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Adsorption and desorption characteristics of 2-methyl-4-chlorophenoxyacetic acid onto activated carbon

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Abstract−Adsorption and desorption characteristics of the 2-methyl-4-chlorophenoxyacetic acid (MCPA) from aqueous solution onto the activated carbon (GAC, F-400) were studied. Adsorption equilibrium capacities of the MCPA increased with decreasing pH and temperature of the solution. Adsorption equilibrium of the MCPA could be represented by the Sips equation. The internal diffusion coefficients were determined by comparing the experimental concentration decay curves with those predicted from surface diffusion model and pore diffusion model. The adsorption model based on the linear driving force approximation (LDFA) was used for simulating the adsorption behavior of the MCPA in a fixed bed. Over ninety five percent desorption of the MCPA could be obtained using distilled water.

Key words: Adsorption, Desorption, 2-Methyl-4-chlorophenoxyacetic Acid, Activated Carbon

INTRODUCTION

Commercial preparations containing 2-methyl-4-chlorophenoxyacetic acid (MCPA) are widely used as herbicides in many countries. Although phenoxyherbicides have been used since the late 1940-1950s, almost no attention has been paid to their toxicological effects on terrestrial ecosystems [Moody et al., 1991; Magnusson et al., 1997; Cho et al., 2003]. The acute toxicity of these pollutants has been determined in laboratory scale in many tests, mainly using individual bacteria, crustaceans, green algae and mammalian cells. Investigations taking into consideration a wide range of organisms are not available, and there are only a few reports about the toxicity of commercial preparations [Zettenberg, 1970; Reddy and Lalwanyi, 1983; Mustonen et al., 1989]. They concern especially genotoxicity and carcinogenicity. It is not easy to assess the environmental fates of phenoxy herbicides. Especially the fate of phenoxy herbicides in fields is interesting because use of phenoxyacetic acid derivatives in agriculture and disposal of unused commercial preparations may result in pollution of arable soil. The concentrations and toxicity in the terrestrial ecosystems for these compounds vary according to the formula used by the manufacturer and different environmental factors: for example, physical and chemical properties of soil, compound solubility in water, condition of organisms. Thus, it is important to avoid the release of these compounds into the environment.

Various treatment techniques have been employed to solve the wastewater problems, including adsorption, precipitation, ion exchange, and reverse osmosis. Among them, adsorption onto solid adsorbents has environmental significance, since it can effectively remove pollutants from both aqueous and gaseous streams. In the wastewater treatment, the activated carbon can be one of the powerful adsorbents because it has the large surface area and the pore volume, which enables it to remove liquid-phase contaminants such as organic compounds, heavy metal ions and coloring matters [Choi et al., 2004; Ramesh et al., 2004; Kim et al., 2005]. In order to design effective activated carbon adsorption units and to develop mathematical models which can accurately describe their operation characteristics, sufficient information is required on both the adsorption and the desorption of individual pollutants under different operating conditions. The main purpose of this work is to study the adsorption and desorption characteristics experimentally as well as theoretically to eliminate the MCPA from aqueous solution.

THEORETICAL MODEL

It is assumed that adsorption occurs instantaneously and equilibrium is established between adsorbates in the fluid and on the surface of the adsorbents. The driving force is the concentration gradient of the adsorbate between the liquid bulk and pore walls. The adsorbed species then diffuse into the pores in the adsorbed state. Provided that surface diffusion is dominant, the rate of adsorption for a spherical particle can be expressed as:

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

And the initial and boundary conditions are,

$$\frac{\partial t}{\partial q} = 0 \qquad \text{at} \qquad r=0 \tag{2}$$

$$q=0 \qquad \text{at} \qquad t=0 \tag{3}$$

$$k_f(C - C_s) = D_s \rho_p \frac{\partial q}{\partial r_p} \qquad \text{at} \qquad r=R_p \tag{4}$$

The mass balance equation in the column and the relevant initial and boundary conditions are,

$$-D_L\frac{\partial^2 C_i}{\partial z^2} + \frac{\partial v C_i}{\partial z} + \frac{\partial C_i}{\partial t} + \frac{1-\varepsilon_b}{\varepsilon_b}\frac{\partial q_i}{\partial t} = 0 \tag{5}$$

$$C_i(z, t=0) = 0 \tag{6}$$

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$$D_L \frac{\partial C_i}{\partial z}\bigg|_{z=0} = -v\left(C_i\big|_{z=0^-} - C_i\big|_{z=0^+}\right) \tag{7}$$

$$\frac{\partial C_i}{\partial z}\bigg|_{z=L} = 0 \tag{8}$$

EXPERIMENTAL

Single species equilibrium adsorption data were obtained by measuring the adsorbate concentration in an aqueous solution of the MCPA, 0.45 mol/m^3.

The solution was kept in a shaking batch at 298 K for 72 h after introducing a given amount of adsorbent.

Batch adsorption experiments were conducted in a Carberry-type batch adsorber. All the experiments were carried out at approximately 400 rpm, since the film mass transfer coefficient, k_f, is practically constant at this condition.

Single-species adsorption was carried out in a fixed bed adsorber which was made of a glass column of 2.54 cm diameter and 50 cm length, respectively. The column was lined with a water jacket, and all experiments were performed at 298 K. The flow rate was regulated with a flow meter. To enhance uniform distribution of the solution, small glass beads were packed in the top and bottom ends of the column.

The samples were withdrawn from the effluent line and analyzed by using a UV spectrophotometer (Shimadzu 1601). The wavelength, corresponding to a maximum absorbance of the MCPA was found to be 279 nm. 2 M HCl and 2 M NaOH solutions were used to adjust pH of the solution. The adsorbent used in this study became the activated carbon, namely, Filtrasorb-400 (GAC, F-400), which was manufactured by Calgon Co., U.S.A.. The particle size of the activated carbon was 0.37-0.54 mm in diameter, the specific surface area and the average pore diameter were 800 m^2/g and 19.02 Å, respectively. All adsorbent particles were dried in vacuum oven to remove impurities prior to use. The physical properties of the MCPA used in this study are shown in Table 1.

RESULTS AND DISCUSSION

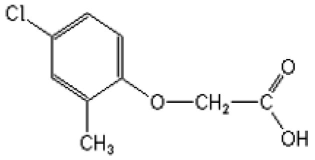
1. Adsorption Equilibrium

The amount of MCPA adsorbed onto the GAC at equilibrium was calculated from the following mass balance equation.

$$q = (C_i - C)\frac{V}{W} \tag{9}$$

The pH of solution is one of the most important parameters affecting the adsorption process. The variation of single species adsorption equilibrium for the MCPA with initial pH is given in Fig. 1.

Table 1. Properties of the adsorbate used in this study

Compound	Structure	Mw	pKa (298 K)
MCPA		200.62	3.2

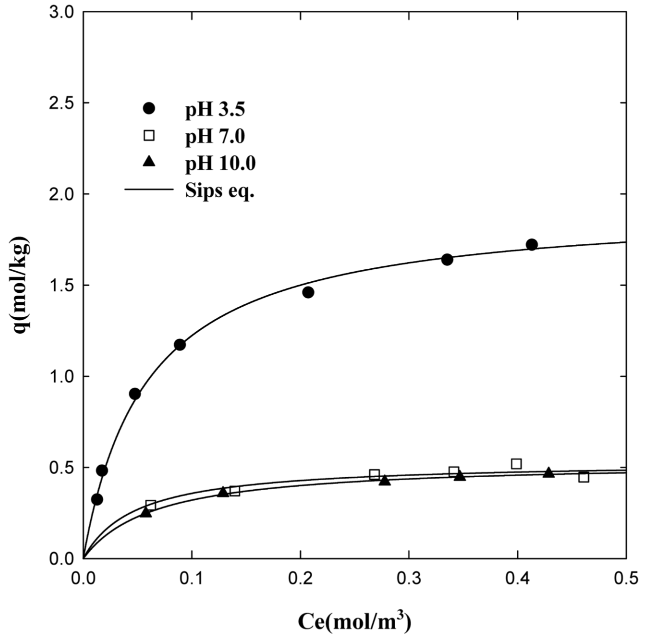


Fig. 1. Adsorption isotherm of the MCPA at different pH (298.15 K).

As can be seen in this figure, the single species adsorption amounts decreased with increasing pH of the solution. It was observed that the adsorption is highly dependent on pH of the solution, which affects the surface charge of the adsorbent, and the degree of ionization and speciation of the adsorbate.

Fig. 2 shows the adsorption capacity of the MCPA at different temperature. The adsorption amounts decreased with increasing temperature of the solution. Compared with Figs. 1 and 2, the pH effect on the adsorption capacity of the MCPA was greater than that of

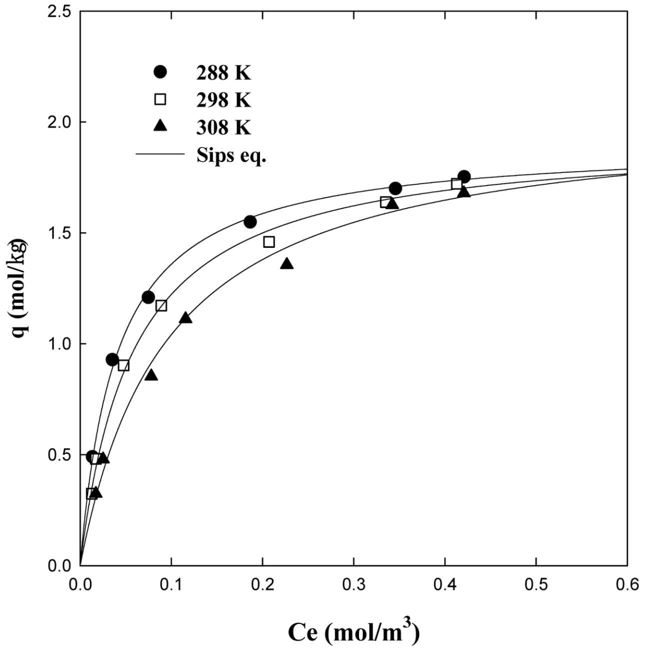


Fig. 2. Adsorption isotherm of the MCPA at different temperature (pH=3.5).

temperature. This suggests that effective separation could be achieved by the adjustment of pH rather than temperature.

In this study, three isotherm models, Langmuir, Freundlich, and Sips, were used to correlate our experimental equilibrium data. Langmuir and Freundlich equations have two parameters and the Sips equation has three parameters. To find the parameters for each adsorption isotherm, the linear least squares method and the pattern search algorithm (NMEAD) were used. The value of the mean percentage error has been used as a test criterion for the fit of the correlations. The mean percent deviation between experimental and predicted values is as follows:

$$\text{Error (\%)} = \frac{100}{N}\sum_{k=1}^{N}\left[\frac{|q_{exp,k} - q_{cal,k}|}{q_{exp,k}}\right] \tag{10}$$

These parameters and the average percent differences between measured and calculated values for the MCPA are given in Tables 2 and 3. As shown in the tables, the Sips equation gives the best fit of our data among the three. From this result, we believe that the Sips equation is suitable for predicting single-component adsorption of the MCPA on activated carbon.

2. Batch Adsorption

For the modeling of the adsorption kinetics, one has to pay attention to two problems: (i) the pore structure of adsorbents and (ii) the mass transfer resistance involved in the adsorption. The adsorption on a solid surface takes place in several steps, such as external diffusion, internal diffusion, and actual adsorption. In general, actual adsorption process is relatively fast compared to the previous two steps. Intraparticle diffusion has been usually considered as the rate-controlling step in liquid-phase adsorption. However, it is important to estimate the order of magnitude of the mass transfer coefficient. There are several correlations for estimating the film mass transfer coefficient, k_f, in a batch system. In this work, we estimated k_f from the initiation concentration decay curve when the diffusion resistance does not prevail. The transfer rate of any species to the external surface of the adsorbent, N_A, can be expressed by

$$N_A=K_fA_s(C-C_s) \tag{11}$$

By rearrangement and approximation for a batch system with adsorption time of less than 300 seconds [Misic et al., 1982].

$$\ln(C/C_i)=-k_fA_st/V_s \tag{12}$$

Where V_s is the volume of solution and A_S is the effective external surface area of adsorbent particles,

$$A_s=3M/\rho_pR_p \tag{13}$$

Fig. 3 is a typical plot to estimate k_f from the initial concentration data of the MCPA at pH 3.5. The value of k_f obtained from Fig. 3 is 5.01×10^{-5} m/s.

Fig. 4 shows the experimental data and model prediction for the adsorption of the MCPA in a batch adsorber. In this study, the pore diffusion coefficient, D_p, and surface diffusion coefficient, D_s, are estimated by pore diffusion model (PDM) and surface diffusion model (SDM) [Moon and Tien, 1987]. The estimated values of k_f, D_p, and D_s for the MCPA are listed in Table 4. The nondimensional Biot number, Bi, in Table 4 was estimated by following equation [Traegner and Suidan, 1989]:

$$\text{Bi}=\frac{k_fd_pc_o}{2D_s\rho_pq_o} \tag{14}$$

The Biot number represents the ratio of the rate of transport across

Table 2. Adsorption equilibrium constants of the MCPA at different pH (298 K)

Isotherm	Parameters	pH 3.5	pH 7.0	pH 10.0
Langmuir	q_m	1.94	0.54	0.53
	b	17.07	18.56	15.07
	error (%)	3.47	4.58	0.93
Freundlich	k	2.89	0.61	0.62
	n	2.23	3.85	3.26
	error (%)	3.39	4.86	3.28
Sips	q_m	1.94	0.53	0.53
	b	16.82	34.78	14.97
	n	1.04	0.80	1.01
	error (%)	3.24	3.54	0.99

Table 3. Adsorption equilibrium constants of the MCPA at different temperature (pH=3.5)

Isotherm type	Parameters	288 K	298 K	308 K
Langmuir	q_m	1.91	1.94	2.04
	b	24.76	17.07	10.38
	error (%)	1.93	3.47	4.49
Freundlich	k	2.61	2.90	2.86
	n	2.87	2.23	2.00
	error (%)	10.99	12.39	7.72
Sips	q_m	1.90	1.93	2.04
	b	24.06	16.82	9.86
	n	1.01	1.00	1.02
	error (%)	1.45	3.44	3.77

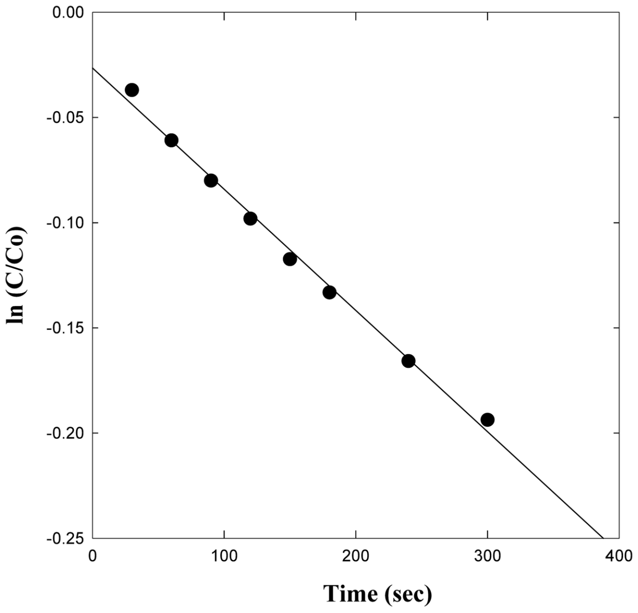


Fig. 3. Determination of k_f from an initial concentration decay plot for the MCPA (298 K, pH=3.5).

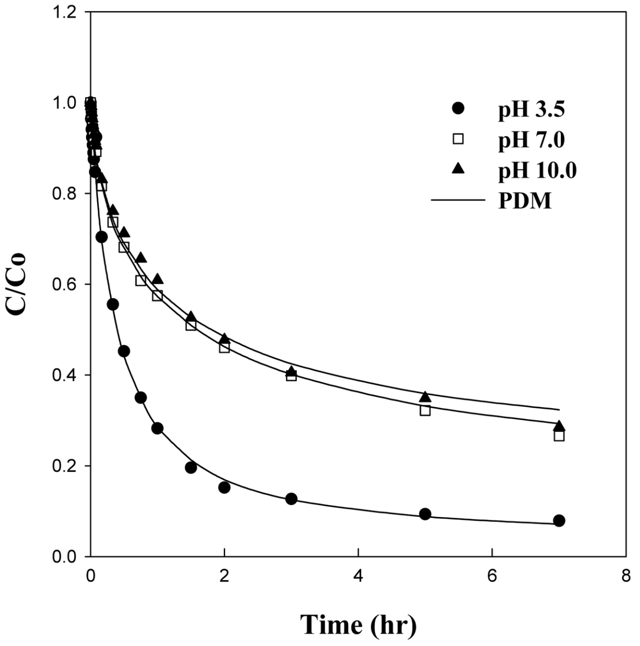


Fig. 4. Concentration decay curves of the MCPA at different pH (298 K).

Table 4. Kinetic parameters of the MCPA in a batch reactor

Adsorbates	$k_f\times10^5$ (m/sec)	$D_s\times10^{13}$ (m^2/sec)	$D_p\times10^9$ (m^2/sec)	Bi (-)
MCPA	5.01	1.72	0.94	19.09

the liquid layer to the rate of diffusion within the particle. For Bi<1, external mass transport resistance is the controlling mass transfer step, while for Bi>100, surface diffusion is the controlling mass transfer mechanism. Bi numbers between 1 and 100 indicated that both mass transfer mechanisms are important for the particular process.

3. Bed Adsorption

For a packed bed adsorber, the main parameters for mass transfer are the axial dispersion coefficient and the external film mass transfer coefficient. Axial dispersion contributes to the broadening of the adsorption front axially due to flow in the interparticle void spaces. Usually it comes from the contribution of molecular diffusion and the dispersion caused by fluid flow. In this study, the axial dispersion coefficient, D_L, for the fixed bed adsorber was estimated by Wakao's correlation [Wakao and Funazkri, 1978]. External film mass transfer is that by diffusion of the adsorbate molecules from the bulk fluid phase through a stagnant boundary layer surrounding each adsorbent particle to the external surface of the solid. The external film mass transfer coefficient, k_f, in a fixed bed adsorber can be estimated by Ranz and Marshall equation [Ruthven, 1984]. Molecular diffusion coefficients, D_m, of the MCPA can be calculated by Wilke-Chang equation [Reid, 1994]. The estimated values of the axial dispersion coefficient, external film mass transfer coefficient, and molecular diffusion in a fixed bed are listed in Table 5.

The breakthrough curves of all species, in general, depend on adsorption equilibrium, intraparticle mass transfer, and the hydrodynamic conditions in the column. Therefore, it is reasonable to consider adsorption equilibrium and mass transport simultaneously in simulating the adsorption behavior in the fixed bed adsorber. On the other hand, the operational factors such as input concentration, pH, flowrate and bed height are important in column designing and optimization. In this work, breakthrough curves were obtained under various experimental conditions mentioned above. In order to demonstrate the effect of the pH on the breakthrough curves of the MCPA, breakthrough curves under different pH values are shown in Fig. 5. The breakthrough time was decreasing with increasing of the pH value, since the hydrogen ion concentration (pH) has a major effect on the degree of ionization of the adsorbate and the surface properties of the adsorbents. These in turn lead to a shift in the sorption capacity of the equilibrium sorption process. This figure also shows that the predicted breakthrough curves by the LDFA model incorporated with Sips equation are fitted well with the fixed bed data.

The dependence of diffusion on adsorbate concentration is important both in process modeling and understanding the mechanism of the diffusion process. Adsorption also depends on adsorbate and adsorbent as well as adsorption conditions such as temperature and concentration. Fig. 6 illustrates the effect of input concentration on experimental breakthrough curves. The breakthrough time decreases with the increase of input concentration. The result can be explained by the concept of the mass transfer zone (MTZ) velocity [Ruthven, 1984]. The velocity of MTZ is a function of interstitial velocity, particle density, bed porosity and slope of the equilibrium isotherm.

Table 5. Values of parameter for the fixed-bed model simulation

Parameter	Symbol (unit)	Value
Axial dispersion coefficient	D_L (m^2/s)	1.13×10^{-5}
Film mass transfer coefficient	k_f (m/s)	2.78×10^{-5}
Molecular diffusion coefficient	D_m (m^2/s)	6.77×10^{-10}
Bed porosity	-	0.27

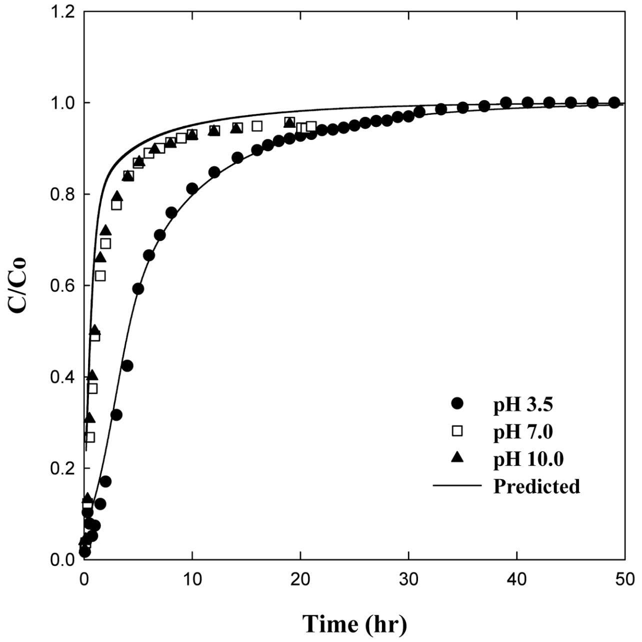


Fig. 5. Effect of pH on adsorption breakthrough curves for the MCPA (Vs=6.23×10^{-3} m/s, H=0.074 m, Co=0.45 mol/m^3).

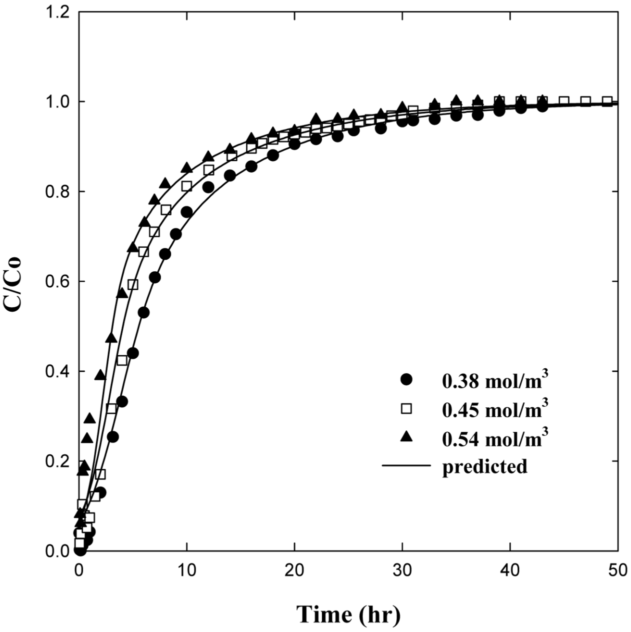


Fig. 6. Effect of concentration on adsorption breakthrough curves for the MCPA (pH=3.5, H=0.074 m, Vs=6.23×10^{-3} m/s).

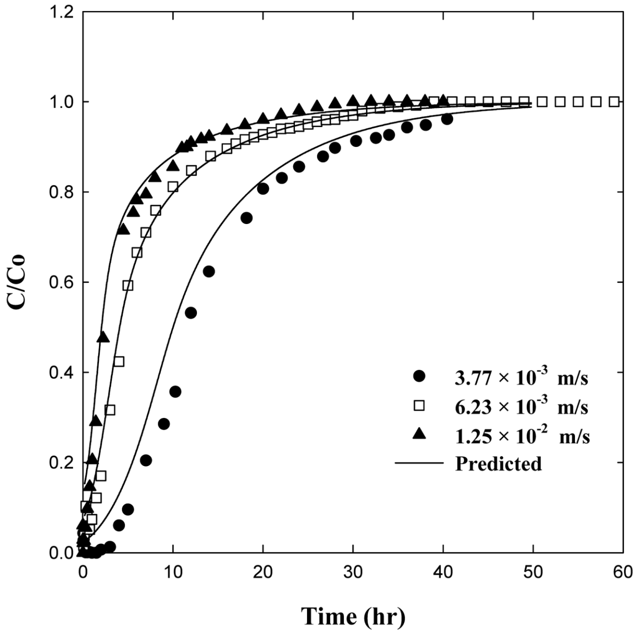


Fig. 8. Effect of flow rate on adsorption breakthrough curves for the MCPA (298 K, pH=3.5, Co=0.45 mol/m^3, H=0.074 m).

For a linear isotherm adsorption system, the velocity of the MTZ is constant. Therefore, the breakthrough time is not affected by input concentrations at constant MTZ velocity. However, the adsorption isotherm of MCPA on GAC is very favorable as shown in Fig. 1. As the input concentration increases, the value of slope of the equilibrium isotherm decreases and the zone velocity increases. Therefore, the breakthrough time becomes shorter under this circumstance.

Fig. 7 shows the effect of bed length on adsorption of the MCPA on GAC. The experimental data of our study show shorter breakthrough times and sharper breakthrough curve for shallow bed compared to those for deeper bed, which is typical in fixed bed adsorber. Since the flow rate is a very important factor in fixed bed design, the effect of flow rate is studied and the results are shows in Fig. 8. This figure shows that the breakthrough time is decreased with increasing flow rate, and the breakthrough curves are steeper for higher flow rates. In general, the breakthrough curves become steeper with increasing flow rate and decreasing bed height. Since the intraparticle diffusivity is usually independent of flow rate, this behavior is due to the external film mass transfer resistance. This resistance is weaker when flow rate is higher, so that the length of the mass transfer zone is reduced, and a sharper breakthrough curve is generated.

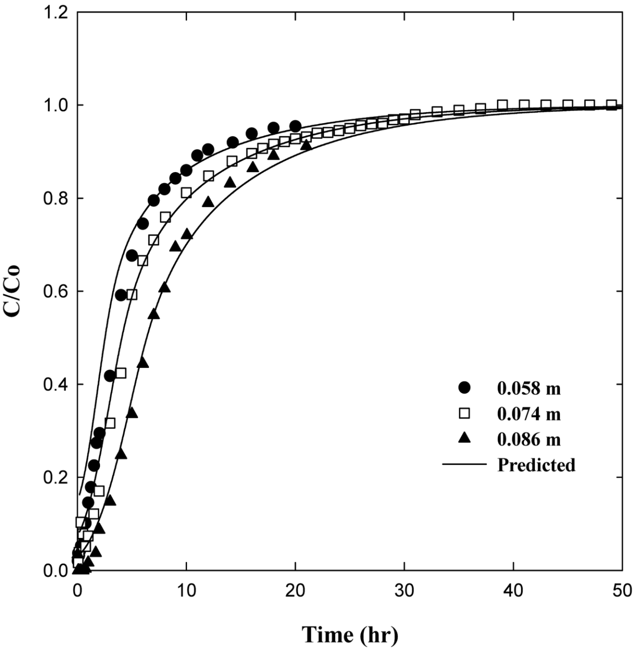


Fig. 7. Effect of bed height on adsorption breakthrough curves for the MCPA (pH=3.5, Vs=6.23×10^{-3} m/s, Co=0.45 mol/m^3).

For the successful application of an adsorption system, the efficient regeneration of the used adsorbent is very important from an economic point of view. In general, there are many regeneration techniques such as thermal, steam, acid or base and solvent regenerations. The choice of a certain regeneration method should depend upon the physical and chemical characteristics of both the adsorbate and the adsorbent. In this study, distilled water was used as desorbate for the MCPA. As shown in Fig. 9, desorption rate of the MCPA in the activated carbon was about 95% using distilled water. The effluent pH increased in the initial stage of adsorption, and decreased to the pH of the initial solution as adsorption proceeded and then increased as desorption proceeded. As discussed previously, the rapid increase of effluent pH in the earlier adsorption stage also implies that large amounts of the MCPA were removed by GAC.

CONCLUSIONS

We have reached the following conclusions:

1. The maximum adsorption capacity of the MCPA was 1.94

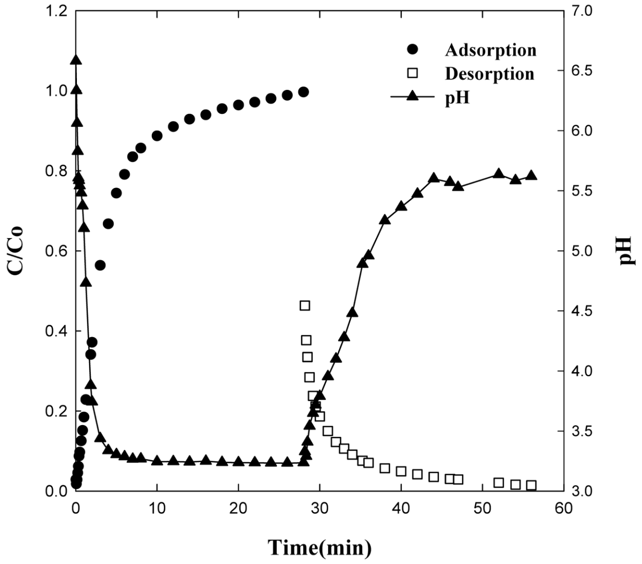


Fig. 9. pH variation during adsorption and desorption process for the MCPA (298 K, pH=3.5, Co=0.45 mol/m^3, Vs=1.02×10^{-2} m/s, H=0.074 m).

mol/m^3 at pH 3.5 and the Sips isotherm was suitable for single component systems among the various isotherms.

2. The adsorption equilibrium capacity of the MCPA onto activated carbon decreased with increasing pH and temperature of the solution.

3. The differences in the rate of adsorption are primarily attributable to the differences in the equilibrium at the various pHs, and the pore diffusion model simulated our data satisfactorily.

4. A simple dynamic model (LDFA) successfully simulated the experimental adsorption breakthrough data under various operation conditions.

5. Desorption rate of the MCPA in the activated carbon was about 95% using distilled water.

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NOMENCLATURE

A_S : surface area of the adsorbent particles [m^2]
C : concentration in the fluid phase [mol/m^3]
C_o : initial liquid phase concentration [mol/m^3]
C_i : initial concentration of bulk fluid [mol/m^3]
C_s : concentration on the surface of adsorbent [mol/m^3]
D_L : axial dispersion coefficient [m^2/sec]
d_p : particle diameter [m]
D_m : molecular diffusion coefficient [m^2/sec]
D_p : effective pore diffusion coefficient [m^2/sec]
D_s : effective surface diffusion coefficient [m^2/sec]
k_f : film mass transfer coefficient [m/sec]
M : total mass of sorbent particle [kg]
N_A : rate of mass transfer of adsorbates to the external surface of the adsorbent [mol/sec]
q_o : initial adsorbed phase adsorbate concentration [mol/kg]
r : radial distance [m]
R_p : particle radius [m]
t : time [sec, hr]
V : volume of solution [m^3]
v : interstitial velocity [m/sec]
v_s : superficial velocity [m/sec]
z : axial distance [m]

Greek Letters

ρ_p : particle density [kg/m^3]
ε_b : bed porosity

Abbreviations

Bi : Biot number
GAC : granular activated carbon
PDM : pore diffusion model
SDM : surface diffusion model

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