

# ADSORPTION AND DESORPTION CHARACTERISTICS OF SOME CHLORINATED HERBICIDES ONTO ACTIVATED CARBON

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**Abstract.** Adsorption and desorption characteristics of some herbicides (CPA, MCPA and 2,4,5-T) from aqueous solution onto the active carbon materials (GAC, F-400) were studied. Adsorption equilibrium capacities of the herbicides increased with decreasing pH of the solution. Adsorption equilibrium isotherms can be represented by the Sips equation. Kinetic parameters were measured in a batch adsorber to analyze the adsorption rates of the 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 for simulating the adsorption behavior of the herbicides in a fixed bed adsorber. Over ninety five percent desorption of the herbicides can be obtained using distilled water.

**Keywords:** adsorption, desorption, herbicide, activated carbon.

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## INTRODUCTION

Worldwide application of intensive agriculture practiced over the past few decades has resulted in the presence of a variety of agrochemicals in the environment. Many pesticides that are commonly used are resistant to natural degradation in the environment; hence, there is a concern about possible adverse human health effects and ecotoxicity.<sup>1-3</sup> Chlorophenoxy herbicides, which have potential toxicity toward humans and animals<sup>4</sup> and are suspect mutagens and carcinogens, are used worldwide on a large scale as plant growth regulators for agricultural and nonagricultural purposes.

Among the numerous agrochemicals in use today, the herbicides selected as model pollutants for the present study were chlorophenoxyacetic acid (CPA), 2-methyl-4-chlorophenoxyacetic acid (MCPA), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). The chemical compounds are highly carcinogenic. Furthermore, their biological degradation is very slow. It is important to avoid the release of these compounds into the environment. These products have potential toxicity towards humans and animals, being considered as moderately toxic by the World Health Organization. When misused or as the result of accidental spillage, these chlorinated herbicides have potential to injure non-target cultivars and microorganisms. In particular, herbicide degraders and others contribute to soil quality or can be used as biocontrol agents, which may cause the adverse side-effects in mammals including humans.<sup>5,6</sup>

Various treatment techniques have been employed to provide 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 enable to remove liquid-phase contaminants such as organic compounds, heavy metal ions and coloring matters.<sup>7</sup> In order

to design effective activated carbon adsorption units and to develop mathematical models which can accurately describe their operation characteristics, it is required for sufficient information 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 of the chlorinated herbicides from aqueous solutions.

## THEORETICAL MODEL

It is assumed that the adsorption and desorption occurs instantaneously and the equilibrium condition is established between adsorbates in the fluid and the surface of the adsorbents. The driving force is the concentration gradient of the adsorbate between the liquid bulk and the pore wall. The adsorbed species then diffuse into the pore space in the adsorbent. Provided that the surface diffusion is dominant, the following equation can be expressed to describe the rate of adsorption for a spherical particle as <sup>8</sup>

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

With initial and boundary conditions

$$\frac{\partial t}{\partial q} = 0 \quad \text{at} \quad r = 0 \quad (2)$$

$$q = 0 \quad \text{at} \quad t = 0 \quad (3)$$

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

The resulting mass balance equation in the column can be represented as

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

In this case we may have the relevant initial and boundary conditions such as

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

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

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

Where  $C$  is concentration in the fluid phase,  $mol/m^3$ ,  $C_i$  is initial concentration of bulk fluid,  $mol/m^3$ ,  $C_s$  is concentration on the surface of adsorbent,  $mol/m^3$ ,  $D_L$  is axial dispersion coefficient,  $m^2/sec$ ,  $D_s$  is effective surface diffusion coefficient,  $m^2/sec$ ,  $k_f$  is film mass transfer coefficient,  $m/sec$ ,  $r$  is radial distance,  $m$ ,  $R_p$  is particle radius,  $m$ ,  $t$  is time,  $sec$ ,  $v$  is interstitial velocity,  $m/sec$ ,  $z$  is axial distance,  $m$ ,  $\rho_p$  is particle density,  $kg/m^3$ , and  $\varepsilon_b$  is bed porosity

## EXPERIMENTAL

The concentration of the herbicides (CPA, MCPA and 2,4,5-T) was determined using the spectrophotometer (Shimadzu 1601). The wavelengths, corresponding to the maximum absorbance of CPA, MCPA and 2,4,5-T were found to be 273nm, 279nm and 211nm respectively. 2M HCl and 2M 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 estimated to be in the ranges of 0.37 and 0.54 mm in diameter. The properties of this adsorbent employed in this work are listed in Table 1. All adsorbent particles were dried in vacuum oven to remove impurities prior to use.

Table 1. Physical properties of the adsorbent employed in this work.

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

Single species equilibrium adsorption data were obtained by measuring the adsorbate concentration in an aqueous solution of the herbicides, 0.45 mol/m<sup>3</sup>. The solution was kept in the 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 using a UV spectrophotometer.

# RESULTS AND DISCUSSION

## 1. Adsorption Equilibrium

The amount of CPA, MCPA and 2,4,5-T adsorbed onto the GAC at equilibrium was calculated from the following mass balance equation.

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

Where  $q$  is equilibrium amount adsorbed on the adsorbent,  $mol/kg$ ,  $V$  is volume of the solution  $m^3$ , and  $W$  is weight of adsorbent,  $kg$ .

The pH of the solution is one of the most important parameters affecting the adsorption process. The variation of single species adsorption equilibrium for the herbicides with initial pH is given in Figures 1 ~ 3. As can be seen in these figures, 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. In this study, three isotherm models ; Langmuir, Freundlich, and Sips, were used to correlate our experimental equilibrium data. Langmuir and Freundlich equations has two parameters and Sips equation have 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 of the correlations. The mean percent deviation between experimental and predicted values is as follow :

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

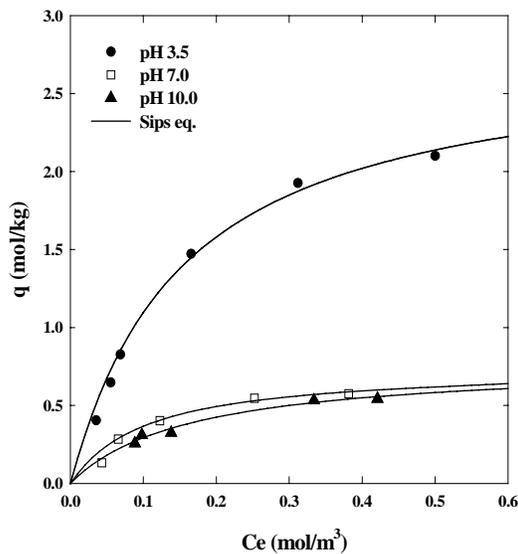


Fig. 1. The adsorption isotherm of CPA for activated carbons at different pH's.

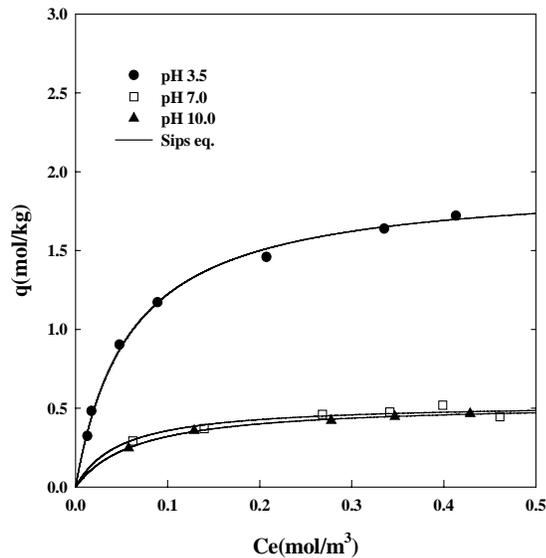


Fig. 2. The adsorption isotherm of MCPA for activated carbons at different pH's.

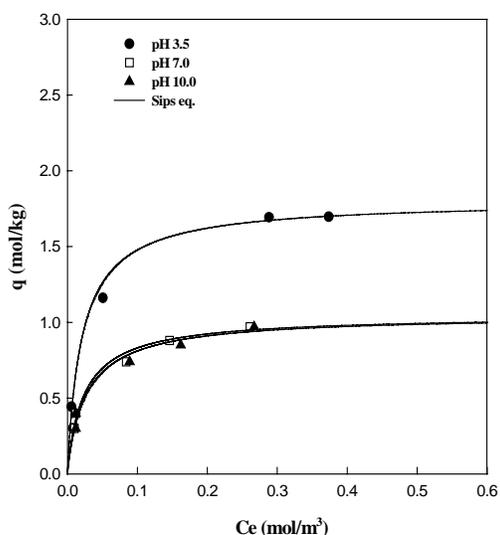


Fig. 3 The adsorption isotherm of 2,4,5-T for activated carbon at different pH's.

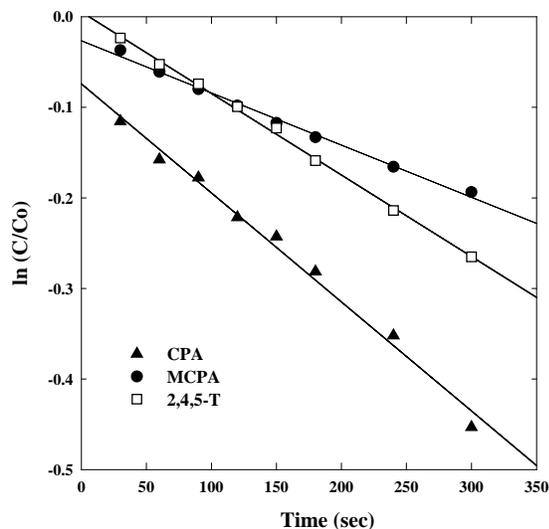


Fig. 4. Determination of  $k_f$  from the  $\ln(C/C_0)$  vs. time plots for the herbicides.

These parameters and the average percent differences between measured and calculated values for the herbicides are given in Table 2. As shown in the Table, 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 herbicides on activated carbon.

Table 2. The adsorption equilibrium constants of the herbicides onto the activated carbon at different pH's (298.15K).

Isotherm	Parameters	PH 3.5			PH 7.0			PH 10.0		
		CPA	MCPA	2,4,5-T	CPA	MCPA	2,4,5-T	CPA	MCPA	2,4,5-T
Langmuir	$q_m$	2.77	1.94	1.68	0.38	0.54	1.01	0.77	0.53	1.05
	$b$	6.59	17.07	60.25	9.90	18.56	46.8	5.86	15.07	34.2
	error (%)	2.66	3.47	5.09	1.98	4.85	5.85	4.99	0.93	6.84
Freundlich	$k$	3.18	2.89	2.54	0.90	0.61	1.65	0.85	0.62	1.58
	$n$	2.09	2.23	3.08	2.44	3.85	2.91	2.14	3.26	2.93
	error (%)	7.32	3.39	8.80	5.26	4.86	7.62	5.38	3.28	7.93
Sips	$q_m$	2.27	1.94	1.80	0.80	0.53	1.05	0.78	0.53	1.05
	$b$	6.86	16.82	41.52	10.3	34.78	33.3	5.88	14.97	29.8
	$n$	0.98	1.04	1.03	0.78	0.80	1.06	1.01	1.01	1.06
	error (%)	2.31	3.24	4.60	1.71	3.54	5.51	5.06	0.99	8.38

## 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

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

By rearrangement and approximation for batch system with adsorption time of less than 300 seconds.<sup>7</sup>

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

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

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

$M$  is the total mass of adsorbent particles loaded and  $\rho_p$  is the particle density. Figure 4 is a typical plot to estimate  $k_f$  from the initial concentration data of CPA, MCPA and 2,4,5-T at pH 3.5. The value of  $k_f$  obtained from Figure 4 is  $7.67 \times 10^{-5}$  m/s,  $5.01 \times 10^{-5}$  m/s and  $4.05 \times 10^{-5}$  m/s respectively.

Figure 5 shows the experimental data and model prediction for the adsorption of CPA, MCPA and 2,4,5-T 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).<sup>8</sup> The estimated values of  $k_f$ ,  $D_p$ , and  $D_s$  for the herbicides are listed in Table 3. The nondimensional Biot number, Bi, in Table 3 was estimated by following equation.<sup>9</sup>

$$Bi = \frac{k_f d_p c_o}{2D_s \rho_p q_o} \quad (14)$$

The Biot number represents the ratio of the rate of transport across the liquid layer to the rate of diffusion within the particle. For  $Bi < 1$ , 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.

Table 3. The kinetic parameters of the herbicides onto activated carbon in a batch reactor.

Adsorbates	$k_f \times 10^5$ [m/sec]	$D_s \times 10^{13}$ [m <sup>2</sup> /sec]	$D_p \times 10^9$ [m <sup>2</sup> /sec]	Biot No. [ - ]
CPA	7.67	6.80	2.90	6.59
MCPA	5.01	1.72	0.94	19.09
2,4,5-T	4.05	3.28	2.93	10.41

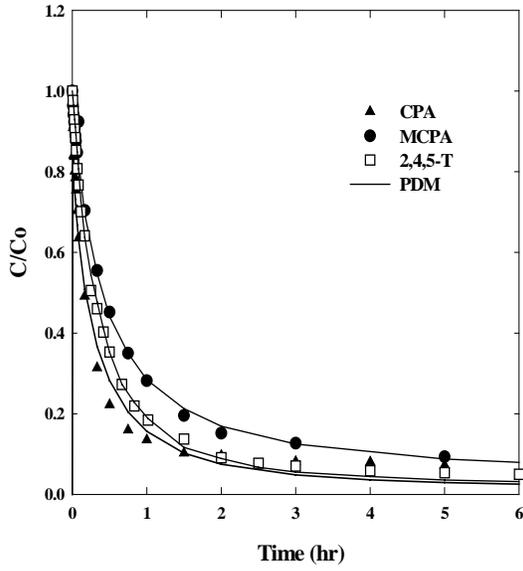


Fig. 5. The concentration decay curves of the herbicides onto active carbon

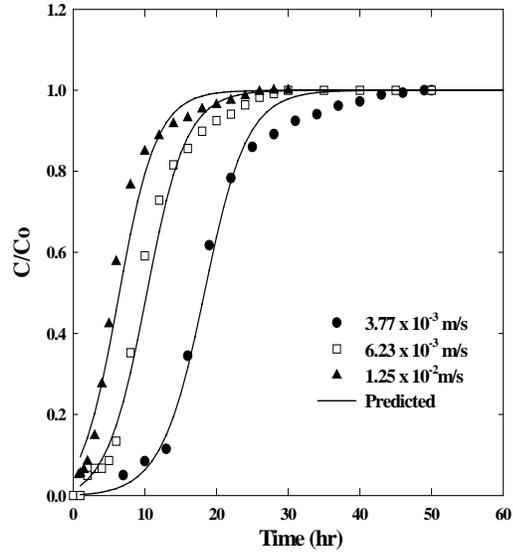


Fig. 6. The effect of flow rate on the adsorption breakthrough curves for CPA onto GAC

## 2. 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.<sup>10</sup>

$$\frac{D_L}{2\nu R_p} = \frac{20}{\xi} \left( \frac{D_m}{2\nu R_p} \right) + \frac{1}{2} = \frac{20}{Re Sc} + \frac{1}{2} \quad (15)$$

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 adsorber can be estimated by Wakao and Funazkri equation.<sup>10</sup>

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

Where  $Sc$  and  $Re$  are Schmidt and Reynolds numbers, respectively. In Eqs. (15) and (16), molecular diffusion coefficients,  $D_m$ , of the herbicides can be calculated by Wilke-Chang equation.<sup>11</sup> The estimated values of axial dispersion coefficient, external film mass transfer coefficient, and molecular diffusion in a fixed bed are listed in Table 4.

Table 4. Model parameter values for the fixed-bed simulation.

	$k_f \times 10^5$ [m/sec]	$D_L \times 10^5$ [m <sup>2</sup> /sec]	$D_m \times 10^{10}$ [m <sup>2</sup> /sec]
CPA	1.04	0.36	2.70
MCPA	2.78	1.13	6.77
2,4,5-T	2.68	0.86	6.42

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.

Since the flow rate is a very important factor in fixed bed design, the effect of flow rate for the herbicides is studied and the results are shown in Figures 6 ~ 8.

Those Figures show that the breakthrough time 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 on flow rate, this behavior is due to the external film mass transfer resistance. This resistance is weakened when flow rate is higher, so that the length of the mass transfer zone is reduced, and sharper breakthrough curve is generated.

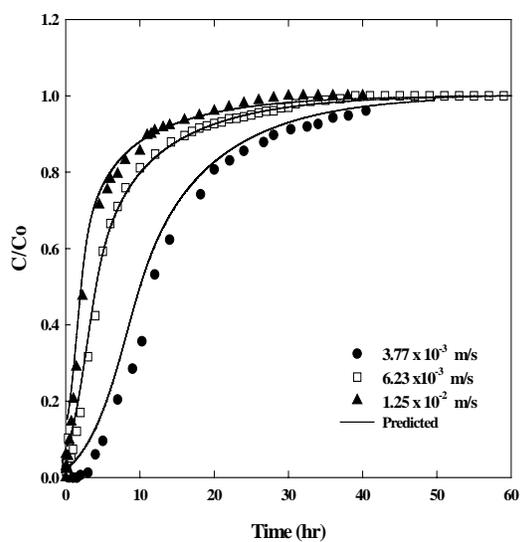


Fig. 7. The effect of flow rate on the adsorption breakthrough curves for MCPA onto GAC.

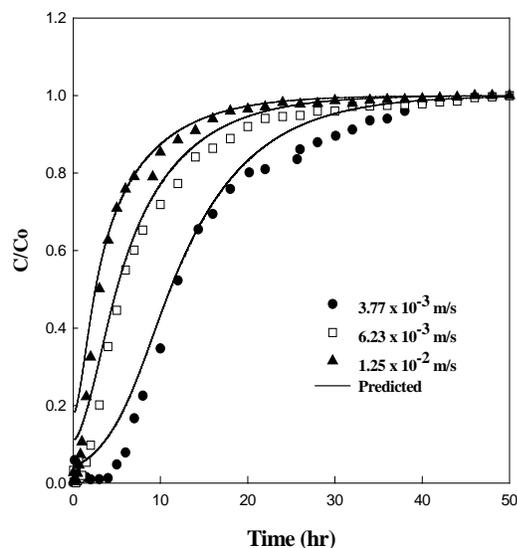


Fig. 8. The effect of flow rate on the adsorption breakthrough curves for 2,4,5-T onto GAC.

For the successful application of an adsorption system, an efficient regeneration of the used adsorbent is very important from the 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 herbicides. As shown in Figures 9 ~ 11, desorption of the herbicides was about 95% only 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 herbicides was removed by GAC.

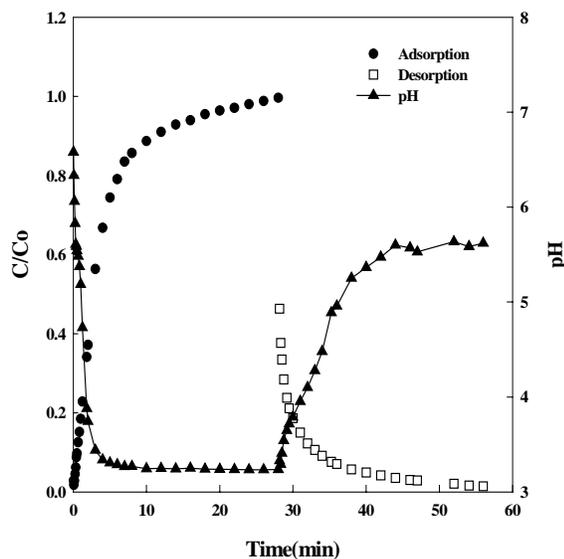
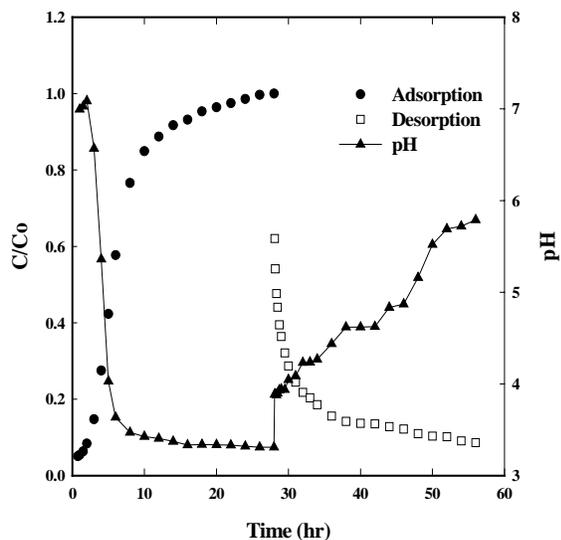


Fig. 9. pH variations during adsorption/desorption process for CPA onto GAC.

Fig. 10. pH variations during adsorption/desorption process for MCPA onto GAC.

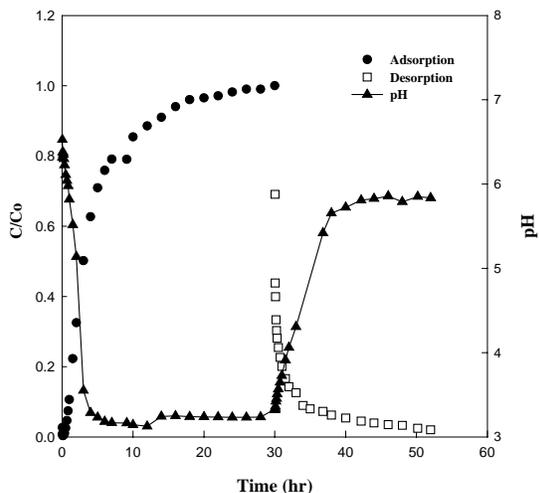


Fig. 11. pH variations during the adsorption/desorption processes for of 2,4,5-T onto GAC.

## CONCLUSIONS

1. The adsorption isotherm of CAP, MCPA, 2,4,5-T onto activated carbon was favorable type, and Sips isotherm was suitable for single component systems among the various isotherms.
2. The adsorption equilibrium capacity of CAP, MCPA and 2,4,5-T onto activated carbon decreased with increasing pH of the solution.
3. Adsorption amounts of the herbicides onto activated carbon was in order of CPA > MCPA > 2,4,5-T.
4. 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.
5. A simple dynamic model (LDFA) successfully simulated the experimental adsorption breakthrough data under various operation conditions
6. Desorption yield of CAP, MCPA and 2,4,5-T was about 95% only using distilled water.

## ACKNOWLEDGEMENT

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