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The Reversibilities of the Adsorption and Desorption of Organic Compounds in Water

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Synopsis. The reversibilities of the adsorption and desorption of seventeen organic compounds in water on a granular activated carbon and a polystyrene adsorbent were examined by means of a batch-adsorption method. The adsorptions of many organic compounds were reversible, but the adsorptions of several phenolic compounds and aniline were irreversible for the activated carbon, because these compounds were adsorbed strongly on the surface of activated carbon by the π-electron combination. On the other hand, the adsorptions of all the organic compounds were reversible for the polystyrene adsorbent.

The applications of adsorption from solutions on solid adsorbents have been considerably developed and become very important in many fields,[1] such as in purification processes, water-treatment processes, and analytical methods. The reversibility of adsorption and desorption is an important characteristic of an adsorbate to consider in selecting the adsorbent and in determining the adsorption conditions in these applications. However, there have been few reports on the reversibilities of the adsorption and desorption[2] of organic compounds in water. In this report, therefore, the reversibilities of the adsorption and desorption of various organic compounds on an activated carbon or a polystyrene adsorbent are investigated.

Experimental

Seventeen organic compounds on a reagent grade were used as the adsorbates. A granular activated carbon and a polystyrene adsorbent whose properties are shown in Table 1 were used in this study.

The adsorption isotherms at 25°C were obtained by the same method as in the previous paper.[3] After measuring the equilibrium concentrations, the solutions of 50—90 cm³ were removed from the flasks and equal amounts of pure water were added. The flasks were then again shake for 4 d at 25±0.5°C. After the equilibrium had been completely attained, the concentrations of the desorbed adsorbates were analyzed and the desorption isotherms were obtained. The reversibilities were examined by a comparison of the desorption isotherms with the adsorption isotherms. The concentrations of the adsorbates were determined from the ultraviolet absorbances and concentrations of the total organic carbon (TOC).

TABLE 1. PROPERTIES OF THE ADSORBENTS USED

Adsorbent	Name	Surface area $m^2\,g^{-1}$	Pore volume/$cm^3\,g^{-1}$ Total	<20 nm
Activated carbon	Filtrasorb 400	1030	0.84	0.52
Polystyrene	XAD-4	640	1.48	1.07

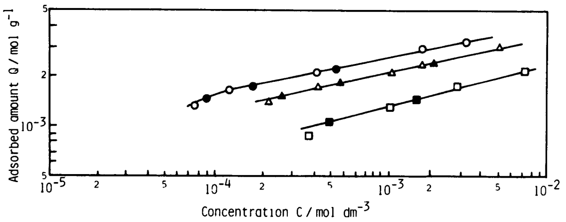

Fig. 1. Adsorption and desorption isotherms of fatty acids for activated carbon at 25°C.
(Open marks show adsorption, and black marks show desorption in Figs. 1—5)
○●: Pentanoic acid, △▲: hexanoic acid, □■: heptanoic acid.

Results and Discussion

Adsorption on Activated Carbon. The adsorption isotherms[3] and the desorption isotherms on the activated carbon are shown in Fig. 1—3 respectively as Freundlich expressions, the logarithmic relationships between the adsorbed amount Q (mol g^{-1}) and the equilibrium concentration C (mol dm^{-3}). The two isotherms agree with one another for many compounds, such as pentanoic acid, hexanoic acid, heptanoic acid, nitrobenzene, benzaldehyde, benzonitrile, benzoic acid, *m*-hydroxybenzoic acid, *m*-hydroxybenzaldehyde, benzenesulfonic acid, *p*-methylbenzenesulfonic acid, and *p*-ethylbenzenesulfonic acid. Therefore, the adsorptions and desorptions of these compounds are reversible. On the other hand, the desorption isotherms for phenol,

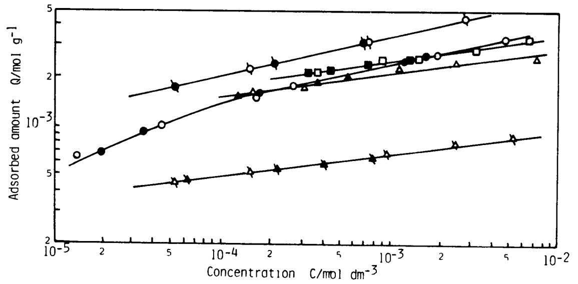

Fig. 2. Adsorption and desorption isotherms of substituted benzenes for activated carbon at 25°C.
○●: Benzoic acid, △▲: *m*-hydroxybenzoic acid, □■: *m*-hydroxybenzaldehyde, ⦸⬤: nitrobenzene, △̸▲̸: *p*-methylbenzenesulfonic acid.

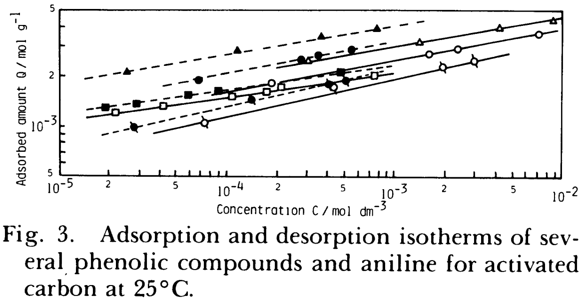

Fig. 3. Adsorption and desorption isotherms of several phenolic compounds and aniline for activated carbon at 25°C.
○●: Phenol, △▲: *m*-cresol, □■: *p*-nitorophenol, ⦸⬤: aniline.

TABLE 2. RATIOS OF k FOR DESORPTION TO ADSORPTION, k_{ds}/k_{ads}

Adsorbent	Phenol	*m*-Cresol	*p*-Nitrophenol	Aniline
Activated carbon	1.3	1.3	1.1	1.1
Polystyrene	1.0	—	1.0	1.0

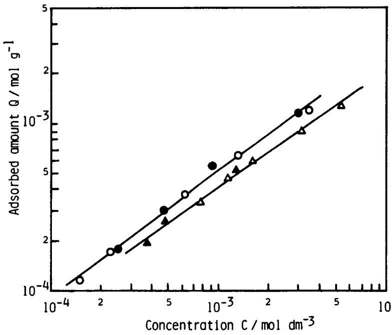

Fig. 4. Adsorption and desorption isotherms of benzoic acid and nitrobenzoic acid for polystyrene adsorbent at 25°C.
○●: Benzoic acid, △▲: *m*-nitrobenzoic acid.

m-cresol, *p*-nitrophenol, and aniline are higher and are parallel with their adsorption isotherms. Therefore, the adsorptions and the desorptions of these several phenolic compounds and aniline are irreversible. However, the values of n in the Freundlich equation, $Q = kC^{1/n}$, for the adsorption and the desorption isotherms are equal to one another. The ratios of the values of k for the desorption to the adsorption, k_{ds}/k_{ads}, show the levels of the irreversibility; they are summarized in Table 2. The ratios are large for phenol and *m*-cresol. Urano *et al.*[3] reported the energy distributions for the adsorptions of those compounds on the activated carbon and showed that the phenol and *m*-cresol adsorbed with especially high energies on the activated carbon. The adsorption energy for aniline was also slightly higher than those for the other aromatic compounds. These high adsorption energies show that those compounds combine strongly with the surface of activated carbons. It is known[2] that there are several electrophilic groups, such as the quinone group and the ketone group, on the surface of activated carbon. Since phenol, *m*-cresol, and aniline act as electron donors, these compounds may be adsorbed by the π-electron combination on the carbon surface. Urano *et al.*[3] reported that the amount of phenol adsorbed decreased with the oxidation of the activated carbon. This decrease may be due to the change in the electrophilic groups into non-electrophilic groups such as the carboxyl group with the oxidation. The reason for the reversible adsorptions of *m*-hydroxybenzoic acid and *m*-hydroxybenzaldehyde, which have a phenolic hydroxyl-group, may be that these compounds do not act as strong electron donors.

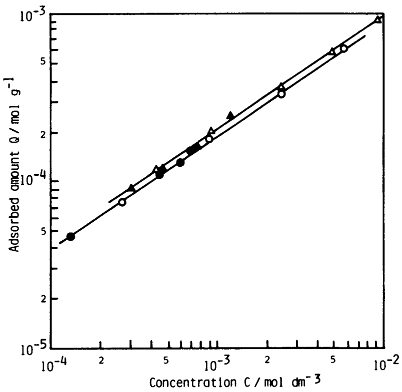

Fig. 5. Adsorption and desorption isotherms of phenol and aniline for polystyrene adsorbent at 25°C.
○●: Phenol, △▲: aniline.

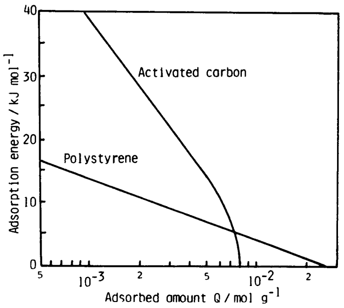

Fig. 6. Distributions of adsorption energy of phenol for activated carbon and polystyrene adsorbent at 25°C.

Adsorption on Polystyrene Adsorbent. The adsorption isotherms and the desorption isotherms on the polystyrene adsorbent are shown in Figs. 4 and 5 respectively. The adsorptions on the polystyrene adsorbent for all the organic compounds were reversible, because the polystyrene adsorbent has no active groups. The energy distribution for the adsorption of phenol on the polystyrene adsorbent was calculated by means of the following equation:[3] $Q=kC_s^{1/n-E_{eq}/nRT}$, where C_s is the saturated concentration, E_{eq} is the adsorption energy at Q, R is the gas constant, and T is the absolute temperature. It is obvious that the adsorption energy for the polystyrene adsorbent is much smaller than the energy for the activated carbon; this shows that the adsorption on the polystyrene adsorbent is completely physical.

References

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