conical flasks. These conical flasks were then capped and placed in an incubator shaker at a pre-set temperature with an uncertainty of ± 0.01 K and shaken under 100 rpm. Sample of solution were withdrawn from the bulk solution at specified time intervals, this was repeated until the constant concentration at equilibrium was achieved, the liquid concentrations were analyzed by 102G gas chromatography (3 mm × 2 m).

Fixed Bed Adsorption Studies. Dynamic column experiments were carried out using a 300 mm long stainless steel column with a 20 mm inside diameter; 4A particle size was (0.8 to 2) mm. The amount of loading was 76 g; the loading density was 780.3 kg·m^{-3}. The zeolite 4A with a known dry weight was put into the column. Nitrogen was used to wash the zeolite in order to remove air bubbles and to rinse the zeolite. A THF + water solution mixture with a known concentration was continuously fed to the top of the column at a desired flow rate controlled by a metering pump until breakthrough happens. In all the column tests, the effluent samples were intermittently collected and measured by gas chromatography. The thermometer had an uncertainty of ± 0.01 K. An electrical balance with an uncertainty of ± 10 μg was used, and the uncertainty of the timer was ± 0.1 s. In this work, the estimated uncertainty of the concentration measurement was less than 0.1 %.

Fixed bed adsorption was studied at two different temperatures: (304.15 and 314.15) K. Experiments at three different initial concentrations [(6.73, 10.60, and 13.65) %] and three different feed flow rates [(3.0, 4.0, and 5.0) mL·min^{-1}] were carried out. Experimental data obtained by carrying out previ-

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ously described adsorption tests were compared with the simulated results from the modeling of different experimental conditions.

Mathematical Model

The underlying important assumptions of HSDM are as follows:[1,2]

(i) The particle is assumed to be a homogeneous solid sphere in which the adsorbate is transported radially by surface diffusion.

(ii) Pore diffusion makes a negligible contribution to mass transport.

(iii) Langmuir isotherm describes adsorption equilibrium.

(iv) At the particle surface, instantaneous equilibrium is assumed to occur between the liquid and adsorbed phases.

(v) Linear driving force describes the liquid film transport resistance at the outer surface of the particle:

$$\text{Column:}\quad \frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - \frac{3(1-\epsilon)}{\epsilon R} k_f (C - C_s) \tag{1}$$

$$\text{Particle:}\quad \frac{\partial q}{\partial t} = D_s\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right) \tag{2}$$

Boundary and initial conditions for the above equations are

$$z = 0,\quad \frac{\partial C}{\partial z} = \frac{v}{D_L}(C - C_0)$$

$$z = L,\quad \frac{\partial C}{\partial z} = 0$$

$$r = 0,\quad \frac{\partial q}{\partial r} = 0$$

$$r = R,\quad \rho_p A D_s \frac{\partial q}{\partial r} = k_f A (C - C_s)$$

$$q_s = \frac{q_m k C_s}{(1 + kC_s)}$$

$$t = 0,\quad q = C = 0$$

where A is the adsorbent surface area, C is the bulk solute concentration (mass fraction of water), C_0 is the initial solute concentration(mass fraction of water), C_s is the solute concentration adjacent to adsorbent surface(mass fraction of water), D_L is the dispersion coefficient, D_s is the surface diffusion coefficient, k_f is the film diffusion coefficient, k is the Langmuir isotherm coefficient, q is the adsorbed solute concentration, q_0 is the adsorbed solute concentration in equilibrium with initial solution concentration C_0, q_s is the adsorbed solution concentration at adsorbent surface, q_m is Langmuir isotherm parameter, r is the distance from the particle core, R is the radius of the sphere, t is the time, ν is the interstitial fluid velocity, z is the axial position along column, and ρ_p is the particle density. The above model equations were solved numerically using a computer program which utilized a combination of orthogonal collocation, fourth-order Runge−Kutta and Newton−Raphson techniques.

Table 2. Effect of Temperature on the Adsorption Kinetics of THF + Water Solution Mixture on Zeolite 4A[a]

T = 304.15 K		T = 314.15 K	
t/min	C/%	t/min	C/%
0	0.098	1	0.021
7	0.083	5	0.025
11	0.072	9	0.020
15	0.091	13	0.023
23	0.089	17	0.025
27	0.154	21	0.025
31	0.160	25	0.027
35	0.102	29	0.024
39	1.289	32	0.594
42	2.907	35.4	3.680
44	4.914	38.4	5.818
47	6.836	41	6.840
50	8.134	44	7.681
53	8.824	47	8.807
56	9.937	49.3	9.464
59	10.364	53.3	10.543
62	10.536	56	10.600
67	10.600	59	10.600
		64	10.600

[a] d_p = (0.8 to 2.0) mm, C_0 = 10.600 %, flow rate = 4.0 mL·min^{-1}.

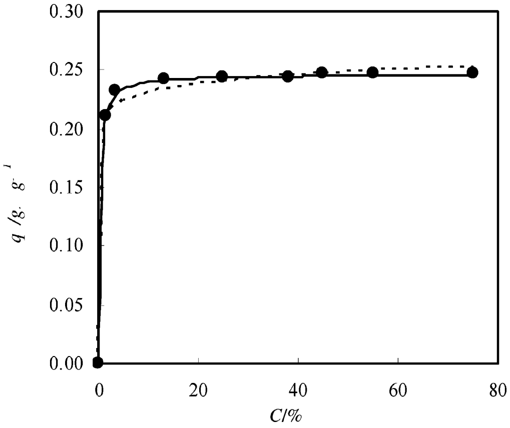

Figure 1. Adsorption isotherm of THF + water solution mixture on zeolite 4A at 298.15 K : ●, experimental data; —, Langmuir model; - - -, Freundlich model.

The film transfer coefficient k_f for the column studies was determined from an empirical correlation. In most correlations, k_f is incorporated in the dimensionless Sherwood number (Sh), which is a function of the Reynolds number (Re) and the Schmindt number (Sc). Roberts et al.[3] compared four such correlations with experimental data and found that the following correlation proposed by Gnielinski gave the best prediction of k_f in water treatment situations:

$$Sh = (2 + 0.644Re^{1/2}Sc^{1/3})[1 + 1.5(1 - \epsilon)] \tag{3}$$

where $Re = 2R\rho v/\mu$, $Sc = \mu/\rho D_m$, $Sh = 2Rk_f/D_m$, D_m is the molecular diffusivity, ϵ is the bed voidage, μ is the solution viscosity, and ρ is the solution density.

Alternatively the Peclet number can be estimated by using correlations to estimate the column dispersion coefficient from the molecular diffusivity D_m of the solute. One such correlation was proposed by Fried[2] to model dispersion effects in soil columns:

$$D_L = D_m[0.67 + 0.5(ReSc)^{1.2}] \tag{4}$$

The surface diffusivity D_s of the THF + water solution mixture on zeolite has been calculated in ref 4:

$$D_s = D_{s0}\exp(-E/RT) \tag{5}$$

where E is the activation energy, D_{s0} is the Pre-exponential

Table 3. Effect of Initial Concentration on the Adsorption Kinetics of THF + Water Solution Mixture on Zeolite 4A[a]

$C_0 = 6.730$		$C_0 = 10.600$		$C_0 = 13.650$	
t/min	C/%	t/min	C/%	t/min	C/%
1	0.053	1	0.021	1	0.153
5	0.053	5	0.025	5	0.095
9	0.058	9	0.020	9	0.091
13	0.031	13	0.023	13	0.061
17	0.028	17	0.025	17	0.048
21	0.036	21	0.025	21	0.049
25	0.048	25	0.027	25	0.540
29	0.039	29	0.024	28	4.166
33	0.041	32	0.594	31	7.058
37	0.042	35	3.680	34	8.895
41	0.058	38	5.818	37	10.530
45	0.042	41	6.840	40	11.900
49	0.019	44	7.681	43	12.990
52	0.994	47	8.807	46	13.370
55	2.597	49	9.464	49	13.680
59	4.174	53	10.54	52	13.650
61	4.849	56	10.600	57	13.650
64	5.206	59	10.600		
67	5.705	64	10.600		
70	5.942				
75	6.545				
79	6.730				
84	6.730				

[a] $T = 304.15$ K, $d_p = (0.8 \text{ to } 2.00)$ mm, flow rate = 4.0 mL·min^{-1}.

Table 4. Effect of Particle Size on the Adsorption Kinetics of THF + Water Solution Mixture on Zeolite 4A[a]

$F = 3$ mL·min^{-1}		$F = 4$ mL·min^{-1}		$F = 5$ mL·min^{-1}	
t/min	C/%	t/min	C/%	t/min	C/%
1	0.032	2	0.017	1	0.021
5	0.022	6	0.017	5	0.025
9	0.026	10	0.029	9	0.023
13	0.052	14	0.021	13	0.027
17	0.035	18	0.018	17	0.029
21	0.041	22	0.024	21	0.016
25	0.060	26	0.025	25	0.289
29	0.040	30	0.018	28	3.688
33	0.047	33	0.015	31	6.427
37	0.053	36	1.255	33	8.210
41	0.065	39	4.154	36	9.019
45	0.909	43	6.398	40	10.440
48	2.844	45	7.715	43	10.510
52	4.870	48	8.380	46	10.540
58	7.016	51	9.097	51	10.600
62	7.882	54	9.887		
66	8.455	57	10.140		
67	8.776	60	10.540		
71	9.196	63	10.520		
74	9.549	67	10.600		
79	10.140				
83	10.490				
87	10.580				
91	10.600				

[a] $T = 294.15$ K, $C_0 = 10.600$ %, $d_p = (0.8 \text{ to } 2.00)$ mm.

factor, and T is the temperature. The values of E and D_{s0} were 21.07 kJ·mol^{-1} and 7.75 × 10^{-7} m^2·s^{-1}, respectively.

Results and Discussion

Adsorption Isotherm. The equilibrium behavior of an adsorption system is an essential requirement for modeling of the system kinetics. A clear review of the various equilibrium isotherms and their applications is in the literature.[5] The isotherm equations used in this study were the Langmuir and the Freundlich equations.

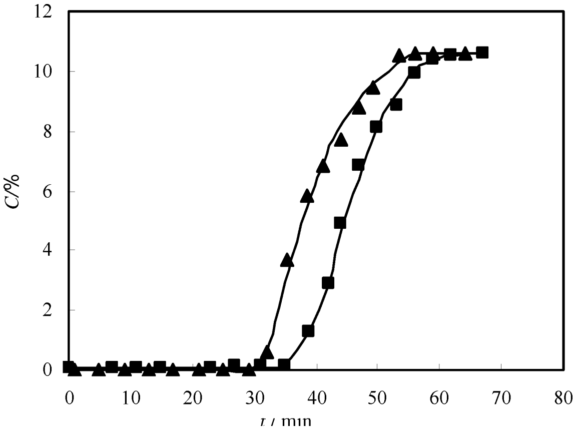

Figure 2. Application of the HSDM to THF + water solution mixture on zeolite 4A fixed bed in different temperatures: ■, 304.15 K; ▲, 314.15 K.

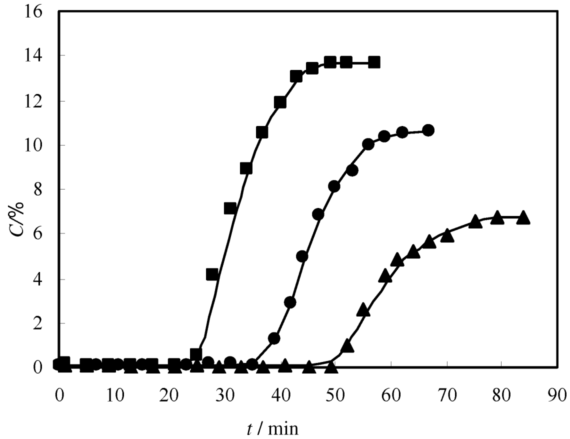

Figure 3. Application of the HSDM to THF + water solution mixture on zeolite 4A fixed bed with different initial concentrations: ■, 13.65 %; ●, 10.6 %; ▲, 6.73 %.

The mathematical form of each model is as follows:

$$\text{Langmuir} \quad q = \frac{q_m kC}{(1 + kC)} \tag{6}$$

$$\text{Freundlich} \quad q = aC^b \tag{7}$$

where a and b are Freundlich isotherm parameters. The amount adsorbed of the THF−H_2O system adsorption on a 4A molecular sieve (see Table 2) was calculated by mass balance according to the following equation:

$$q = \frac{W'}{W} \cdot \frac{C_0 - C}{1 - C} \tag{8}$$

where C_0 is the initial liquid-phase concentration of water (mass fraction), W is the amount of the adsorbent, and W' is the amount of the solution. The Langmuir isotherm selected for this work described the current data with a high degree of accuracy over a wide concentration range (see Figure 1). The estimated values of the parameters are $k = 3.778$ and $q_m = 0.246$. The correlation coefficient is 0.998.

Fixed Bed Adsorption. The effects of temperature, initial concentration, and flow rates on the fixed bed adsorption have been investigated (see Tables 2 to 4). Results of the HSDM application are presented in terms of the concentration curve in Figures 2 to 4. The figures show a good agreement between experimental breakthrough curves results and calculated results.

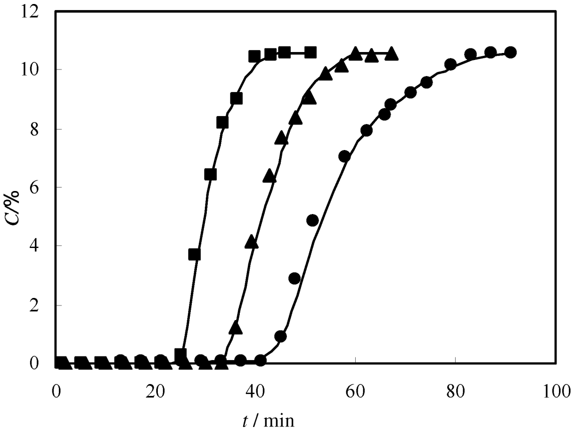

Figure 4. Application of the HSDM to THF + water solution mixture on zeolite 4A fixed bed at different flow rates: ■, 5 mL·min^{-1}; ▲, 4 mL·min^{-1}; ●, 3 mL·min^{-1}.

As shown in Figure 2, the fixed bed adsorption capacity increased when the temperature of operation decreases. The lower the temperature, the later breakthrough times; this is the case because at higher temperature the film transfer coefficient k_f and the surface diffusivity D_s were both decreased as temperature decreased.

As shown in Figure 3, it may be observed that the initial concentration increased leads to shorter breakthrough times and sharper breakthrough curves. This is the case because at higher initial concentration the driving force increase, so the overall diffusion rate increased.

As shown in Figure 4, it may be observed that increasing the flow rate of the feeding leads to shorter breakthrough times and sharper breakthrough curves, but the fixed bed adsorption capacity decreased because the mass transfer time is shorter at higher flow rate.

Conclusion

The adsorption of a tetrahydrofuran + water mixture on zeolite 4A was carried out using a fixed bed. The equilibrium behavior was shown to fit the Langmuir isotherm. A homogeneous surface diffusion model (HSDM) was proposed to predict the adsorption breakthrough curves in the fixed bed with respect to different temperatures, initial concentrations, and feed flow rates. The investigation has shown that the breakthrough times were shorter and breakthrough curves were sharper at higher temperature, flow rate, and initial concentration. Results indicate that the developed model provides a good fit to the experimental data at various temperatures, initial concentrations, and flow rates and that HSDM can be used in the design of a fixed bed.

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