

활성탄에서 염소계 유기화합물의 흡착특성

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Adsorption Characteristics of Chlorinated Organic Compounds onto Activated Carbon

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Introduction

A human being constantly exposed to numerous chemical species present in the environment. Among these compounds, chlorophenoxy acid herbicides are very important because of their wide distribution and extensive use as plant growth regulators. When applied, they are easily transferred to surface and ground waters due to their polar nature and relatively high solubility. Although their decomposition in the presence of oxygen is relatively fast, these herbicides are persistent under reductive conditions and their extended use can lead to pollution of surface and ground waters. The treatment methods aimed at the removal of anthropogenic pollutants from the environment have become the subject of increased interest. Various treatment techniques have been employed to treat the wastewater, including precipitation, adsorption, ion exchange, and reverse osmosis. Among them, adsorption onto solid adsorbents has great environmental significance, since it can effectively remove pollutants from both aqueous and gaseous streams. In wastewater treatment, activated carbon is a powerful adsorbent because it has a large surface area and pore volume, which remove liquid-phase contaminants, including organic compounds, heavy metal ions and coloring matters. 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 the desorption of individual pollutants under different operating conditions is required. The main purpose of this work is to study adsorption characteristics of 2-methyl-4-chlorophenoxyacetic acid (MCPA), para-chlorophenoxyacetic acid (P-CPA) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) from aqueous solution onto a granular activated carbon, experimentally as well as theoretically.

Mathematical Model

It is assumed that adsorption occurs instantaneously and equilibrium is established between adsorbates in the fluid and on the surface of the adsorbents. The driving

force is the concentration gradient of the adsorbate between the liquid bulk and pore walls. The adsorbed species then diffuse into the pores in the adsorbed state. Provided that surface diffusion is dominant, the rate of adsorption for a spherical particle can be expressed as.

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

And the initial and boundary conditions are,

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

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

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

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

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

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

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

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

Result

The concentration of MCPA, P-CPA and 2,4,5-T was measured using a spectrophotometer (Shimadzu 1901). The wavelength, corresponding to a maximum absorbance of MCPA, P-CPA and 2,4,5-T was found to be 279nm, 273nm and 216nm, respectively. The adsorbent used in this study was an activated carbon, Filtrasorb-400, manufactured by Calgon Co.(USA). Single-species equilibrium adsorption data were obtained by measuring the adsorbate concentration in an aqueous solution of MCPA, P-CPA and 2,4,5-T. The solution was kept in the shaking bath for 48 hr after introducing a known amount of the sorbent, and the final adsorbate concentration in the solution was measured. Single-species adsorption isotherms of MCPA P-CPA and 2,4,5-T onto the activated carbon are shown in Fig. 1. 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 Sips equation is more appropriate in predicting our data compared to others isotherm. Since the flow rate is a very important factor in fixed bed design, the effect of flow rate is studied and the results for the herbicides shows in Figs.2-4. These figures show that the breakthrough time is decreased with increasing flowrate, 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.

Acknowledgment

"This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD)"(KRF-2005-D-00014)

Reference

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Table 1. Adsorption equilibrium constants of the chlorinated organic compound onto GAC (pH 3.5, 298K).

Isotherm	Parameters	MCPA	P-CPA	2,4,5-T
Langmuir	q_m	1.94	2.77	1.68
	b	17.07	6.59	60.25
	error (%)	3.47	2.66	5.09
Freundlich	k	2.89	3.18	2.54
	n	2.23	2.09	3.08
	error (%)	3.39	7.32	8.80
Sips	q_m	1.94	2.27	1.80
	b	16.82	6.86	41.52
	n	1.04	0.98	1.03
	error (%)	3.24	2.31	4.60

Table 2. Dynamic Parameters for Model Simulation.

Parameter	Symbol	Component	Value
Axial dispersion coefficient	D_L (m ² /s)	P-CPA	3.36×10^{-6}
		MCPA	1.13×10^{-5}
		2,4,5-T	8.63×10^{-6}
Film mass transfer coefficient	k_f (m/s)	P-CPA	1.04×10^{-5}
		MCPA	2.78×10^{-5}
		2,4,5-T	2.68×10^{-5}
Molecular diffusion coefficient	D_m (m ² /s)	P-CPA	0.27×10^{-9}
		MCPA	6.77×10^{-10}
		2,4,5-T	6.42×10^{-10}

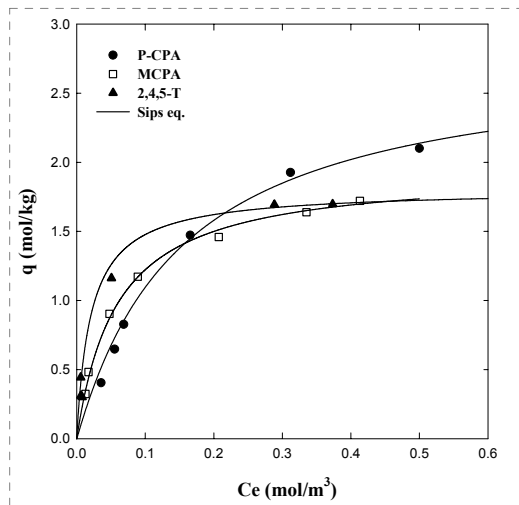


Fig. 1. Adsorption equilibrium data and Sips equation for P-CPA, MCPA, and 2,4,5-T onto GAC at pH 3.5 (298 K)

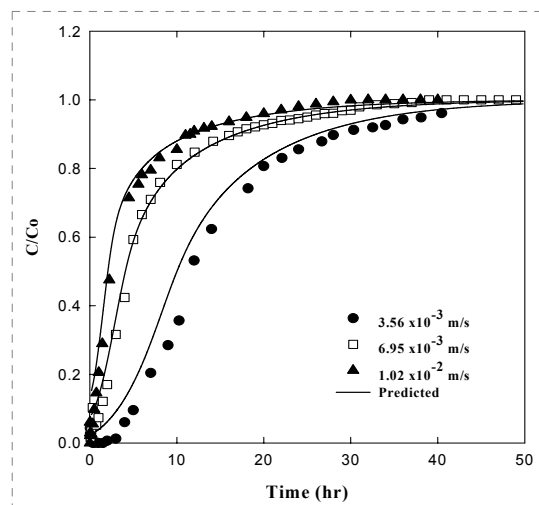


Fig. 2. Effect of flow rate and model prediction of adsorption breakthrough curves for MCPA onto GAC

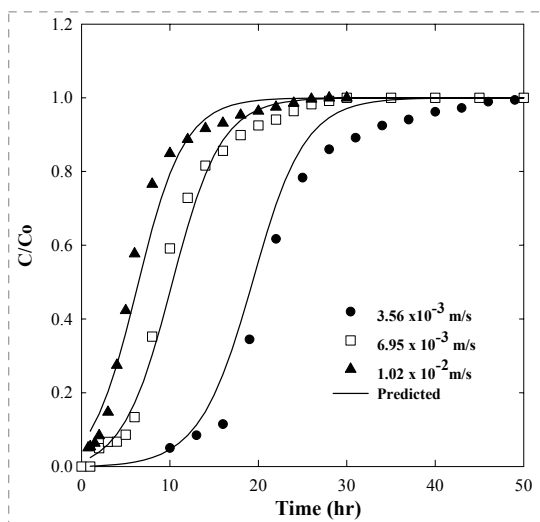


Fig. 3. Effect of flow rate and model prediction of adsorption breakthrough curves for P-CPA onto GAC

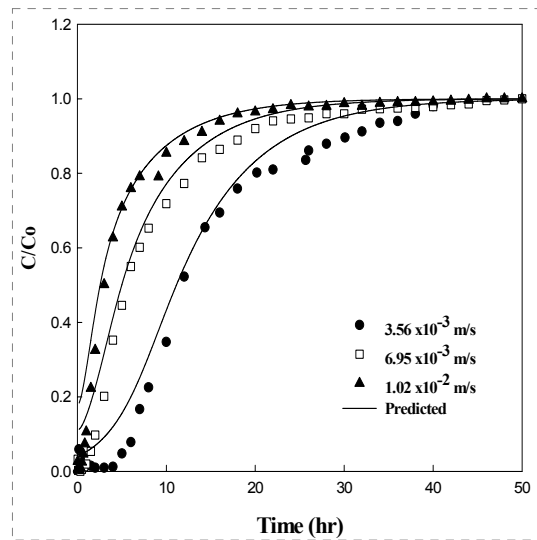


Fig. 4. Effect of flow rate and model prediction of adsorption breakthrough curves for 2,4,5-T onto GAC