Sorption of Anionic Surfactants with Wood Charcoal

Itsusei FUJITA,* Jyo TOMOOKA, and Tsugiharu SUGIMURA
Kumamoto Prefectural Institute of Public Health, 4-33 Minamisendanbata-machi, Kumamoto 860
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Synopsis. The possibility of wood charcoal as an adsorbent, not as an energy source as in the past, was confirmed by the use of an anionic surfactant as the model adsorbate, and a trial sorption of polluting substances in an actual river by a wood charcoal column was conducted.

The rapidly progressing population centralization and the change of life style in urban areas are today having an extremely adverse effects on river environments. Although this has been caused by a delayed construction of basic social facilities (such as sewage disposal facilities) to cope with the increasing population, hasty perfection of social facilities would be difficult in view of the present status of Japan. In order to improve the water environment, it is therefore necessary to reduce the pollution loading amount at each disposal point. As one possible measure, there have been movements to recommend a reduction of polluting materials discarded by each home. In some parts of the country there have also been trial installations of simplified water-purification facilities at disposal points of homes or at nearby small rivers. Simplified water purification facilities include those utilizing catalytic oxidation and those using hydrophytes.

The catalytic oxidation method is a method for cleaning water by the utilization of a self-purifying action of water ways packed with contracting materials covered with a biomembrane. As contracting materials gravel[1] and wood charcoal have commonly been tried.

Wood charcoal, with a history going back to the Heian Era in Japan, was one of national necessaries of life until about 30 years ago. Its annual production sharply decreased from 2 million tons around 1955 to 40 thousand tons at present. The development of new applications of wood charcoal, therefore, not only activates its business circle, but is also expected to stimulate the average person's concern for wood as well as for the concept of "green", leading to a heightened movement fowards "green" cultivation. Wood charcoal has had two major uses: one as an energy source, and the other as a carbon material. The characteristics of wood charcoal as a carbon material are: a large inner surface area with both high reactivity and adsorptivity, high content of valuable minerals, and only a small content of hazardous components. The incorporation of wood charcoal, to which microorgraisms readily adhere, into soil improves the filtration ability and water retention of soil; efficient farming producers, therefore, have applied wood charcoal into soil. From long ago wood charcoal has been used for the filtration of well water; there has also been an idea[2] to use wood charcoal as a water-purifying agent. However, systematic studies concerning the water-purifying function of wood charcoal, which have rarely been carried out, are strongly desired. In the present study, in terms of the above-mentioned background, the possibility of wood charcoal as an adsorbent was investigated using anionic surfactants found in river water as a model substance.

Experimental

Materials and Reagents. The wood charcoal used for the adsorption experiment, a product made from lumber produced by thinning, was presented by the Federation of Kumamoto Forestry Association. The sodium alkylbenzenesulfonate, an anionic surfactant that was used for a batch process experiment, has an alkyl chain of C_{11} to C_{14} and is made by Nacalai Tesque, Inc. The other reagents used were of special reagent grade obtained from commercial sources.

Determination of Surfactants. The determination of surfactants was made by highperformance liquid chromatography.[3] Along with the method using 225 nm ultraviolet absorption, fluorescence spectroscopy using on excitation wavelength of 225 nm and fluorescence light at 285 nm was employed.

Determinations of Other Items. The determination of COD, pH, total nitrogen(T-N), ammonium nitrogen (NH_4-N), nitrite nitrogen (NO_2-N), nitrate nitrogen (NO_3-N), phosphate phosphorus (PO_4-P), and total phosphorus (T-P) was conducted according to Japan Industrial Standad (JIS) K0102. The determination of the chloride ion was made by Mohrs's method.

Sorption Study by Batch Process. One gram of crashed wood charcoal was put into a 300 cm^3 conical flask, and then 100 ml of sodium alkylbenzenesulfonate solution was added. The flask was shaken at 25 °C for 24 h, and the wood charcoal separated by centrifugation. The concentration of sodium alklbenzenesulfonate in the supernatant was measured.

Experimental Conditions of the Wood Charcoal Column for the Adsorption of River Water. A glass column packed with wood charcoal was 15 mm in inner diameter and 500 mm in length. The wood charcoal packed was of crashed irregular shapes with an average diameter of 5 mm. The packed height was 200 mm, and the temperature 25 °C. A 250 cm^3 sample of river water was filtered by suction through a GF/B glass filter, which was washed in 1 ml of methanol and 50 cm^3 of distilled water. The filtrate was passed through a wood charcoal column at a rate of 5 $cm^3 min^{-1}$ to adsorb chemical components in river water; the column effluent was collected at 200 cm^3. Similarly, the filtrate was passed through the activated-carbon column. This column-sorption experiment was triplicated, respectively. The mean concentrations of the chemical components in the eluate are tabulated in the table.

Results and Discussion

Table 1 shows data concerning the wood charcoal used: the specific surface area, ion exchange capacity,[4] chloride ion adsorption, and nitrogen content by ele-

Table 1. Physicochemical Properties of Wood Charcoal

Capacity of anion exchange	8.82×10^{-5} equiv g^{-1}
Sorbed amount of chloride	9.51×10^{-6} mol g^{-1}
Specific surface area	3.57 $m^2\,g^{-1}$
N content (elemental analysis)	0.31%

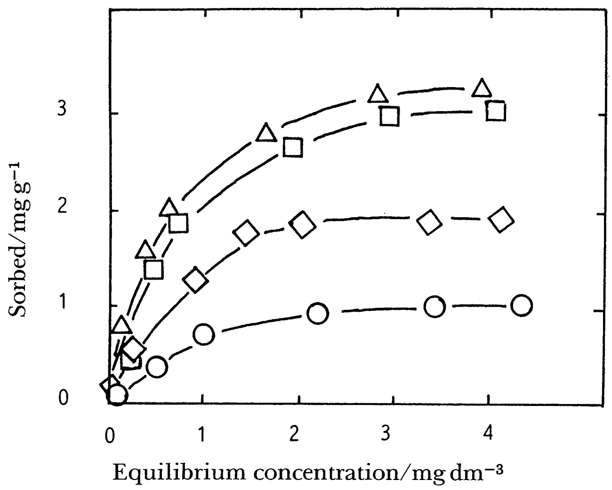

Fig. 1. Sorption isotherm at 25 °C for alkylbenzenesulfonates with wood charcoal.
○: $CH_3(CH_2)_{10}C_6H_4SO_3Na$,
△: $CH_3(CH_2)_{11}C_6H_4SO_3Na$,
□: $CH_3(CH_2)_{12}C_6H_4SO_3Na$,
◇: $CH_3(CH_2)_{13}C_6H_4SO_3Na$.

mental analysis. The specific surface area[5–8] was smaller compared to that of the powdery activated carbon generally used as an adsorbent. Basic groups, the presence of which in low-temperature (300 °C)-treated activated carbon has been reported,[5,6] are supposed to also exist in wood charcoal as a possible precursor of activated carbon.

A surfactant (more specifically, sodium alkylbenzenesulfonate in this experiment), commonly used in adsorption experiments, was used as a model organic substance to be adsorbed by wood charcoal. The experiment was conducted in a batch process. Figure 1 shows the adsorption isotherm, a general means for a comprehensive expression of the adsorption capacity or adsorbed amount of an adsorbent. The adsorbed amount did not show such an increase corresponding to the increase in the length of the alkyl chain of the surfactant.

Figure 2 and Table 2 show the results of an investigation involving the application of Freundlich's adsorption equation, which has been applied to activated carbon. In an adsorbed amount, though wood charcoal showed lower values than did activated carbon, the $1/n$ value which expresses the readiness for adsorption, showed values paralleling those of a previous evaluations.[7]

Wood charcoal, found to have the function described above, was then subjected to an investigation concerning its adsorption capacity in a column of actual river water. Generally, though the particle diameter of an adsorbent to be packed in a column is

Table 2. Freundlich's Absorption Constant

	k	$1/n$
Wood charcoal	4.46×10^{-3}	0.307

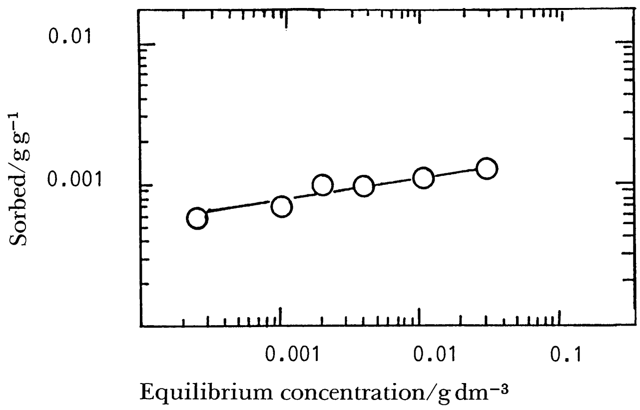

Fig. 2. Sorption isotherm at 25 °C for undecylbenzenesulfonate with wood charcoal.

desinably very small, considering practical applications (to avoid column choking by suspended matter and the removal of river water pollution by the whole experiment system) wood charcoal was powdered to an average diameter of 5.0 mm. Evaluations of the overall pollution loading amount from organic materials in river water has generally been made in terms of the biochemical oxygen demand (BOD); in this experiment, however, it was made in terms of the chemical oxygen demand (COD) owing to its operation simplicity. Evaluations were also made for linear alkylbenzenesulfonate sodium salt (LAS), the principal component of detergents deemed as a model substance of pollution loading by waste water from living, and for nutrient salts (N, P), the loading of which in lakes and ponds is becoming a problem. Water samples taken at Kengun river in a new residential quarter where there were no public water-treatment facilities, were subjected to an investigation concerning their sorption by the wood charcoal column developed in this study.

As can be seen in Table 3, wood charcoal is considered to be efficient as a factor only for the overall removal by sorption. Regarding ionic adsorption of the surfactant, NO_3^-, NO_2^-, and PO_4^{2-}, however, the values remain at the level of about 1/5 of the ion exchange capacity (Table 1). The contact time in the column is very deeply related to this.

The main purpose of using natural materials in conventional water purification processes has been as the carrier of a biomembrane for biological catalytic oxidation. In recent years there have been examples of using wood charcoal for such catalytic oxidation. There have been a number of reports stating that wood charcoal has a greater specific surface area than do conventional materials for catalytic oxidation and is excellent concerning the living conditions of soil bacteria.[2] Wood charcoal might therefore possibly become more useful through additional detailed

Table 3. Sorption of Chemical Components in River Water

	LAS	NH_4-N	NO_2-N	NO_3-N	PO_4-P	T-N	T-P	COD	pH
	$mg\,dm^{-3}$	$mg\,dm^{-3}$	$mg\,dm^{-3}$	$mg\,dm^{-3}$	$mg\,dm^{-3}$	$mg\,dm^{-3}$	$mg\,dm^{-3}$	$mg\,dm^{-3}$	
Original	1.338	5.40	0.09	1.82	0.73	9.20	1.68	30.5	7.7
Elution[a)]	0.706	4.27	0.08	1.41	0.68	7.34	1.58	28.5	7.9
Elution[b)]	0.342	4.87	0.02	0.41	0.57	6.50	1.32	25.6	7.8

a) Wood charcoal. b) Activated carbon.

investigations of the application conditions. Because an improvement in the adsorption activity by a simple treatment was claimed for activated carbon,[5)] such an improvement for wood charcoal is also of interest as a future theme of investigation.

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