

## Efficiency of Wheat Bran for Removal of Organochlorine Compounds and Benzene from Solution

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In 1993, the Environment Agency of Japan brought into effect regulations concerning organochlorine compounds such as dichloromethane and tetrachloroethylene. To protect water sources, it is important to keep the concentrations of these compounds in ground water as low as possible. To remove these compounds from chemical and industrial wastewater, adsorption on activated carbon (Singley et al. 1979; Wood and Demarco 1980) photochemical decomposition by ultraviolet irradiation (Beltran et al. 1994; Latt et al. 1994) or aeration have usually been used. One problem with the use of activated carbon is its cost. Joyce (1979) reported that trichloroethylene was removed through an ammonia-stripping tower with an air-to-water ratio of approximately 3000 to 1, with an efficiency of removal ranging from 69 to 90 %. The aeration process transfers chemicals from water to the atmosphere without treatment. This method is, however, flawed from the viewpoint of air pollution. The object of this work was to investigate several adsorbents for the effective removal of organochlorine compounds and benzene from water.

### MATERIALS AND METHODS

Wheat bran provided by Fujiwara Inc. was used. Adsorbate solutions (100 ml) and wheat bran (0.1–1.0 g) were placed into 100 ml glass stoppered Erlenmeyer flasks and mixed with a stirrer. The reaction mixture was filtered through filter paper (quantitative ashless No.5A Toyo Roshi, Ltd. Japan) to remove the wheat bran. The initial 10 ml of filtrate was discarded because of the adsorption of chemical compounds by the filter paper. In control samples without wheat bran, the subsequent filtrate after the discarded portion contained the same amount of adsorbent as the original solution. Fifty ml of this filtrate was placed in a separatory funnel and 5 ml of m-xylene was added to the solution. The mixture was shaken for 1 min. and the separated m-xylene layer was subjected to gas chromatography (GC) to analyze these organic compounds (Adachi and Kobayashi 1995). To assess the evaporation loss of the adsorbents, control experiments without wheat bran were performed as above. Maximum loss was about 5 % ( $4.7 \pm 0.22\%$ ), although negligible loss was detected in most cases. The removal efficiency of wheat bran was calculated after taking into account the evaporation loss of the organic compounds. Adsorbents were estimated using Shimadzu Model GC-14B gas chromatograph equipped with an electron capture detector and a capillary column (ULBON HR-52, 30 m x 0.53 mm) or Shimadzu Model GC-6A gas chromatograph equipped with a flame ionization detector and

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glass column (3 m x 3 mm ) packed with 20 % silicon DC 550 on 60 - 80 mesh Chromosorb W. Both the column and injection port were maintained at 75 °C, with the detector maintained at 130 °C. Other adsorbents were tested by the same procedure as wheat bran. Treatment with soybean oil was carried out by the same procedure for removal of organochlorine compounds. The experimental conditions were as follows: soybean oil, 0.1 g/L; reaction time; 1.5 hr. Spherosomes were isolated using an improved method based on that of Moreau et al. (1980). Values are shown as means  $\pm$  SD. Data were analyzed using one-way ANOVA and, when appropriate, by the Student-Newman-Keul test. Results were considered significant at  $p < 0.05$ .

## RESULTS AND DISCUSSION

The amount of dichloromethane adsorbed at equilibrium was plotted against the concentration of dichloromethane in solution on a logarithmic scale. Equilibrium was measured after at least three hours of contact. At equilibrium, the adsorption efficiency of wheat bran was higher than that of activated carbon. A linear relationship was obtained, indicating that the adsorption reaction was of a Freundlich isotherm. Adsorption of dichloromethane and chloroform by wheat bran using buffer solutions at a reaction time of 90 min was observed over the range of pH 1-11. Generally, plants store lipids in oil bodies or spherosomes. Spherosomes are organelles rich in lipid and differ in morphology and origin from large oil bodies (Jelsema et al. 1977). The oil body has been suggested to be related

**Table 1.** Removal efficiency of wheat bran or defatted wheat bran for chloroform, dichloromethane and benzene.

Substance	Wheat bran			Defatted wheat bran		
	Concentration(mg/L) Before treatment	Concentration(mg/L) After treatment	Removal efficiency (%)	Concentration(mg/L) Before treatment	Concentration(mg/L) After treatment	Removal efficiency (%)
Chloroform	100	6.7 -15.1	87.8 $\pm$ 2.0*	100	10.4 - 19.3	76.1 $\pm$ 3.5*
Dichloro- methane	100	13.3 - 21.2	83.8 $\pm$ 1.7*	100	6.8 - 22.1	84.0 $\pm$ 3.9*
Benzene	100	9.2 - 15.5	87.5 $\pm$ 1.5*	100	10.8 - 20.3	79.5 $\pm$ 3.5*

\*Data represent the means  $\pm$  SD of four separate samples. Wheat bran :10g/L, Reaction time : 1.5hr, pH : 7.0. Chemical compounds(1.0 g) were dissolved in distilled water, and the solutions were made up to 1000 mL with distilled water. The solution was diluted 10-fold, and 100.0 mL was used for the experiment. A 1.0 g portion of wheat bran was added.

**Table 2.** Removal efficiency of wheat bran or defatted wheat bran for anthracene.

Substance	Wheat bran			Defatted wheat bran		
	Concentration(mg/L)		Removal efficiency (%)	Concentration(mg/L)		Removal efficiency (%)
	Before treatment	After treatment		Before treatment	After treatment	
Anthracene	2.50	0.30 - 0.73	85.3 ± 4.3*	2.50	0.06 - 0.20	93.3 ± 4.7*

\*Data represent the means ± SD of four separate samples. Wheat bran: 10g/L, Reaction time : 1.5hr, pH: 7.0.

**Table 3.** Removal efficiency of spherosome for organochlorine compounds and benzene.

Substance	Concentration(mg/L)		Removal efficiency (%)
	Before treatment	After treatment	
Dichloromethane	100	27 - 34	69.7 ± 0.9*
Chloroform	100	25 - 39	68.0 ± 1.1*
Trichloroethylene	50.0	5.6 - 11	83.3 ± 2.0*
Benzene	100	32 - 41	64.4 ± 1.9*

\* Data represent the mean ± SD of three separate samples. Reaction time: 1.5 hr, pH: 7.0. Spherosomes obtained from wheat bran (5g) were used for this experiment.

to the mechanism of removal, and therefore removal was examined using defatted wheat bran. Table 1 shows the removal of chloroform, dichloromethane and benzene by wheat bran and defatted wheat bran. Defatted wheat bran effectively removed these compounds within the range of 76 - 84 % after 90 min, comparable to wheat bran, which showed 84 - 88 % removal. This finding indicates that the oil body is not related to the removal of compounds by wheat bran. Next, spherosomes were examined; the uptake by spherosomes was studied by a sample reaction with soybean oil. The red color obtained by staining with sudan was confirmed by light microscopy only in the spherosomes after treatment with soybean oil. The reaction was examined using anthracene as a fluorescent compound with high lipophilicity to clarify the uptake by spherosomes. Table 2 shows the removal of this compound by wheat bran or defatted wheat bran. Anthracene in solution at 2.5 mg/L was removed at 85 % by wheat bran, and 93 % by defatted wheat bran. The fluorescence of anthracene was detected only in the spherosomes after treatment by laser micrography. Uptake was further

examined by the direct reaction of isolated spherosomes and compounds to confirm this mechanism. Table 3 shows the removal of organochlorine compounds and benzene by spherosomes isolated ( $0.291 \pm 0.198$  g) from 5 g of wheat bran. The removal by spherosomes is similar to that of wheat bran. These observations indicate directly that organochlorine compounds and benzene are taken up into spherosomes. Spherosomes are widely distributed among plants and fungi but have not been observed in animal cells (Buttrose 1963). Spherosomes tend to be prominent in seeds (Yatsu et al. 1971). The function of spherosomes is not well known. Spherosomes are intracellular oil-containing particles about  $1 \mu\text{m}$  in diameter, with an osmophilic matrix, and are bound by unusual single-line membranes (Yatsu 1972). We suspect these special membranes are related to the uptake of chemical compounds into spherosomes. Based on these results, we concluded that removal of organochlorine compounds and benzene by wheat bran is dependent on the uptake of these compounds into spherosomes.

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