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Separation characteristics of some phenoxy herbicides from aqueous solution

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Abstract The adsorption and desorption characteristics of some phenoxy herbicides (CPA 2,4-D, and MCPA) from an aqueous solution on the active carbon materials (GAC, F-400) were studied. Adsorption equilibrium capacities of the phenoxy herbicides increased with a decrease in pH of the solution. Adsorption equilibrium isotherms were represented by the Sips equation. Kinetic parameters were measured in a batch adsorber to analyze the adsorption rates of the phenoxy herbicides. The internal diffusion coefficients were determined by comparing the experimental concentration curves with those predicted from the surface diffusion model and the pore diffusion model. The adsorption model based on the linear driving force approximation (LDFA) was used to simulate the adsorption behavior of the phenoxy herbicides in a fixed bed adsorber. Over 95 percent desorption of the phenoxy herbicides was obtained using distilled water.

Keywords Adsorption · Desorption · CPA · 2,4-D · MCPA · Activated carbon

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Nomenclatures

A_s	surface area of the adsorbent particles, m^2
b	isotherm parameter, m^3/mol
c	equilibrium concentration of the solution, 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
$D_{e,p}$	effective diffusion coefficient, m^2/sec
D_L	axial dispersion coefficient, m^2/sec
D_m	molecular diffusion coefficient, m^2/sec
d_p	particle diameter, m
D_p	effective pore diffusion coefficient, m^2/sec
D_s	effective surface diffusion coefficient, m^2/sec
k	isotherm parameter, $[mol/kg][mol/m^3]^{-1/n}$
k_f	film mass transfer coefficient, m/sec
M	total mass of sorbent particle, kg
n	isotherm parameter, –
N_A	rate of mass transfer of adsobates to the external surface of the adsorbent, mol/s
q_m	maximum adsorption capacity of adsorbent, mol/kg
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/s
W	weight of adsorbent, kg

Greek letters

ρ_p	particle density, kg/m^3
ε_b	bed porosity

ε_p	particle porosity
τ_p	tortuosity factor

Abbreviations

Bi	Biot number
GAC	granular activated carbon
PDM	pore diffusion model
Re	Reynolds number
Sc	Schmidt number
SDM	surface diffusion model

1 Introduction

Water pollution by pesticides, particularly herbicides, has been recognized in agricultural areas of the world for many years, and considerable evidence suggest that many water resources are contaminated by organic pesticides (Cohen 1986). Pesticides are used worldwide in agriculture to control plagues and in order to increase crops yields. Common agricultural practices, accidental spillage or uncontrolled release of contaminated waters due to of washing of pesticide containers or industrial effluents in the environment have resulted in the contamination of air, soils, and surface and ground water as well as living organisms. The contamination of the environmental and trophic chain with pesticides has serious negative impacts on public health and biological diversity. Many commonly used pesticides are resistant to natural degradation in the environment; hence, there is concern about possible adverse human health effects and ecotoxicity (Hodgson and Levi 1996). Phenoxy acid herbicides have been extensively used to control weed growth in agriculture. A majority of the herbicides used in Europe are acidic herbicides, and phenoxy acid herbicides such as 2,4-dichlorophenoxyacetic acid (2,4-D), 2-methyl-4-chlorophenoxyacetic acid (MCPA), dichlorprop (DCPP), and mecoprop (MCPP) are among the 10 most important pesticides in Europe (Fielding et al. 1992). Due to their high solubility in water, phenoxy acid herbicides easily enter surface or ground waters through natural drainage or infiltration, and have been widely detected in groundwater (Thorstensen et al. 2000). Large amounts of agrochemical products are used to produce foods to feed the growing world population today, and the removal and disposal of pesticides and other chemicals represents an important problem as the environment becomes increasingly exposed to the harmful effects of these chemicals and pesticides.

Among the numerous agrochemicals in use today, phenoxy herbicides selected as model pollutants for the present study were 2,4-dichlorophenoxyacetic acid (2,4-D), chlorophenoxyacetic acid (CPA) and 2-methyl-4-chlorophenoxyacetic acid (MCPA). Chlorophenoxyacetic acid (CPA) is used worldwide as a plant growth regulator for both agricultural and non-agricultural purposes. Typically, it is employed on a large scale for weed control on cereal crops and lawns. 2,4-dichlorophenoxyacetic acid (2,4-D), a member of the phenoxy herbicide group, has been widely applied to control broad leaf weeds (Mangat and Elefsiniotis 1999). 4-chloro-2-methylphenoxyacetic acid (MCPA) is a systemic foliar herbicide used to control annual and perennial weeds in small grains, grassland and turf. MCPA is usually formulated as either an aqueous salt (e.g. dimethylamine (DMA) or sodium salts) or as an ester (e.g. 2-ethylhexyl, 2-EHE). Formulations of MCPA are registered worldwide for use on agricultural crops such as cereals, grasses, and pulses, and in non-crop areas (Ravenzwaay et al. 2004).

When misused or as a result of accidental spillage, these herbicides have the potential to injure non-target cultivars and microorganisms, in particular herbicide degraders and others contributing to soil quality and to cause adverse side effects in mammals, including humans.

Various treatment techniques have been employed to address the wastewater problems, including adsorption, precipitation, ion exchange, air stripping, incineration and chemical treatment, and reverse osmosis. Among them, adsorption onto solid adsorbents has environmental significance, since it can effectively remove pollutants from both aqueous and gaseous streams (Aksu and Kabasakal 2004; Kah and Brown 2007; Areerachakul et al. 2007).

Adsorption of herbicides onto solid adsorbents is very important, since it can effectively remove pollutants from both aqueous and gaseous streams. In order to design effective activated carbon adsorption units and to develop mathematical models which can accurately describe their operation characteristics, sufficient information on both the adsorption and desorption of individual pollutants under different operating conditions is required. The main purpose of this work is to study the adsorption and desorption characteristics of the phenoxy herbicides experimentally as well as theoretically to better remove them from aqueous solution.

2 Experimental

Since adsorption equilibrium is the most fundamental property, a number of studies have been conducted to determine the amount of species adsorbed under a given set of conditions including concentration and temperature. When an adsorbent is in contact with the surrounding fluid of a certain composition, adsorption takes place. After a sufficiently long time, the adsorbent and the surrounding fluid reach equilibrium. The amount of the component adsorbed on the surface, mainly the micropore of the adsorbent, is determined in this state.

Adsorption isotherms were determined by contacting a volume of the solution with a carefully weighed amount of GAC in a conical flask. The amounts of carbon were varied

(0.001 to 0.25 g), and the volume of the solution was 200 ml in a single solute test. The flasks were shaken for 4 days to provide enough time and contact for equilibrium between the solid and liquid phases. Prior to analysis of the sample taken from the flask, it was filtered to remove suspended carbon particles. The concentration of the phenoxy herbicides (CPA, 2,4-D, and MPCA) was determined using the spectrophotometer (Shimadzu 1961) at $\lambda = 273$ nm, 284 nm and 279 nm, respectively.

Among several adsorbents, the activated carbon was selected in this study, namely, Filtrasorb-400 (GAC F-400) manufactured by Calgon Co., USA. The particle size of the activated carbon was estimated to be within the range 0.37 to 0.54 mm in diameter. The physical characteristics of the adsorbent in this work are listed in Table 1. Shown in Table 2 are the structural properties of the phenoxy herbicides investigated in this study. All adsorbent particles were dried in a vacuum oven to remove impurities prior to use.

Table 1 Physical characteristics of the adsorbent employed in this work

Physical properties	F400, coal-based
Particle diameter	0.37 ~ 0.54 [mm]
Particle density	682 [kg/m^3]
Particle porosity	0.62 [–]
BET surface area	800 [m^2/g]
Micropore area	490 [m^2/g]
Average pore diameter	19.02 [Å]

Batch adsorption experiments were conducted using a Carberry-type batch process. All experiments were carried out at approximately 400 rpm, when the film mass transfer coefficient, k_f, practically becomes constant.

Single species adsorption was carried out in a fixed bed system, which was made of a glass column of 2.54 cm in diameter and 50 cm in length. The column was lined with a water jacket, and all experiments were performed at 298 K. The flow rate was regulated with the flow meter. To enhance the uniform distribution of the solution, small glass beads were introduced at the top and the bottom ends of the column. The samples were taken from the effluent line and analyzed by UV spectrophotometry.

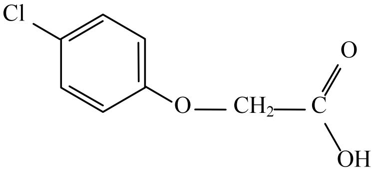
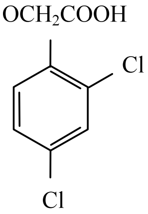
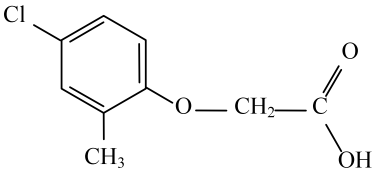
3 Results and discussion

The amount of the phenoxy herbicides adsorbed onto GAC under equilibrium conditions were calculated from the following mass balance equation

$$q = (C_i - C)\frac{V}{W} \tag{1}$$

where q is the equilibrium amount adsorbed on the adsorbent (mol/kg), C_i is the initial concentration of bulk fluid

Table 2 Structural properties of the adsorbates employed in this study

Compounds	Structure	Molecular weight	pKa (298 K)
CPA		186.6	3.1
2,4-D		221.04	2.8
MPCA		200.6	3.2

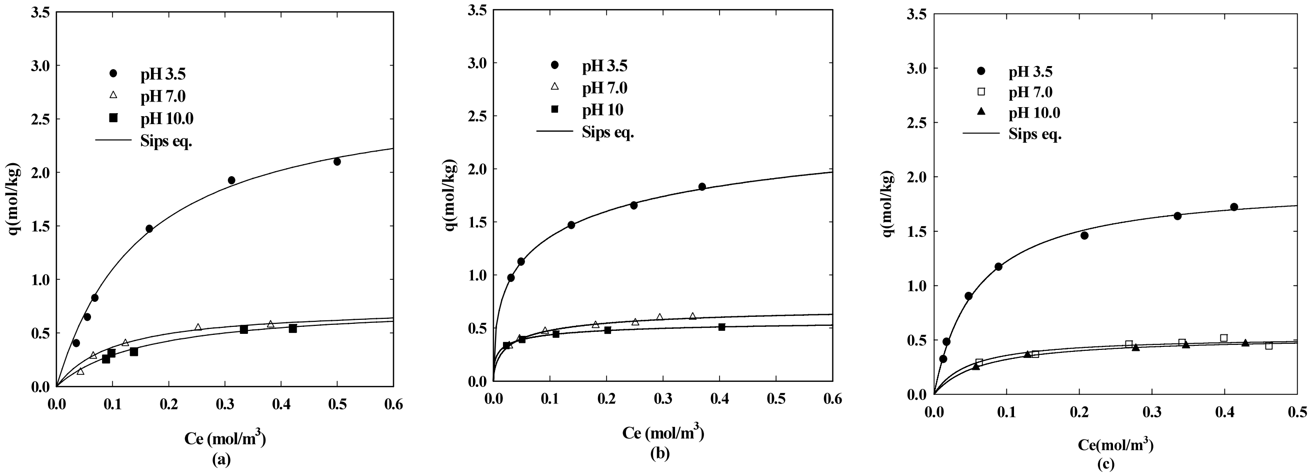


Fig. 1 Adsorption data and isotherms of the herbicides for different pH (298 K) (**a**) CPA, (**b**) 2,4-D, (**c**) MCPA

(mol/m^3), C is the equilibrium concentration of the solution (mol/m^3), V is the volume of solution (m^3), and W is the weight of adsorbent (kg).

The pH is one of the most important parameters affecting the adsorption process in an aqueous solution. The single-species adsorption isotherms for the system of CPA, 2,4-D and MPCA with the initial pH variations are illustrated in Fig. 1. As can be seen in this figure, the adsorption amounts for single species decreased with increasing solution pH values. Such adsorption processes are highly dependent on the pH values of the solution, which can affect the surface charge of the adsorbent, the degree of ionization, and the speciation of the adsorbate. The magnitude of adsorption capacity for the phenoxy herbicides onto the GAC was in order of CPA > 2,4-D > MCPA.

In this study, three isotherm models including Langmuir, Freundlich, and Sips predictions were used to correlate our experimental equilibrium data (Langmuir 1918; Freundlich 1907; Sips 1948). The Langmuir and Freundlich equations have two parameters, while the Sips equation requires three parameters. To find the parameters for each adsorption isotherm, the linear least square method and the pattern search algorithm (NMEAD) were used. The value of the mean percentage error has been used as a test criterion for fit. The mean percent deviation between experimental and predicted values is defined as following:

$$error(\%) = \frac{100}{N}\sum_{k=1}^{N}\left[\frac{|q_{\exp,k} - q_{\mathrm{cal},k}|}{q_{\exp,k}}\right]_i. \tag{2}$$

These parameters and average percent differences between the measured and calculated values for the phenoxy herbicides are listed in Table 3. Under all three sets of pH variations investigated in this study, the Freundlich equation shows relatively larger errors, particularly in the low concentration regime, compared with the Langmuir and the Sips equations of the relative error less than 5%. From the result shown in Table 3 together with isotherm curves displayed in Fig. 1, we believe that the Sips equation is suitable for predicting the single-component adsorption isotherm for CPA, 2,4-D, and MPCA on the activated carbon.

For the modeling of the adsorption kinetics, there are two problems considered: (i) the pore structure of adsorbents, and (ii) the mass transfer resistance involved in the adsorption process. The adsorption on a solid surface takes place in several steps, such as the external diffusion, the internal diffusion, and the actual adsorption. In general, the actual adsorption process is relatively fast compared to the previous two steps. The intraparticle diffusion has been usually considered as the rate-controlling step in the liquid-phase adsorption. However, it is important to estimate the order of magnitude for 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 initial 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

$$N_A = K_f A_s (C - C_i). \tag{3}$$

For the batch system with the adsorption time of less than 300 seconds, one may have an approximation (Misic et al. 1982)

$$\ln(C/C_i) = -k_f A_s / V \tag{4}$$

where V is the volume of solution. In this equation, the effective external surface area of adsorbent particles, A_S, can be expressed as

$$A_s = 3M/\rho_p R_p \tag{5}$$

Table 3 Adsorption equilibrium isotherms of the herbicides onto activated carbon for different pH at 298 K

Isotherm	Parameters	pH 3.5			pH 7.0			pH 10.0		
		2,4-D	CPA	MCPA	2,4-D	CPA	MCPA	2,4-D	CPA	MCPA
Langmuir	q_m [mol/kg]	1.86	2.77	1.94	0.62	0.38	0.54	0.50	0.77	0.53
	b [m^3/mol]	33.9	6.59	17.07	40.7	9.90	18.56	83.8	5.86	15.07
	error (%)	3.11	2.66	3.47	2.94	1.98	4.58	2.71	4.99	0.93
Freundlich	k [mol/kg][mol/m^3]$^{-1/n}$	2.37	3.18	2.89	0.77	0.90	0.61	0.59	0.85	0.62
	n [–]	3.97	2.09	2.23	4.45	2.44	3.85	6.82	2.14	3.26
	error (%)	1.35	7.32	3.39	2.34	5.26	4.86	2.01	5.38	3.28
Sips	q_m [mol/kg]	3.03	2.27	1.94	0.75	0.80	0.53	0.63	0.78	0.53
	b [mol/m^3]$^{-1/n}$	2.36	6.86	16.82	7.32	10.3	34.78	6.58	5.88	14.97
	n [–]	2.16	0.98	1.04	1.62	0.78	0.80	2.61	1.01	1.01
	error (%)	1.02	2.31	3.24	1.70	1.71	3.54	0.27	4.98	0.99

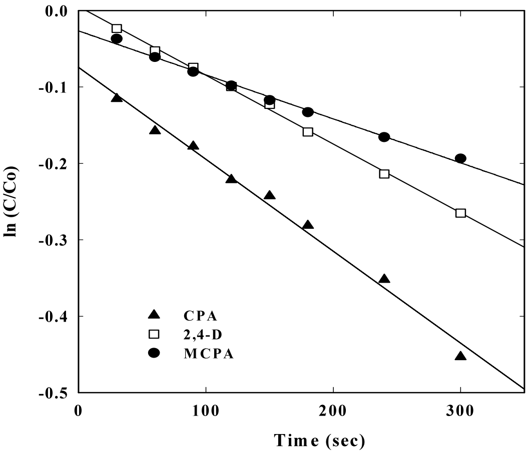


Fig. 2 Concentration-time plot for the determination of k_f (298 K, pH 3.5)

which M is the total mass of adsorbent particles loaded and ρ_p is the particle density, respectively.

Figure 2 is a typical plot to estimate the k_f values from the initial concentration data at 298 K and pH = 3.5.

The values of k_f for CPA, 2,4-D, and MPCA obtained from the slope in Fig. 2 are 8.01×10^{-5} m/s, 5.82×10^{-5} m/s, and 3.62×10^{-5} m/s, respectively. The coefficients of determination between measurement and calculation from the slope are 0.98, 0.99, and 0.99, respectively.

Figure 3 shows the experimental data and the model prediction for the adsorption in a batch system. In this study, the pore diffusion coefficient, D_p, and surface diffusion coefficient, D_s, are estimated by the pore diffusion model (PDM) and the surface diffusion model (SDM), respectively (Ma and Lee 1976; Masamune and Smith 1964). The estimated values of k_f, D_p, and D_s for CPA, 2,4-D and MPCA are listed in Table 4.

Table 4 Kinetic parameters of the herbicides in a batch reactor (298 K, pH 3.5)

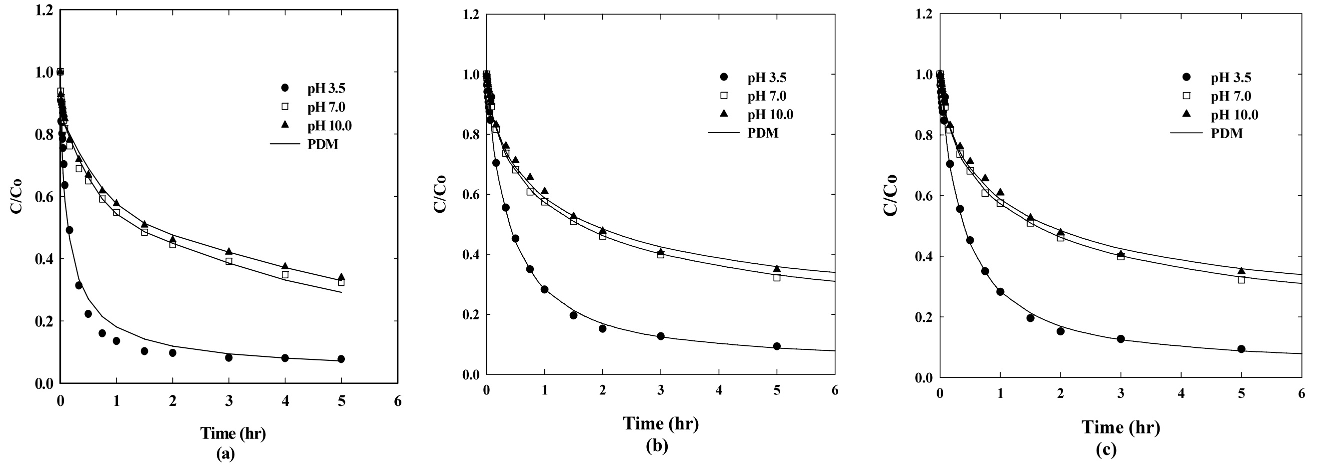
Adsorbates	$k_f \times 10^{-5}$ [m/sec]	$D_s \times 10^{-14}$ [m^2/sec]	$D_p \times 10^{-11}$ [m^2/sec]	Bi [–]
2,4-D	5.82	5.01	2.09	96.2
CPA	8.01	6.58	4.99	65.1
MCPA	3.62	4.63	1.99	53.3

The nondimensional Biot number, Bi, in Table 4 was estimated by the following relationship (Traegner and Suidan 1989)

$$\mathrm{Bi} = \frac{k_f d_p c_o}{2 D_s \rho_p q_o}. \tag{6}$$

The Biot number represents the ratio of the rate of transport across the liquid layer to the rate of diffusion within the particle. For Bi < 1, the external mass transport resistance is the controlling mass transfer step, whereas, for Bi > 100, the surface diffusion is the controlling mass transfer mechanism. Bi numbers between 1 and 100 indicate that both mass transfer mechanisms are important in the mass transfer process.

For a packed bed system, the main parameters for mass transfer can be both the axial dispersion and the external film mass transfer. The axial dispersion contributes to the broadening of the adsorption front axially due to flow in the interparticle void spaces. This usually comes from the contribution of molecular diffusion and the dispersion caused by fluid flow. In this study, the axial dispersion coefficient,



(a)

(b)

(c)

Fig. 3 Concentration decay curves of the herbicides in a batch adsorber (298 K, pH 3.5) (**a**) CPA, (**b**) 2,4-D, (**c**) MCPA

D_L, for the fixed bed system was estimated by Wakao's correlation (1978).

$$\frac{D_L}{2vR_p} = \frac{20}{\mathrm{ReSc}} + \frac{1}{2}. \tag{7}$$

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 system can also be estimated by the Wakao and Funazkri equation (1978)

$$k_f = \frac{D_m}{2R_p}(2.0 + 1.1\mathrm{Re}^{06}\mathrm{Sc}^{0.33}) \tag{8}$$

where Sc and Re are, respectively, Schmidt and Reynolds dimensionless numbers. In (8), the molecular diffusion coefficients, D_m, of CPA, 2,4-D, and MPCA can be calculated by the Wilke-Chang equation (Reid et al. 1994). The estimated values of the axial dispersion coefficient, the external film mass transfer coefficient, and the molecular diffusion in a fixed bed are listed in Table 5.

From the Tables 4 and 5, the molecular diffusion coefficient is higher than the pore diffusion coefficient. Generally, the intraparticle diffusion of an organic molecule in a GAC can be due to Fick diffusion and the effective diffusivity, $D_{e,p}$, can be estimated using the following equation

$$D_{e,p} = \frac{\varepsilon_p D_m}{\tau_p} \tag{9}$$

where ε_p is the particle porosity of the GAC, τ_p is the tortuosity factor, and D_m is the molecular diffusivity of an herbicides molecule in water. The particle porosity of the GAC used in this study is 0.62 and Leyva-Ramos recommended a τ_p of 3.5 for granular activated carbon. The molecular diffusion coefficient should be greater than the pore diffusion coefficient to satisfy (9). This model has been used very successfully to interpret the adsorption rate of organic compounds on activated carbons (Roberto and Geankoplis 1994; Roberto et al. 2005).

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

Parameter	Symbol (unit)	Species	Value
Axial dispersion coefficient	D_L (m^2/s)	CPA	3.36×10^{-6}
		2,4-D	2.98×10^{-5}
		MCPA	1.13×10^{-5}
Film mass transfer coefficient	k_f (m/s)	CPA	1.04×10^{-5}
		2,4-D	3.67×10^{-5}
		MCPA	2.78×10^{-5}
Molecular diffusion coefficient	D_m (m^2/s)	CPA	7.23×10^{-10}
		2,4-D	6.91×10^{-10}
		MCPA	6.77×10^{-10}

The breakthrough curves of all species depend on the adsorption equilibrium, the intraparticle mass transfer, and the hydrodynamic conditions in the column. Therefore, it is reasonable to consider the adsorption equilibrium and the mass transport simultaneously in simulating the adsorption behavior in the fixed bed system. On the other hand, the operational factors such as the input concentration, pH, the flow rate and the bed height are important in column design and optimization.

In order to demonstrate the effect of initial pH on the breakthrough curves of the phenoxy herbicides, breakthrough curves under different initial pH values (pH = 3.5,

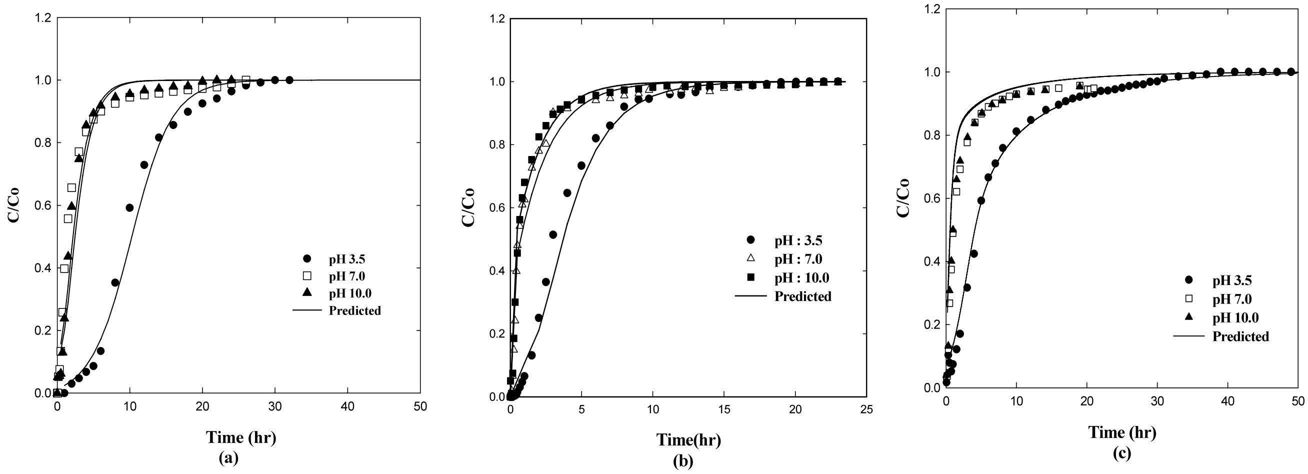


Fig. 4 Effect of pH and model prediction of adsorption breakthrough curves for herbicides onto GAC (T 298 K, V_s 6.59×10^{-3} m/s, H 0.10 m, C_o 0.45 mol/m^3) (**a**) CPA, (**b**) 2,4-D, (**c**) MCPA

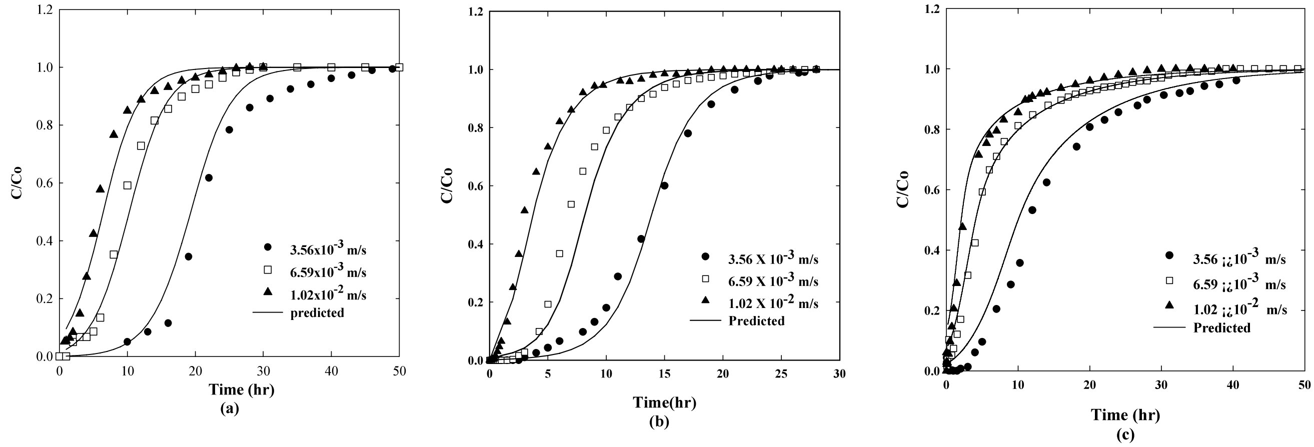


Fig. 5 Effect of flow rate and model prediction of adsorption breakthrough curves for the herbicides onto GAC (T 298 K, pH 3.5, H 0.10 m, C_o 0.45 mol/m^3) (**a**) CPA, (**b**) 2,4-D, (**c**) MCPA

7.0, 10.0) are shown in Fig. 4. The breakthrough time decreased with increasing 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. As shown in Fig. 4, the breakthrough time of CPA is longer than that of 2,4-D and MPCA because the adsorption amount of CPA is greater than that of 2,4-D and MCPA. Figure 4 also shows that the predicted breakthrough curves by the LDFA model incorporated with the Sips equation fit well with the fixed bed data.

Since the flow rate is a profoundly important factor in the fixed bed design, to investigate the effect of flow rate on the herbicides adsorption, the influent herbicides concentration was held constant at 0.45 mol/m^3, and the superficial flow rates were 3.56×10^{-3}, 6.59×10^{-3}, and 1.02×10^{-2}, respectively. And the results of CPA, 2,4-D, and MPCA are shown in Fig. 5. As shown in Fig. 5, the breakthrough time decreased with increasing flow rate. On the other hand, the breakthrough curves were steeper for higher flow rates. This result can be explained by the concept of the moving velocity of the mass transfer zone (MTZ) (Ruthven 1984), V_{mtz}, which is defined as follow:

$$V_{mtz} = \left(\frac{\partial z}{\partial t}\right)_C = \frac{V}{1 + \rho_p \frac{1-\varepsilon_b}{\varepsilon_b} (\frac{\partial q^*}{\partial c})_C}. \tag{10}$$

Equation (10) suggests that MTZ is a function of interstitial velocity, particle density, bed porosity, and $\frac{\partial q^*}{\partial c}$. Intraparticle diffusivity is generally believed to be independent of flow rate. From Fig. 5, however, the breakthrough curves were found to be steeper at higher flow rate. This phenomenon is attributed to external film mass transfer resistance. This resistance is smaller when flow rate is higher, so length of

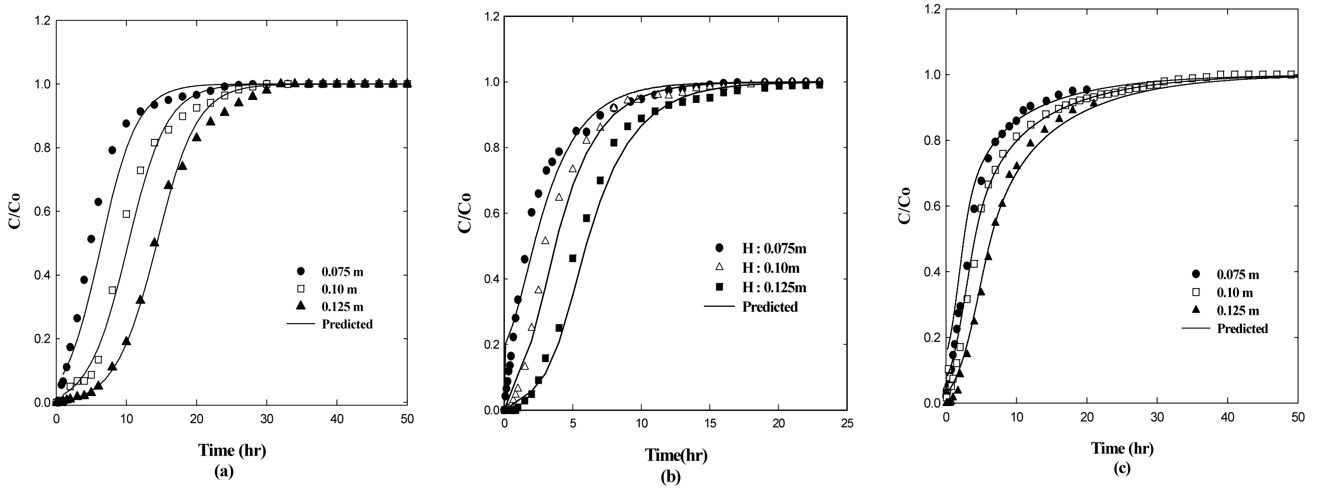


Fig. 6 Effect of bed height and model prediction of adsorption breakthrough curves for herbicides onto GAC (T 298 K, pH 3.5, V_s 6.59 × 10^{-3} m/s, C_o 0.45 mol/m^3) (**a**) CPA, (**b**) 2,4-D, (**c**) MCPA

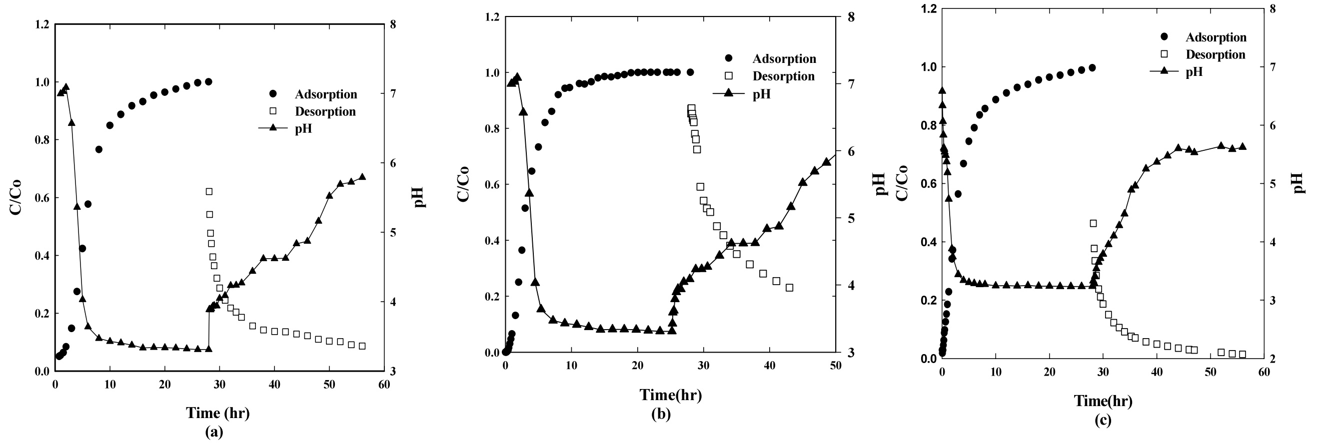


Fig. 7 The pH variations during the adsorption/desorption processes for the system (T 298 K, pH 3.5, V_s 1.02 × 10^{-2} m/s, C_o 0.45 mol/m^3) (**a**) CPA, (**b**) 2,4-D, (**c**) MCPA

MTZ is reduced and a sharp breakthrough curve is generated. Figure 6 shows the effect of bed length on adsorption of the phenoxy herbicides on GAC. Initially, the feed solution was in contact with the fresh adsorbent at the bottom of the column. The herbicides were adsorbed progressively on the sorbent as it flowed upward. As more fluid fed into the column, the bottom portion of the adsorbent becomes saturated with the herbicides. Thus, the adsorption zone moves upwards. The concentration of solute in the lower portions of the packed bed is usually higher than that in the top portions. If the breakthrough curves are obtained at different column lengths, their shapes should be similar because all of the other operative conditions are the same. However, Fig. 6 shows the experimental result, that the breakthrough curve has a sharper shape for a shorter column. Generally, this result can be observed when the column length is shorter than the zone length. However, the concentration profile in the MTZ becomes a constant pattern after traveling some finite distance, which is usually much longer than the zone length. From our experimental results, the breakthrough curve for 0.075 m of bed length becomes increasingly steeper.

For the successful application of adsorption systems, the efficient regeneration of adsorbents can be another important issue from an economic point of view. There are many regeneration techniques such as the thermal, the steam, and the solvent regenerations. The choice of a specific regeneration method may depend upon the physical and chemical characteristics of both adsorbates and adsorbents. In this study, distilled water was used as a solvent for phenoxy herbicides.

Figure 7 shows adsorption and desorption of the phenoxy herbicides in the fixed bed adsorber. The mass of adsorbent is 0.01 kg and initial pH of the herbicides solution is 3.5. As shown in Fig. 7, the desorption yield was above 95% for the phenoxy herbicides only using distilled water. The pH of the herbicides solution through the fixed bed increased from 3.5 to 7.1 at the front of the breakthrough point, and then decreased from 7.1 to 3.5 at the back of the breakthrough point in the fixed bed. As shown in Fig. 7, the rapid increase of effluent pH at the initial stage of adsorption in the fixed bed implies that large amounts of the phenoxy herbicides can be removed by the adsorption method using the activated carbon materials as adsorbents.

4 Conclusion

In the present study, we investigated the adsorption and desorption characteristics of some phenoxy herbicides including CAP, 2,4-D, and MPCA on activated carbon materials. The adsorption isotherm of CAP, 2,4-D, and MPCA on activated carbon exhibited the favorable type, in which the Langmuir and the Sips equations were found to be suitable to describe adsorption isotherms for the single component system. Adsorption equilibrium capacities of these phenoxy herbicides increased with decreasing pH values. Kinetic parameters such as the mass transfer coefficients and controlling-step diffusion coefficients were evaluated from several correlation approximations. Such simple dynamic models successfully simulated the experimental adsorption breakthrough curves under various operation conditions. The desorption yield of the phenoxy herbicides in the activated carbon was about 95% using distilled water as a solvent.

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References

Aksu, Z., Kabasakal, E.: Batch adsorption of 2,4-dichlorophenoxy-acetic acid (2,4-D) from aqueous solution by granular activated carbon. Sep. Pur. Technol. **35**, 223–240 (2004)

Areerachakul, N., Vigneswaran, S., Ngo, H.H.: Kandasamy Granular activated carbon (GAC) adsorption-photocatalysis hybrid system in the removal of herbicide from water. Sep. Pur. Technol. **55**, 206–211 (2007)

Cohen, D.B.: Groundwater contamination by toxic substances—a California assessment. In: Garner, W.Y., Honeycutt, R.C., Nigg, H.N. (eds.) Evaluation of Pesticides in Groundwater. ACS Symposium Series, vol. 315, pp. 499–529. American Chemical Society, Washington (1986)

Fielding, M., Barcelo, D., Helweg, A., Galassi, S., Torstensson, L., Zoonen, P., Wolte, R., Angeletti, G.: Pesticides in ground and drinking water. Water Pollution Research Report 27, Commission of the European Communities, Brussels (1992)

Freundlich, H.: Uber die adsorption in loesungen. J. Phys. Chem. **57**, 385–470 (1907)

Hodgson, E.P., Levi, E.: Pesticides: an important but underused model for the environmental health science. Environ. Health Perspect. **104**, 97–105 (1996)

Kah, M., Brown, C.D.: Changes in pesticide adsorption with time at high soil to solution ratios. Chemosphere **68**, 1335–1343 (2007)

Langmuir, I.: Adsorption of gases on plain surfaces of glass mica and platinum. J. Am. Chem. Soc. **40**, 1361–1403 (1918)

Ma, Y.H., Lee, T.Y.: Transient diffusion in solids with a bipore distribution. AICHE. J. **22**, 147–152 (1976)

Mangat, S.S., Elefsiniotis, P.: Biodegradation of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) in sequencing batch reactors. Water Res. **33**, 861–867 (1999)

Masamune, S., Smith, J.M.: Adsorption rate studies-significance of pore diffusion. AICHE. J. **10**, 246–252 (1964)

Misic, D.M., Sudo, Y., Suzuki, M., Kawazeo, K.: Liqiid to particle mass transfer in a stirred batch adsorptiom tank with nonlinear isotherm. J. Chem, Eng. Jpn. **15**, 490 (1982)

Ravenzwaay, B.V., Pigott, G., Leibold, E.: Absorption, distribution, metabolism and excretion of 4-chloro-2-methylphenoxyacetic acid (MCPA) in rats. Food Chem. Toxicol. **42**, 115–125 (2004)

Reid, R.C., Prausnitz, J.M., Pokung, B.E.: The Properties of Gases and Liquidss. MaGraw-Hill Co., New York (1994)

Roberto, L.R., Geankoplis, C.J.: Diffusion in liquid filled pores of activated carbon. I: Pore volume diffusion. Can. J. Chem. Eng. **72**, 262–271 (1994)

Roberto, L.R., Rangel, J.R., Bernal, L.A., Berber, M.S.: Intraparticle diffusion of cadmium and zinc ions during adsorption from aqueous solution on activated carbon. J. Chem. Technol. Biotechnol. **80**(8), 924–933 (2005)

Ruthven, D.M.: Principles of Adsorption and Adsorption Processes. Wiley, New York (1984)

Sips, R.: On the structure of a catalyst surface. J. Chem. Phys. **16**(5), 490–495 (1948)

Traegner, U.K., Suidan, M.T.: Evaluation of surface and film diffusion coefficients for carbon adsorption. Water Res. **23**, 267–273 (1989)

Thorstensen, C.W., Lode, O., Christiansen, A.L.: Development of a solid-phase extraction method for phenoxy acids and bentazone in water and comparison to a liquid-liquid extraction method. J. Agric. Food Chem. **48**, 5829–5833 (2000)

Wakao, N., Funazkri: Effect of fluid dispersion coefficient on particle to fluid mass transfer coefficients in packed bed. Chem. Eng. Sci. **33**, 1375–1384 (1978)