2-Methyl-4-Chlorophenoxyacetic Acid의 흡착 특성에 관한 연구

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Separation Characteristics of 2-Methyl-4-Chlorophenoxyacetic Acid onto GAC

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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 pollutions under different operating conditions is required. The main purpose of this work is to study adsorption characteristics of 2-methyl-4-chlorophenoxyacetic acid (MCPA) from aqueous solution onto a granular activated carbon, experimentally as well as theoretically.

Mathematical Model

A mathematical model was developed, which takes into account the non-ideality of adsorbable species in the adsorbed phase under equilibrium. For the modeling of the adsorption kinetics, attention has to be paid to two problems i) the pore structure of adsorbents and ii) the transfer resistance involved in adsorption.

1) External Diffusion

There are some correlation for estimating the film mass transfer coefficient k_f, in a batch system. The value of k_f was estimated experimentally from the initial concentration decay

curve when the diffusion resistance dose not significantly prevail. The transfer rate of any species to the external surface of the adsorbent, N_A, can expressed by

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

The Eq.(1) can be arrange and approximated to Eq.(2) in a batch system.

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

$$A_s = \frac{3w}{\rho_p R_p} \tag{3}$$

k_f can be obtain from the experimental data by plotting the $\ln(C/C_i)$ vs t.

2) Internal Diffusion

The rate of adsorption in porous materials is generally controlled by transport within the pore network.

a) Surface Diffusion Model

A material valance for particle results in the following mass transfer equations:

$$\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 D_s \frac{\partial q}{\partial r}\right) \tag{4}$$

$$k_f(C - C_s) = D_s \rho_p \frac{\partial q}{\partial r} \qquad at \quad r = R_p \tag{5}$$

$$\frac{\partial q}{\partial r} = 0 \qquad at \quad r = 0 \tag{6}$$

b) Pore Diffution Model

In the pore diffusion model, it is assumed that the adsorbate diffuses into the pores in the fluid phase and is taken up by adsorption on the walls of the pores. It assumes (i) a spherical particle, (ii) dilute solution, (iii) local equilibrium, then the equations which describe the adsorbate mass transfer are as follows:

$$\varepsilon_p \frac{\partial C_p}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{\varepsilon_p}{r^2} \frac{\partial}{\partial r}\left(r^2 D_p \frac{\partial C_p}{\partial r}\right) \tag{7}$$

$$k_f(C - C_s) = \varepsilon_p D_p \frac{\partial C_p}{\partial r} \qquad at \quad r = R_p \tag{8}$$

$$\frac{\partial C_p}{\partial r} = 0 \qquad at \quad r = 0 \tag{9}$$

$$C_p = C_{p0}, \qquad q = q_0 \qquad at \quad t = 0 \tag{10}$$

Result

The concentration of 2-methyl-4-chlorophenoxyacetic acid was measured using a spectrophotometer (Shimadzu 1901). The wavelength, corresponding to a maximum absorbance of MCPA, was found to be 279nm. 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. 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. Adsorption amounts are measured at different initial pH and temperature. Adsorption isotherms of MCPA onto the activated carbon at three different pH and temperature are shown in Figs. 1 and 2. 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. Batch adsorption experiments were conducted in a Carberry-type batch adsorber. All the experiments were carried out at the mixing rate of approximately 400rpm, since the film mass transfer coefficient, k_f, is practically constant at this condition [1]. Fig. 3 is a typical plot to estimate k_f from the initial concentration data of MPCA at pH 3.5. Fig. 4. shows the concentration decay curves for the MCPA 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) [2]. The estimated values of k_f, D_p, D_s for MCPA are listed in Table 2.

Acknowledgment

Reference

1. Moon, H. and W. K. Lee, J. Colloid Interface Sci., **96**, 162-166, (1983).
2. Kim, T. Y., Kim, S. J. and Cho, S. Y., Korean J. Chem. Eng., *18*, 5, 2001

Table 1. Adsorption equilibrium isotherm parameters of MCPA onto Activated carbon

Isotherm type		pH 3.5	pH 7.0	pH 10
Langmuir	q_m	1.94	0.53	0.53
	b	17.07	18.56	15.07
	error (%)	3.47	4.58	0.94
Freundlich	k	2.89	0.61	0.62
	n	2.23	3.85	3.27
	error (%)	3.39	4.86	3.29
Sips	q_m	1.94	0.53	0.53
	b	16.82	34.78	14.97
	n	1.04	0.80	1.01
	error (%)	3.24	3.54	0.99

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

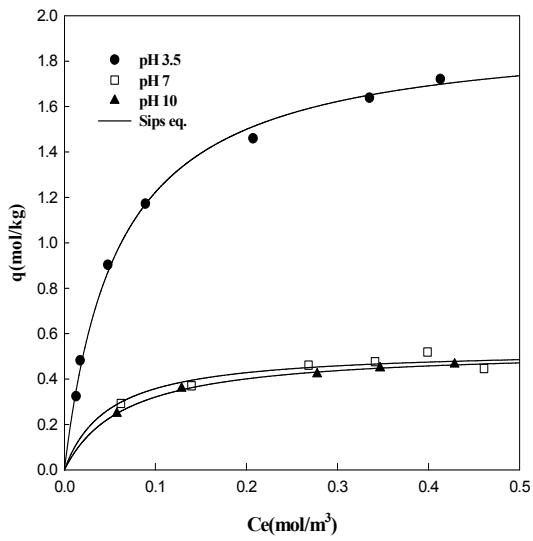| Adsorbate species	pH	k_f x 10^{-5} [m/s]	D_p x 10^{-10} [m^2/s]	D_s x10^{-13} [m^2/s]
MCPA	3.5	5.01	9.35	1.72
	7.0	4.22	3.75	4.06
	10.0	3.53	3.64	3.78

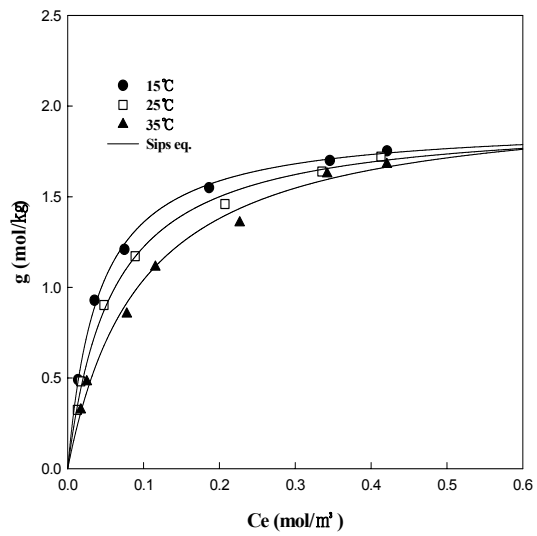Fig. 1. Adsorption equilibrium isotherms of MCPA at different pH (298K)

Fig. 2. Adsorption equilibrium isotherms of MCPA at different temperature (pH;3.5)
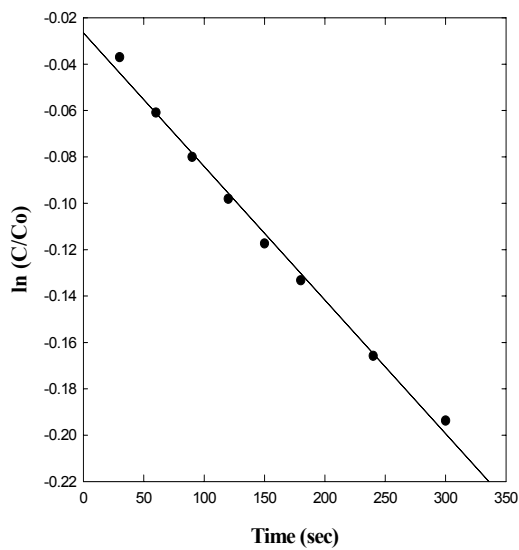

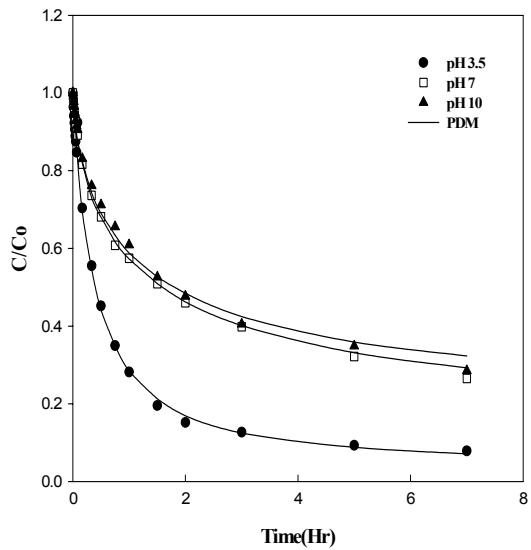Fig. 3. Determination of k_f from an initial concentration decay plot

Fig. 4. Concentration decay curves of MCPA in terms of pH.