Adsorption of Chlorinated Hydrocarbons by Charcoal Produced from Coniferous Trees

Ikuo ABE1), Nobuo IKUTA1), Isao KAWAFUNE1), Hideki TATSUMOTO2) Mitsunori HITOMI3), Hiroshi KOMINAMI3) and Yoshiya KERA3)
Osaka Municipal Technical Research Institute1)
Department of Applied Chemistry, Faculty of Engineering, University of Chiba2)
Department of Applied Chemistry, Faculty of Science and Engineering, University of Kinki3)

Summary

Although it has been known since antiquity that charcoal has adsorptive ability, it is used today mainly as a fuel. Charcoal produced from broad-leaf trees is well suited as fuel because of its high density, whereas charcoal produced from coniferous trees is not since it is extremely porous. The authors discovered however that charcoal produced from such conifers as Japanese cypress (C. ohtusa) and Japanese cedar (C. japonica) has remarkable adsorption power superior to that of commercially available activated carbon. Particularly when it comes to adsorbing the small quantities of chloroform and trichloroethylene in tap water and ground water (which have recently become a health hazard), such charcoal is superior to the latest forms of fibrous activated carbon both in terms of adsorption capacity and adsorption rate. The supposition that the outstanding adsorption power of charcoal from coniferous trees is based on its pore structure was confirmed by means of studies on pore-size distribution and by scanning electron micrography.

Keywords: Charcoal, Activated carbon, Adsorption, Chloroform, Trichloroethylene

1. Introduction

Although it has been known since antiquity that charcoal has adsorptive ability, it is used today mainly as a fuel. Charcoal produced from broad-leaf trees is well suited as fuel because of its high density, whereas charcoal produced from coniferous trees is not since it is extremely porous. Charcoal was previously used as a material for basic research on adsorption. However, with the development of activated carbon, such use ceased. In an attempt to develop inexpensive adsorption materials, the authors tested charcoal, a material known from ancient times, and attempted a reassessment of its adsorption properties. Porous structure and adsorption behavior of gas and liquid phases was examined in commercially available charcoals produced from a variety of woods; it was found that charcoal from coniferous trees is more suited as an adsorption material than charcoal from broad-leaf trees [1].

It is well known that trace amounts of chloroform and trichloroethylene are contained in tap water and ground water. These compounds must be removed because of their carcinogenicity; but there is no adsorbent with high enough adsorption capacity. In the present study, charcoals were prepared from Japanese cypress and Japanese cedar and their adsorption of chloroform and trichloroethylene was investigated.

2. Experimental

2.1 Materials

Charcoals were prepared by a simple process from the sapwood of Japanese cypress (C. ohtusa) and Japanese cedar (C. japonica) obtained from a timber dealer. The wood was cut into pieces measuring 30×25×120mm. These were placed in a metal container measuring 60×50×240mm which was covered and inserted in an electric muffle furnace which was heated to 900°C at a speed of 5°C/min. The materials were maintained at this temperature for 2h and then cooled to obtain charcoal. For the sake of comparison, studies were made on the following products: two commercial charcoals (Japanese oak (Q. mongolica) and evergreen oak (Q. phillyraeoides)) as well as four representative brands of...
commercial activated charcoal (decolorizing type, water processing type, gas processing type and high performance fibrous activated carbon for the latest water purifiers). All the porous carbon was pulverized and passed through a 75µm sieve, after which it was washed with distilled water and sufficiently dried at 110°C before being used in the adsorption test.

2.2 Analytical method of chlorinated hydrocarbon

The concentration of chlorinated hydrocarbon in water was determined by the head space method with a vial and gas chromatograph Shimadzu Model GC-4CM (Japan) equipped with an electron capture detector. The head space gas in a closed vial, which had been kept at 25°C for over 2h, was injected into the gas chromatograph and the concentration was determined. The concentration of C_L (µg/l) in the standard solution for calibration was calculated by equation (1):

\[ C_L = \frac{b}{V_L + HV_G} \]  

where \( b \) (µg) is the amount of chlorinated hydrocarbon added to the vial, \( V_L \) (liters) is the volume of solution in the vial, \( V_G \) (liters) is the volume of the air phase in the vial, and \( H \) (-) is the partition coefficient of gas phase to water phase.

2.3 Procedure for adsorption of chlorinated hydrocarbon

Adsorption tests to obtain the isotherms of chlorinated hydrocarbon were carried out according to the procedure reported by Urano et al. [2]. The adsorbent (M (g)) was put into 100ml of water in a vial (water was purified by distillation, followed by treatment with activated carbon and ion-exchanger columns). A certain volume of the methanol solution of chlorinated hydrocarbon was injected by a microsyringe into the water, and the vial was sealed tightly with a butyl gum septum and an aluminum cap. The vial was set in a water-bath at 25°C and shaken for 1 day. After attaining equilibrium, the head space gas was injected into the gas chromatograph, and the equilibrium concentration \( C_L \) (µg/L) of chlorinated hydrocarbon in water was determined by the calibration curve. The amount adsorbed at equilibrium per gram of adsorbent \( X \) (µg/g) was calculated by equation (2):

\[ X = \frac{b_0 - C_L V_L}{M} \]  

where \( b_0 \) (µg) is the initial injected amount of chlorinated hydrocarbon.

To measure adsorption rate, samples of porous carbon with a particle size ranging between 53 and 75µm were inserted in a vial at a rate of 10mg. A chloroform solution of 100ml with an initial concentration of 1µmol/l was added and the vial was hermetically sealed. The solution was placed in a constant temperature bath at a temperature of 25°C and shaken regularly. The remaining concentration was then measured to obtain the amount adsorbed.

2.4 Measurement of porosity

Specific surface area and pore volume were determined based on the adsorption isotherm of nitrogen using the Carlo Erba Sorptomatic Series 1800 (Italy). Specific surface area \( (S) \) was calculated by BET plots in the relative pressure range 0.01 to 0.15 [3]. The volume of pores smaller than 15 nm in radius was calculated using the Cranston-Inkley method [4]. The mean pore diameter \( (D) \) was calculated from \( D=4V/S \), the pore system being assumed to be made up of uniform cylindrical nonintersecting capillaries [5]. Observations by electron microscope were performed with the JEOL Model JSM-5800LV.

3. Results and Discussion

Figures 1 and 2 show the adsorption isotherms of chloroform and trichloroethylene at 25°C. The adsorption isotherms were approximated by the Freundlich equation:

\[ \log X = \log K + \frac{1}{n} \log C_L \]  

where \( K \) and \( n \) are constants.

![Adsorption isotherms of chloroform from an aqueous solution onto various porous carbons (25°C).](image)

- [A], [B], [C], [D], [E], [F], [G], [H]
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Fig. 2 Adsorption isotherms of trichloroethylene from an aqueous solution onto various porous carbons (25°C).

where \( C \) is the equilibrium concentration (µg/l), \( X \) is the amount of solute adsorbed (µg/g), and \( K \) and \( 1/N \) are adsorption constants. These adsorption constants are presented in Table 1. The Japanese cypress charcoal showed remarkable adsorption capacity, greater than that of any type of activated carbon. The Japanese cedar charcoal also showed a high adsorption capacity. The commercially available charcoal likewise exhibited an adsorption capacity on a level with that of activated carbon for water purification.

In order to clarify the origin of the high adsorption capacity of the Japanese cypress charcoal, the relation with pore-size distribution was examined. Table 1 shows the specific surface area (S), the pore volume (V), the mean pore diameter (D), and the amount of chlorinated hydrocarbon adsorbed (X₁₀) at 10 µg/l. An examination of the interrelationship between surface area expressing adsorption capacity, pore volume, and \( X₁₀ \) showed that carbon with a high adsorption capacity does not always exhibit a large \( X₁₀ \) value. Fig. 3 shows the relationship between the mean pore diameter and the \( X₁₀ \) value. This shows that the smaller the D value of the carbon, the larger the \( X₁₀ \) value.

Adsorption onto adsorbents 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 [6]. The reason why the Japanese cypress charcoal has a high adsorption power is that, compared to activated carbon, it is composed of pores with a very small pore diameter, which is suited to the size of chloroform and trichloroethylene. However, pores with too small a pore diameter cannot adsorb these substances because of a molecular sieving effect.

When it comes to use as an adsorbent, it is not only necessary that the adsorption capacity be large but also that the adsorption rate be fast.

Fig. 4 shows the adsorption rate profile of the Japanese cypress charcoal, a commercial oak charcoal (deciduous charcoal, \( Q. phillyraeoides \)), and a fibrous activated carbon

Table 1. Physical properties of porous carbons and Freundlich's adsorption constants for chlorinated hydrocarbons

<table>
<thead>
<tr>
<th>Carbon No.</th>
<th>Type of carbon</th>
<th>Raw material</th>
<th>Specific surface area (S/m²/g)</th>
<th>Pore volume (V/ml/g)</th>
<th>Mean pore diameter (D/nm)</th>
<th>Chloroform</th>
<th>Trichloroethylene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>K (mg/g)</td>
<td>1/N</td>
</tr>
<tr>
<td>[A]</td>
<td>Activated</td>
<td>C. obusa</td>
<td>1,293</td>
<td>1.03</td>
<td>3.19</td>
<td>5.7</td>
<td>0.909</td>
</tr>
<tr>
<td>[B]</td>
<td>Activated</td>
<td>Coal</td>
<td>872</td>
<td>0.276</td>
<td>1.27</td>
<td>45.1</td>
<td>0.693</td>
</tr>
<tr>
<td>[C]</td>
<td>Activated</td>
<td>Coconut shell</td>
<td>1,359</td>
<td>0.344</td>
<td>1.01</td>
<td>107</td>
<td>0.639</td>
</tr>
<tr>
<td>[D]</td>
<td>Activated</td>
<td>Phenol resin</td>
<td>1,493</td>
<td>0.300</td>
<td>0.80</td>
<td>182</td>
<td>0.469</td>
</tr>
<tr>
<td>[E]</td>
<td>Charcoal</td>
<td>Q. phillyraeoides</td>
<td>95.14</td>
<td>0.053</td>
<td>2.23</td>
<td>18.0</td>
<td>0.835</td>
</tr>
<tr>
<td>[F]</td>
<td>Charcoal</td>
<td>Q. mongolica</td>
<td>314</td>
<td>0.115</td>
<td>1.46</td>
<td>25.6</td>
<td>0.818</td>
</tr>
<tr>
<td>[G]</td>
<td>Charcoal</td>
<td>C. obusa</td>
<td>641</td>
<td>0.122</td>
<td>0.76</td>
<td>213</td>
<td>0.625</td>
</tr>
<tr>
<td>[H]</td>
<td>Charcoal</td>
<td>C. japonica</td>
<td>529</td>
<td>0.122</td>
<td>0.92</td>
<td>73.1</td>
<td>0.845</td>
</tr>
</tbody>
</table>

[A] ~ [F]: Commercially available charcoals and activated carbons, [G] and [H]: trial products in our laboratory

--- (15) ---
Fig. 3  Relationship between amount of chloroform adsorbed at 10μg/L and mean pore diameter.

![Fig. 3](image)

Fig. 4  Adsorption rate profile of chloroform onto various porous carbons (25°C).

![Fig. 4](image)

Fig. 5  Scanning electron microscope photographs.

(a): Japanese cypress charcoal (C. obtusa), (b): Oak charcoal (Q. phillyraeoides), Scale bar: 10μm

which is known to have a high adsorption rate; the Japanese cypress charcoal has the fastest adsorption rate.

Fig. 5 shows a scanning electron microscope photograph of the Japanese cypress charcoal and the oak charcoal. The Japanese cypress charcoal exhibits a structure characterized by many pores surrounded by an extremely thin wall with a thickness of about 2μm, and a large number of micropores with high adsorption power opening directly onto the wall surface. This is thought to give it high contact efficiency with aqueous solution. As for oak charcoal, as the picture shows, the pore walls are extremely thick, which means low contact efficiency. Activated carbon fibers are of very low thickness and micropores open onto the fiber surface. This structure is thought to give high contact efficiency with aqueous solution and a very fast adsorption rate. However, the thickness of an activated carbon fiber, at 5-20μm, is greater than that of the pore walls of Japanese cypress charcoal.

Charcoal can be produced very simply and at low cost by charring of wood materials. Charcoal differs greatly in its pore-size distribution according to the type of tree used. If it is possible to make effective use of the natural pores in natural wood materials, we can expect an even wider range of uses. The present paper indicates the need for scientific research to focus once again on the adsorption properties of natural charcoal.

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