

ADSORPTION AND DESORPTION CHARACTERISTICS OF CHLORINATED PHENOXYACETIC ACIDS ONTO THE ACTIVATED CARBON

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The adsorption and desorption characteristics of chlorinated phenoxyacetic acids were studied for chlorophenoxyacetic acid and 2-methyl-4-chlorophenoxy acetic acid from the aqueous solution onto the activated carbon materials. Adsorption equilibrium capacities of these phenoxyacetic acids increased with decreasing the pH values of the solution. A good agreement for adsorption isotherms was found with theoretical equations, in which Langmuir and Sips equations indicated relatively small errors to the experimental data than Freundlich predictions. Kinetic parameters were measured in the batch system to analyze the adsorption rate of chlorinated phenoxyacetic acids. 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 model based on the linear driving force approximation was also used for simulating in the fixed bed system.

INTRODUCTION

Chlorinated phenoxyacetic acids are known to be selective agricultural herbicides, which are widely used to control broad-leaved weeds and other vegetations. They are inexpensive and very potent even at low concentrations. Because of their high water solubility with toxicological risks, the monitoring for the presence of herbicides is carefully required in both ground and drinking water. Much increasing concerns have also been paid over the surface water pollution. Major sources contributed to this pollution may include the direct application, the domestic usage, the surface run-off from the agricultural land, the industrial waste, and the large scale of weed control operations on industrial sites.¹⁻³ Among numerous agrochemicals available, the pesticides investigated in this study as model pollutants were chlorophenoxyacetic acid (CPA) and 2-methyl-4-chlorophenoxyacetic acid (MCPA). Both chemical compounds are found to be highly carcinogenic, and, furthermore, their biological degradation process is very slow. It is important to understand how to avoid the release of these hazardous compounds into the environment. When misused, these products, considered as moderately toxic by the World Health Organization, have potential toxicity towards animals and human beings. As in the result of accidental spillage, these chlorinated phenoxyacetic acids have proven their potential to injure non-target cultivars and microorganisms, which can cause the adverse side effect in mammals including human beings. In this regard, herbicide degraders and related techniques can make great contributions to improve better soil qualities as biocontrol agents.^{4,5}

Recently, various technical treatments have been employed to solve the wastewater problems including adsorption, precipitation, ion exchange, and reverse osmosis. Among them, the adsorption onto solid adsorbents has become the environmental-friendly method with some advantages since the adsorption

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method 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 with the well-developed pore volume, which enable to remove liquid-phase contaminants such as the organic compounds, the heavy metal ions and the coloring matters.⁶ In order to design the effective adsorption/desorption processes, and also to develop the mathematical model which can accurately describe those operation processes, it is required to obtain detailed information on both the adsorption and the desorption characteristics for individual pollutants under different operating conditions. The main purpose of this research work is to study the adsorption/desorption characteristics, experimentally as well as theoretically, in order to eliminate the chlorinated phenoxyacetic acids from the aqueous solutions.

THEORETICAL MODEL

It is assumed that the transport processes for adsorption and desorption occurs instantaneously between the adsorbate in the fluid and the surface of the adsorbent. The driving force under equilibrium conditions is the concentration gradient of the adsorbate between the liquid bulk and the pore wall. The adsorbed species then diffuse into the pore space confined within the adsorbent. Provided that the surface diffusion coefficient, D_s , is a dominant factor, the following equation can be assumed to describe the rate of adsorption for spherical particles⁷

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

with initial and boundary conditions

$$q_i(r, t=0) = 0 \quad (2)$$

$$\left. \frac{\partial q_i}{\partial r} \right|_{r=0} = 0 \quad (3)$$

$$D_s \rho_p \left. \frac{\partial q_i}{\partial r} \right|_{r=R} = k_f (C_i - C_{si}) \quad (4)$$

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

$$-D_L \frac{\partial^2 C_i}{\partial z^2} + \frac{\partial v C_i}{\partial z} + \frac{\partial C_i}{\partial t} + \frac{1-\epsilon_b}{\epsilon_b} \frac{3}{R} (C_i - C_{si}) = 0 \quad (5)$$

$$C_i(z, t=0) = 0 \quad (6)$$

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

$$\left. \frac{\partial C_i}{\partial z} \right|_{z=L} = 0 \quad (8)$$

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 such as concentration and temperature. When an adsorbent is in contact with the surrounding fluid of a certain composition, adsorption takes place and after a sufficiently long time, the adsorbent and the surrounding fluid reach equilibrium. In this state the amount of the component adsorbed on the surface mainly of the micropore of the adsorbent is determined.

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 ~ 0.25g), and the volume of the solution was 200 ml in single solute test. The flasks were shaken for 7 days to provide enough time and contact for equilibrium between the solid and liquid phase. Prior to

analysis of the sample taken from the flask, it was filtered to remove suspended carbon particles. The concentration of the chlorinated phenoxyacetic acids (CPA and MPCA) was determined using the spectrophotometer (Shimadzu 1601) at $\lambda=273$ 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., U.S.A. The particle size of the activated carbon was estimated to be within the range 0.37 - 0.54 mm in diameter. The physical characteristics of the adsorbent in this work are listed in Table 1. Also shown in Table 2 are the structural properties of the chlorinated phenoxyacetic acids investigated in this work. All adsorbent particles were dried in vacuum oven to remove impurities prior to use.

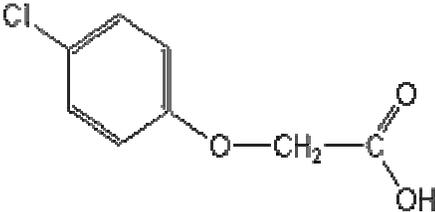
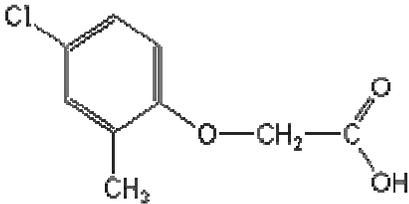
Table 1

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 [\AA]

Table 2

Structural properties of the adsorbates employed in this study.

Compounds	Structure	Molecular Weight	pKa (298 K)
CPA		186.6	3.1
MPCA		200.6	3.2

Batch adsorption experiments were conducted using a Carberry-type batch process. All the 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, respectively. 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.

RESULTS AND DISCUSSION

Adsorption equilibrium

The amount of chlorinated phenoxyacetic acids adsorbed onto GAC under equilibrium conditions were calculated from the following mass balance equation.

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

Where q is the equilibrium amount adsorbed on the adsorbent (mol/kg), C_i is the initial concentration of bulk fluid (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 control of solutions is observed to be one of the most important parameters affecting the adsorption process. The single-species adsorption isotherms for the system of CPA and MPCA with the initial pH variations are illustrated in Figs. 1 and 2, respectively. As can be seen in these figures, the adsorption amounts for single species decreased with increasing the pH values of the solution. Such adsorption processes are highly dependent on the pH values of the solution, which can affect the surface charge of the adsorbent, and the degree of ionization, and the speciation of the adsorbate. The adsorption capacity of CPA onto GAC was greater than that of MPCA.

In this study, three isotherm models including Langmuir, Freundlich, and Sips predictions were used to correlate our experimental equilibrium data. 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 the fit. The mean percent deviation between experimental and predicted values is defined as following:

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

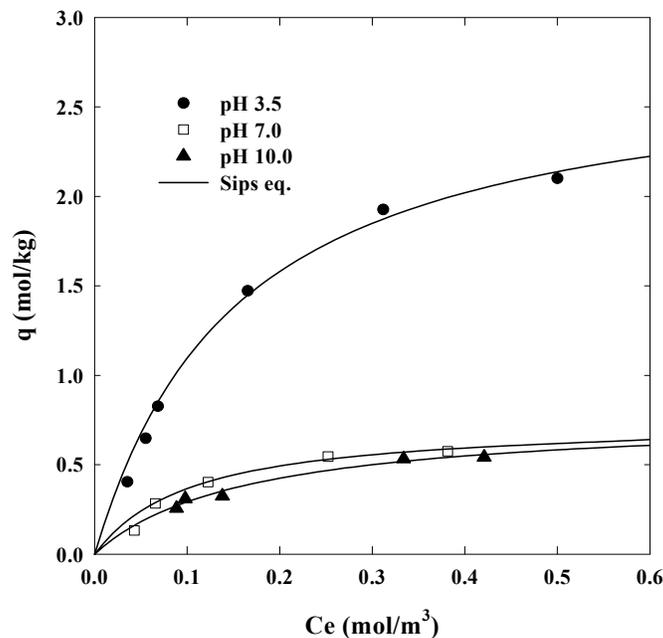


Fig. 1 – The adsorption isotherm of CPA for the activated carbon at different pHs (298 K).

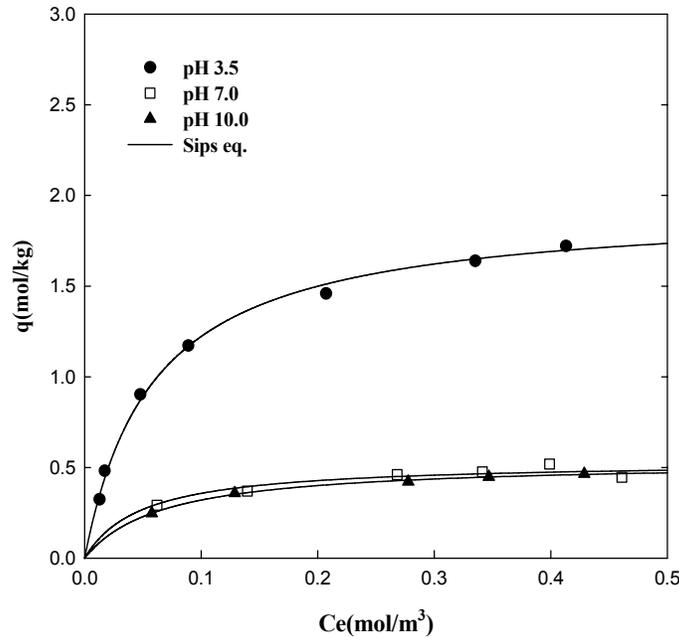


Fig. 2 – The adsorption isotherm of MPCA for the activated carbon at different pHs (298 K).

These parameters and the average percent differences between the measured and the calculated values for CPA and MPCA are listed in Table 3. Under all three sets of pH variations investigated in this work, 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 this result in Table 3 together with isotherm curves displayed in Figs. 1 and 2, we believe that the Langmuir and the Sips equations is suitable for predicting the single-component adsorption isotherm for CPA and MPCA on the activated carbon.

Table 3

The adsorption equilibrium constants of chlorinated phenoxyacetic acids onto the activated carbon at different pHs (298.15K)

Isotherm	Equation	Parameters	pH=3.5		pH=7.0		pH=10.0	
			CPA	MPCA	CPA	MPCA	CPA	MPCA
Langmuir	$q = \frac{q_m b C}{1 + b C}$	$q_m [mol/kg]$	2.77	1.94	0.38	0.54	0.77	0.53
		$b [-]$	6.59	17.07	9.90	18.56	5.86	15.07
		error(%)	2.66	3.47	1.98	4.58	4.99	0.93
Freundlich	$q = k C^{1/n}$	$k [-]$	3.18	2.89	0.90	0.61	0.85	0.62
		$n [-]$	2.09	2.23	2.44	3.85	2.14	3.26
		error(%)	7.32	3.39	5.26	4.86	5.38	3.28
Sips	$q = \frac{q_m b C^{1/n}}{1 + b C^{1/n}}$	$q_m [mol/kg]$	2.27	1.94	0.80	0.53	0.78	0.53
		$b [-]$	6.86	16.82	10.31	34.78	5.88	14.97
		$n [-]$	0.98	1.04	0.78	0.80	1.01	1.01
		error(%)	2.31	3.24	1.71	3.54	5.06	0.99

Batch bed adsorption

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

$$N_A = K_f A_s (C - C_s) \quad (11)$$

For the batch system with the adsorption time of less than 300 seconds, one may have an approximation⁶

$$\ln(C/C_i) = -k_f A_s / V_s \quad (12)$$

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

$$A_s = 3M / \rho_p R_p \quad (13)$$

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

Fig. 3 is a typical plot to estimate the k_f -values from the initial concentration data at 298K and pH=3.5. The values of k_f for CPA and MPCA obtained from the slope in Fig. 3 are 7.67×10^{-5} m/s and 5.01×10^{-5} m/s, respectively.

Fig. 4 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.⁷ The estimated values of k_f , D_p , and D_s for CPA and MPCA are listed in Table 4.

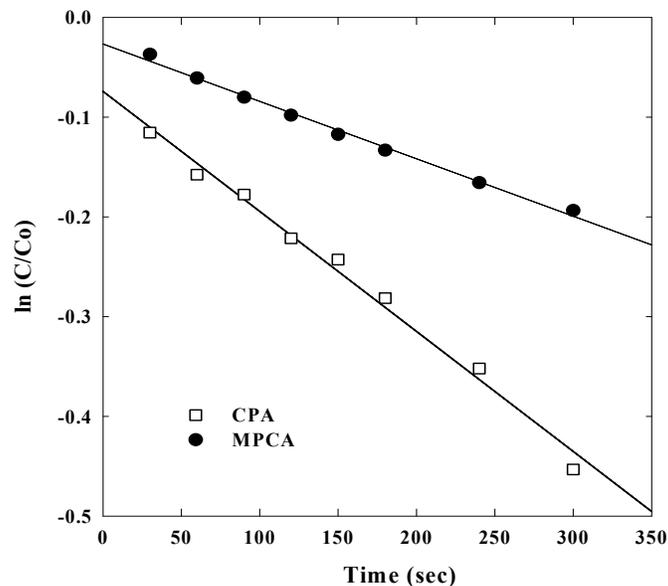


Fig. 3 – Determination of k_f from $\ln(C/C_0)$ vs. time plots for chlorinated phenoxyacetic acids (298 K and pH=3.5).

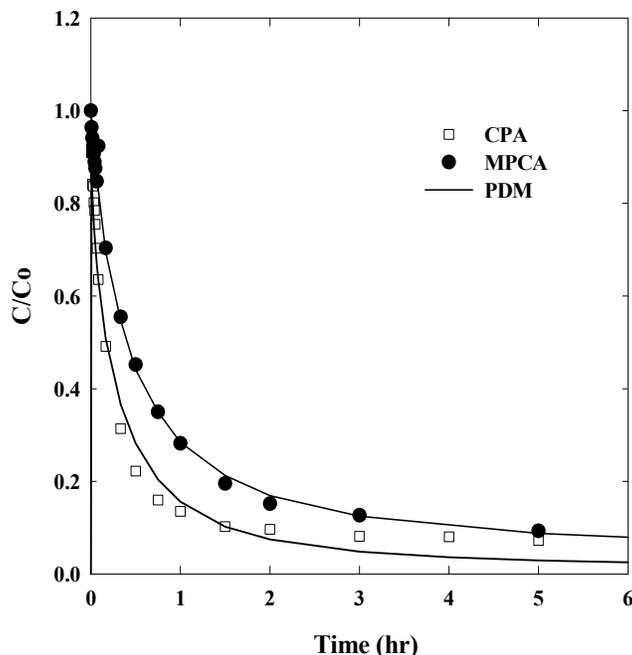


Fig. 4 – The concentration decay curve of chlorinated phenoxyacetic acids onto the activated carbon (298 K and pH=3.5).

Table 4

The kinetic parameters of chlorinated phenoxyacetic acids onto the activated carbon in a batch reactor.

Adsorbates	$k_f \times 10^5$ [m/sec]	$D_s \times 10^{13}$ [m ² /sec]	$D_p \times 10^9$ [m ² /sec]	Biot No. [-]
CPA	7.67	6.80	2.90	6.59
MPCA	5.01	1.72	0.94	19.09

The nondimensional Biot number, Bi, in Table 4 was estimated by the following relationship,⁹

$$Bi = \frac{k_f d_p c_o}{2D_s \rho_p q_o} \tag{14}$$

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.

Packed bed adsorption

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. 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 system was estimated by the Wakao’s correlation¹⁰

$$\frac{D_L}{2vR_p} = \frac{20}{Re Sc} + \frac{1}{2} \tag{15}$$

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 equation¹⁰

$$k_f = \frac{D_m}{2R_p} (2.0 + 1.1 Re^{0.6} Sc^{0.33}) \quad (16)$$

where Sc and Re are, respectively, Schmidt and Reynolds dimensionless numbers. In Eqs. (15) and (16), the molecular diffusion coefficients, D_m , of CPA and MPCA can be calculated by the Wilke-Chang equation.¹¹ 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.

Table 5

Model parameter values for the fixed-bed simulation.

	$k_f \times 10^5 [m/sec]$	$D_L \times 10^5 [m^2/sec]$	$D_m \times 10^{10} [m^2/sec]$
CPA	1.04	0.36	2.70
MPCA	2.78	1.13	6.77

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 designing and optimization.

Fig. 5 shows the breakthrough curves of CPA and MPCA at the same operation condition. As can be seen in this figure, the breakthrough time of CPA is longer than that of MPCA because the adsorption affinities of MPCA are lower than that of CPA. This figure also shows that the predicted breakthrough curves by the linear driving force approximation (LDFA) model incorporated within the Sips equation are fitted well with the fixed bed data for the single component system.

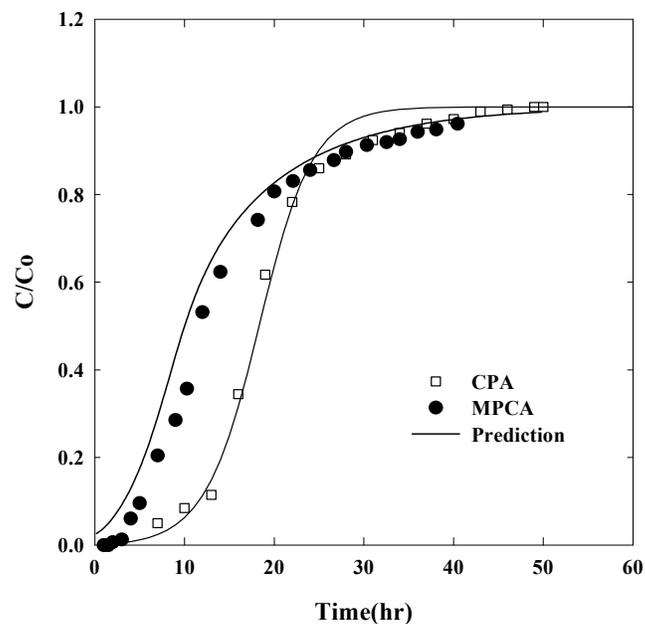


Fig. 5 – Breakthrough curves of chlorinated phenoxyacetic acids onto the activated carbon (298 K, pH=3.5, $v=3.77 \times 10^{-3}$ m/sec, $C_0=0.45$ mol/m³, and H=0.1 m).

Since the flow rate is a profoundly important factor in the fixed bed design, the effect of the flow rate was investigated, and the results of CPA and MPCA are shown in Figs. 6 and 7, respectively. Those figures show that (i) the breakthrough time decreases with increasing the flow rate, and (ii) the breakthrough curves are steeper for higher flow rates. In general, the breakthrough curves become steeper with increasing the flow rate and with decreasing the bed height. Since the intraparticle diffusivity is usually independent on the flow rate, this suggests the external film mass transfer resistance. This resistance is weak when the flow rate is higher, so that the length of the mass transfer zone is reduced and the sharper breakthrough curve is generated.

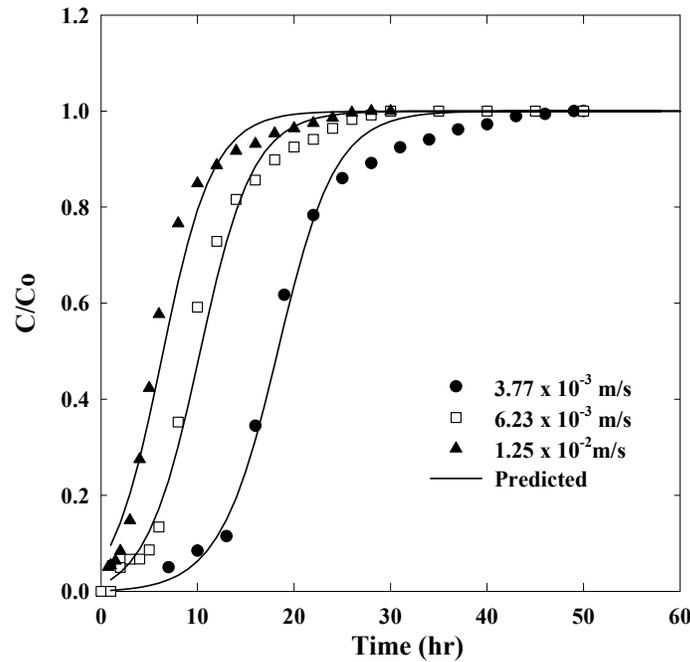


Fig. 6 – Effects of the flow rate on the experimental results and the model predictions of adsorption breakthrough curves for the system of CPA onto GAC (298 K, pH=3.5, $C_0=0.45 \text{ mol/m}^3$, and $H=0.1 \text{ m}$).

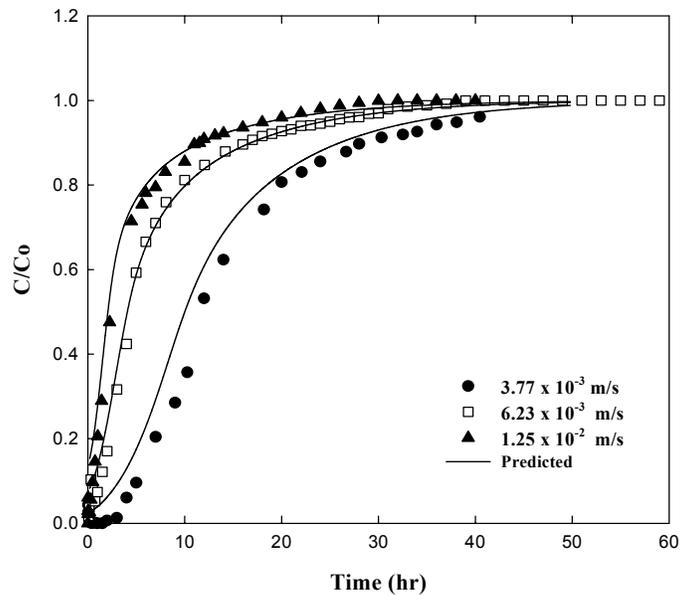


Fig. 7 – As in Fig. 6 but for the system of MPCA onto GAC.

For the successful application of adsorption systems, the efficient regeneration of adsorbents can be another important issue from the 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, the distilled water was used as solvent (effluent) for chlorinated phenoxyacetic acids. As shown in Figs. 8 and 9, the desorption yield was above 90 % for CPA and above 95 % for MPCA only using the distilled water. The effluent pH increased in the initial stage of adsorption, and decreased to the pH of the initial solution during the adsorption process, while increased during the desorption process. The rapid increasing of effluent pH in the earlier adsorption stage also implies that large amounts of chlorinated phenoxyacetic acids can be removed by the adsorption method using the activated carbon materials as adsorbents.

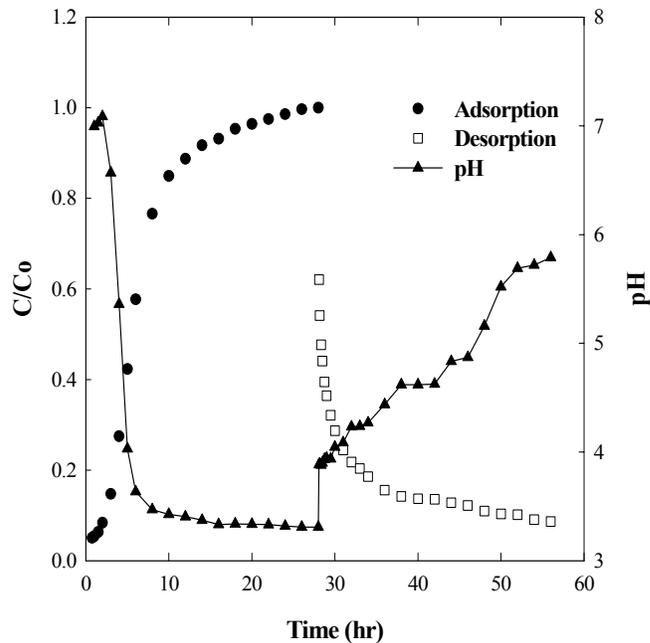


Fig. 8 – The pH variations during the adsorption/desorption processes for the system of CPA onto GAC (298 K, pH=3.5, $C_0=0.45 \text{ mol/m}^3$, $V_s=1.02 \times 10^{-2} \text{ m}^3$, and $H=0.1 \text{ m}$).

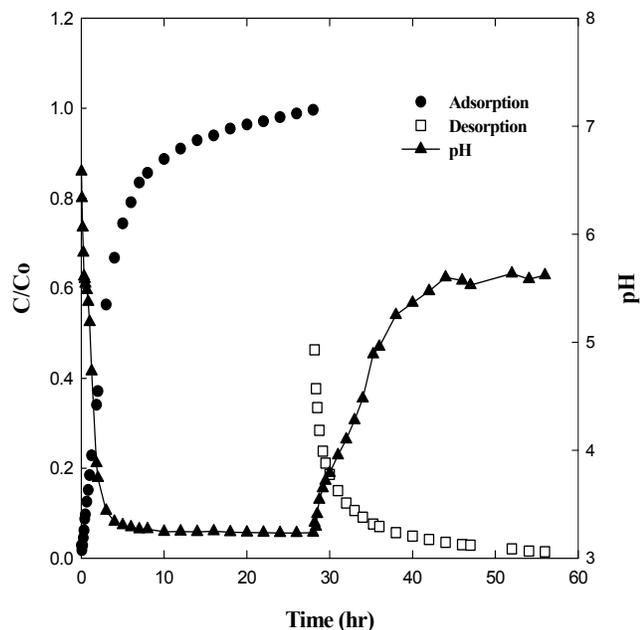


Fig. 9 As in Fig. 8 but for the system of MPCA onto GAC.

CONCLUSIONS

In the present work, we have investigated the adsorption and desorption characteristics of chlorinated phenoxyacetic acids including CAP and MPCA onto the activated carbon materials. The adsorption isotherm of CAP and MPCA onto the activated carbon exhibited the favorable type, in which the Langmuir and the Sips equations can be suitable to describe adsorption isotherms for the single component system. Adsorption equilibrium capacities of these phenoxyacetic acids increased with decreasing the pH values of the solution. 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 MPCA was higher than that of CAP, and both were above 90% only using the distilled water as solvent.

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Nomenclatures

A_S	surface area of the adsorbent particles, m^2
b	isotherm parameter
C	equilibrium concentration of the solution, 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_m	molecular diffusion coefficient, m^2/sec
d_p	adsorbent particle diameter, m
D_p	effective pore diffusion coefficient, m^2/sec
D_s	effective surface diffusion coefficient, m^2/sec
k	isotherm parameter
k_f	film mass transfer coefficient, m/sec
M	total mass of sorbent particle, kg
n	isotherm parameter
N	number of data point
N_A	rate of mass transfer of adsorbates to the external surface of the adsorbent, mol/sec
q	equilibrium amount adsorbed on the adsorbent, mol/kg
q_i	Concentration in particle phase, mol/kg
q_m	fixed number of surface sites, i. e. 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/sec
v_s	superficial velocity, m/sec
W	weight of adsorbent, kg
z	axial distance, m

Greek Letters

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

Abbreviation

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

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