

Removal of 4-Nonylphenol by Carbonaceous Materials Produced from Cottonseed Shell as Organic By-products

Ikuo ABE*, Takahiro TABUCHI**, Osamu SHINOHARA**,
Satoshi IWASAKI*, Naohito KAWASAKI***, and Seiki TANADA***

Abstract

The recycling of organic by-products has attracted much interest. In this paper, techniques for producing carbonaceous adsorbents from an organic by-product and the application to removal of endocrine disruptors are described. Cottonseed shell as an organic by-product was carbonized at 873 K, and the cottonseed shell char was then activated in a rotary kiln with steam at 1123 K for different lengths of time to obtain microporous carbons. The specific surface area of the carbons obtained was nearly equal to those of commercial activated carbons. The amount of 4-nonylphenol adsorbed at equilibrium concentration above 20 g/L was high for the carbon with large specific surface area. The adsorption at extremely low concentrations such as 1 g/L was high for the carbon with a small mean pore diameter. Microporous carbons were produced next by air activation of cottonseed shell in a one-step treatment. Although the specific surface area of the carbon was small, pore size was adequate for adsorbing 4-nonylphenol at low concentration. Therefore 4-nonylphenol could be efficiently removed from an aqueous solution.

Key Words: Zero Emission, By-product, Carbonization, 4-Nonylphenol

1. Introduction

Zero Emissions aims at reducing the environmental load on the earth to near zero. One component of the strategy is to make use of organic by-product resources, thus mitigating the consumption of resources¹⁾. The building of recycling society is realized by changing new industries, the economy, the social system, and the lifestyles etc. There are many techniques to decrease the by-products of individual production processes. New collection techniques for the by-products and techniques to give additional value to by-products are needed²⁾. The technology to increase sustainable development has been reported, as have the technique for efficient collection of foaming polystyrene or the replay material and the technique to reuse by collecting the dyestuff from used ink ribbons³⁾. For example, a polymer was decomposed to a monomer by super-

critical water⁴⁾. To promote "zero emissions" of organic by-products, it is necessary to build a carbon circulation process. By changing the difficult recycling of an organic by-product into carbon materials without disposing of it as in the past, it is possible to reduce the discharge quantity of carbon dioxide, which is equivalent to the carbon contents in the carbon material.

Activated carbons are widely used in the industry for separation, purification, and recovery processes. The demand for environmental protection has tended to increase every year. Any inexpensive materials with high carbon content can be used as a raw material for the production of activated carbon. It is suspected that some chemicals function like hormones in the living body and have serious effects on internal secretion. Such chemicals, which are called endocrine-disrupting chemicals, have recently become a social issue.

* Osaka Municipal Technical Research Institute,
1-6-50 Morinomiya, Joto-ku, Osaka 536-8553, Japan

** Faculty of Science and Engineering, Kinki University,
3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502, Japan

*** Faculty of Pharmaceutical Science, Kinki University,

4-Nonylphenol is categorized as such a chemical because it has a weak estrogen-like effect. The establishment of a technology for 4-nonylphenol removal is therefore desirable³⁾. In Japan, 170,000 ton/y of cottonseed is imported to produce cotton oil and effective utilization of the cottonseed shell as a by-product is required. The purpose of this study is to investigate the feasibility of manufacturing carbonaceous adsorbents from the agricultural by-product cottonseed shell and to apply to the removal of 4-nonylphenol. The carbonaceous adsorbents will be used again and again by steam activation. That decreased the adsorbability of 4-nonylphenol will be thermal recycle. The adsorbed 4-nonylphenol onto the carbonaceous adsorbents will be degraded to water and carbon dioxide.

2. Materials and Methods

Carbonization of by-products

The by-product used was cottonseed shell. The composition of cottonseed shell is 34~40 cellulose, 37~42 hemicellulose, 13~18 lignin, and 5~7 minerals. The cottonseed shell was inserted in a metal container which was covered and inserted in an electric furnace which was heated to 873 K at a speed of 5 K/min. The materials were maintained at this temperature for 1 h and then cooled to obtain char.

Steam-based activation

A steam-based activation method was used to form micropores in the char. Figure 1 shows the apparatus for steam-based activation. The 10 g of cottonseed char was inserted in the rotary kiln which was heated to 1123 K at a speed of 5 K/min in a nitrogen stream of 300mL/min. At 1123 K, steam was introduced into the kiln at a speed of 10g/h for various periods of time, and the kiln was then cooled to obtain microporous carbon.

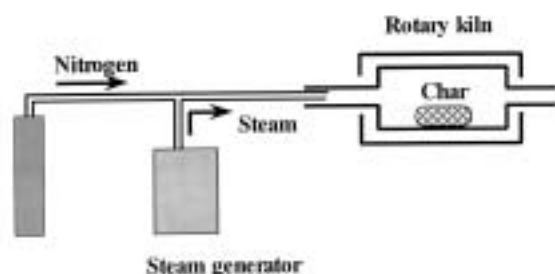


Fig. 1 Apparatus for steam-based activation

Air-based activation

In the case of the air-based activation method, air was used as activation reagent instead of steam.

Figure 2 shows the apparatus for air-based activation. The cottonseed shell was inserted in the furnace which was heated to 1173 K at a speed of 5 K/min in an air stream of 15 mL/min. The materials were maintained at this temperature for the prescribed time and then cooled to obtain microporous carbon.

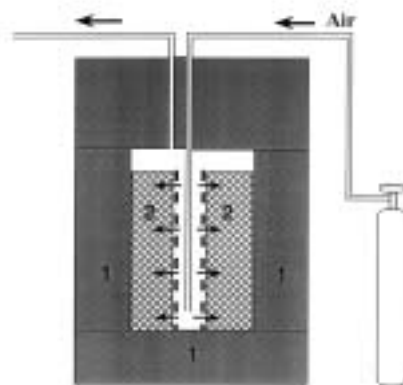


Fig. 2 Apparatus for air-based activation
1: electric furnace, 2: cottonseed shell

Measurement of porosity

The specific surface area and pore volume of the microporous carbons were determined from nitrogen adsorption isotherms using the Nihon Bell Belsorp 18SA (Osaka, Japan). Specific surface area (S) was calculated from BET plots in the relative pressure range of 0.01 to 0.15. The volume (V) of pores smaller than 30 nm in diameter was determined from the amount of nitrogen adsorbed at a relative pressure of 0.931. The mean pore diameter (D) was calculated from $D = 4V/S$, the pore system being assumed to consist of uniform cylindrical nonintersecting capillaries. The amount of iodine adsorbed at equilibrium concentration 2.5g/l was measured according to JIS (Japanese Industrial Standard) K1474.

Measurement of 4-nonylphenol adsorption

4-Nonylphenol ($C_9H_{19}-C_6H_4-OH$, molecular weight=220.4) was obtained from Tokyo Chemical Industry (Tokyo, Japan). It was confirmed by thin-layer chromatography and nuclear magnetic resonance that 4-nonylphenol was a mixture of some branched isomers. Water used for 4-nonylphenol adsorption was purified by distillation, followed by treatment with activated carbon adsorption and ion-exchange.

The adsorption isotherms were obtained by adding various quantities of microporous carbon to 100-mL vial tubes. An aliquot of 100 mL of a 4-nonylphenol solution of 100 g/L was added to the tube and the tube was capped. The tubes were shaken in a bath maintained at 298 K for 15 h. Preliminary

experiments showed that adsorption was essentially complete within 15 h. After equilibration, a sample was taken from each tube and filtered through a glass-fiber filter paper to remove any suspended carbon. The 4-nonylphenol content in the filtrate solution was measured using a spectrofluorophotometer, Shimadzu RF-5300PC (Kyoto, Japan). The excitation wavelength and emission wavelength were 221.0 nm and 304.0 nm, respectively. The equilibrium amount adsorbed was calculated using the following equation:

$$X = (C_0 - C)V/W \quad (1)$$

where X is the equilibrium amount adsorbed per gram of carbon (mg/g), C_0 and C are the initial and equilibrium concentrations ($\mu\text{g/L}$), V is the volume of solution (L), and W is the weight of the carbon (mg).

3. Results and Discussion

Preparation of microporous carbon

Carbonaceous material was obtained in a 30.3 % yield by carbonizing cottonseed shell. Table 1 shows the physical properties of cottonseed shell char. Table 2 shows the results of steam activation of cottonseed shell char. The activation yield decreased and ash increased with an increase in activation time. This suggests that the weight of minerals in the char did not appreciably change though the carbon weight decreased through the activation process. The specific surface area, pore volume, and iodine adsorption capacity increased

Table 1 Properties of cottonseed shell char

Specific surface area (m^2/g)	252
Pore volume (mL/g)	0.132
Mean pore diameter (nm)	2.10
Iodine adsorption capacity (mg/g)	140
Ash (%) ^{a)}	4.7

Table 2 Steam activation of cottonseed shell char

Samples	Activation time (h)	Activation yield ^{a)} (%)	Ash (%)	Specific surface area (m^2/g)	Pore volume (mL/g)	Mean pore diameter (nm)	Iodine adsorption capacity (mg/g)
SA-A	2.0	55.8	9.3	1039	0.469	1.81	970
SA-B	2.5	27.7	16.8	1464	0.705	1.93	1300
SA-C	3.0	13.6	32.2	948	0.494	2.08	960

^{a)}Cottonseed shell base The yield of cottonseed char produced from cottonseed shell was 30.3%

Table 3 Air activation of cottonseed shell char

Samples	Activation time (h)	Activation yield (%)	Ash (%)	Specific surface area (m^2/g)	Pore volume (mL/g)	Mean pore diameter (nm)	Iodine adsorption capacity (mg/g)
AA-A	2.0	14.2	30.1	450	0.209	1.86	520
AA-B	4.0	8.2	39.6	611	0.279	1.83	640

AA-A: Cottonseed shell charged was 37.2 g. AA-B: Cottonseed shell charged was 18.3 g.

^{a)} Tested by JIS K1474

area is due to the enlargement of micropore size and with an increase in activation time up to 2.5 h and then decreased. The increase in specific surface area is due to the growth of micropores by the activation reaction. The decrease in specific surface area the increase in ash content by carbon loss. The ash content of the microporous carbons prepared from cottonseed shell was high. That of commercial activated carbon prepared from coconut shell is about 1 %. The specific surface areas per unit mass of carbon of [SA-A], [SA-B], and [SA-C] were 1150, 1760, 1400 $\text{m}^2/\text{g-C}$, respectively. Table 3 shows the results of air activation of cottonseed shell char. The specific surface area and pore volume were lower than those for steam activation. This air activation method can accomplish both carbonization and activation in a single treatment. In practice, the carbonization proceeds in the range of about 500 900 K and the activation proceeds above 1100 K. The main activation reaction is expressed by equation (2), which is a reaction between carbon and carbon dioxide evolved in the combustion reaction ⁶⁾.



Although this air activation method has a disadvantage in that the reaction rate of activation is lower than that of steam activation, the method needs only a furnace. In spite of the specific surface area of [AA-B] being low, the mean pore diameter was similar to that of [SA-A] with high specific surface area. A activated carbon which was produced by steam activation is the smaller mean pore diameter. The result that the mean pore diameter of [AA-B] was higher than predicted may be attributed to an effect of the combustion reaction, the reaction between carbon and oxygen in air.

Adsorption properties of 4-nonylphenol

The adsorption isotherms of 4-nonylphenol on microporous carbons produced by steam activation are shown in Figure 3. The order of the amount of 4-nonylphenol adsorbed at equilibrium concentration above 18 g/L was [SA-B] > [SA-C] > [SA-A]. Although the adsorption amount for [AC-B] with a high specific surface area was very

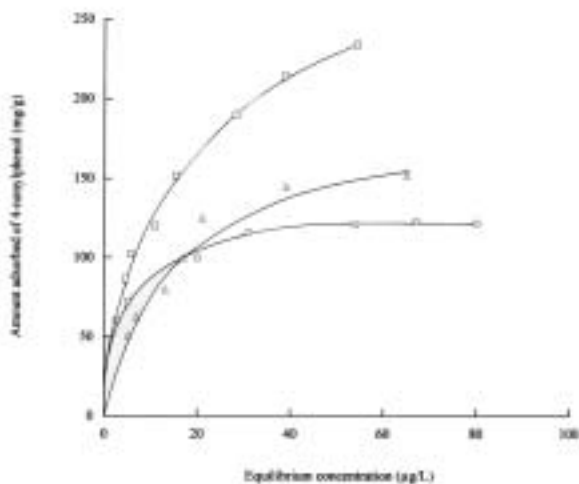


Fig. 3 Adsorption isotherms of 4-nonylphenol onto carbonous materials produced from cottonseed shell by water steam activation.

, SA-A; , SA-B; , SA-C

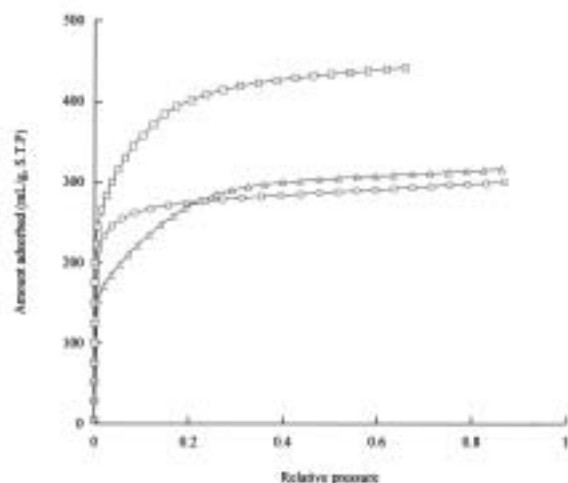


Fig. 4 Adsorption isotherms of nitrogen at 77K of resulting activated carbons at various extents of burn-off from steam activation.

, SA-A; , SA-B; , SA-C

high, the order was not in accord with that of specific surface area. Figure 4 shows the adsorption isotherms of nitrogen gas on [SA-A], [SA-B], and [SA-C] at 77 K. The shape of isotherms for nitrogen was similar to that for 4-nonylphenol. The order of

the amount of 4-nonylphenol adsorbed above 18 g/L was the same adsorption amount was as the order of the amount of nitrogen adsorbed at relative pressure above about 0.23. Furthermore, the order of the amount of 4-nonylphenol adsorbed in the range 5 18 g/L was the same as the order of the amount of nitrogen adsorbed in the relative pressure range in which the specific surface area was determined. The adsorption isotherms of 4-nonylphenol were approximated by the Freundlich equation:

$$\log X = \log K + (1/N) \log C \quad (3)$$

where K and 1/N are adsorption constants. The adsorption constants were estimated by linear regression analysis and are shown in Table 4. The K value is the same as the amount of 4-nonylphenol adsorbed at 1 g/L and it increased with the decreasing mean pore diameter. The constant 1/N increased with the mean pore diameter. The constant 1/N expresses an affinity between the adsorbate and adsorbent. An increase in affinity

Table 4 Freundlich adsorption constants of 4-nonylphenol onto microporous carbons

Samples	Freundlich constants	
	K	1/N
SA-A	64	0.17
SA-B	49	0.39
SA-C	28	0.46
AA-A	4.2	0.26
AA-B	27	0.26

causes a decrease in the constant 1/N. Adsorption onto carbon whose surface is hydrophobic is mainly based on the London dispersion force which is part of the van der Waals force.

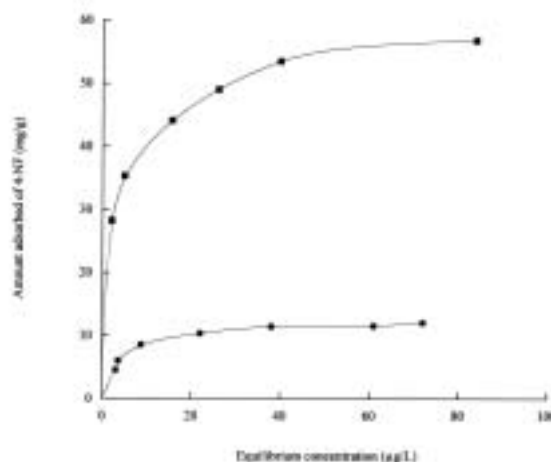


Fig. 5 Adsorption isotherms of 4-nonylphenol onto carbonous materials produced from cottonseed shell by air activation.

, AA-A; , AA-B

The more closely the adsorbate molecules in the pores are located to the surrounding pore walls, the higher will be the adsorption force⁷⁾. The adsorption at very low concentration such as 1 g/L occurs mainly in the pores with high adsorption force. It was considered that elongation of the activation time increased the mean pore diameter, decreased the adsorption force and then increased the constant 1/N.

The adsorption isotherms of 4-nonylphenol on microporous carbons produced by air activation are shown in Figure 5. The adsorption isotherms of nitrogen gas are shown in Figure 6. The adsorption amount of 4-nonylphenol or nitrogen was higher for

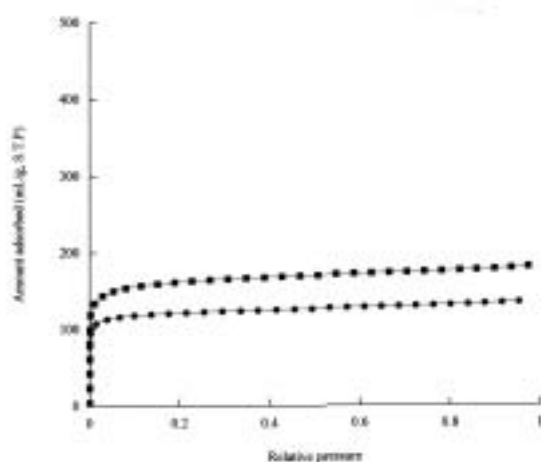


Fig. 6 Adsorption isotherms of nitrogen at 77K of resulting activated carbons at various extents of burn-off from air activation.

, AA-A; , AA-B

the carbon with higher specific surface area. Although the specific surface area of [AA-B] was

low, the amount of 4-nonylphenol adsorbed was higher than predicted. This indicates that the pore size of [AA-B] was adequate for adsorbing 4-nonylphenol at low concentration.

It is concluded that the microporous carbons, which are produced from organic by-products, could be used as adsorbents. Moreover, this technique could provide zero emission for the organic by-products and no discharge of carbon dioxide in the environment.

Acknowledgements

This research was supported partly by Grant 11128252 from Ministry of Education, Science, and Culture, Japan.

References

- 1) Takebayashi, M. (1999) Development of Resource-Recycling Society: From a Company's Point of View. *Chem. Eng. Jpn.*, **63**(2), 76-78.
- 2) Suzuki, M. (1999) Zero Emission Oriented Industrialized Society, *Chem. Eng. Jpn.*, **63**(2), 69-72.
- 3) Watanabe, H. (1999) Technical Development for Decrease of Environmental Load, *Chem. Eng. Jpn.*, **63**(2), 79-81.
- 4) Adschiri, T. (1993) Non-catalytic Conversion of Cellulose in Supercritical and Subcritical Water, *J. Chem. Eng. Jpn.*, **26**, 676-680.
- 5) Abe, I. (1999) Adsorption Properties of Endocrine Disruptors onto Activated Carbon, *J. Water Waste*, **41**, 43-47.
- 6) Abe, I., Hitomi, M., Ikuta, N., Tatsumoto, H., Kera, Y. (1996) Production of Microporous Carbon by Air Activation, *Tanso*, **1996**, 137-141.
- 7) Kondo, S., Ishikawa, T., Abe, I. (1991) *in Science of Adsorption*, Maruzen, Tokyo.