

Adsorption and Mass Transfer Characteristics of Metsulfuron-Methyl on Activated Carbon

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Abstract—Removal of a synthetic organic herbicide, metsulfuron-methyl (MSM), from aqueous solutions has been studied in batch and stirred tank adsorbers charged with granular activated carbon particles. Two kinetic parameters, film mass transfer and intraparticle diffusion coefficients, were estimated from concentration decay curves obtained in the batch adsorber. Based on these kinetic parameters, the concentration profiles measured in the stirred tank adsorber were simulated. From experimental and simulated results, it was proven that the film mass transfer at external surfaces of carbon particles controls the overall mass transfer, particularly at low mixing (rotation of blades), during the adsorption of MSM by granular activated carbon particles.

Key words: Removal of Herbicide, Adsorption of Metsulfuron-Methyl, Granular Activated Carbon, Kinetic Parameters

INTRODUCTION

In recent years, developing and applying efficient and cost-effective technologies for treatment of waters contaminated with synthetic organic compounds (SOC) has become important. Synthetic organic compounds are the products of a wide range of manufacturing processes, and some are classified as hazardous to animal and human health. Occasionally, these compounds find their way into natural water sources by means of accidental spills, dumping, or leaching to groundwater aquifers. Many organic compounds present in drinking water are of major concern because they are potentially mutagenic, carcinogenic, and toxic. The US Environmental Protection Agency (U.S. EPA) has set maximum contaminant levels for several organic compounds and many other compounds are currently being added to the list [Oxenford and Lykins, 1991].

Metsulfuron-methyl (MSM) is an organic herbicide that has been widely used to control broad-leaved weeds. After application they permeate into soil and can subsequently run off from cropland into rivers and lakes, causing surface water pollution. This compound may persist in the environment for many months. Therefore, the removal of this potentially harmful compound from water has emerged as an important issue of environmental protection [Yang et al., 1997; Holloway et al., 1995].

As a water clean-up technique, the adsorption of trace organic pollutants by granular activated carbons (GAC) has proved to be economical and effective. The application of this technique to herbicide removal has been cited as having great potential [Toth and Milhanm, 1975] and has been routinely used in water treatment industries.

This paper presents the adsorption of MSM onto activated carbon. The objectives of this study are to investigate the adsorption characteristics of MSM onto activated carbon and to obtain reli-

able information that will be applied in analyzing and simulating the adsorption dynamics of MSM in activated carbon adsorbers used in removing synthetic organic compounds from water. First, isotherm parameters of MSM on activated carbon were determined from experimental equilibrium data that were measured under specific conditions such as concentration and temperature. Kinetic parameters, namely film mass transfer and intraparticle diffusion coefficients, were also estimated by matching concentration decay curves with corresponding model predictions. A reliable adsorption model will be used to simulate the adsorption dynamics of MSM in a stirred tank adsorber.

EXPERIMENTAL METHODS

The adsorbent used, F400, was a commercial granular activated carbon, purchased from Calgon Co., USA. Prior to use, all carbon particles were boiled in distilled water for 24 hr and washed in distilled water to remove impurities. After drying in an oven at 103-105 °C, the carbon particles were classified into two groups. One was passed through 20 mesh and retained on 30 mesh (ASTM), and the other was passed through 16 mesh and retained on 20 mesh. The average particle diameters were estimated to be 0.84 and 0.59 × 10⁻³ m from the sieve openings, respectively. The physical properties are summarized in Table 1, and the pore size distribution of the carbon measured by Hovath-Kawazoe method is shown in Fig. 1.

Table 1. Physical properties of activated carbon

Physical properties	Units	Activated carbon
Particle density	kg/m ³	748
Total pore volume	m ³ /kg	7.27 × 10 ⁻⁴
Average pore diameter	Å	26.14
BET surface area	m ² /g	1112
Average particle diameter	m	5.9 × 10 ⁻⁴ , 8.4 × 10 ⁻⁴

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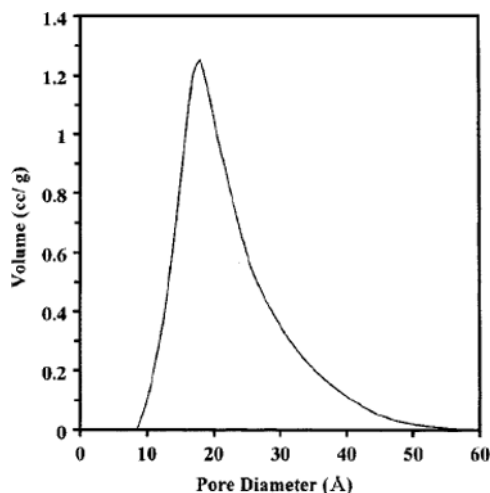


Fig. 1. Horvath-Kwawzoe differential pore volume with pore size of activated carbon.

This activated carbon was suitable for liquid-phase adsorption of organic compounds from aqueous solutions because it has a mean pore radius of about 1.31 nm. The working solution of MSM was prepared by dissolving a commercial grade product into water without any purification. The MSM used here is a white crystal form and its chemical formula is $C_{14}H_{13}N_5O_6S$.

Adsorption equilibrium data were obtained by introducing known weights of activated carbon particles into 2 L MSM solution in a Carberry-type batch adsorber. Four baffles were fixed in the vessel. The agitation rod was equipped with a four-bladed impeller of 0.03 m wide and 0.05 m high. This rod was connected to a variable speed motor. The cages of 30-mesh stainless steel wire screen were attached on the circumference of the impeller blades to sustain the adsorbent particles. The vessel was placed in a constant temperature water bath to regulate the temperature and covered with a cover of 20 mm opening. This facilitated sampling and prevented vapor loss. All runs were carried out at 25 °C.

The solution was agitated at 500 rpm for three days to give sufficient contact time for equilibrium. After equilibrium was obtained, a sample was taken from the solution. The concentration of MSM was determined by using an UV spectrophotometer. The amount of adsorption at equilibrium was calculated from the following mass balance equation:

$$q = (C_0 - C) \frac{V}{w} \quad (1)$$

where V is the volume of solution, C_0 is the initial concentration, and w is the weight of adsorbent.

The stirred tank adsorber (STA) used in this work is shown in Fig. 2. The tank was the same one that was used as the batch adsorber. The flow rate of the solution was regulated by precision liquid pumps (QSY, Fluid Metering, Inc., USA). The revolution speed in the batch and stirred tank adsorbers was varied from 0 to 500 rpm in order to study the contribution of the film mass transfer to the overall mass transfer of MSM during its adsorption onto activated carbon particles.

ADSORPTION EQUILIBRIUM

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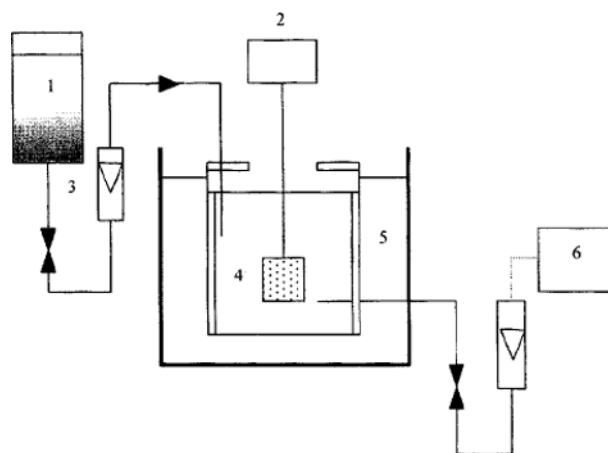


Fig. 2. Experimental apparatus for STA.

- | | |
|------------------------|------------------------------------|
| 1. Solution tank | 4. Basket impeller |
| 2. Motor | 5. Constant temperature water bath |
| 3. Fluid metering pump | 6. UV-spectrometer |

Since adsorption is one of the fundamental surface phenomena, it is important to have a satisfactory description of an equilibrium state in order to successfully represent the dynamic adsorption behavior of any species from the fluid to the solid phase, [Noll et al., 1992]. In this work, three well-known adsorption isotherms were employed to represent the equilibrium data of MSM on activated carbon. They are Langmuir and Freundlich equations with two isotherm parameters and Sips equation with three isotherm parameters.

$$q = \frac{q_m b C}{1 + b C} \quad (2)$$

$$q = k_f C^{1/n} \quad (3)$$

$$q = \frac{q_m b C^{1/n}}{1 + b C^{1/n}} \quad (4)$$

The adsorption isotherms of MSM are shown in Fig. 3. It shows that the Langmuir equation is not adequate for fitting equilibrium data. However, a good agreement between measured and predicted

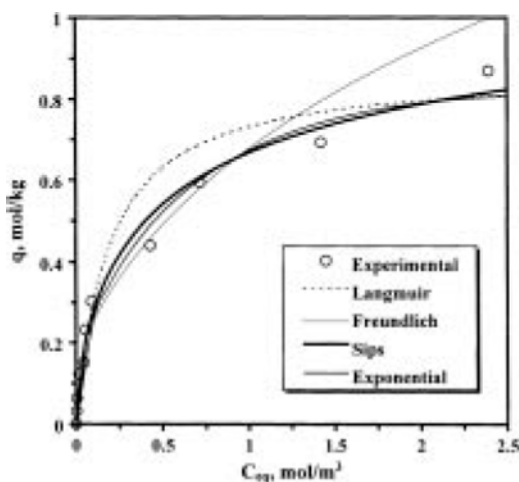


Fig. 3. Adsorption isotherm of metsulfuron-methyl on activated carbon at 298.15 K.

Table 2. Adsorption equilibrium isotherms of metsulfuron-methyl by granular activated carbon at 298.15 K

Isotherm type	Parameters	
Langmuir	q_m	0.87
	b	5.21
	$E(\%)$	27.07
Freundlich	k_F	0.68
	n	2.17
	$E(\%)$	17.04
Sips	q_m	1.17
	b	1.32
	n	1.59
	$E(\%)$	13.48

$$E(\%) = \frac{100}{N} \sum_{k=1}^M \left[\frac{|q_{exp,k} - q_{cal,k}|}{q_{exp,k}} \right]$$

values was obtained for the Sips. The average percent differences in the amount adsorbed are 17.04% for the Freundlich and 13.48% for the Sips as listed in Table 2. Unlike these isotherms, the Langmuir isotherm showed a difference of 27.07%. This implies that the Langmuir isotherm based on a homogeneous adsorption energy is not suitable for dealing with adsorption equilibrium data of MSM on activated carbon.

The surface heterogeneity, therefore, plays an important role in the adsorption on solids. For a heterogeneous adsorbent, the adsorption energy of a given molecule depends on its position on the solid surface. Most investigations of adsorption on heterogeneous adsorbent surfaces are based on the integral equation of the adsorption isotherm over a domain, Ω [Rudzinski and Everett, 1992]:

$$\theta_i(C) = \int_{\Omega} \theta(E, C) x(E) dE \quad (5)$$

where $\theta_i(C)$ is the total surface coverage, q/q_m , $\theta(E, C)$ is the local isotherm for an arbitrarily chosen homogeneous patch of the surface with E , and $x(E)$ is the normalized adsorption energy distribution function characterizing the energetic heterogeneity of the adsorbent surface.

Adsorbent heterogeneity may be calculated from adsorption data and several methods have been proposed for such a purpose. One simplest method is the application of an exponential equation to describe adsorption equilibrium data [Jaroniec and Moffat, 1987].

$$q = \exp \left[- \sum_{n=0}^m B_n \left\{ RT \ln \frac{C_0}{C} \right\}^n \right] \quad (6)$$

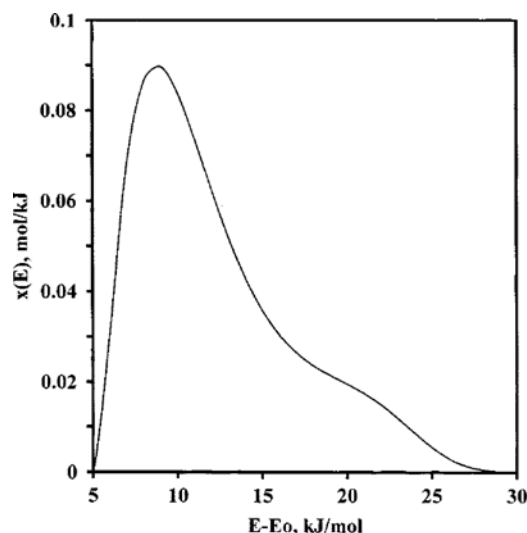
where q , C , and C_0 are the amount adsorbed, the equilibrium concentration, and the saturated concentration that can be calculated from its solubility, respectively. B_n ($n=1, 2, \dots, m$) are parameters related to the energetic heterogeneity. The energy distribution function, $x(E)$, corresponding to the exponential isotherm, Eq. (6), may be written as

$$x(E) = \left[\sum_{n=1}^m n B_n (E - E_0)^{n-1} \right] \exp \left[- \sum_{n=1}^m B_n (E - E_0)^n \right] \quad (7)$$

where E is the adsorption energy related to the equilibrium con-

Table 3. Adsorption equilibrium isotherms of metsulfuron-methyl on activated carbon at 298.15 K

MSM activated carbon	
$T(K)$	298.15
C_0 (mol/m ³)	24.90
m	4
B_0	1.79E+00
B_1	-7.00E-04
B_2	9.97E-08
B_3	-4.97E-12
B_4	9.21E-17
$E(\%)$	11.5%

**Fig. 4. Energy distribution calculated according to Eq. (7) for MSM adsorption on activated carbon at 298.15 K.**

centration and E_0 is the minimum adsorption energy.

The parameters, B_n , in Table 3 were determined by minimizing the mean percent deviation between experimental and predicted amounts adsorbed. The mean percent deviation is 11.5%, which is relatively low compared with other isotherms. The energy distribution for the MSM-activated carbon system is shown in Fig. 4.

TRANSPORT PHENOMENA

In most of the adsorption processes where highly porous adsorbents are used, the solution-particle mass transfer resistance could not be neglected as compared to intraparticle diffusion. There are some correlations available for estimating the film mass transfer coefficient, k_f , in a batch system. In this work, k_f was determined from the initial concentration history that might be approximated by the following equation when the adsorption time is less than 300 seconds [Moon et al., 1991].

$$\ln(C/C_0) = k_f A t / V \quad (8)$$

where V is the volume of solution and A denotes the effective external surface area of adsorbent particles. A can be calculated from

Table 4. Mass transfer coefficients and effective diffusion coefficients estimated in a batch adsorber

Species	$d \times 10^3$ (m)	RPM (ω)	$k_f \times 10^5$ (m/s)	$D_p \times 10^8$ (m ² /s)	$D_s \times 10^{13}$ (m ² /s)
Metsulfuron- methyl	0.59	0	0	0	0
		50	0.26	0.00583	0.143
		120	0.39	0.334	3.2
		200	1.25	0.102	1.74
		300	1.33	0.152	2.2
	0.84	0	0	0	0
		50	0.35	0.0107	0.272
		120	0.56	0.53	5.3
		200	1.32	0.141	2.08
		300	1.45	0.143	2.18
500	3.5	0.105	2.22		

$$A = \frac{3w}{\rho_p R_p} \quad (9)$$

where ρ_p is the particle density of adsorbent, R_p is the particle radius, and w is the weight of adsorbent charged.

The film mass transfer coefficients for the MSM-activated carbon system are in the range of $0.26\text{--}3.5 \times 10^{-5}$ m/s as shown in Table 4. As expected, the film mass transfer coefficient was found to increase with particle size and rotation speed. However, it should be noted that the mass transfer coefficient varied almost linearly with the rotation speed unlike other adsorption systems [Moon and Lee, 1983; Ditl et al., 1978]. In this work the film mass transfer coefficient was simply correlated with the rotation speed and the particle size as follows:

$$k_f = 3.60 \times 10^{-5} \omega^{0.01} d^{0.916} \quad (10)$$

where ω is the revolution per minute and d is the average particle diameter.

This correlation will be used in simulating and predicting the adsorption dynamics of MSM in batch and stirred tank adsorbers.

Since the intraparticle diffusion is usually the rate-controlling step in most adsorption processes, the determination of diffusion coefficient is an essential step. There are various methods for determining the diffusion coefficient in the literature [Mistic et al., 1982; Moon et al., 1991; Kim et al., 1996; Keum and Lee, 1989]. The most general method for this is to compare the experimental concentration history with predicted one from a specified diffusion model. Since the diffusion coefficient obtained by this method reflects all kinds of mass transfer resistance inside a particle, it was termed "an effective diffusion coefficient".

The rate of adsorption in porous adsorbents is generally controlled by transport within the pore network. On the internal pore surface, an adsorbed molecule may hop along the surface when it attains sufficient activation energy and when an adjacent adsorption site is available. Although the mobility of the adsorbed phase is generally smaller than that in the solution, a significant contribution to the flux is possible when the concentration is very high.

When adsorption occurs at the outer surface of the particle, followed by diffusion of adsorbate molecules in the adsorbed state

along the pore walls, a material balance for a spherical particle may be written as follows:

$$\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_s \frac{\partial q}{\partial r} \right) \quad (11)$$

$$q = q_b \quad \text{at } t = 0 \quad (12)$$

$$k_f(C - C_s) = D_s \rho_p \frac{\partial q}{\partial r} \quad \text{at } r = R_p \quad (13)$$

$$\frac{\partial q}{\partial r} = 0 \quad \text{at } r = 0 \quad (14)$$

The partial differential equation representing the model was first reduced to a set of ordinary differential equations by the orthogonal collocation method. The kinetic data were well predicted by SDM model incorporated with Sips equation. The resulting set of the ordinary differential equations was then integrated numerically in the time domain by LSODE employing Gear's stiff method with variable order and step size [Gardini, 1985; Bahattacharya et al., 1988; Yu et al., 1989].

The effective diffusion coefficient of MSM was evaluated from the experimental concentration curve by a simple parameter search technique. The effective surface diffusion coefficient, D_s , estimated in this work was found to be in the range of $0.1\text{--}3.5 \times 10^{-13}$ m²/s as listed in Table 4. In this table, the effective pore diffusion coefficient, D_p , obtained by the pore diffusion model (PDM) [Moon and Lee, 1983] is also listed for comparison.

Figs. 5 and 6 represent the experimental and simulated data for MSM in a batch adsorber at different revolution speeds. It is noteworthy that the revolution speed significantly affected the concentration decay curve in the range of 0–120 rpm, and the mass transfer was extremely slow when there was no agitation. The effect of the particle size is shown in Figs. 7 and 8. In Fig. 7, the concentration decay curves were fitted by two different diffusion models to check which model is more plausible in representing these kinetic data. Very little difference was found between two models. This implies that any diffusion model can be used in fitting kinetic data

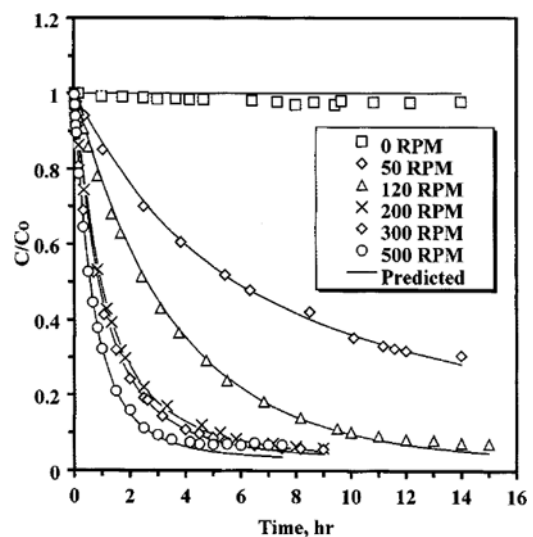


Fig. 5. Effect of RPM on concentration decay curves.
($V = 2$ L, $w = 3$ g, $d = 0.59$ mm)

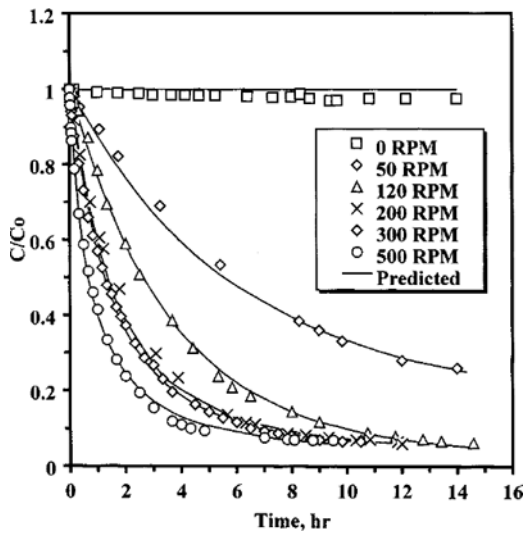


Fig. 6. Effect of RPM on concentration decay curves. (V=2 L, w=3 g, d=0.84 mm)

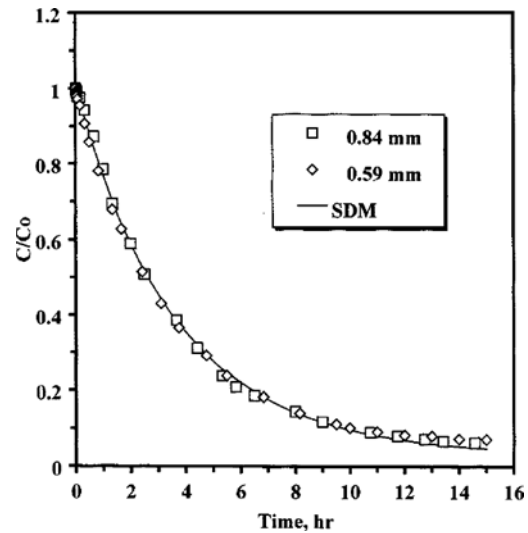


Fig. 8. Effect of particle size on concentration decay curves. (V=2 L, w=3 g, ω=120)

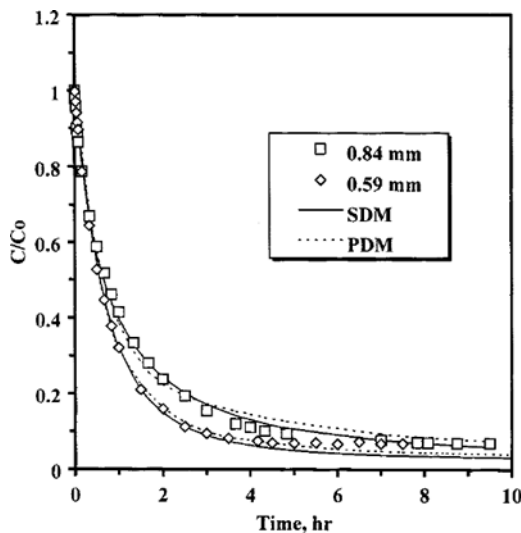


Fig. 7. Effect of particle size on concentration decay curves. (V=2 L, w=3 g, ω=500)

obtained in the batch adsorber. As expected, the equilibrium time increased with the particle size (Fig. 7). However, Fig. 8 shows that the two curves are almost identical at 120 rpm regardless of the particle size. Similar results were found at low revolution speed less than 120 rpm as shown in Figs. 5 and 6. This means that the film mass transfer might control the overall mass transfer of MSM during adsorption when the rotation speed is low.

ADSORPTION IN STIRRED TANK ADSORBER

Similar to adsorption in the batch adsorber, calculations in stirred tank adsorbers were made by using an appropriate macroscopic conservation equation with the intraparticle diffusion equation. Consequently, all the methods and procedures discussed in the preceding section for batch adsorption can be easily adopted to calculate adsorption in stirred tank adsorbers.

When a mixed tank is initially filled with a solution of volume

V and concentration C_m and at time $t=0$ the solution commences to flow in and out at a volumetric flow rate of Q, the mass balance around the tank at time t can be given by the following equation:

$$V \frac{dC_b}{dt} = Q(C_m - C_b) - k_y A(C_b - C_s) \quad (15)$$

where C_b and C_s denote concentrations in the bulk phase and at the particle surface, respectively. The corresponding initial conditions are

$$C_b = C_m \text{ and } C_s = 0 \text{ at } t=0 \quad (16)$$

Fig. 9 shows the comparison of experimental and simulated data of MSM in a stirred tank adsorber at different flow rates. In the stirred tank adsorber, the concentration of MSM initially decreased very quickly and then slowly increased with time. This result can be expected from the limit of adsorption capacity of carbon parti-

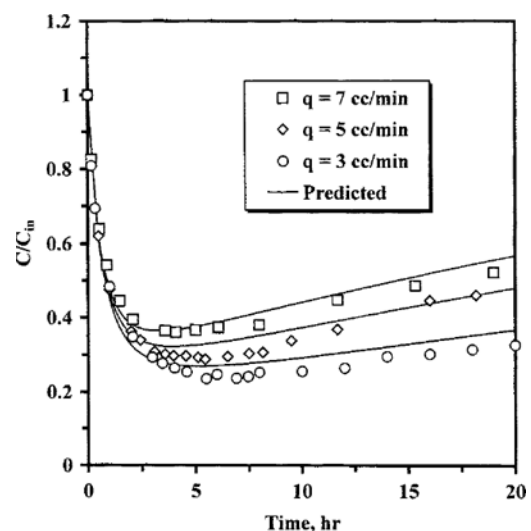


Fig. 9. Comparison of experimental data with simulated results for a STA run using the surface diffusion model. ($C_0=0.05$ mmol/L, $\omega=500$, $d=0.59$ mm)

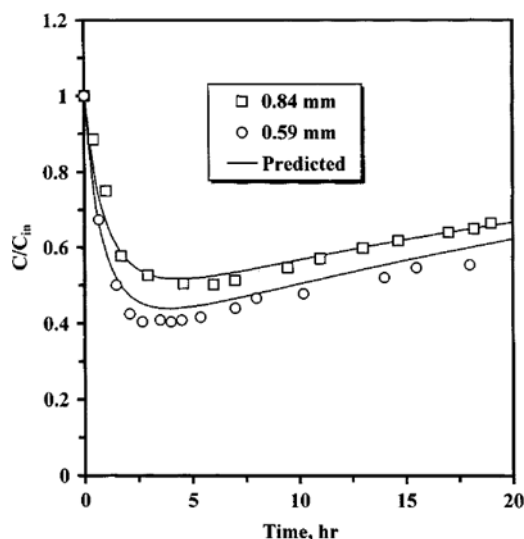


Fig. 10. Effect of particle size with simulated results for a STA run using the surface diffusion model.
($C_0=0.1$ mmol/L, $\omega=300$, $Q=7$ cc/min)

cles. The effect of the particle size in the stirred tank adsorber was similar to the batch adsorption as shown in Fig. 10 since the rotation speed is high enough (300 rpm).

CONCLUDING REMARKS

From the experiments and model simulation on the adsorption of MSM onto granular activated carbon particles in batch and stirred tank adsorbers, several concluding remarks could be made. The equilibrium data of MSM on activated carbon could be fitted with the Sips equation quite satisfactorily since the surface heterogeneity is predominant. This fact was confirmed by obtaining the adsorption energy distribution. From kinetic studies in a batch adsorber it was found that the film mass transfer controlled the overall adsorption rate of MSM when the revolution speed is low. To confirm this result, the effect of the particle size was also investigated at low revolution speeds. In the MSM-activated carbon system, the film mass transfer coefficient is extremely low as compared to other cases. Therefore for this system, stirred tank and fluidized bed adsorbers will be more effective than the conventionally used fixed bed adsorber since the film mass transfer can be mechanically enhanced.

In this work, the adsorption of MSM in a stirred tank adsorber was also carried out to check its applicability in removing MSM from water. In the stirred tank adsorber the adsorption rate is good enough, as expected, but the operation itself is not satisfactory because of the limited adsorption capacity.

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NOMENCLATURE

A : effective external surface area of adsorbent particle [m^2]

- b : isotherm parameters in Langmuir and Sips equations [m^3/mol or $(m^3/mol)^{1/n}$]
 B_n : parameter related to the energetic heterogeneity [-]
 C : concentration of fluid phase [mol/m^3]
 C_0 : initial concentration of fluid phase [mol/m^3]
 C_{in} : inlet concentration [mol/m^3]
 C_b : concentration in the bulk phase [mol/m^3]
 C_s : concentration at the particle surface [mol/m^3]
 d : average particle diameter [m]
 D_s : intraparticle surface diffusion coefficient [m^2/s]
 D_p : intraparticle pore diffusion coefficient [m^2/s]
 E : adsorption energy [kJ/mol]
 E_0 : minimum adsorption energy [kJ/mol]
 k_f : external film mass transfer coefficient [m/s]
 k_f : equilibrium constant of Freundlich isotherm [$(m^3/mol)^{1/n}$]
 m : order of exponential isotherm
 n : reciprocal of exponent in Freundlich and Sips equations or exponent in Eqs. (6) and (7)
 Q : volumetric flow rate [m^3/s or cc/min]
 q : equilibrium amount adsorbed on the adsorbent [mol/kg]
 q_m : maximum adsorption capacity of adsorbent [mol/kg]
 r : radial coordinate in particles
 R_p : particle radius [m]
 t : time [s or hr]
 T : temperature [K]
 V : volume of solution [m^3]
 w : weight of adsorbent charged [kg]
 $x(E)$: adsorption energy distribution [-]

Greek Letters

- θ : fractional surface coverage, or fractional filling of micropores [-]
 $\theta(E, C)$: localized adsorption isotherm [-]
 ρ_p : particle density of adsorbent particles [kg/m^3]
 ω : revolution per minute
 Ω : domain of adsorption energy distribution

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