수용액으로부터 2,4,5-Trichlorophenoxyacetic Acid의 분리 특성

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Separation Characteristics of 2,4,5-Trichlorophenoxyacetic Acid from Aqueous Solution

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Introduction

Environmental contamination by toxic xenobiotic chemicals is a serious worldwide problem. These contaminants arise predominantly from agricultural and industrial sources. A human being constantly exposed to agricultural chemicals species present in the environment. Agricultural chemicals are very important because of their wide distribution and extensive use as plant growth regulators. Among these compounds, 2,4,5-trichlorophenoxy¹⁾ acetic acid (2,4,5-T) are potential danger to human health. also, the widespread usage of pesticides has a potential negative impact on the ecosystem.²⁾ Some of the applied herbicides are continuously discharged into aquatic environments through the runoff, and such discharge can lead to contaminated aquatic environments which are hazardous to resident organisms. Among the numerous agrochemicals in use today, the herbicide, 2,4,5-trichlorophenoxy acetic acid, a member of the phenoxy herbicide group, has been widely applied to control broad leaf weeds. Adsorption processes are used economically for various separations processes in the chemical industries and toxic matter. Activated carbon has long been used for removal of toxic matters from industrial adsorption process and environmental pollution.³⁾ Activated carbon is a powerful adsorbent because it has a large surface area and pore volume. The main purpose of this work is to select a proper adsorbent for elimination of 2,4,5-T from its aqueous solution, and to study their adsorption and desorption characteristics experimentally as well as theoretically.

Theory

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

$$N_A = k_f A_s \left(C - C_s \right) \tag{1}$$

By rearrangement and approximation for batch system with adsorption time of less than 300 seconds.

$$\ln\left(C / Co\right) = -\frac{k_f A_s t}{V} \tag{2}$$

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

$$A_s = \frac{-3M}{\rho_p R_p} \tag{3}$$

M is the total mass of adsorbent particles loaded and ρ_p is the particle density

Experimental

The adsorbent used in this study was an activated carbon, Filtrasorb-400, manufactured by Calgon Co.(USA). The particle size of the activated carbon was $0.37 \,^{\sim} 0.54$ mm in diameter. All adsorbent particles were dried in vacuum oven to remove impurities prior to use.

Equilibrium adsorption data were obtained by measuring the adsorbate concentration in an aqueous solution of 2,4,5-trichlorophenoxyacetic acid, 0.45mol/m³. The solution was kept in the shaking batch at 298K for 72 hr after introducing a given amount of sorbent. The concentration of 2,4,5-trichlorophenoxyacetic acid was determined using a spectrophotometer (Shimadzu 1601). The wavelength, corresponding to a maximum absorbance of 2,4,5-trichlorophenoxyacetic acid, was found to be 273nm. 2M HCl and 2M NaOH solutions were used to adjust solution pH.

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 2.54cm diameter and 50cm length. The column was lined with a water jacket, and all experiments were performed at 298K. The flow rate was regulated with a flow meter. To enhance uniform distribution of the solution radially, 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

Single-species adsorption equilibrium data were obtained by measuring the adsorbate concentration in an aqueous solution of 2,4,5-T at different initial pH. Adsorption isotherms of 2,4,5-T onto the activated carbon at three different pH are shown in Fig. 1. As can be seen in this figure, the adsorption capacity of 2,4,5-T onto GAC increased with decreasing pH of

the solution. Single-species isotherm data were correlated by well-known Langmuir, Freundlich and Sips equations. These parameters and the average percent differences between the measured and calculated values are given in Table 1. Among these isotherms, the Langmuir equation is more appropriate in predicting our data compared to others isotherm. Batch adsorption experiments were conducted in a Carberry-type batch adsorber. Fig. 2 is a typical plot to estimate k_f from the initial concentration data of 2,4,5-T at pH 3.5. The value of k_f obtained from fig. 2 is 4.05×10^{-5} m/s. Fig. 3. shows the concentration decay curves for the 2,4,5-T in a batch adsorber. In this study, the pore diffusion coefficient, D_p , and surface diffusion coefficient, Ds, are estimated by pore diffusion model (PDM) and surface diffusion model (SDM)⁴. The estimated values of k_f , D_p , D_s for 2,4,5-T are listed in Table 2.

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Isotherm type		pH 3.5	pH 7.0	pH 10
Langmuir	q_m	1.1786	1.0055	1.0491
	b	59.5214	46.759	34.1695
	error (%)	1.0524	5.8531	7.8356
Freundlich	k	2.0789	1.6453	1.5843
	n	2.8521	2.9142	2.9309
	error (%)	12.228	7.6206	7.9313
Sips	q_{m}	1.1827	1.0524	1.0491
	b	55.8393	33.3363	29.7576
	n	1.0121	1.0563	1.0644
	error (%)	1.1387	5.5146	8.3821

Table 1. Adsorption equilibrium isotherm parameters of 2,4,5-T onto Activated carbon

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Adaarhata anaajaa	рН	$k_f \ge 10^{-5}$	$D_{p} \ge 10^{-8}$	$D_{s} \times 10^{-12}$
Ausorbate species		[m/s]	$[m^2/s]$	$[m^2/s]$
	3.5	4.05	2.93	3.28
2,4,5-T	7.0	3.40	1.04	1.32
	10.0	3.38	1.03	1.23

Table 2. Kinetic parameters in a batch adsorber (298K)



Fig. 1. Adsorption equilibrium isotherms of 2,4,5-T at different pH (298K)



Fig. 2. Determination of k_j from an initial concentration decay plot



Fig. 3. Concentration decay curves of 2,4,5-T in terms of pH.