고정층과 유동층에서 TCA의 흡착 특성

최하춘[1], 김태영[2], 김승재[2,3], 조성용[2], 김진환[1,*], 이호연[1]
[1]전남대학교 응용화학공학부, [2]전남대학교 환경공학과, [3]전남대학교 환경연구소
(jhkim@chonnam.ac.kr*)

Adsorption Characteristics of TCA in a Fixed and Fluidized Beds

H. C. Choi[1], T. Y. Kim[2], S. J. Kim[2,3], S. Y. Cho[2], J. H. Kim[1,*], H. Y. Lee[1]
[1]Faculty of Applied Chemical Engineering, [2]Department of Environmental Engineering,
[3]Environmental Research Institute, Chonnam National University
(jhkim@chonnam.ac.kr*)

Introduction

Trichloroacetic acid (TCA) is a natural organohalogen in soil that may be produced from chlorination of organic substances as reported previously [1,2]. And also, it is a secondary atmospheric pollutants formed by photo oxidation of chlorinated organics in the atmosphere, and is considered as one of the stress factors. The concentration of TCA in conifer needles in Central Europe was roughly between 1 and 150 ppb, but it is decreasing in recent years [3]. The widespread and intensive use of chlorinated acid herbicides in agriculture and forestry may give rise to a number of toxicological and environmental problems, even though, when used at recommended application rates and procedures, the concentrations of TCA in the environment will be well below the levels generally considered to be of concern. When misused or as the result of accidental spillage, these herbicides have potential to injure non-target cultivars and microorganisms, in particular herbicide degraders and others contributing to soil quality, and can cause adverse side-effects in mammals, including humans.

Various treatment techniques have been employed to treat the wastewater, including precipitation, adsorption, ion exchange, and reverse osmosis. Among them, adsorption onto solid adsorbents is very important, 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 can 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 the adsorption and desorption of individual pollutants under different operating conditions is required. The main purpose of this work is to study its adsorption characteristics experimentally as well as theoretically to remove TCA from aqueous solution.

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 concentration of trichloroacetic acid (TCA) was measured using a spectrophotometer (Shimadzu 1601). The wavelength, corresponding to a maximum absorbance of TCA, was found to be 216nm with an accuracy of ±0.3 nm. HCl and NaOH solutions were used to adjust pH of the solution. 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 ~ 0.54 mm in diameter. All sorbent particles were dried in vacuum oven to remove impurities prior to use.

Results

The pH is one of the most important parameters affecting the adsorption process in an aqueous solution. The variation of adsorption equilibrium for TCA with initial pH is shown in Fig. 1. As can be seen in this figure, the adsorption amount decreased with increasing pH of the solution. The adsorption is highly dependent on pH of the solution which affects the surface charge of the adsorbent, degree of ionization and speciation of the adsorbate. TCA has weak acidic character and may exist as anions below pKa, 0.52, and the ionic state of TCA will be preferred by the positively charged surface of the carbon adsorbent.

Single-species isotherm data were correlated using well-known Langmuir, Freundlich and Sips equations. The parameters of each isotherm were obtained by the least square fitting with experimental data. These parameters and the average percent differences between measured and calculated values are given in Table 1. As shown in the table, the Sips equation gives the best fit of our data among the three. From this result, we believe that the Sips equation is suitable for single-component equilibrium adsorption of TCA on activated carbon.

Fig. 2 shows the experimental data and model prediction for the TCA concentration 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). The estimated values of , D_p, and D_s for TCA are listed in Table 2. Table 2 shows that the magnitude of D_s is smaller than D_p by order of two, which implies that the diffusion inside a particle is a rate-controlling step.

Since the flow rate is a very important factor in a fixed bed design, the effect of flow rate is studied and the results are shows in Fig. 3. This figure shows that the breakthrough time decreased with increasing flow rate, 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 of 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.

Fig. 4 shows the breakthrough curve for respective beds, 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.

Acknowledgment

The authors wish to acknowledge a grant-in-aid for BK 21 Team for Environmentally Friendly Core Material and Process Development.

Reference

1. Heal M. R., Deckay A.., Cape J. N. and HealK. V., *Atmospheric Environment*, **37**, 4447 -4452, 2003.
2. Schroder P., Matucha M., Forczek S. T., Uhirova H., Fuksova K. and Albrechtoca, *J. Chemosphere*, **52**, 434-442, 2003.
3. Suedee R., Srichana T., Sangpagia C., Tunthana C. and Vanichapichat P., *Anslytica Chimica Acta*, **504**, 89-100, 2004.

Table 1. Adsorption equilibrium constants of TCA onto GAC at different initial pHs (298 K)

Isotherm	Parameters	pH		
		3.5	7.0	10.0
Langmuir	q_m	1.01	0.64	0.48
	b	13.40	1.19	1.84
	error(%)	2.91	5.81	5.90
Freundlich	k	1.01	0.38	0.33
	n	4.66	1.52	1.83
	error(%)	0.46	5.80	4.97
Sips	q_m	3.55	1.00	0.48
	b	0.43	0.56	1.81
	n	3.61	1.19	1.03
	error(%)	0.44	5.73	4.21

Table 2. Kinetic parameters of TCA onto GAC t 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	4.46	5.93	9.47
pH 7.0	1.62	0.73	0.29
pH 10.0	1.17	0.18	0.22

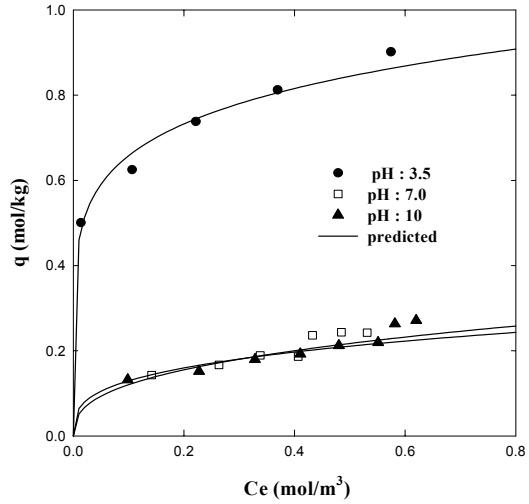

Fig. 1. Adsorption isotherms of TCA onto GAC at different pHs.

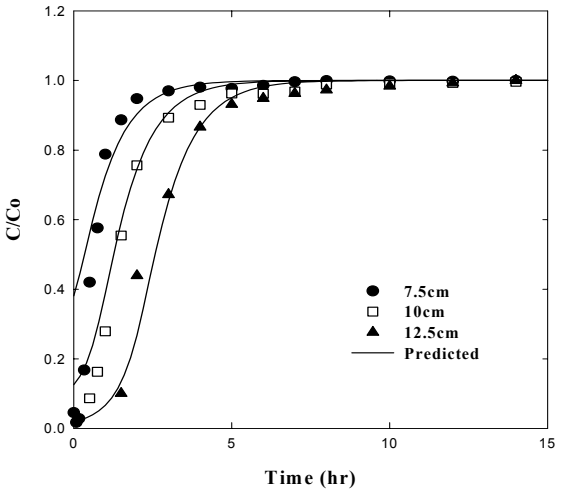

Fig. 3. Effect of bed height on the adsorption breakthrough curves for TCA

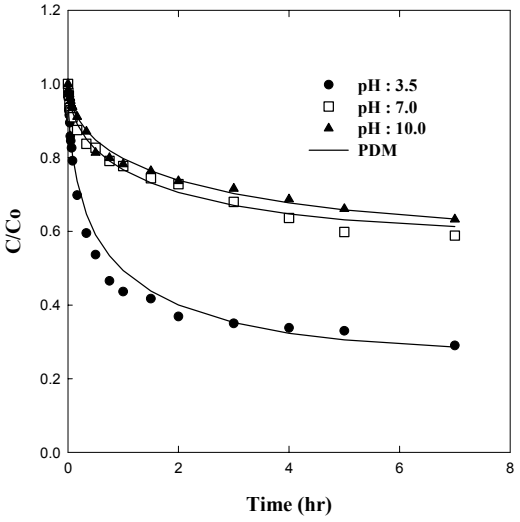

Fig. 2. Concentration decay curves of TCA onto GAC at different pHs.

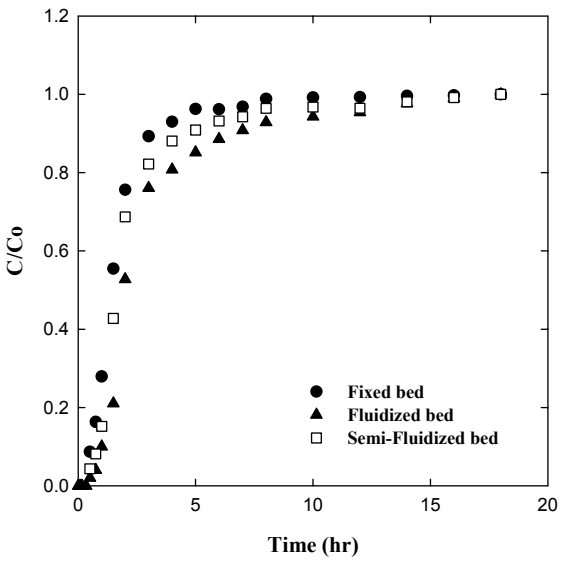

Fig. 4. Comparison of breakthrough curves for TCA in terms of bed types