Removal of Endocrine-Disrupting Chemicals in Water using Textile-Related Wastes. I Removal of 4-Nonylphenol by Microporous Carbons Prepared from Cotton Waste

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Abstract: For recycling of textile wastes and for environmental preservation, preparation of carbonaceous adsorbent from cotton waste and its application to removal of endocrine-disrupting chemicals in water were investigated. In cotton towel carbonized at 600°C and activated at 850°C with steam, increasing activation time caused a decrease in microporous carbon yield and a linear increase in specific surface area. The specific surface area of microporous carbon with 50 % yield was approximately 1000 m²/g. Activation with air produced an equal yield of microporous carbon to steam activation, but a smaller mean pore diameter. The amount of 4-nonylphenol adsorbed onto both of the cotton waste-based microporous carbons was very high, even in extremely dilute solution, and efficient removal from aqueous solution was achieved.

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1. Introduction

Japanese textile industry faces two important challenges: environmental preservation and recycling. Textile-processing mills use large quantities of water and chemicals, some of which are discharged into rivers or sewers. Nonionic surfactants are typical textile-processing chemicals. Nonylphenol ethoxylates, currently used in the textile industry in a volume of between 50 and 100 thousand of tons a year, produce nonylphenol through decomposition in water. Because of its weak estrogen-like effect [1, 2], nonylphenol is categorized as one of the so-called endocrine-disrupting chemicals which have recently become a social issue due to their suspected hormone-like function in the living body and resulting serious effects on internal secretion. The establishment of a technology for nonylphenol removal is therefore desirable.

Various methods are used for recycling textile wastes, including material recycling, chemical recycling — often applied to nylon and polyester — and thermal recycling. There is however no effective recycling method for cotton.

The present study investigated the use of cotton wastes in the adsorption removal of nonylphenol in water. Microporous carbons were prepared by carbonizing and activating cotton wastes and adsorption isotherms were measured to obtain fundamental data.

2. Experimental

2.1 Materials

The waste cotton product used was cotton towel. 4-nonylphenol was obtained from Tokyo Kasei Kogyo Co., Ltd.

2.2 Carbonization

Three sheets of cotton towel in a metal container were heated in an electric furnace to 600°C at a speed of 5°C/min. The materials were maintained at this temperature for 1 h and then cooled to obtain carbon material. Yield of carbonization was obtained from the weight of dry sample before and after carbonization. In order to produce more micropores, activation with steam or air was carried out.

2.3 Steam activation

For steam activation the carbon material was cut into 30 × 30 mm pieces. These 10 g carbon pieces were inserted into a Shinyo Rotary Kiln (Osaka), which was heated to 850°C at a speed of 5°C/min in a nitrogen stream of 500 mL/min. After a temperature of 850°C had been reached, steam was introduced into the kiln at a speed of 10 g/h for a certain time, and the kiln was then cooled to obtain microporous carbon. Figure 1 shows the apparatus for steam activation. Yield of microporous carbon Y_s (%) was determined by equation (1):

$$Y_s = M / M_0 \times 100 \quad (1)$$

where M (g) is mass of microporous carbon obtained and M_0 is mass of cotton char.

Fig. 1 Apparatus for steam activation. A: nitrogen, B: generator of steam, C: pump, D: water, and E: rotary kiln.

2.4 Air activation

For air activation, cotton towel and not carbon was used as starting material. Sixty gram of cotton towel in a metal container measuring $250 \times 100 \times 50$ mm was heated in an electric furnace to 900°C at a speed of $5^\circ\text{C}/\text{min}$. The materials were maintained at this temperature for 1 h and then cooled to obtain microporous carbon. Yield of microporous carbon $Y_a(\%)$ was determined by equation (2):

$$Y_a = W / W_0 \times 100 \quad (2)$$

where W (g) is mass of microporous carbon obtained and W_0 is mass of cotton.

2.5 Measurement of microporosity

Specific surface area and pore volume were determined on the basis of nitrogen adsorption isotherms using a BELSORP 28SA. Specific surface area (S) was calculated using BET plots in the relative pressure range 0.01 to 0.15 [3]. The pore volume (V) was determined from the amount of nitrogen adsorbed at relative pressure 0.931 [4]. Mean pore diameter (D) was calculated from

$$D = 4V / S \quad (3)$$

with the pore system assumed to be made up of uniform cylindrical nonintersecting capillaries [5].

2.6 Procedures for adsorption of iodine and 4-nonylphenol

The amount of iodine adsorbed at equilibrium concentration 2.5 g/L was measured using JIS K 1474. The adsorption isotherms of 4-nonylphenol were obtained by adding various quantities of activated carbon to 120 mL vial tubes. An aliquot of 100 mL of $100 \mu\text{g/L}$ 4-nonylphenol solution was added to the tube and the tube capped. The tubes were then shaken in a bath maintained at 25°C for 17 h. Preliminary experiments showed that adsorption was essentially complete within 17 h. After equilibrium, a sample was taken from each tube and filtered through a glass-fiber filter paper to remove any suspended carbon. The 4-nonylphenol content of the filtrate solution was measured using a fluorescence spectrophotometer (Shimadzu RF5300PC, excitation at 221 nm and emission at 304 nm). The equilibrium amount adsorbed was calculated using the following equation:

$$X = (C_0 - C) V / M \quad (4)$$

where X is equilibrium amount of 4-nonylphenol adsorbed per gram of activated carbon (mg/g), C_0 and C are in initial and equilibrium concentration of 4-nonylphenol ($\mu\text{g/L}$), V is volume of solution (L) and M is weight of microporous carbon (mg).

3. Results and discussion

3.1 Preparation of microporous carbon

Table 1 shows the result of carbonization of cotton towel. The carbonization yield was 18 %; ash content was very low, which gives a good raw material for production of microporous carbon. The specific surface area of carbon derived from cotton was similar in magnitude to that of various wood charcoals [6].

Table 2 shows the results of steam activation. The reaction of steam activation is the so-called water gas reaction shown in equation (5), which occurred at temperature above 750°C [7].

Table 1 Carbonization of cotton towel.

Sample code	Original weight (g)	Product (g)	Yield (%)	Ash (%)	Specific surface area (m^2/g)	Pore volume (mL/g)	Mean pore diameter (nm)	Iodine adsorption capacity (mg/g)
AC0	270	48.6	18.0	0.5	389	0.175	1.80	330

Table 2 Steam activation of carbon prepared from cotton towel.

Sample code	Activation time (min)	Original weight (g)	Product (g)	Yield (%)	Specific surface area (m ² /g)	Pore volume (mL/g)	Mean pore diameter (nm)	Iodine adsorption capacity (mg/g)
AS90	90	11.0	7.7	70	648	0.298	1.84	780
AS120	120	10.1	6.3	62	736	0.401	2.18	800
AS150	150	10.3	6.1	59	843	0.426	2.02	950
AS180	180	11.8	6.1	52	873	0.510	2.34	950
AS210	210	11.3	5.8	51	970	0.455	1.88	1050

Fig. 2 Relationship between steam activation time and yield. **Fig. 3** Relationship between steam activation time and specific surface area.

Figures 2 and 3 show the effect of increasing activation time on activated carbon yield, which decreased; and on specific surface area, which showed a linear increase. Mean pore diameter, however, was not correlated with activation time.

Fig. 4 Cumulative pore-volume curve of microporous carbons prepared by steam activation. ◇:AS90, ●:AS120, □:AS150, △:AS180, ○:AS210.

In general prolongation of activation time increases mean pore diameter [7, 8]. The mean pore diameter of AS210 was unexpectedly low, which may be due to non-uniformity of reaction between the steam and fibrous carbon. The specific surface area of microporous carbon with 50 % yield was approximately 1000 m²/g. As clear from Fig. 4, which shows the cumulative pore-volume curve of microporous carbon prepared from cotton towel, the pores in all the carbon produced were made up of micropores.

Table 3 shows the result of air activation, during which the reactions noted below occurred. First there occurred a carbonization reaction of the cotton fiber with rising temperature, followed by a combustion reaction with oxygen contained in air, as shown in equation (6).

At temperature above 850°C occurred a reaction of C and CO₂ generated by combustion, as shown in equation (7). This is the activation reaction [7, 9].

Table 3 Preparation of microporous carbon by air activation.

Sample code	Activation time (min)	Yield (%)	Specific surface area (m ² /g)	Pore volume (mL/g)	Mean pore diameter (nm)	Iodine adsorption capacity (mg/g)
AA60	60	11.3	867	0.403	1.86	750

Although air activation includes a combustion reaction which decreases the weight of the carbon, it produced no lower a yield of microporous carbon than steam activation, but a smaller pore diameter.

3.2 Adsorption removal of 4-nonylphenol by microporous carbons

Figure 5 shows the isotherms of 4-nonylphenol adsorption onto microporous carbons prepared by steam activation. X (mg/g) in vertical axis and C (μg/L) in horizontal axis are equilibrium amount of 4-nonylphenol adsorbed per gram of activated carbon and equilibrium concentration of 4-nonylphenol, respectively. As shown in Fig. 5, the amount of 4-nonylphenol adsorbed was very high even in extremely dilute solution. Efficient 4-nonylphenol removal from aqueous solution was thus achieved. The isotherms were expressed by Freundlich adsorption equation with X and C used also in Fig. 5:

$$\log X = \log K + (1/N) \log C \quad (8)$$

where K and $1/N$ are the adsorption constants. The adsorption constants were estimated by linear regression analysis and are shown in Table 4. Figure 6 shows the relationship between specific surface area and constant K : the latter increased with the former. However, adsorption constant $1/N$ was not correlated with specific surface area or pore diameter.

Figure 7 shows the isotherm of 4-nonylphenol adsorption onto microporous carbons prepared by air activation. The usefulness of the material was reflected in the high adsorption at low concentration. The Freundlich adsorption constants were calculated and are shown in Table 5. This constant $1/N$ expresses the affinity between adsorbate and adsorbent and decreases in value with increasing affinity. Adsorption onto carbon, whose surface is hydrophobic, is mainly based on the London dispersion force, which is part of the van der Waals force. The more closely the adsorbate molecules in the pores are located to the surrounding pore walls, the higher the adsorption force [10].

It is known that nonylphenol ethoxylates are strongly adsorbed by activated carbon [11, 12]. The chemical

Fig. 5 Adsorption isotherms of 4-nonylphenol on the microporous carbons prepared by steam activation. ◇: AS90, ●: AS120, □: AS150, △: AS180, ○: AS210.

Table 4 Freundlich adsorption constants of 4-nonylphenol on microporous carbons prepared by steam activation.

Microporous carbon	K (-)	$1/N$ (-)	Correlation coefficient
AS90	10	0.34	0.987
AS120	39	0.32	0.983
AS150	41	0.12	0.927
AS180	72	0.14	0.907
AS210	60	0.16	0.923

Fig. 6 Relationship between specific surface area and adsorption constant K .

structure of nonylphenol, with its greater hydrophobicity due to the lack of a hydrophilic ethoxylate chain, also suggests high adsorbability, which was confirmed in the present study. The air activation method requires no boiler for steam generation, and produces carbonaceous adsorbent from textile wastes at low cost. The study results present a potential contribution to environmental preservation and recycling.

Fig. 7 Adsorption isotherm of 4-nonylphenol onto the microporous carbon, AA60, prepared by air activation.

Table 5 Freundlich adsorption constants of 4-nonylphenol on microporous carbon, AA60, prepared by air activation.

Microporous carbon	K (-)	$1/N$ (-)	Correlation coefficient
AA60	60	0.059	0.940

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