SIZE AND SURFACE EFFECTS OF ACTIVATED CARBONS ON THE ADSORPTION BEHAVIORS OF INDOLE AND AMYLASE

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Introduction

Recently, special activated carbons which can remove wastes from the body to reduce the burden of kidneys are commercialized. So far, the adsorption behaviors of such porous carbons have not been carefully investigated. In this study, the present authors examined pore size and structural effects of activated carbons on the molecular adsorption behaviors to optimize their adsorption capacity and selectivity for the body waste removals. Indole and amylase were selected as model adsorptive bio-materials because they have much different molecular size and polarity. Activated carbon fiber having small average pore size of about 0.65 nm showed the highest adsorption capacity of indole, though, from the point of view of the adsorption rate, a little bit wider micropores of about 0.7 nm seemed to be suitable. Amylase adsorption amount was limited, maybe because amylase having large molecular size can not be well adsorbed in micropores.

Experimental

Indole and α-amylase were purchased from Wako Pure Chemical Industries, Ltd., and used without further purification. As the activated carbons, pitch-based activated carbon fibers (OG series: OG5A, OG7A, OG10A, OG15A, and OG20A, Osaka Gas Co., Ltd.) were used in this study, because they have relatively uniform micropores of different average pore size. A commercialized spherical oral activated carbon (OAC) of 200-300 μm in diameter and another type of spherical activated carbon (SAC) of 100-200 μm in diameter were also used. Pore structural parameters of obtained from αs-analyses of N_2 adsorption isotherms at 77 K for all samples used in this study are summarized in Table 1.

Adsorption tests of indole or amylase were performed as below. First, aqueous solutions of indole or amylase were prepared by dissolving indole or amylase to purified water at desired concentrations. Then, 8 mg of porous carbon samples was dispersed in the indole aqueous solution (40 cm^3), and stirred during the desired adsorption periods (3 min ~ 96 h) at 25°C. After the set time passed, the suspensions were filtrated using 0.20 μm membrane filter, and then absorption spectra of the filtrate were measured by using UVvisNIR spectrometer. Concentration of indole or amylase in the filtrate was calculated from absorbance at 269 nm or 279 nm, the maximum absorption wavelength of indole or amylase, respectively, using the pre-measured calibration curves.

Results and Discussion

Adsorption isotherms of indole on the OG series at 25°C are shown in Figure 1. With increasing of specific surface area or pore volume, the adsorption amount of indole at the same equilibrium concentration became larger from OG5A to OG15A; however OG20A showed lower adsorption capacity than OG15A. This suggests that the micropores of OG20A were too wide for the indole molecules to be adsorbed efficiently, namely an overlapping of potential curves from opposite pore walls was insufficient to provide deep adsorption potentials for the indole molecules. In Figure 2, a relationship between average pore size and the specific adsorption amount of indole normalized by the specific surface area is shown. Monotonic decrease of the specific adsorption amount with an increase of pore size indicates that narrower micropores work more effective adsorption space for the indole molecules.

Figure 3 shows adsorption kinetic profiles of indole on the OG series at 0.004 wt% of the initial indole concentration. Here, the abscissa is shown in logarithmic scale. The wider the pore size, the faster the adsorption rate; especially for OG5A of very narrow pore size, 0.65 nm, showed much slower adsorption rate as compared from others. Thus, we concluded that, from the results for the OG series, the micropores of about 0.7 nm are suitable for the indole adsorption not only from the adsorption capacity, but also from the adsorption rate.

The indole adsorption isotherms for OAC and SAC almost agreed with each other (data not shown), though distinct differences were observed in the adsorption kinetics especially at initial adsorption stage (Fig. 4). This observed different adsorption rate is considered to be due to different particle size of OAC and SAC; it may take longer time for the indole solution to diffuse into the inner part of particles for OAC having larger particle size. The specific adsorption amounts of indole normalized by the specific surface area for OAC and SAC are also plotted in Figure 2. Here, the specific adsorption amount of indole for SAC was calculated using the micropore surface area, but a point for SAC was almost on the correlation curve for the OG series, indicating that mesopores of SAC did not work as effective adsorption sites for indole. For OAC, on the other hand, an upward deviation from the correlation curve was observed, but reason is not well understood at present.

The adsorption kinetic measurements of amylase showed very slow adsorption rate for all activated carbons (data not shown). The adsorptions were still in progress at 12 h after the introduction of amylase. Removal rate, calculated as a ratio between the amylase concentration in the filtrate at 12 h and the initial concentration, was less than 10% for all samples. Given that the large molecular size of amylase to be adsorbed in the micropores, most of the removed amylase molecules are likely to be adsorbed on the external surface.

Table 1. Pore structure parameters of samples calculated by αs-analyses of N_2 adsorption isotherms at 77 K.

	Specific surface area (m^2/g)				Pore volume (cm^3/g)			Pore width (nm)	
	Total	External	Micropore	Mesopore	Total	Micropore	Mesopore	Micropore	Mesopore
OG5A	677	1	676	0	0.22	0.22	0	0.65	0
OG7A	988	3	984	0	0.34	0.34	0	0.68	0
OG10A	1212	5	1206	0	0.46	0.46	0	0.77	0
OG15A	1488	14	1474	0	0.66	0.66	0	0.90	0
OG20A	1817	16	1801	0	0.97	0.97	0	1.08	0
OAC	1216	4	1212	0	0.56	0.56	0	0.92	0
SAC	960	-	931	29	0.55	0.32	0.23	0.68	32

Conclusions

Pore size was found to strongly influence on the indole adsorption capacity and rate; the suitable pore size was about 0.7 nm in size for the indole adsorption. On the other hand, amylase was not adsorbed remarkably in micropores, maybe due to its large molecular size. Thus, as the oral applications to selectively remove the wastes in the body such as indole but not useful molecules such as amylase, the activated carbons having abundant micropores of about 0.7 nm in size but minimum external surface area would be suitable.

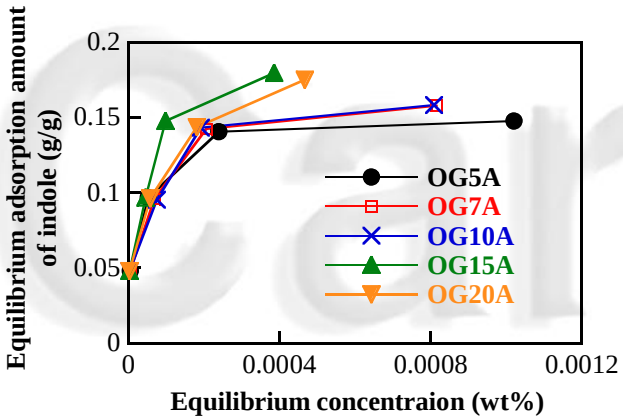

Fig. 1 Adsorption isotherms of indole on OG series at 25°C.

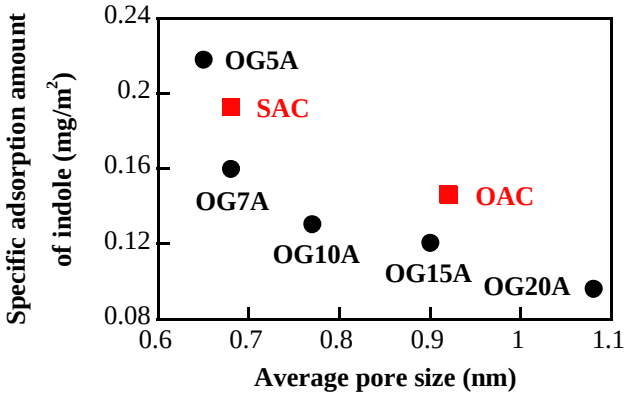

Fig. 2 Relationship between average pore size and specific adsorption amount of indole normalized by specific surface area. (Initial concentration of indole: 0.004 wt%)

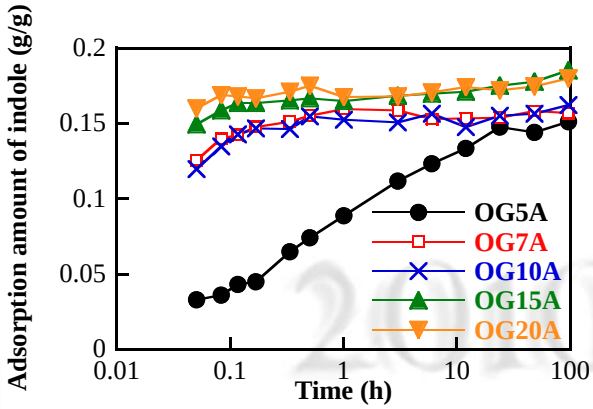

Fig. 3 Adsorption kinetic profiles of indole on OG series at 25°C. (Initial concentration of indole: 0.004 wt%)

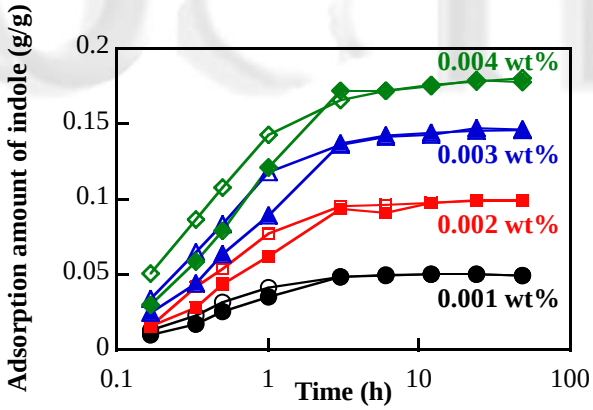

Fig. 4 Adsorption kinetic profiles of indole on OAC (open symbols) and SAC (closed symbols) at 25°C.

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