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Adsorption and Separation Characteristics of Herbicides onto Activated Carbon

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Abstract. Adsorption and desorption characteristics of the herbicides (CPA, 2,4-D and 2,4-DNP) in aqueous solution for a GAC, F-400, were studied at pH 3.5, 7.0 and 10.0. Adsorption equilibrium capacities of the herbicides onto GAC increased with decreasing pH of the solution. An 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. Ninety percent desorption of 2,4-D can be obtained using distilled water.

Keywords: adsorption, desorption, herbicides, activated carbon

1. Introduction

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 are still one of the important problems since the environment are exposed to the harmful effects of these chemicals and pesticides (Mehmet et al., 2000). Among the numerous agrochemicals in use today, 2,4-dichlorophenoxyacetic acid (2,4-D), a member of phenoxy herbicide group, has been widely applied to control broad leaf weeds (Mangat et al., 1999).

Chlorophenoxyacetic acid (CPA) is used worldwide as a plant growth regulators for agricultural and non-agricultural purposes. Typically, it is employed on a large scale for weed control on cereal crops and lawns. 2,4-dinitrophenol (2,4-DNP) is used in making dyes, wood preservatives, explosives, insect control substances, and photographic developer, and releases into the air, water and soil. The ingestion of 2,4-DNP causes harmful effects on human being. When misused or as a result of accidental spillage, these herbicides have 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.

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 pollutant under different operating conditions is required. The main purpose of this work is to

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study the adsorption and desorption characteristics of the herbicides experimentally as well as theoretically to remove them from aqueous solution.

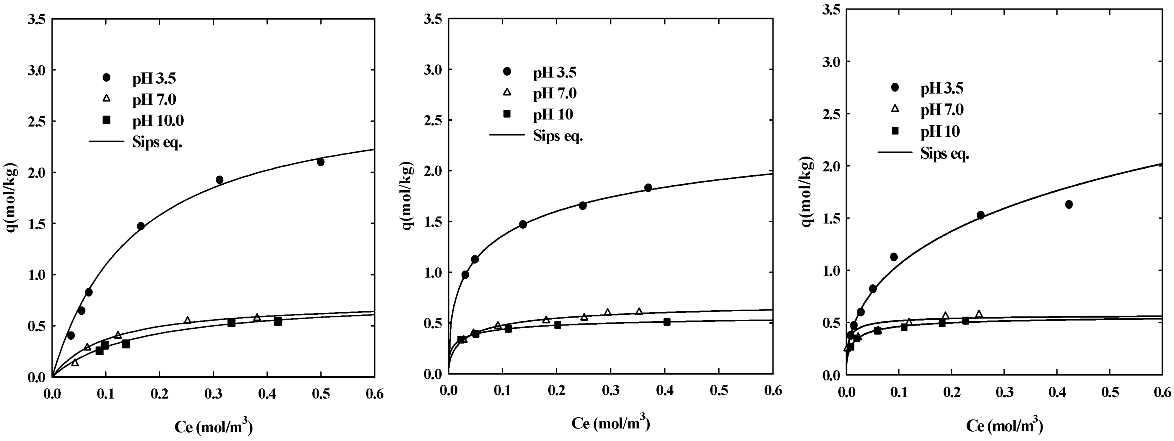
2. Experimental

The concentration of the herbicides (CPA, 2,4-D, 2,4-DNP) was measured using a spectrophotometer (Shimadzu 1601). The wavelengths, corresponding to a maximum absorbance of CPA, 2,4-D and 2,4-DNP, were found to be 273 nm, 284 nm and 325 nm, respectively. HCl and NaOH were used to adjust pH of the solution. The adsorbent used in this study was an activated carbon, Filtrasorb-400, manufactured by Calgon Co. (USA). The particle size of the granular activated carbon (GAC), BET surface area, porosity and average pore diameter were 0.37–0.54 mm, 800 m^2/g, 0.62 and 19.0 Å, respectively.

Single species equilibrium adsorption data were obtained by measuring the adsorbate concentration in an aqueous solution of the herbicides, initially at 0.45 mol/m^3. The solution was kept in the shaking bath at 298 K for one week after introducing a known amount of sorbent, and the final adsorbate concentration in the solution was measured. Batch adsorption experiments were conducted in a Carberry-type batch adsorber. All the experiments were carried out at the mixing rate of approximately 400 rpm, since the film mass transfer coefficient, k_f, is practically constant at this condition. A single-species adsorption experiment was carried out in a fixed bed adsorber which was made of a glass column of 25.4 mm in diameter and 500 mm in length, respectively. A desorption experiment of the herbicides from the sorbents was performed using distillated water. The samples were withdrawn from the effluent line and analyzed using a UV spectrophotometer.

3. Results and Discussion

The single species adsorption equilibrium data of the herbicides for different pHs are shown in Fig. 1. As can be seen in this figure, the adsorption amount decreased with increasing pH of the solution. 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 shift in the sorption capacity of the equilibrium adsorption. Anions are favorably adsorbed on the surface of adsorbents at low pH. And the magnitude of adsorption capacity for the herbicides onto the GAC was in the order of CPA > 2,4-D > 2,4-DNP. In this study, three isotherm models; Langmuir, Freundlich, and Sips were used to correlate our experimental equilibrium data. 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 correlation. The model parameters and the average percent differences between measured and calculated values are given in Table 1. As shown in the table, the Sips equation gives the best fit of our data among the three. From this result,



(a) (b) (c)

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

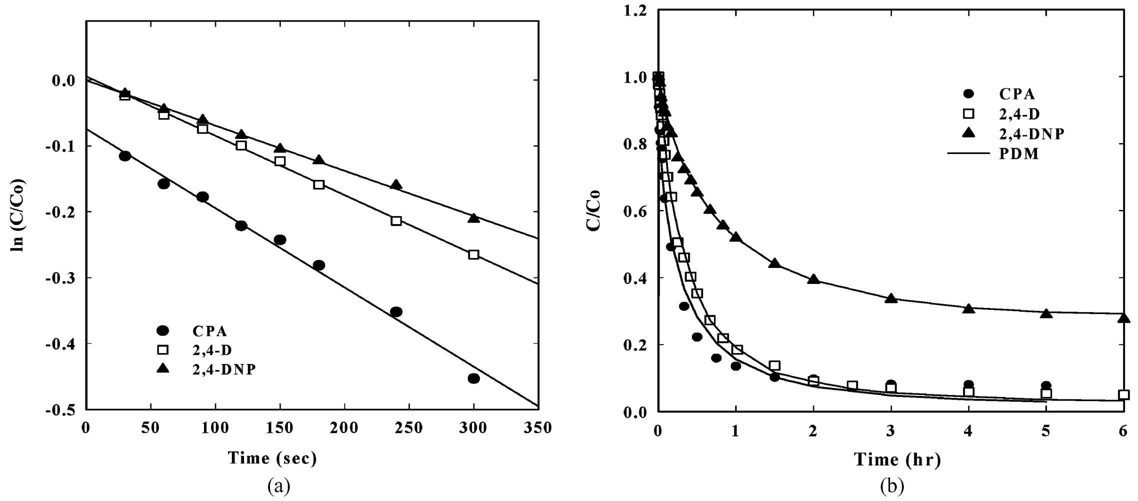
Table 1. Adsorption equilibrium isotherms of the herbicides onto activated carbon for different pH at 298 K.

		pH 3.5			pH 7.0			pH 10.0		
Isotherm	Parameters	CPA	2,4-D	2,4-DNP	CPA	2,4-D	2,4- DNP	CPA	2,4-D	2,4- DNP
Langmuir	q_m	2.77	1.86	1.81	0.38	0.62	0.53	0.77	0.50	0.50
	b	6.59	33.9	20.5	9.90	40.7	385	5.86	83.8	124
	error (%)	2.66	3.11	9.79	1.98	2.94	4.84	4.99	2.71	3.43
Freundlich	k	3.18	2.37	2.54	0.90	0.77	0.75	0.85	0.59	0.69
	n	2.09	3.97	2.54	2.44	4.45	5.87	2.14	6.82	5.22
	error (%)	7.32	1.35	5.73	5.26	2.34	5.00	5.38	2.01	2.99
Sips	q_m	2.27	3.03	6.99	0.80	0.75	0.58	0.78	0.63	0.58
	b	6.86	2.36	0.51	10.3	7.32	32.4	5.88	6.58	15.8
	n	0.98	2.16	2.16	0.78	1.62	1.62	1.01	2.16	1.62
	error (%)	2.31	1.02	4.59	1.71	1.70	2.40	5.06	0.27	1.51

we believe that the Sips equation is suitable for representing single-component equilibrium adsorption data of the herbicides on activated carbon.

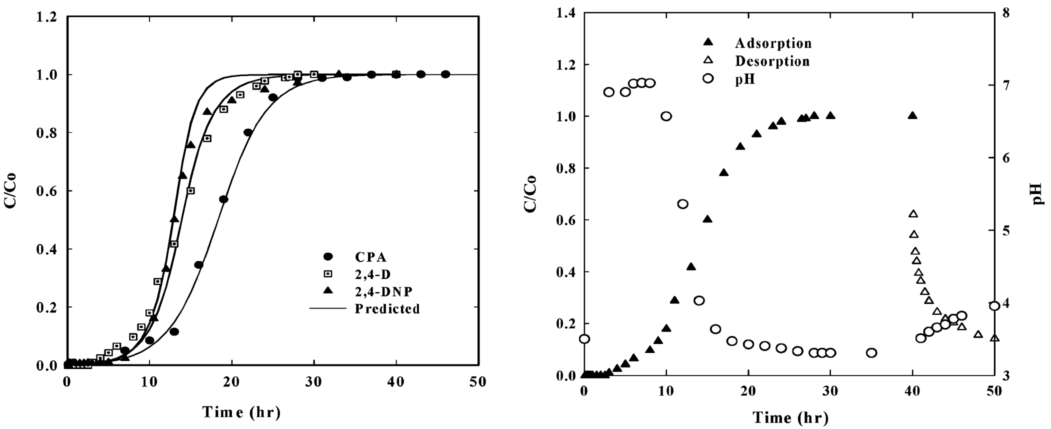
Adsorption on a solid surface takes place in several steps, such as external diffusion, internal diffusion, and actual adsorption. In general, the actual adsorption process is relatively fast compared to the previous two steps. However, it is important to estimate the order of magnitude of the mass transfer coefficient to prove it. 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 (Kim et al., 2004). Figure 2(a) is a typical plot to estimate k_f from the initial concentration data of the herbicides at pH 3.5. The value of k_f obtained from Fig. 2(a) is given in Table 2.

Figure 2(b) represents the experimental data and model prediction for single species concentration in a batch adsorber at pH 3.5. The pore diffusion model (PDM) shows satisfactory prediction of concentration decay curves. 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 herbicides are



(a) (b)

Figure 2. (a) Concentration-time plot for the determination of k_f (298 K, pH 3.5), (b) Concentration decay curves of the herbicides in a batch adsorber (298 K, pH 3.5).



(a) (b)

Figure 3. (a) Comparison of breakthrough curves of the herbicides, (b) pH variations during adsorption and desorption process for 2,4-D (298 K, pH; 3.5, V; 3.77 × 10^{-3} m/sec, Co; 0.45 mol/m^3, H; 0.1 m).

listed in Table 2. The Biot number in Table 2 represents the ratio of the rate of transport of diffusion within the GAC. 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 (Traegner and Suidan, 1989).

The breakthrough curves of all species, in general, depend on adsorption equilibrium, intraparticle mass transfer, and hydrodynamics in the column. Therefore, it is reasonable to consider adsorption equilibrium and mass transfer simultaneously in simulating the adsorption behavior in the fixed bed adsorber. Single species breakthrough data of CPA, 2,4-D and 2,4-DNP were obtained in a fixed-bed, and the data were fitted by LDFA model (Kim et al., 2004).

Figure 3(a) shows the breakthrough curves of CPA, 2,4-D and 2,4-DNP at the same operation condition. As can be seen in this figure (a), the breakthrough time of CPA is longer than those for 2,4-D and 2,4-DNP because the adsorption affinities of 2,4-D and 2,4-DNP are lower than that for CPA. 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 for single component systems. For the successful application of an adsorption system, efficient regeneration of the used adsorbent is very important. In this study, distilled water was used as desorbate for 2,4-D. As shown in Fig. 3(b), the equilibrium desorption rate of 2,4-D, was about 90% 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.

Table 2. Kinetic parameters of the herbicides in a batch reactor (298 K, pH 3.5).

Adsorbates	$k_f \times 10^{-5}$ (m/sec)	$D_s \times 10^{-13}$ (m^2/sec)	$D_p \times 10^{-9}$ (m^2/sec)	Bi (−)
CPA	7.67	6.80	2.90	9.91
2,4-D	5.00	1.90	1.42	21.58
2,4-DNP	4.29	7.48	4.79	4.73

4. Conclusion

The adsorption isotherm of CPA, 2,4-D and 2,4-DNP onto GAC was favorable type, and Sips equation was most suitable for single component system among the three isotherms. The adsorption equilibrium capacity of CPA, 2,4-D and 2,4-DNP onto GAC decreased with increasing pH of the solution. The differences in the adsorption rates among the herbicides are primarily attributable to the differences in the amount of equilibrium adsorption, and the pore diffusion model simulated our data satisfactorily. A simple dynamic model (LDFA) successfully simulated the experimental adsorption breakthrough data, and ninety percent desorption of 2,4-D can be obtained using distilled water.

Acknowledgment

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