고정층과 반유동층에서 2,4-D의 흡착 특성

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Adsorption Characteristics of 2,4-D in a Fixed and Semi-Fluidized Beds

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Introduction

Among the numerous agrochemicals in use today, the herbicide 2,4-Dichlorophenoxyacetic acid (2,4-D), a member of the phenoxy herbicide group, has been widely applied to control broad leaf weeds. 2,4-D is a regulated compound due to its toxicity; solids containing 2,4-D in excess of 1,000ppm are classified as hazardous. 2,4-D is used as agricultural herbicides against broad leaf weeds in cereal crops as well as on pastures and lawns, in parks, and on golf courses [1]. Various treatment techniques have been employed to treat the wastewater, including precipitation, adsorption, ion exchange, and reverse osmosis [2]. Among them, adsorption onto solid adsorbents has environmental significance, since it can effectively remove pollutants from in wastewater. In wastewater treatment, activated carbon is a powerful adsorbent because it has a large surface area and pore volume, which allows the removal of liquid-phase contaminants, including organic compounds, heavy metal ions and colors [3]. The pollutant content, pH, and temperature of wastewater are likely to vary with time, so design of suitable adsorption systems is not that simple; this difficulty is compounded by the fact that the influence of these variables on the equilibrium amount of adsorption is not extensively studied. In this work, a main idea is to select a proper adsorbent for separating of 2,4-D from its aqueous solution and to find its adsorption characteristics by conducting experimental and theoretical works.

Materials and Methods

The adsorbent used in this study was granular activated carbon (GAC), F400, manufactured by Calgon Co.. Before washing it with distilled water a few times to remove impurities and carbon powder and then stored after drying it in the vacuum oven at 120℃ for 24hr. The adsorbate investigated was 2,4-D. The purity and manufacturer of 2,4-D is 99.0% (Acros Co.). All chemicals were used as received without further treatment. The solution pH was adjusted to 3.5, 7.0, 10.0 by the addition of NaOH and HCl.

Results

The adsorption equilibrium of 2,4-D onto GAC was favorable type. The adsorption amount of 2,4-D onto GAC increased with decreasing initial pH of the solution. 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 Sips equation have three parameters. To find the parameters for each adsorption isotherm, the linear least squaresmethod 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 :

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

These parameters and the average percent differences between measured and calculated values for the 2,4-D in terms of pH are given in Table 1.

Fig. 2 shows the experimental data and model prediction of concentration profiles for the adsorption of 2,4-D onto GAC 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), repectively. The estimated values of k_f, D_p, and D_s for 2,4-D are listed in Table 2.

Fig. 3 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. Velocity of MTZ is a function of interstitial velocity, particle density, bed porosity and slope of the equilibrium isotherm. 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 2,4-D 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. 4 shows the breakthrough curve for packed, semi-fluidized, and fluidized beds. It is seen that the breakthrough curve obtained from semi-fluidized bed lies between those obtained from the packed and fluidized beds, since a semi-fluidized bed possesses the features of both the fluidized and packed beds. This figure also shows that the shape of the breakthrough curve for the packed bed is steeper than that for the fluidized bed, since mass transfer of axial direction in a liquid-solid packed bed operation is more predominant effects than that of radial direction. On the other hand, since fluidized bed operation has whole bed as adsorption zone and mass transfer of radial direction prevails in the bed, the breakthrough curve in fluidized bed is smoother than any other curve. Also, effluent concentration of the fluidized bed as compared with other beds exceeds rapidly the breakthrough concentration in this figure. It is due to back mixing of the liquid which occurs at high velocity.

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Table 1. Adsorption equilibrium constants of 2,4-D onto GAC at different initial pHs (298 K)

Isotherm	Parameters	pH		
		3.5	7.0	10.0
Langmuir	q_m			
	b	1.857	0.615	0.503
		33.86	40.69	83.83
	error(%)	3.111	2.937	2.710
Freundlich	k			
	n	2.369	0.771	0.598
		3.974	4.451	6.819
	error(%)	1.354	2.335	2.011
Sips	q_m			
	b	3.025	0.747	0.629
	n	2.361	7.324	6.584
		2.164	1.623	2.156
	error(%)	1.020	1.701	0.270

Table 2. Kinetic parameters of 2,4-D onto GAC at different initial pHs in a batch adsorber (298 K).

	$k_f \times 10^5$ m/sec	$D_S \times 10^{13}$ m^2/sec	$D_P \times 10^9$ m^2/sec
pH 3.5	5.00	1.90	1.42
pH 7.0	2.31	2.99	0.425
pH 10.0	2.24	3.64	0.429

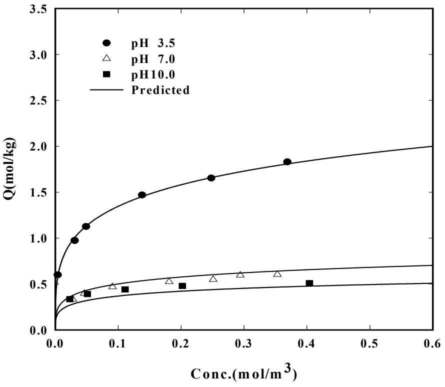

Fig. 1. Adsorption isotherms of 2,4-D onto GAC at different pHs.

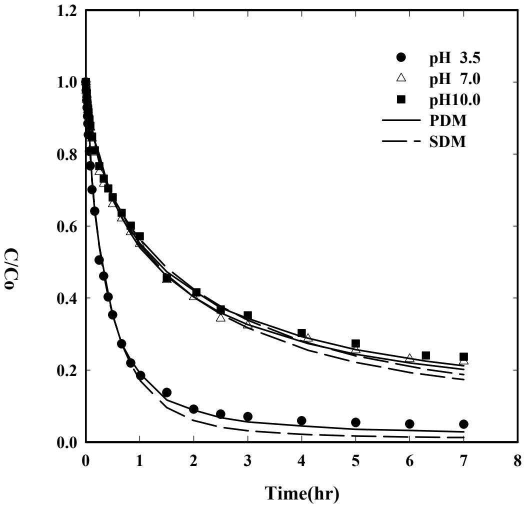

Fig. 2. Concentration decay curves of 2,4-D onto GAC at different pHs.

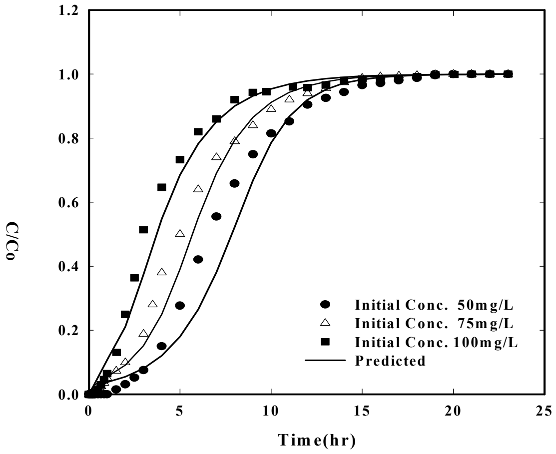

Fig. 3. Effect of bed height on the adsorption breakthrough curves for 2,4-D

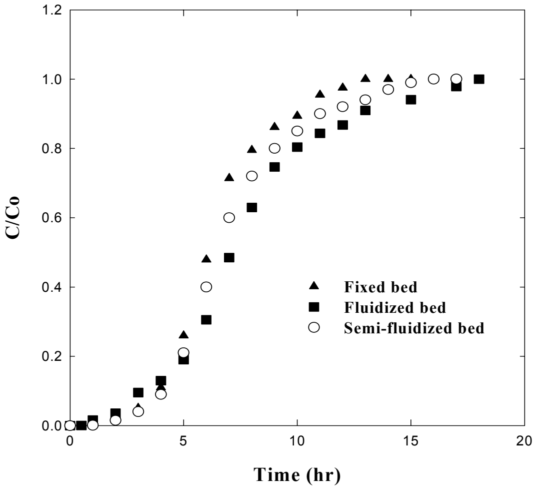

Fig. 4. Comparison of breakthrough curves for 2,4-D in terms of bed types