JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Use of Beer Bran as an Adsorbent for the Removal of Organic Compounds from Wastewater

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Beer bran was found to effectively adsorb several organic compounds, such as dichloromethane, chloroform, trichloroethylene, benzene, pretilachlor, and esprocarb. Equilibrium adsorption isotherms conformed to the Freundlich isotherm (log−log linear). Adsorption of these organic compounds by beer bran was observed in the pH range of 1−11. At equilibrium, the adsorption efficiency of beer bran for benzene, chloroform, and dichilorometháne was higher than that of activated carbon. The removal of these organic compounds by beer bran was attributed to the uptake by intracellular particles called spherosomes. The object of this work was to investigate several adsorbents for the effective removal of organic compounds from wastewater.

KEYWORDS: Dichloromethane; chloroform; pesticide; beer bran; spherosome

INTRODUCTION

In 1993, the Environment Agency of Japan brought into effect regulations concerning organochlorine compounds such as dichloromethane and trichloroethylene. To protect water sources, it is important to keep the concentrations of these compounds in groundwater as low as possible. To remove these compounds from chemical and industrial wastewater, activated carbons are widely used in industry (*1*−*6*). However, one problem with the use of activated carbon is its high cost. The purpose of this study is to develop a new technique for treating wastewater using beer brans. Beer bran is a byproduct of making beer from barley. Therefore, beer bran is very inexpensive, with a cost of 1/100−1/50 of that of active carbon, and thus, its use would significantly lower the cost of wastewater treatment. The present study is the first to use beer bran as an adsorbent for the removal of organic compounds, such as dichloromethane, chloroform, trichloroethylene, benzene, and pesticides from wastewater.

MATERIALS AND METHODS

Apparatus. Shimadzu Model GC-6A gas chromatograph equipped with a flame ionization detector and glass column (3 m × 3 mm) packed with 20% silicon DC 550 on 60−80 mesh Chromosorb W was used for the analysis of dichloromethane, chloroform, trichloroethylene, and benzene. The column was maintained at 90 °C, and both the injection port and detector were maintained at 120 °C. The assay of pretilachlor and esprocarb was performed on a Shimadzu Model GC-14B gas chromatograph equipped with a flame ionization detector and a capillary column (ULBON HR-52, 30 m × 0.53 mm). The column was maintained at 250 °C, and both the injection port and detector were maintained at 280 °C.

Materials. Beer bran was provided by Kirin Beer, Inc. The composition of the beer bran is shown in **Table 1**. The beer bran was used for the adsorption experiment after air-drying at room temperature for 48 h. The moisture content of the beer bran was 11%. Standards of dichloromethane, chloroform, trichloroethylene, benzene, pretilachlor, and esprocarb were purchased for water analysis from Wako Pure Chemical Industries Ltd. (Amagasaki, Japan). Activated carbon (powder, coal-base carbon) was purchased for the practical grade from Wako. Wastewater samples were taken from a chamber storing wastewater collected from chemical laboratories (Kobe Pharmaceutical University). The quality of the wastewater is shown in **Table 2**.

Table 1. Composition of Beer Bran

constituent	concentration (g/100 g)
water	65.6
protein	8.8
lipid	2.5
carbohydrate	20.5
ash	2.6

Table 2. Water Quality of Wastewater from the Chemical Laboratories

substance	assayed value in wastewater
pH	∼5.5–8.9
BOD (mg/L)	∼10–33
SS (mg/L)	∼5–120
n-hexane extract (mg/L)	ND[a] ∼5
chloroform (mg/L)	ND ∼0.017
dichloromethane (mg/L)	ND ∼0.13
benzene (mg/L)	ND ∼0.08
pretilachlor (mg/L)	ND
Cd (mg/L)	<0.005
Pd (mg/L)	<0.01
Cr^{6+} (mg/L)	<0.01
As (mg/L)	ND ∼0.017
Hg (mg/L)	ND ∼0.033

[a] ND = not determind.

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10.1021/jf061082z CCC: $33.50
Published on Web 07/26/2006

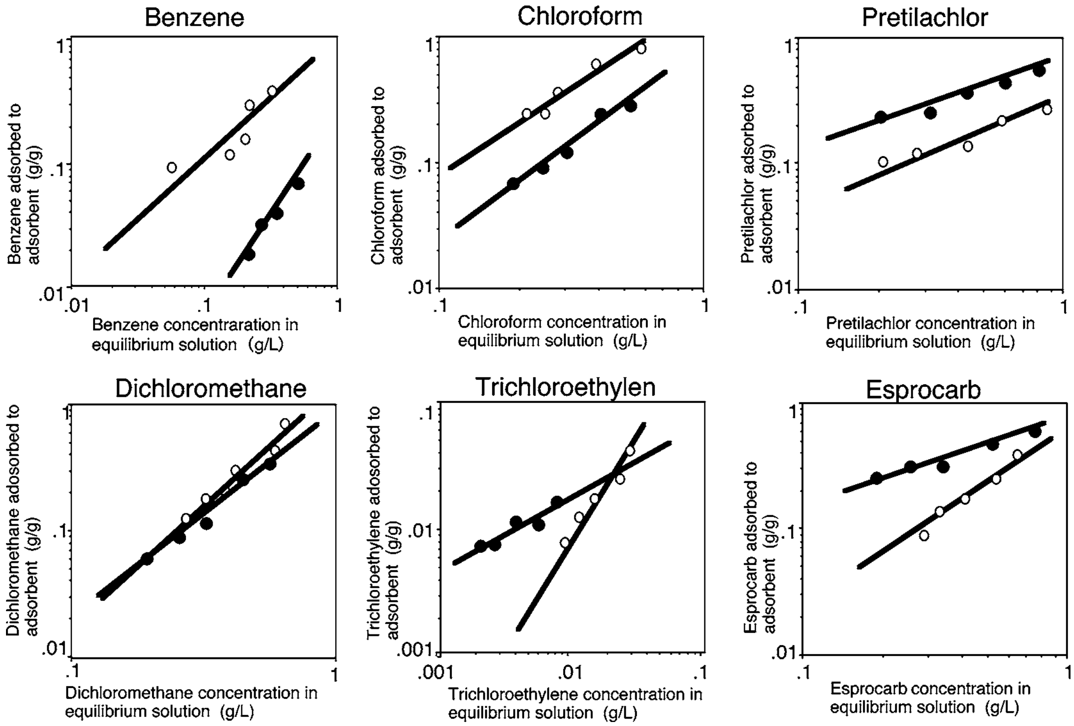

Figure 1. Freundlich's adsorption isotherm of organic compounds. Data represent the mean ± standard deviation (SD) of three separate samples. Reaction time, 3 h; chemical compounds, 1 g/L; pH 7. (○) Beer bran and (●) activated carbon.

Table 3. Removal Efficiency of Beer Bran for Organic Compounds[a]

	concentration (mg/L)		
substance	before treatment	after treatment	removal efficiency (%)
benzene	100	~22.5–24.5	76.2 ± 1.1
chloroform	100	~23.1–24.5	76.2 ± 0.7
dichloromethane	100	~13.5–22.5	81.2 ± 1.1
trichloroethylene	50	~3.54–3.59	92.5 ± 0.3
pretilachlor	5	~1.18–1.36	76.5 ± 1.8
esprocarb	5	~0.20–0.36	94.3 ± 1.6

[a] Data represent the mean ± SD of three separate samples. Beer bran, 10 g/L; reaction time, 90 min; pH 7.0.

Adsorption Experiment. A 100 mL of sample solutions containing chemical compounds or wastewater containing 0.1 g/L dichloromethane was taken in a 100 mL glass stoppered Erlenmyer flask, to which 0.1−1.0 g (dry weight basis) of beer bran, activated carbon, or all spherosomes from beer bran (1 g, dry weight basis) was added, and the solution was mixed with a stirrer at room temperature (22 ± 2 °C). The reaction mixture was filtered through filter paper (quantitative ashless No.5A Toyo Roshi, Ltd., Japan) to remove the beer bran, activated carbon, or spherosome. The initial 10 mL of filtrate was discarded because of the adsorption of chemical compounds by the filter paper. In control samples without beer bran, the subsequent filtrate after the discarded portion contained the same amount of chemical compounds as those in the original solution. The filtrate (50 mL) was placed in a separatory funnel, and 5 mL of *m*-xylene was added to the solution. The mixture was shaken for 1 min. The separated *m*-xylene layer was subjected to gas chromatography (GC) to assess the concentrations of these compounds. To quantify the evaporation loss of the chemical compounds, control experiments were performed following the same procedure as the sample treatment, except for the absence of beer bran or activated carbon. The removal efficiency of beer bran was calculated by eliminating the contribution because of evaporation loss.

Isolation of Spherosomes. Spherosomes were isolated using an improved method based on that of Moreau et al. (*7*). Samples of 1 g (dry weight basis) of beer bran were ground in 40 mL of grinding medium consisting of 20 mM sodium succinate at pH 5.6 containing 10 mM $CaCl_2$ with a mortar and pestle. The paste was filtered through four layers of cheesecloth, and the filtrate was centrifuged at 30000*g* for 20 min. The spherosome pad was removed from the surface with a spatula and washed by resuspending in 40 mL of fresh medium. This suspension was recentrifuged at 30000*g* for 20 min. This process was repeated 2 more times, and the final pellet was used as the spherosome fraction.

RESULTS AND DISCUSSION

Adsorption Rate. Table 3 shows efficiencies of beer bran for the removal of dichloromethane, chloroform, trichloroethylene, benzene, pretilachlor, and esprocarb at a reaction time of 90 min. The average removal efficiencies for these chemical compounds by beer bran range from 76.2 to 94.3%. For esprocarbe, a large removal efficiency was found in these compounds.

Adsorption Isotherm. The amount of dichloromethane, chloroform, trichloroethylene, benzene, pretilachlor, and esprocarb adsorbed in the equilibrium state was plotted against the concentration of these compounds in solution on a logarithmic scale. Equilibrium was measured after at least 3 h of contact. A linear relationship was obtained, indicating that the adsorption reaction was of a Freundlich type (**Figure 1**). At equilibrium, the adsorption efficiency of beer bran for benzene, chloroform, and dichiloromethane was higher than that of activated carbon.

Effect of pH on Adsorption. Figure 2 shows the effect of pH on the adsorption of chloroform, pretilachlor, and esprocarb by beer bran using buffer solutions at a reaction time of 90 min. Adsorption was observed over the range of pH 1−11. Therefore, it can be applied for the treatment of industrial wastewater over a wide pH range.

Application to Wastewater Treatment. When beer bran was applied to wastewater containing 0.1 g/L dichloromethane (**Figure 3**), the percent removal was slightly better than that in pure water because the pH of the wastewater was 10. This observations indicate that beer bran can be used for the treatment of wastewater.

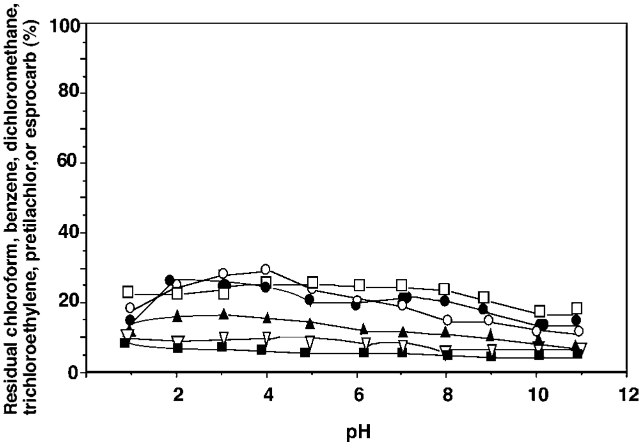

Figure 2. Effect of pH on the adsorption of chloroform, benzene, dichloromethane, trichloroethylene, pretilachlor, and esprocarb by beer bran. Data represent the mean ± SD of three separate samples. Beer bran, 10 g/L; reaction time, 90 min; chloroform, 0.1 g/L; pretilachlor, 0.005 g/L; esprocarb, 0.005 g/L. Solutions of HCl, citric acid–phosphate buffer, and carbonate buffer were used for preparation of pH 1–2, 3–7, and 8–11 solutions, respectively. (○) chloroform, (□) benzene, (▲) dichloromethane, (▽) trichloroethylene, (●) pretilachlor, and (■) esprocarb.

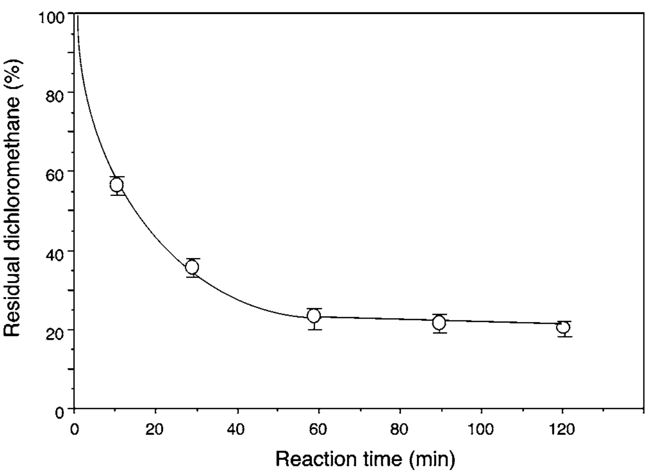

Figure 3. Efficiency of the removal of dichloromethane in chemical wastewater by beer bran. Data represent the mean ± SD of three separate samples. Beer bran, 10 g/L; dichloromethane, 0.1 g/L; pH 10. Dichloromethane (1.0 g) was dissolved in chemical wastewater, and the solution was made of 1000 mL with chemical wastewater. In addition, it was diluted 10-fold, and this 100.0 mL was used for the experiment. A 1.0 g aliquot of beer bran was added.

Adsorption Mechanism. We investigated the mechanism of removal. We have previously reported that rice bran was effective in removal of organochlorine compounds such as chloroform, dichloromethane, and benzene (*8*). Furthermore, it was confirmed that the spherosomes isolated from rice bran were effective in removing these organic compounds. Analytical and laser microscopic data have confirmed that the removal of organochlorine compounds and benzene is dependent upon the uptake of these compounds into intracellular particles called spherosomes (*8*). Spherosomes are intracellular particles about 10 μm in diameter and widely distributed among plants and fungi (*9*). Neither the function of spherosomes nor its analysis is well-understood. Spherosomes are organelles rich in lipid, and they differ in morphology and origin from large oil bodies (*10*). **Table 3** shows the removal efficiency of chloroform and esprocarb by both beer bran and spherosomes isolated from 1 g (dry weight basis) of beer bran. The removal by spherosomes was similar to that of beer bran. We regarded the special membranes to be related to the uptake of chemical compounds into spherosomes. The chemical nature of the spherosomes is uncertain. On the basis of these results, we concluded that removal by beer bran is dependent upon the uptake into spherosomes.

When the findings of this study are taken together, they suggested that the use of beer bran as an adsorbent is an efficient and cost-effective method for removal of several organic compounds from wastewater.

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Received for review April 18, 2006. Revised manuscript received June 30, 2006. Accepted July 3, 2006.

JF061082Z