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Original Research Article

A simplified technique to determine intraparticle diffusivity of macro-reticular resins

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ABSTRACT

Both resins and activated carbons are commonly used as adsorbents in water and wastewater treatment. In general, intraparticle diffusion mechanisms within macro reticular resin particles (such as XAD-2000) are different from those in activated carbon particles. Currently, completely mixed batch reactor (CMBR) technique can be used to determine the intraparticle diffusivity for phenolic compounds adsorbed onto activated carbon systems. However, the technology cannot determine the intraparticle diffusivity accurately if the fluid-film resistance is significant, such as synthetic macro-reticular resins. Therefore, this study develops a technique to determine the intraparticle diffusivities of XAD-2000 resin. This paper characterized the concentration decay curves of para-nitrophenol in CMBR to determine effective pore diffusivity (D_P) of the resin. The obtained mean and standard deviation of D_P are about 1.1×10^{-5} and 3.2×10^{-6} ($cm^2\ s^{-1}$), respectively. The technology developed in this study has the advantages of significant chemical saving and easy operation.

1. Introduction

Liquid-phase adsorption has been used in the purification of synthetic compounds and environmental pollution control. A typical separation process is a fixed bed adsorption process due to its efficiency and easy process control [1–3]. Many design methods for fixed bed adsorbers are presented for single component and multi-component systems [4–7]. To properly design a fixed bed process, the adsorption equilibrium and kinetic parameters of the systems are required. In general, kinetic parameters include fluid-film mass transfer coefficient and intraparticle diffusivity. The former describes the mass transport from the bulk phase to the geometric surface of adsorbent particles and can be estimated using empirical formula [8–10]. The latter coefficient describes the mass transport of adsorbate molecules within adsorbent particles and is often the rate-controlling step in the adsorption process.

Both resins and activated carbons are commonly used as adsorbents. This study focuses on resins' macro reticular resin particles (such as XAD-2000, Tokyo Organic Chemical Industry. Japan). XAD-2000 resin has wide application in wastewater treatment [3]. XAD-2000 particles are made of many micro-particles and exhibit bi-dispersed particle behaviors. In general, intraparticle diffusion mechanism within macro reticular resin particles (such as XAD-2000) is different from that in activated carbon particles. XAD-2000 has the same chemical structure as the other styrene-divinyl-benzene resins (such as XAD-4) but with different physical properties. The migration resistance of phenolic from one micro-particle to an adjacent micro-particle predominates over other transfer resistance. The traditional and simple pore diffusion model is useful for the design of synthetic resin fixed bed adsorber with small intraparticle diffusivity. However, the model cannot be applied to macro reticular resins such as XD-2000 with large intraparticle diffusivities [11]. Three commonly used experimental techniques for the determination of intraparticle diffusivities include long bed, shallow bed and completely mixed batch reactor (CMBR) techniques (Table 1). Both of long bed and shallow bed techniques require significant amount of test solutions, while CMBR technique requires minimum amount of fluid volume. Fujiki et al. [12] applied CMBR technique to determine the intraparticle diffusivity for phenolic compounds adsorbed onto activated carbon systems. However, it was only valid for the case of intraparticle diffusion resistance being much larger than that of fluid-film resistance (Biot number (B_i) larger than 30). B_i represents the

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Table 1
Characteristics of various techniques for determination of intraparticle diffusivities.

Experiments	Long bed	Shallow bed	CMBR
Liquid volume	~20 L	~200 L	~3 L
Time interval for concentration determination	10–30 min	2–90 min	10–300 min
Fluid-film resistance	Significant	Negligible	Significant
Technical difficulty of the experiment	Difficult	Difficult	Easy

ratio of the rate of transport across the liquid layer to the rate of intraparticle diffusion. Therefore, the technology cannot determine the intraparticle diffusivity accurately if the fluid-film resistance is significant, such as XAD-2000 synthetic macro-reticular resin. Therefore, the main focus of the study is to develop a technique to determine the intraparticle diffusivities of resins.

2. Materials and methods

2.1. Adsorbent and adsorbate

XAD-2000 was employed as the adsorbent in this study. The resin was prepared by being soaked and washed in isopropanol to remove monomer and impurities. After being washed with isopropanol, the resin was subjected to successive washing with methanol and distilled water. The resultant resin was preserved with distilled water in a glass bottle before further tests. The characteristics of the resin are listed in Table 2. The mean particle diameter was determined to be 0.194 mm with the procedure defined in Furuya and Takeuchi [11]. para-nitrophenol (PNP) is a typical phenolic compound found in aqueous solution. It was used as a surrogate in this study. The reagent grade of PNP was employed as the adsorbate. The concentration of PNP was measured by UV spectrophotometry (Shimazu, UV1700, Japan) at the wave length of 318 nm.

2.2. Equilibrium adsorption studies

For the adsorption test, a known amount of resin (0.5 g) (XAD-2000) was added into a series of 125 mL glass bottles that contained 100 mL of known concentrations of adsorbate (PNP). These bottles were mixed for 7 d (at 20 °C). The adsorption capacity (q_e, mg of adsorbate adsorbed/g of absorbent) was determined using Eq. (1).

$$q = \left(\frac{V}{m}\right)(c_0 - c_e) \quad (1)$$

where q was the adsorption capacity of resins (mg g^{-1}), c_0 and c_e were initial and equilibrium concentrations of PNP (mg L^{-1}), respectively, V was the solution volume, and m was the mass of adsorbent (g). Selected samples were analyzed in triplicate within accepted analytical error (±5%).

2.3. Kinetic studies

A baffle-basket-type CMBR equipment was employed in this study. A typical experimental setup of CMBR reactor is illustrated in Fig. 1. A known amount of the resin particles were immersed in the PNP solution, whereas the resin particles were packed in the baskets of CMBR. Each basket was filled with an equal amount of resin particles. A known concentration of PNP solution (1 L) was prepared and added to a 2 L glass vessel, and agitation was started immediately. This was taken as time zero for the kinetic experiment. The vessel was immersed in a constant temperature bath (20 °C) at the stirring speed of approximately 200 rpm. The stirring speed was measured by a tachometer (HT-4200, Ono Sokki, Japan). The aliquot amounts of solution (1 mL) were periodically sampled to determine the PNP concentrations. Selected samples were analyzed in triplicate within accepted analytical error (±5%).

Table 2
Characteristics of XAD-2000.

Resin	Particle size (mm)	Pore volume (mL g^{-1})	Mean pore diameter (Å)	ρ_s (g mL^{-1})	Specific surface area (m^2 kg^{-1})
XAD-2000	0.194	0.73[a]	45[a]	0.666	$6.2*10^5$

[a] Provided by Organo Corporation, Japan with mercury intrusion methods.

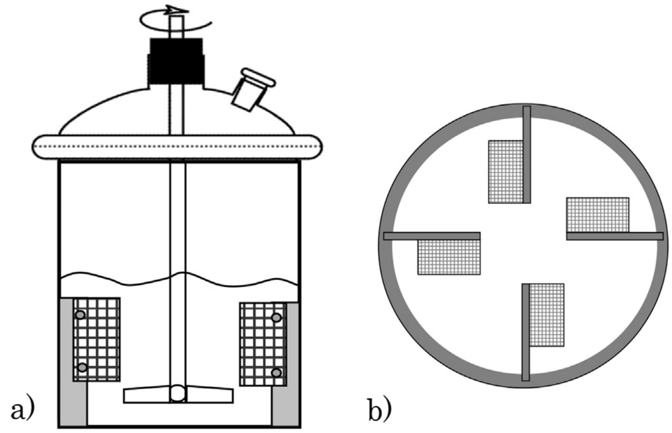

Fig. 1. Experimental setup of CMBR a) Side view and b) top view.

3. Results and discussion

3.1. Numerical studies

The fundamental equations (Eqs. (2)–(4)) of the PNP adsorption in the CMBR are based on the following assumptions that (a) pore diffusion model can be applied, (b) adsorption equilibrium is established momentarily at the geometric surface of solid particles, (c) all particles are spherical with same diameters, and (d) constant temperature is maintained within the reactor. Furuya and Takeuchi [11] have demonstrated that the pore diffusion is the rate controlled process for XAD-2000 resin. The fundamental equations for intraparticle diffusion of the system are derived as follows:

Intraparticle diffusion

$$\rho_S\left(\frac{\partial q_m}{\partial t}\right) = \left(\frac{D_P}{r^2}\right)\frac{\partial}{\partial r}\left(r^2\frac{\partial c_m}{\partial r}\right)\cdot q_m = f(c_m)\ \ at\ \ r = r_P \quad (2)$$

For CMBR technique, the mass transfer resistance within the fluid-to-solid film is significant and hence the following equation is derived.

Fluid-to-solid film transport

$$\rho_S\left(\frac{\partial q_t}{\partial t}\right) = k_F a_P (c_t - c_S) \quad (3)$$

To solve the above equation, the boundary conditions (B.C.) at the center and the geometric surface of particles are required.

$$\text{B.C. 1}\ \left(\frac{\partial c_m}{\partial r}\right)_{r=0} = 0 \quad (4)$$