Use of Tea or Coffee Lees as Adsorbent for Removal of Benzene from Wastewater

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The object of this work was to investigate several adsorbents to determine their effective removal of benzene from wastewater. Tea and coffee lees were found to effectively adsorb benzene. Equilibrium adsorption isotherms conformed to the Freundlich isotherm (log-log linear). Adsorption of benzene by tea or coffee lees was observed in the pH range of 1 to 11. At equilibrium, the adsorption efficiency of tea or coffee lees for benzene was lower than that of activated carbon. The removal of benzene by tea or coffee lees was attributed to the uptake by intracellular particles called spherosomes. Ninety minutes after application of lees to wastewater (pH 10) containing 0.1 g/l of benzene, 75 to 82% of the benzene had been removed.

Key words —— benzene, tea lees, coffee lees, spherosome, Freundlich isotherm

INTRODUCTION

Benzene has been used for a number of years as a raw material in the manufacture of ethylbenzene, styrene, cyclohexane, nylon, dyes, resins and detergents.

The hematoxicity of benzene is well established in humans and experimental animals, chronic or repeated exposure resulting in lymphocytopenia, pancytopenia, and aplastic anemia.[1–3] The estimated annual production of benzene in Japan is over 4800000 tons.[4] In 2002 the amount of benzene released and transferred in the country was 19000 tons based on Pollutant Release and Transfer Register (PRTR) data. In 1993, the Environment Agency of Japan established regulations concerning benzene (0.01 mg/l). To protect water sources, it is important to keep the concentrations of benzene in ground water as low as possible. To remove benzene from chemical and industrial wastewater, activated carbons are widely used in industry.[5–7] However, one problem with the use of activated carbon is its high cost. The object of this work was to investigate several adsorbents for the effective removal of benzene from wastewater.

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MATERIALS AND METHODS

Apparatus —— An assay of benzene 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 90°C, and both the injection port and detector were maintained at 150°C.

Materials —— Coffee lees was provided by UCC Ueshima Inc. (Kobe, Japan), Used tea leaves (sencha) were used. Both coffee and tea lees were powdered using a blender, and the composition of both is shown in Table 1. Moisture content was determined by drying a sample for 6 hr at 110°C. The nitrogen content (%) was analyzed by the Kjeldahl method.[8] The protein content (%) was calculated from the nitrogen content by multiplying it by the nitrogen-protein conversion factor 6.25. Lipids were extracted by the Bligh and Dyer method.[9] The mass of the total lipid was determined by drying an aliquot of chloroform extract in a vacuum oven overnight and weighing the resulting lipid residue. Carbohydrate (glucide) was determined by Anthrone method.[10] Tea and coffee lees were used for the adsorption experiment after air-drying at room temperature for 48 hr. Standards of benzene

Table 1. Composition of Tea and Coffee Lees

Constituent	Concentration (g/100 g)	
	Tea lees	Coffee lees
Water	7.6	8.5
Protein	29.1	13.5
Lipid	6.0	10.1
Carbohydrate	54.3	66.5
Ash	3.0	1.4

was purchased for water analysis from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Activated carbon (powder, coal base carbon) was purchased as 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 water is shown in Table 2.

Adsorption Experiment —— One hundred ml sample solutions containing benzene or wastewater containing 0.1 g/l of benzene was placed in a 100 ml glass stoppered Erlenmyer flask, to which 0.1–2.0 g (dry weight basis) of tea or coffee lees, activated carbon, or all spherosomes from the lees (1.5–3.0 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.5 A Toyo Roshi, Ltd., Tokyo, Japan) to remove the tea, coffee lees, activated carbon or spherosomes. The initial 10 ml of filtrate was discarded because of the adsorption of benzene by the filter paper. In control samples without tea or coffee lees, the filtrate remaining after this portion had been discarded contained the same amount of benzene as the original solution. The filtrate (50 ml) was placed in a separatory funnel, and 5 ml of m-xylene was added to the solution, then the mixture was shaken for 1 min. The separated m-xylene layer was subjected to gas chromatography (GC) to assess the benzene concentration. To quantify the evaporation loss of the benzene, control experiments were performed following the same procedure as the sample treatment, except for the absence of tea lees, coffee lees or activated carbon. The removal efficiency of tea or coffee lees was calculated by eliminating the contribution due to evaporation loss.

Isolation of Spherosomes —— Spherosomes were isolated using an improved method based on that of Moreau *et al.*[11] Samples of 0.5–3.0 g (dry weight basis) of tea or coffee lees were ground in 40 ml of grinding medium consisting of 20 mM sodium succinate, 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 centrifuged at $30000 \times g$ 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 $30000 \times g$ for 20 min. This process was repeated two more times, and the final pellet was used as the spherosome fraction.

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[a]– 0.017
Dichloromethane (mg/l)	ND[a]– 0.13
Benzene (mg/l)	ND[a]– 0.08
Cd (mg/l)	< 0.005
Pd (mg/l)	< 0.01
Cr^{6+} (mg/l)	< 0.01
As (mg/l)	ND[a]– 0.017
Hg (mg/l)	ND[a]– 0.033

a) ND = not determined.

RESULTS AND DISCUSSION

Adsorption Rate

Table 3 shows efficiencies of tea or coffee lees for removal of benzene at the reaction time of 90 min. The average removal efficiencies for benzene by tea and coffee lees were 72.8% and 72.1%, respectively, being very similar in the two lees.

Adsorption Isotherm

The amount of benzene adsorbed in the equilibrium state was plotted against the concentration of these compounds in solution on a logarithmic

Table 3. Removal Efficiency of Tea or Coffee Lees for Benzene

Substance	Tea lees			Coffee lees		
	Concentration (mg/l)		Removal efficiency (%)	Concentration (mg/l)		Removal efficiency (%)
	Before treatment	After treatment		Before treatment	After treatment	
Benzene	5	1.39–1.46	72.8 ± 1.0[a]	5	1.37–1.42	72.1 ± 0.4[a]

a) Data represent the mean ± S.D. of three separate determinations. Tea or coffee lees: 15 g/l; Reaction time: 90 min.

scale. Equilibrium was measured after at least three hours of contact. A linear relationship was obtained, indicating that the adsorption reaction was of a Freundlich type (Fig. 1). At equilibrium, the adsorption efficiency of tea or coffee lees for benzene was lower than that of activated carbon.

Effect of pH on Adsorption

Figure 2 shows the effect of pH on the adsorption of benzene by tea and coffee lees using buffer solutions at a reaction time of 90 min. Adsorption was observed over the range of pH 1 to 11 in a profile similar to rice bran.[12] The amount of adsorption was almost constant regardless of pH-values, because benzene adsorption by spherosomes of both lees is caused by hydrophobic interactions. Therefore, it can be applied for the treatment of industrial wastewater over a wide pH range.

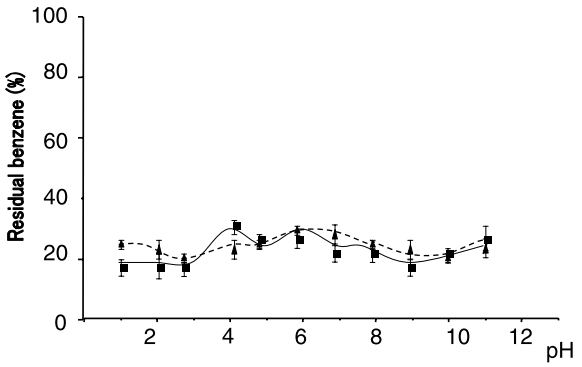

Fig. 2. Effect of pH on the Adsorption of Benzene

Data represent the mean ± S.D. of three separate determinations. Tea or coffee lees: 15 g/l, Reaction time: 90 min, Benzene: 5 mg/l, Each solution of HCl, citric acid-phosphate buffer, and carbonate buffer was used for the preparation of pH 1–2, pH 3–7 and pH 8–11 solutions, respectively. ■——■: Tea lees, ▲- - - -▲: Coffee lees.

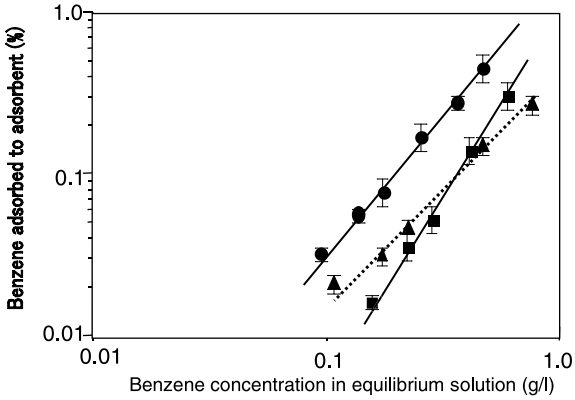

Fig. 1. Freundlich's Adsorption Isotherm of Benzene

Data represent the mean ± S.D. of three separate determinations. Tea or coffee lees and activated carbon: 1–20 g/l, Reaction time: 3 hr, Benzene: 5 mg/l, pH: 7, ■——■: Tea lees, ▲- - - -▲: Coffee lees, ●——●: Activated carbon.

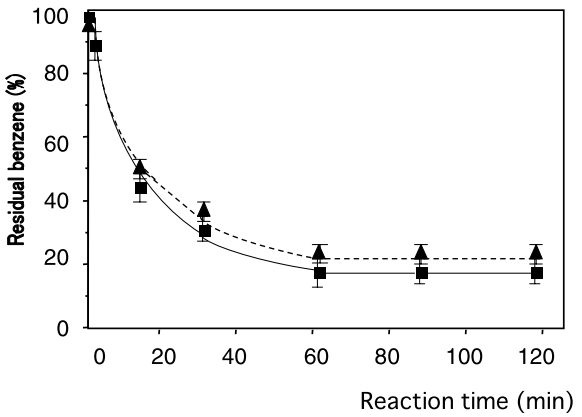

Fig. 3. Removal Efficiency of Tea or Coffee lees for Benzene Added to Chemical Wastewater

Tea or coffee lees: 15 g/l, Reaction time: 90 min, Data represent the mean ± S.D. of three separate determinations. Benzene at 0.1 g was dissolved in chemical wastewater, and the solution was extended to 1000 ml with chemical wastewater, and 100.0 ml was used for the experiment. ■——■: Tea lees, ▲- - - -▲: Coffee lees.

Table 4. Removal Efficiency of Spherosomes Isolated from Various Amounts of Tea or Coffee Lees for Benzene

	Amount of tea or coffee lees used (g)	Amount of spherosome isolated (g)	Benzene concentration (mg/l)		Removal efficiency (%)
			Before treatment	After treatment	
Tea lees	0.5	0.04	5	3.0–3.9	31.4 ± 7.8[a)]
	1.5	0.12	5	2.3–2.4	52.8 ± 0.9[a)]
	3.0	0.21	5	0.6–1.1	83.4 ± 8.8[a)]
Coffee lees	0.5	0.05	5	2.9–3.5	33.4 ± 6.9[a)]
	1.5	0.16	5	2.1–2.2	56.5 ± 1.7[a)]
	3.0	0.31	5	0.4–0.8	87.4 ± 6.8[a)]

a) Data represent the mean ± S.D. of three separate determinations. Reaction time: 90 min.

Application to Wastewater Treatment

When tea or coffee lees was applied to wastewater containing 0.1 g/l of benzene (Fig. 3), the percent removal was slightly better than that in pure water because the pH of the wastewater was 10. These observations indicate that tea and coffee lees can be used for the treatment of wastewater.

Adsorption Mechanism

We investigated the mechanism of removal. We previously reported that rice bran was effective in removal of organochlorine compounds such as chloroform, dichloromethane and benzene.[12] It was also confirmed that the spherosomes isolated from rice bran were effective in removing the organic compounds in wastewater. Analytical and laser microscopic data have confirmed that the removal of organochlorine compounds and benzene is dependent on the uptake of these compounds into intracellular particles called spherosomes.[12] Spherosomes are intracellular particles about 10 μm in diameter and widely distributed among plants and fungi.[13] Neither the function of spherosomes nor their analysis is well understood. They are organelles rich in lipid, and they differ in morphology and origin from large oil bodies.[14] Table 4 shows the removal efficiency of benzene by spherosomes isolated from 0.5–3.0 g (dry weight basis) of the tea or coffee lees; that efficiency increased in response to spherosome amount. We previously reported that the number of spherosomes in lees materials increased with the removal efficiency of organochlorine compounds and benzene by these materials.[15] We regarded the special membranes as related to the uptake of chemical compounds into spherosomes. The chemical nature of the spherosomes is uncertain. Based on these results, we concluded that removal by tea or coffee lees is dependent on their uptake into spherosomes.

Tea and coffee lees are waste matter. Taking into account their reuse and the price of activated carbon, the findings of this research are useful and contribute to the recycling of unused tea or coffee lees from an environmental viewpoint.

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