CAC Bead를 이용한 Copper Ions과 2,4-Dichlorophenoxyacetic Acid의 흡착특성

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Adsorption Characteristics of Copper Ions and 2,4-Dichlorophenoxyacetic Acid onto CAC Bead

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Introduction

Heavy-metal ions are often toxic even at low concentrations and are not biodegradable, they must be removed from the contaminated water in order to meet increasingly stringent environmental quality standards. Agrochemical in use today, the 2,4-dichlorophenoxy acetic 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 herbicide 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 wastewater, including precipitation, adsorption, ion exchange, and reverse osmosis [2,3]. Among them, adsorption onto solid adsorbents has an environmental significance, since it can effectively remove pollutants from wastewater. This will require the development of new separation technologies utilizing novel solid adsorbents that are capable of recovering low-concentration heavy metal ions and organics from wastewater.

Activated carbon possesses a large capacity for adsorption of organic matters due to its large surface area. Polysaccharide biopolymers isolated from marine organisms are a new class of potentially inexpensive and environmentally benign solid adsorbents that exhibit a high specificity toward metal ions. Particular interest is the amine biopolymer chitosan, which selectively binds to virtually all group III transition-metal ions.

In this work, several type of chitosan beads containing entrapped powdered activated carbon were prepared by reaction with sodium hydroxide. The adsorption characteristics of copper ions and 2,4-D onto CAC bead was studied experimentally as well as theoretically.

Materials and Methods

Although chitosan has an intrinsically high affinity and selectivity for transition metal ions, the adsorbent raw material (flake type) is not suitable for processing an aqueous waste stream or the treatment of ground water. Chitosan is usually obtained in a flaked or powdered form that are both nonporous adsorbents. The powdered chitosan was dissolved in a 2wt% acetic acid solution to produce a viscous solution with approximately 3wt% chitosan. And then, the amine biopolymer chitosan solution was cast into beads by a phase-inversion technique using 2M NaOH solution.

A 0.5wt% of CAC solution were prepared by mixing 15g of activated carbon with 1000ml of 3wt% chitosan solution, and a 0.5wt% of CAC beads were made by reaction with sodium hydroxide.

The concentration of 2,4-D was measured using a spectrophotometer (Shimadzu 1901). The wavelength, corresponding to a maximum absorbance of 2,4-D was found to be 284 nm. The activated carbon used in this study was Filtrasorb-400, manufactured by Calgon Co.(USA).

The concentration of copper ion was determined using an ISE (ion selective electrode) meter. The amount of copper ion and 2,4-D onto the adsorbents at equilibrium was calculated from the mass balance equation as follows:

$$q = (C_i - C)\frac{V}{W} \qquad (1)$$

Here q is the equilibrium amount adsorbed onto the adsorbent (*mol/kg*), C_i is the initial concentration of bulk fluid (*mol/m*^{3}), C is the equilibrium concentration of the solution (*mol/m*^{3}), V is the volume of solution (m^3), and W is the weight of adsorbent (*kg*).

Result

Single species equilibrium adsorption data were obtained by measuring the adsorbates concentration in aqueous solution of copper ion and 2,4-D. The single species solution was kept in the shaking bath for 48 hr after introducing a known amount of the adsorbents, and the final adsorbates concentration in the solution was measured. Adsorption isotherms of copper ion onto four different adsorbents are shown in Fig. 1. As can be seen in this Figure, the magnitude of adsorption capacity of copper ion was in the order of chitosan bead > 0.5wt% CAC > 1wt% CAC > activated carbon. Since the amount of chitosan increased with increasing adsorption capacity for copper ion. The estimated values of parameters for adsorption isotherms of copper ion onto four different adsorbents are listed in Table 1.

Figs. 2 and 3 show the adsorption equilibrium isotherms of 2,4-D onto 0.5wt% and 1wt% CAC. As can be seen in this Figure, adsorption amount of 2,4-D onto the adsorbents increased 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 adsorption capacity of the equilibrium adsorption process. Single-species isotherm data were correlated by well-known Langmuir, Freundlich and Sips equations. Among these isotherms, the Sips equation is more appropriate in predicting our data compared to the Langmuir and Freundlich equation. Fig. 4 shows the concentration decay curves for 2,4-D in a batch adsorber. Adsorption rate of 2,4-D was in the order of activated carbon > 1wt% CAC > 0.5wt% CAC > chitosan bead.

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Table 1. Adsorption equilibrium constants of copper ion onto different adsorbents (pH 3, 298K)

Isotherm	Parameters	0.5wt% CAC	1wt% CAC	Chitosan bead	Activated carbon
Langmuir	q_m	0.99	1.13	1.68	0.16
	b	27.33	20.98	30.05	10.70
	error(%)	5.99	5.42	3.58	5.08
Freundlich	k	0.95	1.08	1.68	0.16
	n	4.64	6.65	6.32	3.66
	error (%)	5.03	4.86	2.19	3.45
Sips	q_m	0.97	1.13	1.88	0.16
	b	32.19	21.24	6.32	9.28
	n	1.08	1.17	2.13	1.23
	error(%)	4.30	3.16	2.93	3.40

Table 2. Adsorption equilibrium constants of 2,4-D onto different adsorbents (298K)

Isotherm	Parameters	pH 3		pH 7		pH 10	
		0.5wt%	1wt%	0.5wt%	1wt%	0.5wt%	1wt%
Langmuir	q_m	0.46	0.70	0.19	0.41	0.16	0.32
	b	24.57	32.84	30.60	63.17	17.69	24.39
	error(%)	4.82	5.64	5.38	6.42	5.58	6.58
Freundlich	k	0.64	0.80	0.21	0.58	0.18	0.42
	n	2.91	4.52	4.51	2.47	3.38	2.95
	error (%)	2.55	2.28	4.86	4.86	4.21	4.19
Sips	q_m	0.54	0.70	0.19	0.40	0.16	0.32
	b	11.02	18.61	24.06	26.34	18.17	17.84
	n	1.12	1.44	1.14	1.15	1.12	1.23
	error(%)	2.56	2.08	4.16	4.16	4.13	4.13

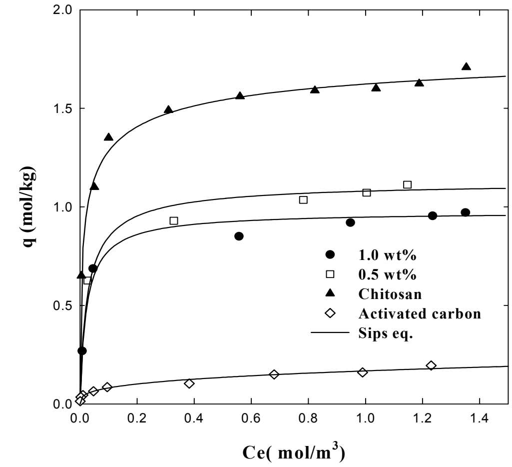

Fig. 1. Adsorption isotherms of copper ions onto different adsorbents (298K)

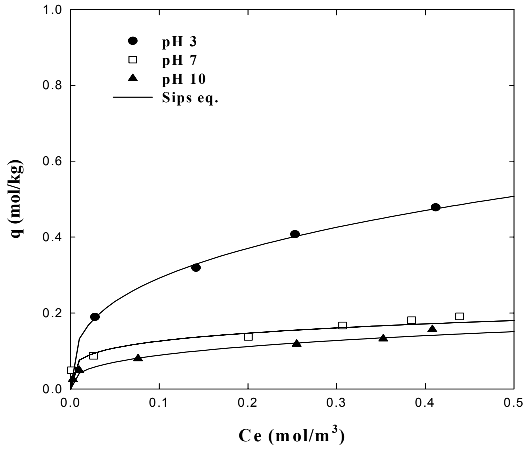

Fig. 2. Adsorption isotherms of 2,4-D at different pH (298K, 0.5wt% CAC)

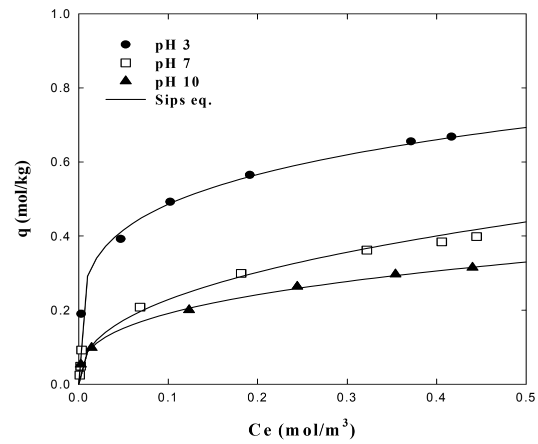

Fig. 3. Adsorption isotherms of 2,4-D at different pH (298K, 1wt% CAC)

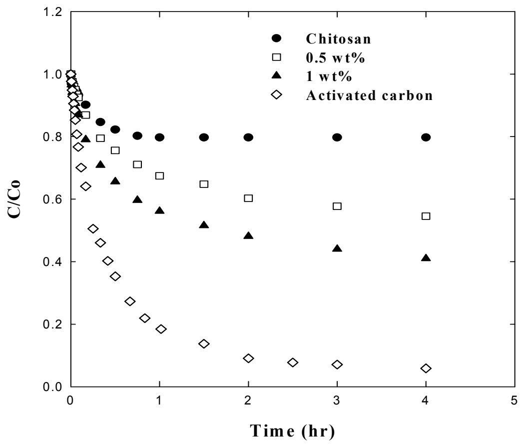

Fig. 4. Concentration decay curves of 2,4-D onto different adsorbents (pH 3, 298K)