Preparation of Activated Carbon from Wastepaper and Adsorption of Endocrine Disrupting Chemicals

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ABSTRACT

Activated carbon is proposed as a new application of wastepaper recycling other than the paper-making. Waste kraft bag is considered to be a suitable raw material for activated carbon because of its low ash content. Small pellets of wastepaper squeezed out from the continuous kneader were carbonized in a nitrogen atmosphere and activated using carbon dioxide.

The BET specific surface areas of activated carbon prepared from waste kraft bag was 1,285 m^2/g, which is higher than commercially available activated carbons. The activated carbon prepared from wastepaper has a well-developed porous structure, particularly in mesopore and macropore ranges. As a result, activated carbon with iodine adsorption capacity of 1,400 mg/g was obtained from waste kraft bag.

In this paper, adsorption amount of Bisphenol A (BPA) was determined to investigate adsorbability of activated carbon from waste kraft bag. Adsorption measurements were on solutions ranging from 0.1 μg/L to 100 mg/L. The activated carbon from waste kraft bag gave higher BPA adsorbabilities over a wide range, compared with commercially available activated carbons.

INTRODUCTION

The world annual consumption of paper and paperboard reached 357 million tons in 2004[1]. The recovery rate of waste paper increased up to 47.7 %.

The wastepaper recovery rate in individual countries is dependent on the situation regarding its fiber resources and paper industry, as well as the per capita paper and paperboard.

In 2004, the paper consumption was 31 million tons in Japan and the per capita paper consumption was also more than 240 kg. In spite of a large amount of paper consumption, wastepaper recovery in Japan has exceeded 71%[2]. However, waste paper utilization remained around 60 % in recent years. Japan exports of recovered paper rose from 1.7 % of all the recovered paper recovered in Japan in 2000 to 13.2 % in 2004. In that year, recovered paper exports reached 2.8 million tons, compared with 370 thousand tons in 2000. Most of this increase was in exports to China, which stepped up production dramatically during the 2000's. Chinese papermakers have to import a large amount of their raw materials due to limited domestic

supplies of pulp fiber. This tendency will force Japanese papermakers to utilize recovered paper of lower grades. However, the utilization of recovered paper for higher grades of paper such as printing, writing, information and tissue papers has been restricted because of the demand for their quality. On the other hand, environmental issues are still serious and controversial, because 30-40 % of garbage is paper and paperboard.

It is important to find new processes to utilize waste papers other than paper to paper recycling. In this paper, activated carbons prepared from waste kraft bag were investigated to develop other applications for recycling of waste paper.

Activated carbon has been used as an adsorbent in many industrial fields. In recent years, it has been used for controlling air pollution, water pollution, odors, etc., and for environmental protection, and demand for it is increasing. Studies on activated carbons, which use scrap wood, organic waste sludge, bean-curd refuse, bagasse, almond shell, waste phenol resin, etc. as raw materials, have been carried out to explore recycling options for organic waste materials[3)-9)]. We have previously manufactured activated carbon using waste newspaper as raw material, and examined its adsorbability and pore structure[10)-13)]. The waste newspaper activated carbon exhibited an adsorbability of almost the same level as that of commercially available activated carbon, and had well-developed pores in mesopore and macropore range.

However, we found that the adsorbability of the wastepaper activated carbon decreased with an increase in ash content of wastepaper. It is considered that a compaction of the raw material is necessary in the pretreatment process. In this paper, kraft bag, which has low ash content, was torn and compacted into granules for use as raw material. The waste kraft bag was extruded to form granules without an

adhesive, and the granules were carbonized in a nitrogen atmosphere and then activated in a carbon dioxide atmosphere in a rotary kiln.

In recent years, endocrine disrupting chemicals (EDC) have been reported by many researchers as one of the problem of environmental pollution. Bisphenol A is categorized as an EDC because of its weak estrogen-like effect. Bisphenol A (BPA) is a typical product of the industrial society produced in large quantities worldwide, 90 % or more being used as a monomer for the production of polycarbonate, epoxy resins, and unsaturated polyester-styrene resins. We investigated the adsorbability of BPA in water onto the wastepaper activated carbon and some commercial activated carbons in this paper.

EXPERIMENTAL

Preparation of activated carbon

The waste kraft bags were cut into small pieces using a shredder. The moisture contents of the pieces were controlled in the range of 20 to 23 % based on oven-dried fiber. Small pellets of waste kraft bag were squeezed out from the continuous kneader as the sample material for carbonization. Each pellet was approximately 6 mm diameter and 10 mm long.

The sample was placed in a stainless steel tube in a tubular furnace. The air present in the tube was replaced by nitrogen at room temperature. The temperature was increased by 10 °C/min. under a nitrogen flow rate of 150 mL/min. to a final temperature of 800 °C. The temperature was maintained at 800 °C for 2 h to complete the carbonization process.

The carbonated pellets were activated in the furnace. The furnace was increased at a rate of 10 °C/min. in the nitrogen flow and kept at a predetermined temperature within the range 900-1100 °C. Carbon dioxide gas was introduced into the stainless steel tube at a flow rate of 500 mL/min. after the

temperature was reached. The activation temperature was maintained within the range 30-90 min.

Measurement of porous structure

The activated pellets prepared at various conditions were ground to a particle diameter of 53-150 μm. The nitrogen adsorption isotherm at liquid nitrogen temperature was determined using automatic vapor adsorption apparatus (BELSORP18, assembled by Bell Japan, Inc.). The specific surface area was calculated by the BET equation, and the pore distribution curve was determined by the t-method, the Molecular-Probe method and the Dollimore-Heal method. The commercially available coconut shell activated carbon and the chemical reagent activated carbons were used as reference samples.

Adsorbability of iodine and methylene blue

The adsorbability was evaluated by the amounts of iodine and methylene blue adsorbed. The adsorbabilities were measured based on JIS K 1474 (Method of testing activated carbon).

Measurement of bisphenol A adsorption

Bisphenol A (BPA) Standard was obtained from Wako Pure Chemical Industries Co., Ltd. (Osaka, Japan). The MilliQ water was used for measurement of the BPA adsorption. The BPA Standard was dissolved in water containing 10 % of methanol. Measurements of the adsorption capacity were made on the solutions ranging in three concentrations of BPA from 0.1 μg/L to 100 mg/L.

The adsorption isotherms of BPA were obtained by adding various quantities of activated carbon to Erlenmeyer flasks. The volume of activated carbon was varied over a range of 0.5-15 mg. An aliquot of 50 mL of 100 mg/L BPA solution was added to the flasks and the flasks was capped. The flasks were shaken at room temperature for 24 h. After equilibration, the solution was filtered through a glass syringe filter to remove any suspended activated carbon.
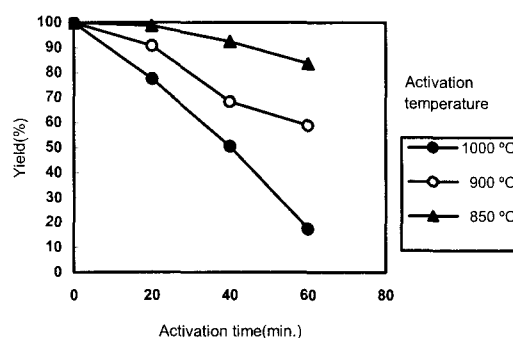

Fig. 1 Effect of activation conditions
on yield of waste kraft bag AC

The BPA content in the filtrate solution was directly determined by using a UV spectrophotometer at 276.5 nm wavelength in the case of 100 mg/L BPA solution.

On the other hand, changes in lower initial concentrations of the BPA solution such as 500 μg/L and 0.1 μg/L were determined by enzyme-liked immunosorbent assay (ELISA). The ELISA kit[14] was obtained from Takeda Chemical Industries, Co., Ltd. (Tokyo, Japan). Lately immunosensors have been applied as biological analytical tools for the analysis of micropollutants in the environment.

Immunosensors incorporate either antigens or derived antigens or antibodies, intimately associated with or integrated within a physico-chemical transducer, which, in contrast to immunoassays, is permanently fixed in the construction of the device[15]. The monitoring of BPA in solution was performed using an optical immunosensor and measuring absorbance at 450 nm. Preconcentration of the samples was carried out using the solid-phase extraction[16] in the case of 0, 1 μg/L initial concentration of BPA in water.

RESULTS AND DISCUSSION

Activation condition and pore structure of activated carbon

Fig. 1 shows the effect of activation conditions for the carbonized product prepared from waste kraft bag

on the yield of activated carbon prepared from the carbonized product. The yield of activated carbon decreased with the increase of activation temperature and activation time. The adsorbability of activated carbon depends on the size of the effective adsorption area and the amount of adsorption caused by capillary condensation[1]. Therefore, the surface area has a large effect on the adsorption capacity.

Fig. 2 shows the relationship between the yields of activated carbon prepared from waste kraft bag under various activation conditions and the specific surface area. The specific surface area of waste kraft bag activated carbon proportionally increased with the yield decreased. On the other hand, the specific surface area of waste newspaper activated carbon reached a maximum value at a yield of about 40 %, which is related to 3.6 % of ash content in waste newspaper.
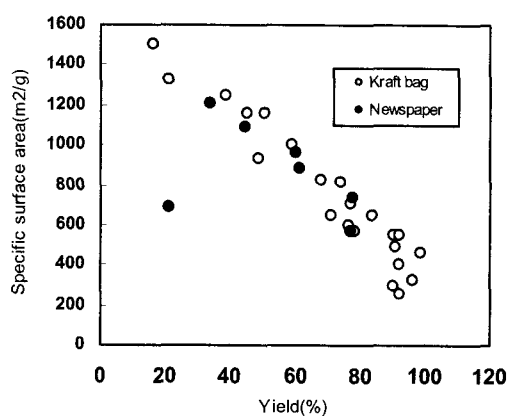

Fig. 2 Yield and specific surface area of activated carbon

The increase of specific surface area may be caused by the development of micropores formed on the surface of carbonized product during the activation treatment. The pores of activated carbon can be divided into micropores (<1 nm), mesopores (1-25 nm) and macropores (>25 nm). The size, shape and distribution of the pores, and their specific surface area, as well as other physical properties, can significantly affect the adsorption properties. In particular, when the pore size is in the range four to

five times the diameter of the adsorbed molecules, the interaction between the adsorbed molecules and the porous wall may act in three dimensions, which provides a large adsorption force[17]. These micropores are the principal structures in which many currently manufactured activated carbons consist of well-developed micropores.

On the other hand, activated carbons used for water purification are required to have more mesopores and macropores. Activated carbon with well-developed mesopores provides better selective adsorption properties towards larger molecules compared with activated carbon with well-developed micropores only[18,19].

Table 1 gives the specific surface areas and pore volumes of waste kraft bag activated carbon and commercially available activated carbons. The waste kraft bag activated carbon had a higher specific surface area compared with coconut shell and chemical reagent activated carbons. The high grade of activated carbon used in advanced water purification showed the highest specific surface area in this study. The micropore volume of waste kraft bag activated carbon determined by nitrogen adsorption was similar to that of commercially available activated carbons. However, the mesopore volume was higher than that in coconut shell and chemical reagent activated carbons and lower than that in the high grade of activated carbon.

Table 1 BET specific surface area (SSA) and pore volume of waste kraft bag activated carbon and commercially available activated carbons (AC)

AC Samples	BET SSA (m²/g)	Pore volume (mL/g)		
		Total	Micro-pore	Meso-pore
Waste kraft bag	1285	1.05	0.52	0.53
Coconut shell	807	0.49	0.42	0.07
Chemical reagent	923	0.63	0.44	0.20
High grade AC	1500	1.69	0.55	1.14

Adsorbability of bisphenol A onto activated carbon

Fig. 3 shows changes in residual concentration of 100 mg/L BPA solution with amount of activated carbon added. The results can be seen in Fig. 3, where the concentration of BPA adsorbed by activated carbon increased with amount of activated carbon added while the concentration in water decreased with amount of activated carbon added. The residual concentration of BPA solution with equilibration being reached in 24 h shaking decreased with increasing amount of activated carbon added. The amount of BPA adsorbed onto the high grade of activated carbon was higher even at small amount of activated carbon added. Efficient BPA removal from aqueous solution at high concentration of 100 mg/L was also performed using the waste kraft bag activated carbon.
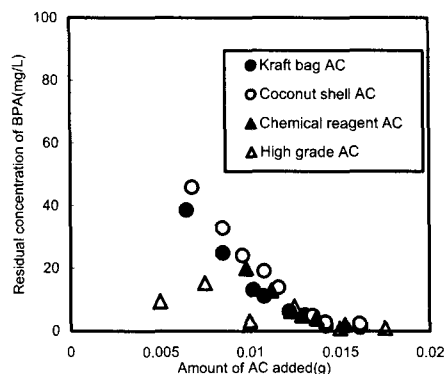

Fig. 3 Adsorbability of BPA in 100 mg/L
solution onto activated carbons

The amount of BPA adsorbed onto the waste kraft bag activated carbon at lower initial concentration of 500μg/L was higher than onto coconut shell and chemical reagent activated carbons, and somewhat lower than onto the high grade of activated carbon (Fig. 4).

The adsorption of 500μg/L BPA solution onto waste kraft bag activated carbon was faster than that onto other activated carbons within the initial 10 min. The
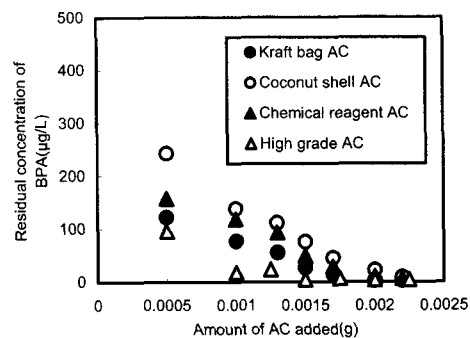

Fig. 4 Adsobability of BPA in 500 μg/L
solution onto activated carbons

waste kraft bag activated carbon also gave the highest momentary adsorbability of BPA at initial concentration of 100μg/L in water.

The concentration levels of BPA detected in river waters were quite high in some of them (up to 0.4 μg/L) and expected to increase as a consequence of its widespread application. Therefore, it is important to determine the adsorption of BPA onto activated carbons at initial concentration of 0.1 μg/L solution. The determination of BPA in 0.1 μg/L solution was performed using both the ELISA kit and the solid-phase extraction. The waste kraft bag activated carbon showed almost the same amount of BPA adsorbed as the high grade of activated carbon and much higher adsorbability compared with other commercially available activated carbons, as shown in Fig. 5.
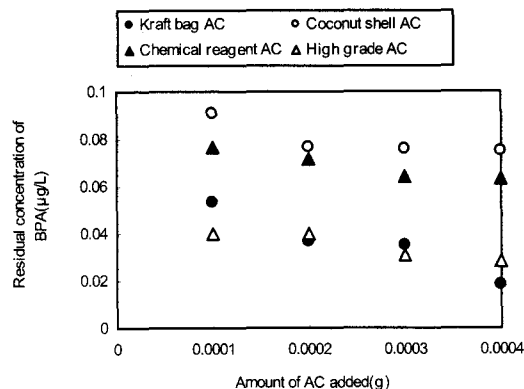

Fig. 5 Adsorbability of BPA in 0.1 μg/L
solution onto activated carbons

CONCLUSIONS

To develop applications for the recycling of wastepaper, the pore structure and the adsorbability of activated carbon prepared from waste kraft bag that was compacted and extruded to granules were compared with commercially available activated carbons. The adsorbability of BPA in 0.1 μg/L solution onto activated carbon was determined using both the ELISA and the solid-phase extraction. The amounts of BPA adsorbed in the range of 0.1 μg/L-500 mg/L were higher in the waste kraft bag activated carbon. The adsorption of BPA onto waste kraft bag activated carbon was faster than that onto commercially available activated carbons at lower concentrations.

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