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Removal of trichloroethylene from aqueous solution by pyrolyzed Japanese cedar bark

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Abstract The bark of Japanese cedar (*Cryptomeria japonica* D. Don) was heated in an N₂ atmosphere at 300°–900°C for 3 h to investigate the surface properties of the pyrolyzed residues and their ability to remove trichloroethylene (TCE) from aqueous solutions. The specific surface areas (S_N) and total pore volumes (V_N) of the pyrolyzed barks steadily increased with rising pyrolysis temperature; no significant differences in the average pore diameters (D_N) were observed at higher temperatures (600°–900°C). The adsorption capacities of the pyrolyzed residues for TCE were determined under batch mode conditions using an aqueous solution containing 500 $\mu\text{g TCE dm}^{-3}$. The adsorption data were well fitted to the Freundlich equation. The adsorption capacity of the bark pyrolyzed at 900°C was about five times larger than that of commercial activated carbon.

Key words Removal of trichloroethylene · Adsorption · Pyrolyzed bark · Japanese cedar · *Cryptomeria japonica* D. Don

Introduction

Volatile chlorinated hydrocarbons are a major concern as potential health hazards in drinking water, because they are suspected carcinogens and are highly resistant to biodegradation in the environment. Among these agents, trichloroethylene (TCE), a degreasing and cleaning agent

for metals and electronic parts, is a common contaminant at hazardous waste sites. Since 1989 the maximum allowable concentration level for TCE in drinking water has been set at 30 $\mu\text{g dm}^{-3}$ by the Ministry of Health and Welfare of Japan in accordance with the guideline assigned by the World Health Organization.¹

Traditional clean-up methods for water contaminated with volatile chlorinated hydrocarbons include techniques such as aeration and adsorption by synthetic resins or activated carbons. For water that has high concentration of organic compounds, adsorption onto activated carbon appears to be the most effective treatment. However, high capital and regeneration costs deter widespread adoption of activated carbon adsorption,² although this method may be justified when used for separation and recovery of valuable products such as gold from dilute cyanide solution. Recently, it has been reported that carbonized slash pine bark could be used as a promising alternative for the removal of phenol from aqueous solutions.³ Abe et al.⁴ also reported that charcoals prepared at 900°C showed larger adsorption capacities for TCE and chloroform than those of commercial activated carbons, indicating the potential utility of low rank carbonaceous materials such as charcoal and peat to remove volatile chlorinated hydrocarbons from aqueous systems.

Wood barks discharged as by-products from wood industries are widely available and of little economic value. In this study we investigated the efficiency of pyrolyzed bark of Japanese cedar (*Cryptomeria japonica* D. Don) for reducing TCE in contaminated water. The effects of pyrolysis temperature and contact time on the TCE adsorption were examined.

Material and methods**Materials and analytical procedure**

The barks of Japanese cedar were air-dried and ground in a Wiley mill to pass through a 0.5-mm screen. A commercial

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activated carbon (WG-460, 8–30 mesh; Kurita Water Industry, Tokyo, Japan) was used as a reference adsorbent. A TCE aqueous solution was prepared using analytical grade TCE (1g TCE dm⁻³ in methanol) (GL Science, Tokyo, Japan) and distilled and deionized water.

Three replications of 12g of the barks in 120-cm³ crucibles were heated in a closed vessel at 300°–900°C for 3h using an electric oven. Before the heating, air in the vessel was replaced with N₂. The oven temperature was programmed to reach the desired temperature within 17°–22°Cmin⁻¹.

Specific surface areas (S_N), total pore volumes (V_N), and average pore diameters (D_N) were determined using a NOVA 1200 (Quantachrome, Boynton Beach, FL, USA) at 77°K. Outgas of the samples was carried out in vacuo at 200°C for 4h before use. The S_N was calculated from the BET plots in the relative pressure range between 0.01 and 0.15.⁵ V_N was obtained from the amount of N₂ adsorbed at the relative pressure ($P \cdot P_0^{-1} = 0.99$), and D_N was calculated using the following equation.⁶

$$D_N = 4V_N S_N^{-1} \quad (1)$$

Batch adsorption experiments

Adsorption experiments were carried out in a 110-ml glass tube stoppered by a screw cap. Each adsorbent was heated in an electric oven at 105°C for 24h before use. A known quantity of the adsorbent (1–600mg) was placed in 100ml of the TCE aqueous solution. The initial concentration of TEC in the solution was 500µgdm⁻³. The glass tubes were shaken at 20°C for 24h.

The TCE concentrations were determined using a GCMS-QP5000 (Shimadzu, Kyoto, Japan) equipped with an HS-40 head-space sampler (Perkin-Elmer, Norwalk, CT, USA). A DB-624 column (0.32mm × 60m, 1.8µm film thickness) (J & W Scientific, Folsom, CA, USA) was used. Helium was used as carrier gas (0.75MPa). The initial temperature, 40°C, was maintained for 1min and then was increased to 200°C at 10°Cmin⁻¹; it was held at 200°C for 3min. Temperatures of the injector and detector were 150°C and 230°C, respectively. Operating conditions of the head-space sampler were as follows: sample temperature 60°C, needle and transfer temperatures 120°C, thermostat

time 20min, pressurizing time 3min, injection time 0.17min, carrier gas pressure 135kPa.

Results and discussion

Yield and surface properties of pyrolyzed Japanese cedar barks

Table 1 shows the yield and surface properties of Japanese cedar barks heated at temperatures ranging from 300° to 900°C. The yield of pyrolysis solid residue decreased as the temperature rose. A large difference in the yield was observed in the temperature range 300°–400°C. Of the major components of lignocellulosics, hemicelluloses are the most thermally susceptible and decompose within the temperature range of 200°–260°C.⁷ Cellulose and lignin are more thermally stable, and their decomposition occurred at the higher temperature ranges of 325°–375°C and 250°–500°C, respectively.⁸ Therefore, a distinct change in the yield between 300° and 400°C is mainly due to the thermal decomposition of cellulose, lignin, and condensed tannin present in the bark.

Pyrolysis of lignocellulosics at 500°C or higher produces microporous chars of low surface areas. Recently, Abe et al.⁹ and Kitamura et al.¹⁰ reported that when coniferous woods were carbonized at a temperature of 600°–1000°C the specific surface areas (S_N) and total pore volumes (V_N) of the resulting charcoals decreased as the carbonization temperature increased. To improve the surface properties, activation with steam, air, or CO₂ at higher temperatures (750°–1100°C) is widely employed. In general, the greater surface area results in an increased adsorption capacity. However, Abe et al.⁴ reported that carbons with high adsorption capacity for TCE do not always have large surface areas. The S_N and V_N reflect the number of adsorption sites, whereas the average pore diameter (D_N) is considered to relate closely to the adsorption capacity.¹¹ Consequently, the availability of the adsorbent surface for the adsorbate depends on its molecular dimensions and the size of the micropores. The extent of the adsorption is also affected by the surface chemistry of the adsorbent.

The S_N , V_N , and D_N values calculated from the N₂ adsorption isotherm are listed in Table 1. Unexpectedly, the

Table 1. Yield and surface properties of pyrolyzed Japanese cedar (*Cryptomeria japonica* D. Don) barks

Pyrolysis temperature (°C)	Yield (%)	Specific surface area (S_N , m ² g ⁻¹)	Total pore volume (V_N , cm ³ g ⁻¹)	Average pore diameter (D_N , nm)
900	29.7	596	0.259	1.74
800	29.9	492	0.236	1.92
700	34.0	334	0.166	1.99
600	35.7	362	0.176	1.94
500	39.7	62	0.061	3.97
400	46.3	–	–	–
300	62.6	–	–	–
Activated carbon	–	1059	0.575	2.17

S_N and V_N values of the pyrolyzed barks increased with a rising pyrolysis temperature, whereas no significant difference in the D_N was recorded at 600°C or higher. These D_N values suggest that significant shrinkage of pores does not occur during pyrolysis at higher temperatures (600°–900°C).

Trichloroethylene adsorption

The solid–liquid contact time is an important parameter in adsorption studies. Equilibration times ranging from 2 h to 1 day have been reported for the TCE adsorption onto activated carbons^{12,15} and charcoals.⁴ Figure 1 shows the effect of contact time on the removal of TCE from an aqueous solution containing 500 $\mu\text{g TCE dm}^{-3}$ by the pyrolyzed barks at 20°C. As shown in Fig. 1, the amounts of TCE removed from the solution increased rapidly during the first few hours, then gradually increased, and finally reached equilibrium within 16–24 h.

Figure 2 shows that the adsorption isotherms of TCE at 20°C have the general shape of the type I isotherm in the Brunauer classification.¹⁴ The experimental data fit well to the Freundlich equation:

$$q = kc^{1/n} \quad (2)$$

where c is the equilibrium concentration in solution ($\mu\text{g dm}^{-3}$), q is the adsorbed phase concentration (mg g^{-1}), and k and n^{-1} are Freundlich constants. If logarithms are applied to Eq. (2), a linear relation between q and c is found:

$$\log q = \log k + n^{-1} \log c \quad (3)$$

The intercept of the straight line, $\log k$, roughly indicates the adsorption capacity, and its slope (n^{-1} , the adsorption intensity) is closely related to the affinity between adsorbate and adsorbent. When the n^{-1} value is much smaller than 1 ($0 < n^{-1} \ll 1$), the shape of the isotherm becomes a pla-

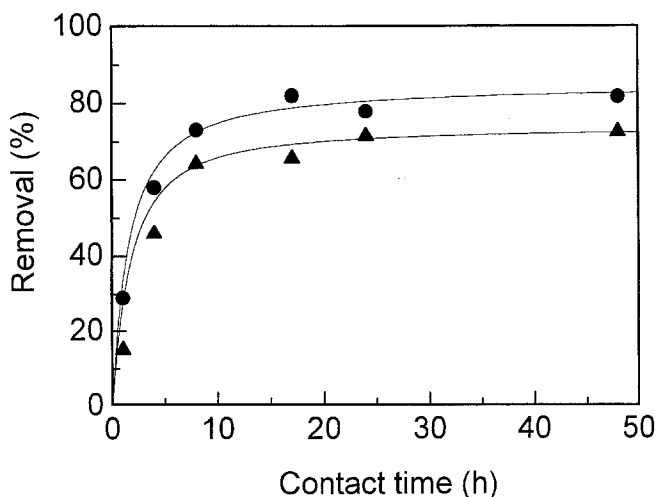


Fig. 1. Time course of trichloroethylene (TCE) adsorption onto pyrolyzed Japanese cedar, *Cryptomeria japonica* D. Don, barks. Triangles, 600°C; circles, 900°C. Adsorbents (6 mg) were shaken with an aqueous solution containing 500 $\mu\text{g TCE dm}^{-3}$ at 20°C

teau that is nearly horizontal, suggesting that the adsorbent has a certain capacity for the adsorbate over a wide concentration range of adsorbate.¹⁵ Freundlich constants of the pyrolyzed barks and commercial activated carbon for TCE are given in Table 2. The k and n^{-1} values of the pyrolyzed barks prepared at high temperatures are higher and lower, respectively, than those of commercial activated carbon, indicating that these adsorbents are promising as scavengers for TCE in contaminated waters. However, the barks pyrolyzed at low temperatures (300°–500°C) showed only limited capacity for TCE.

Conclusion

Japanese cedar barks pyrolyzed at a temperature range of 600°–900°C showed large adsorption capacities for TCE from aqueous solutions. Their high adsorption capacities may be due to the increased specific surface areas (S_N), the total pore volumes (V_N), or both without significant

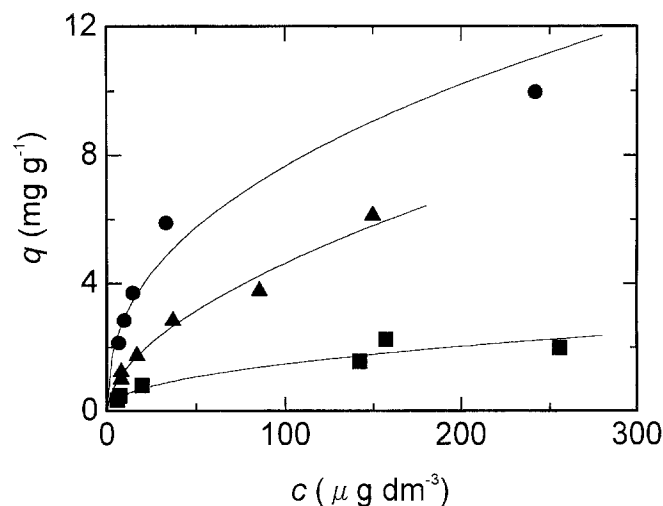


Fig. 2. Adsorption isotherms of TCE onto pyrolyzed Japanese cedar barks and commercial activated carbon. c , equilibrium concentration; q , adsorbed phase concentration; triangles, 600°C; circles, 900°C; squares, activated carbon. Adsorbent (1–600 mg) was shaken with an aqueous solution containing 500 $\mu\text{g TCE dm}^{-3}$ at 20°C for 24 h

Table 2. Freundlich constants for TCE adsorption onto pyrolyzed Japanese cedar barks and commercial activated carbon^a

Pyrolysis temperature (°C)	k	n^{-1}	r^b
900	0.85	0.488	0.992
800	0.81	0.496	0.999
700	0.55	0.420	0.991
600	0.35	0.558	0.992
500	0.14	0.700	0.991
400	0.02	0.719	0.972
300	0.01	0.736	0.997
Activated carbon	0.18	0.456	0.979

^aThe adsorbent (1–600 mg) was shaken with an aqueous solution containing 500 $\mu\text{g trichloroethylene (TCE) dm}^{-3}$ at 20°C for 24 h

^bCorrelation coefficient

shrinkage of the micropores formed. The bark carbonized at high temperatures (600°–900°C) is promising as a scavenger for TCE in contaminated water.

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