

# Study of Removal Effect of Bisphenol A and $\beta$ -Estradiol by Porous Carbon

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The adsorption properties of bisphenol A (BPA), suspected as endocrine disrupting chemicals (EDCs), and  $\beta$ -estradiol (E2) were examined in this study. Based on the adsorption isotherm results, the adsorption amount of BPA increased as the carbonization temperature increased. The adsorption effect of a porous carbon carbonized at 400°C was minimal, while the adsorption effect of a porous carbon carbonized at 1000°C was significant. Although the adsorption effect of the activated carbon was also significant, that of activated carbon was lower than that of the 1000°C porous carbon in the low concentration range, while that of the activated carbon was higher than that of the 1000°C porous carbon in the high concentration range. The adsorption amount of E2 increased as the carbonization temperature increased. The adsorption effect of the activated carbon was midway between 700 and 1000°C. Porous carbon carbonized at 1000°C with a low surface polarity was more effective for the removal of EDCs from environmental water than activated carbon with a large pore volume. It is expected that the 1000°C porous carbon can be used with activated carbon, which has already been used in waste water treatment, in purification plants, *etc.*

**Key words** — porous carbon, endocrine disrupting chemical, bisphenol A,  $\beta$ -estradiol, carbonization temperature

## INTRODUCTION

Bisphenol A (BPA), which has been suspected as endocrine disrupting chemicals (EDCs), is used for the production of polycarbonate and epoxy resin and as a stabilizer of polyvinyl chloride resin. It is a problem that BPA eluting from these products, such as tableware, affect living organisms.<sup>1)</sup>

$\beta$ -Estradiol (E2) is a natural female hormone, and the total estrogen excreted from female urine is from several tens to sixty  $\mu\text{g}$  per day and from 200 to 400  $\mu\text{g}$  during the early days of a pregnancy. Furthermore, a contraceptive pill concluding synthetic estrogen was approved by the Pharmaceutical Affairs Law of Japan in 1999, and the pill contains 30–

40  $\mu\text{g}$  of ethynylestradiol (EE). Although satisfactory knowledge to what degree estradiol or estrone of the natural female hormone influences aquatic life has not been obtained, these hormones of comparatively high concentration have been detected in various environments.<sup>1)</sup>

Removal methods of EDCs from water, such as electrochemical methods,<sup>2,3)</sup> and a method using a biological membrane<sup>4)</sup> have been reported. Although the removal performance for EDCs by activated carbon has also been reported,<sup>5–10)</sup> Nakanishi *et al.*<sup>11)</sup> has only reported the relationship between the carbonization temperature of woody carbon, such as bamboo charcoal and sugi charcoal, and the removal performance.

Surface properties such as the pore structure and chemical structure of woody porous carbon change due to the carbonization temperature,<sup>12)</sup> so that the adsorption properties of chemicals are different based on the carbonization temperature. Furthermore, activated carbon produced by activation of charcoal changes the adsorption properties by de-

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veloping a pore structure. Porous carbon, such as activated carbon with a large surface area and pore volume, is effective for the adsorption of common chemicals, but it is presumed for chemicals at trace concentrations, such as EDCs, that the affinity between the adsorbate and adsorbent rather than the adsorption volume, such as surface area and pore volume, influence the removal of these chemicals. In previous reports,<sup>13-15</sup> we described the relationship between the carbonization temperature of porous carbon and the removal effects of harmful gases, such as problem chemicals, on "Sick Building Syndrome" or the "Chemical Sensitivity" and odorous gases.

In this study, the relationship between the carbonization temperature of porous carbon and the removal effects for BPA and E2 as pollutants in environmental water, a comparison with commercial activated carbon, and the effective porous carbon for the removal of EDCs from environmental water were examined. Furthermore, the adsorption properties of BPA and E2 were compared due to examine those as EDCs.

## MATERIALS AND METHODS

**Production of Porous Carbon** — Porous carbon from Moso bamboo (*Phyllostachys pubescens*) was produced using an electric charcoal kiln KTC (Kankyo Techno Consul, Kobe, Japan). Three types of porous carbon were carbonized at 400, 700, and 1000°C of the final temperature. Each porous carbon was labeled PC<sub>400</sub>, PC<sub>700</sub>, and PC<sub>1000</sub>, respectively. The temperature program rate was 1.3°C/min from room temperature to 100°C, and 5°C/min from 100 to 400°C after drying at 100°C for 1 hr under the final temperature of 400°C. At the final temperature of 700°C, the temperature program rate was 6.7°C/min from 100 to 500°C after drying at 100°C for 1 hr, and 3.3°C/min from 500 to 700°C after thermolysis at 500°C for 1 hr. Under the final temperature of 1000°C, the temperature program rate was 2.0°C/min from 500 to 1000°C after thermolysis at 500°C for 1 hr. After reaching these final temperatures, each material was maintained at this temperature for 1 hr and then cooled to obtain a porous carbon. The activated carbon (hereafter referred to AC) for comparison was that used for chromatograph (Wako Pure Chemical Industries, Osaka, Japan). Each porous carbon was crushed and sieved, and porous carbon powders with a particle diameter

under 125  $\mu\text{m}$  were obtained. With regard to the samples for the experiments, the porous carbon powder was dried for 3 hr at 115°C, and then stored in a desiccator.

**Surface Properties of Porous Carbon** — Nitrogen adsorption isotherms from 0.01 to 1.0 at 77.4 K were obtained using an Autosorb 1C-VP-2 (Quantachrome, U.S.A.). Before the adsorption isotherms were obtained, each sample was treated in a vacuum at 200°C for 3 hr. The specific surface area and total pore volume were determined by a BET plot from 0.01 to 0.1 relative pressure, and at a 0.98 relative pressure, respectively.

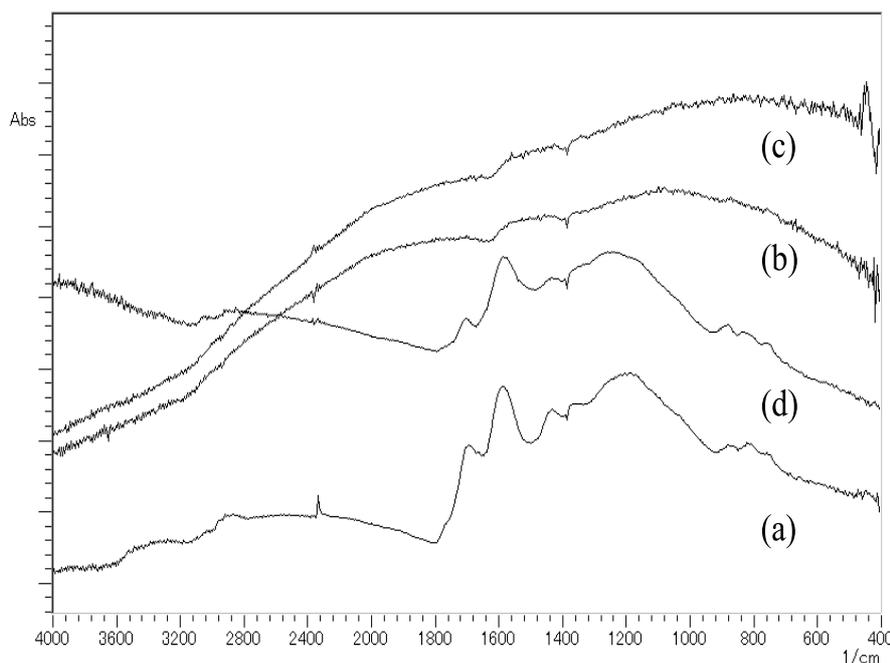
**Identification of Surface Functional Groups by Fourier Transform-Infrared Spectrometry (FT-IR)** — The FT-IR spectra of each porous carbon sample were obtained using IRPrestige-21 (Shimadzu, Kyoto, Japan) in the 400–4000  $\text{cm}^{-1}$  wavenumber range by the KBr method. Five mg Pellets were made mixing 10 mg of each porous carbon sample with 500 mg of KBr powder in a mortar.

**Adsorption Isotherm Measurement of BPA and E2** — The concentrations of BPA and E2 were determined by high performance liquid chromatography (HPLC). The HPLC system consisted of two LC-10AT (Shimadzu) pumps, a CTO-10A (Shimadzu) column oven, a SPD-10A (Shimadzu) detector, and an Inertsil ODS-3 (150  $\times$  4.6 mm i.d.: GL-Sciences, Yokohama, Japan) analytical column. Aqueous 70% (v/v) methanol, used as the mobile phase, was pumped at 1.0 m/min. The column temperature was set 40°C, and the wavelength of the detector was 280 nm. All injections were 20  $\mu\text{l}$  using a sample loop.

Standard solutions (1000 mg/l) of the BPA and E2 were prepared using methanol, and then the test solutions were prepared by dilution using purified water. Methanol was then added to the test solutions for a 2% total concentration. The primary concentration in the test solutions of different concentrations was determined by HPLC, and then 0.01 g of each porous carbon sample was added to 100 ml of each test solution. The test solutions were shaken in an incubator maintained at 23°C for 24 hr. The equilibrium concentration of the filtered test solutions after 24 hr was determined by HPLC. The adsorption amount was calculated from the difference between the primary concentration and the equilibrium concentration, and then the adsorption isotherms were measured. The adsorption isotherms were applied to the Freundlich equation:

**Table 1.** BET Surface Area and Total Pore Volume of Porous Carbon and Activated Carbon

	BET Surface Area (m <sup>2</sup> /g)	Total Pore Volume (ml/g)
PC <sub>400</sub>	2.50	< 0.01
PC <sub>700</sub>	251	0.143
PC <sub>1000</sub>	300	0.153
AC	1350	0.605

**Fig. 1.** FT-IR Spectra of Porous Carbon and Activated Carbon; (a) PC<sub>400</sub>, (b) PC<sub>700</sub>, (c) PC<sub>1000</sub>, (d) AC

$$\log W = \log K + (1/n) \log C$$

where  $C$  is the equilibrium concentration (mg/l),  $W$  is the adsorption amount (mg/g), and  $K$  and  $1/n$  are constants, and then  $K$  and  $1/n$  were then calculated. It describes that the constant  $1/n$  shows the affinity between the adsorbent and adsorbate and  $K$  shows an adsorption capacity in addition to the affinity between the adsorbent and adsorbate.<sup>16)</sup>

## RESULTS AND DISCUSSION

### Surface Properties of Porous Carbon

The BET surface area and total pore volume of each porous carbon sample are shown in Table 1. The BET surface area and total pore volume of the porous carbon increased as the carbonization temperature increased. The difference in those of the PC<sub>400</sub> and PC<sub>700</sub> was significant, but the difference

between the PC<sub>700</sub> and PC<sub>1000</sub> was minimal. Furthermore, the BET surface area and total pore volume of the AC was 4.5 and 4.0 times greater than those of the PC<sub>1000</sub>. Generally, the physical adsorption effect increases as the surface area and pore volume increase. Therefore, the physical adsorption effect increased as the carbonization temperature increased.

### Surface Functional Groups of Porous Carbon

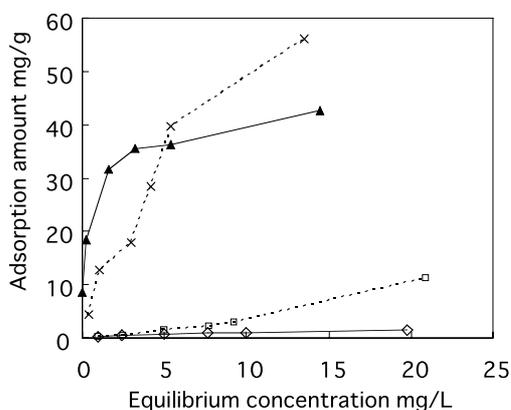
Figure 1 shows the FT-IR spectrum of each sample. For the PC<sub>400</sub> and AC, the bands at 1700, 1600, and 1425 cm<sup>-1</sup> indicate the absorbance by the stretching vibration of C=O, stretching vibration of C=C, and deformation vibration (bending in plane) of O-H, respectively. Therefore, this indicated that much functional groups including oxygen such as the carboxyl group exist on the surface of the PC<sub>400</sub> and AC. However, these absorbencies for the PC<sub>700</sub> and PC<sub>1000</sub> were unclear, so that few functional groups were indicated. Therefore, it is thought that

the surface polarity decreased due to a decrease in the carboxyl group as the carbonization temperature increased. Furthermore, the surface polarity of the AC was midway between the PC<sub>400</sub> and PC<sub>700</sub>.

### Adsorption Isotherms and Freundlich's Adsorption Constants of BPA and E2

The adsorption isotherms of BPA are shown in Fig. 2, and Freundlich's adsorption constants and correlation coefficients are shown in Table 2. From the results of the adsorption isotherms, the adsorption amount of BPA increased as the carbonization temperature increased. The adsorption effect of the PC<sub>400</sub> was slight, while that of PC<sub>1000</sub> was significant. The adsorption effect of the AC was lower than that of the PC<sub>1000</sub> in the low concentration range, while that of the AC was higher than that of the PC<sub>1000</sub> in the high concentration range. An inversion of the adsorption isotherms between the AC and the PC<sub>1000</sub> took place at about a 5 mg/l equilibrium concentration. The result of application to Freundlich's equation to BPA showed a linearity over 0.98, and the adsorption isotherms of BPA were approximated by the Freundlich equation. Therefore, the constant 1/n

and K of the Freundlich equation can be used for discussions of adsorption properties. The constant 1/n of the PC<sub>1000</sub> was the smallest, and that of the PC<sub>700</sub> was the largest. The constant 1/n of the AC was midway between the PC<sub>700</sub> and the PC<sub>1000</sub>. The constant 1/n of the Freundlich plot shows a slope for the adsorption isotherm based on logarithmic calculations. Therefore, it was reasoned that the constant 1/n of the PC<sub>1000</sub> was small because of the significant adsorption amount in the low concentration range and the low adsorption amount in high concentration range. The constant K of the PC<sub>1000</sub> was the largest, and that of the AC, the PC<sub>400</sub>, and the PC<sub>700</sub> followed. Although the value of the 1/n constant of the AC was larger than that of PC<sub>1000</sub>, the adsorption effect of the PC<sub>1000</sub> was the largest in the low concentration range. From the result of the surface pore properties by nitrogen adsorption, the BET surface area and total pore volume of AC were greater than those of the PC<sub>1000</sub>, so that the adsorption sites of the AC were greater than that of the PC<sub>1000</sub>. However, from the result of the surface chemical structure by FT-IR, the amounts of the surface functional groups on the PC<sub>1000</sub> were less than those of the AC, so that it was postulated that the surface hydrophobicity of the PC<sub>1000</sub> was greater than that of the AC. Furthermore, it was presumed that the affinity between the PC<sub>1000</sub> and hydrophobic chemicals, which had low solubilities in water such as BPA [120 mg/l at 25°C (Hazardous Substances Data Bank, United States National Library of Medicine, <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>)], was strong. Therefore, the PC<sub>1000</sub> had a more effective the BPA adsorption, which becomes a problem in trace concentrations, than the AC. The adsorption isotherms of E2 are shown in Fig. 3, and the Freundlich's adsorption constants and correlation coefficients are shown in Table 2. From results of the adsorption isotherms, the adsorption amount of E2 increased as the carbonization temperature increased. The adsorption effect of the AC was midway between the PC<sub>700</sub> and the PC<sub>1000</sub>. The result of



**Fig. 2.** Adsorption Isotherms of Bisphenol A on Porous Carbon and Activated Carbon

◇, PC<sub>400</sub>; □, PC<sub>700</sub>; ▲, PC<sub>1000</sub>; ×, AC.

**Table 2.** Freundlich's Adsorption Constants of Bisphenol A and  $\beta$ -Estradiol

	Bisphenol A			$\beta$ -estradiol		
	1/n	K	r	1/n	K	r
PC <sub>400</sub>	0.53	0.30	0.996	0.51	0.26	0.998
PC <sub>700</sub>	1.4	0.14	0.998	0.62	0.79	0.998
PC <sub>1000</sub>	0.24	25	0.988	0.49	15	0.990
AC	0.71	9.9	0.980	0.85	4.6	0.991

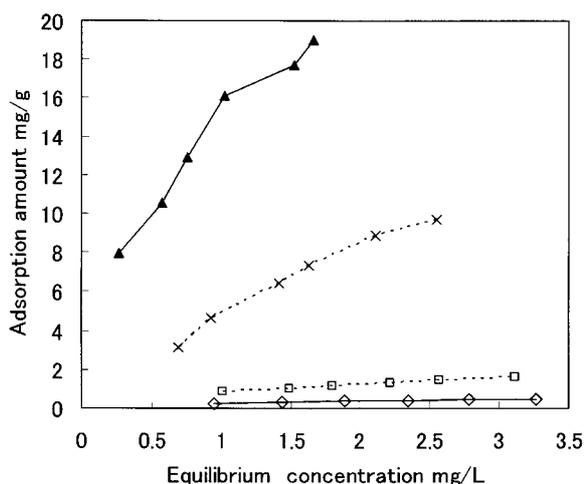


Fig. 3. Adsorption Isotherms of  $\beta$ -Estradiol on Porous Carbon and Activated Carbon

◇, PC<sub>400</sub>; □, PC<sub>700</sub>; ▲, PC<sub>1000</sub>; ×, AC.

the application using the Freundlich equation for E2 showed a linearity of over 0.99, and the adsorption isotherms of E2 were also approximated by the Freundlich equation. The constant  $1/n$  of the AC was the largest, and that of the PC<sub>700</sub>, the PC<sub>400</sub> and the PC<sub>1000</sub> followed. Although that of the PC<sub>1000</sub> was the lowest, the reason was thought to be the same as BPA. The constant  $K$  of the PC<sub>1000</sub> was the highest, and that of the AC, the PC<sub>700</sub>, and the PC<sub>400</sub> followed. Therefore, the adsorption of E2 to the PC<sub>1000</sub> was the most effective. The inversion of the adsorption isotherms between the PC<sub>1000</sub> and the AC occurred in BPA, but did not occur in E2. It is postulated that this is caused by the solubility in water. The solubility in water of E2 [3.60 mg/l (Hazardous Substances Data Bank, United States National Library of Medicine, <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>); 0.01 mol/l] is low, and the hydrophobicity is high in contrast to that of BPA (120 mg/l; 0.53 mmol/l), so that the adsorption amount of the AC didn't exceed that of the PC<sub>1000</sub> within the solubility in water of E2. Therefore, the adsorption properties of EDCs influence the solubility in water. The PC<sub>1000</sub> with a low surface polarity is effective for the adsorption of a high hydrophobic substance, and the AC with a high pore volume is effective as the solubility in water increases.

Especially, a trace concentration becomes a problem in EDCs, and most EDCs have a high hydrophobicity. Therefore, the PC<sub>1000</sub> with a strong affinity due to a low surface polarity was more effective for the removal from environmental water than the

AC with a large adsorption capacity due to a large pore volume. It is expected that the PC<sub>1000</sub> will be used with the AC, which has been used in waste water treatment, in purification plants, etc.

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