Efficiency of Rice Bran for the Removal of Fe^{3+} from Solution

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Rice bran was found to adsorb Fe^{3+} effectively over the range of pH 1–12. Therefore rice bran is applicable for uses in the food industry over a wide pH range. Fe^{3+} was successfully removed from water samples with an average removal efficiency of 88.5% after 90 min when rice bran was added to water samples containing 5 mg/l Fe^{3+}. The removal of Fe^{3+} by rice bran was attributed to the chelating properties of phytic acid. Here, we report a fundamental study on the efficiency of rice bran for the removal of Fe^{3+} using a batch system on a laboratory scale and describe the elucidation of the mechanism of Fe^{3+} removal by rice bran.

Key words —— Fe^{3+}, rice bran, phytic acid, chelate

INTRODUCTION

Hydrogen sulfide is an end product resulting from the action of many varieties of bacteria on organic material containing protein.[1] Osada *et al.*[2] stated that hydrogen sulfide is one of the substances formed during the thermal processing or storage of canned meat . The reaction between Fe^{3+} and hydrogen sulfide results in the formation of sulfide darkening,[2] which causes significant damage to food. Therefore the removal of hydrogen sulfide or Fe^{3+} has been investigated.

To remove hydrogen sulfide from canned meat, adsorption on zinc acetate was reported.[1] Synthetic chelating agents such as EDTA form complexes with Fe^{3+} and therefore have the potential to remobilize Fe^{3+} from sediments and aquifers.[3] Boki *et al.*[4] reported the thermodynamics of the adsorption and desorption of hydrogen sulfide in micropores of activated carbon. Phytic acid is a major component of all plant seeds, constituting 1–3% by weight of many cereals and oilseeds.[5] The unique structure of phytic acid suggests tremendous chelating potential and it precipitates Fe^{3+} quantitatively at low pH. This property forms the basis of most methods for the determination of phytic acid.[5] O'Dell *et al.*[6] reported that phytic acid was primarily found in the outer layers of rice bran, and we also noted phytic acid in rice bran.

This study was carried out in an attempt to provide data on the removal of Fe^{3+} using rice bran.

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MATERIALS AND METHODS

Materials —— Rice bran was purchased at a local market (Daiei, Kobe, Japan). Fe^{3+} standard, phytic acid solution, cellulose, and celite were purchased from Wako Pure Chemical Industries (Amagasaki, Japan).

Procedure for Removal —— Sample solutions (100 ml) and rice bran (1.0 g) were placed in 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 rice bran. The initial 10 ml of filtrate was discarded because of the adsorption of chemical compounds by the filter paper. In control samples without rice bran, the subsequent filtrate after the discarded portion contained the same amount of chemical compound as the original solution. The concentration of Fe^{3+} in the filtrate was determined colorimetrically using the bathophenanthroline method.[7]

Determination of Fe^{3+} —— Ten milliliters of the filtrate from the removal procedure was placed in a 100-ml separating funnel with 1 ml of 10% hydroxylamine solution and 4 ml of 10% sodium acetate solution. This gave a solution with a pH value of approximately 4. Four milliliters of 0.002 M bathophenanthroline and 10 ml of isoamyl alcohol were added and mixed. After shaking, isoamyl alcohol extract solution was read at 533 nm using isoamyl alcohol to set the spectrophotometer.

A blank containing only Fe^{3+} was used to monitor the stability of Fe^{3+} with respect to time. Then the removal efficiency for Fe^{3+} was calculated with the following equation:

Removal efficiency (%) = $[(Co - Ca)/Co] \times 100$

where Co is the initial concentration of Fe^{3+} and Ca is the residual concentration of Fe^{3+} after reaction.

Determination of Phytic Acid ——— The phytic acid concentration in the rice bran was determined using the colorimetric method.[8] Five grams of rice bran was extracted with 100 ml of 2.4% HCl for 1 hr at room temperature and centrifuged. The extract was diluted to 20-fold with distilled water. Ten milliliters of diluted sample was passed through an AG1-X8 chloride anion-exchange column (200–400 mesh). Inorganic phosphorus eluted with 15 ml of NaCl 0.1 M was followed by the elution of phytate with NaCl 0.7 M. Three milliliters of this extract was pipetted into a 15-ml conical centrifuge tube and 1 ml of modified Wade reagent was added. The solution was mixed in a vortex mixer for 5 sec, centrifuged for 10 min, and the supernatant read at 500 nm using water to set the spectrophotometer.

Rice Bran without Phytic Acid ——— Rice bran without phytic acid was prepared by removing phytic acid.[9] Ten g of rice bran was treated with 200 ml of 1.2% HCl containing 10% Na_2SO_4 and stirred for 18–24 hr. After the reaction period, the mixture was filtered to give the desired rice bran without phytic acid.

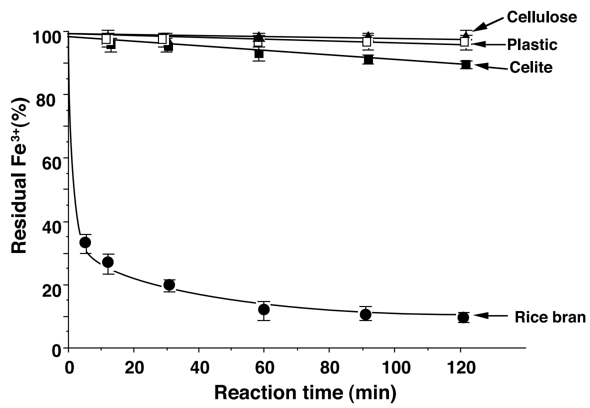

Fig. 1. Removal Efficiency of Fe^{3+} in Distilled Water by Cellulose, Celite, Plastic, and Rice Bran

Data represent the mean ± S.D. of three separate determinations. Cellulose, celite, plastic, rice bran, 10 g/l; Fe^{3+}, 5 mg/l. Fe^{3+} (1 g/l) standard solution was diluted 200-fold with distilled water, and 100.0 ml was used for the experiment. A 1.0-g aliquot of cellulose, celite, plastic, or rice bran was added.

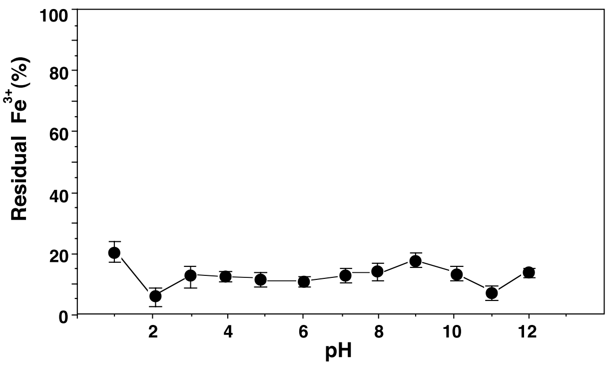

Fig. 2. Effects of pH on the Removal of Fe^{3+} by Rice Bran

Data represent the mean ± S.D. of three separate determinations. Rice bran, 10 g/l; Fe^{3+}, 5 mg/l. Fe^{3+} (1 g/l) standard solution was diluted 200-fold with buffer solution, and 100.0 ml was used for the experiment. Each solution of HCl, citric acid-phosphate buffer, carbonate buffer, and calcium hydroxide buffer was used for the preparation of pH 1–2, 3–7, 8–11, and 12 solutions, respectively. A 1.0 g aliquot of rice bran was added.

RESULTS AND DISCUSSION

Figure 1 shows Fe^{3+} removal efficiencies in distilled water as a function of time for cellulose, celite, plastic, and rice bran. Rice bran was the most effective of these substances. Fe^{3+} was removed from water with an average removal efficiency of 88.5% after 90 min when rice bran was added to distilled water containing 5 mg/l Fe^{3+}. After 60 min of reaction time, the removal appeared to plateau.

Figure 2 shows the effects of pH on the removal of Fe^{3+} by rice bran using buffer solution with a reaction time of 90 min. The removal reaction was observed over the range of pH 1–12 and exhibited a fixed value. Therefore it can be applied in the food industry over a wide pH range.

Next, we investigated the mechanism of removal. Phytates can be found in a wide variety of foods, as was demonstrated in an early study by Averill and King,[10] who reported a wide range of phytate levels influenced by the type and product of numerous cereals and nuts. Juliano[11] reported that phytic acid is abundant in rice grains and is a potent chelator of essential minerals. Phytic acid is a good antioxidant, and the iron-phytate chelate is totally inert in the Fenton reaction. Unlike most chelators, it forms a complex with Fe^{3+} that lacks iron-coordinated water and thus is unable to catalyze the formation of hydroxyl radicals in the Fenton reaction and Haber-Weiss cycle.[5] Its main function in seeds is believed to be protection against oxidative damage during storage. Graf[5] successfully applied this antioxidant property of phytic acid to the preservation of fresh fruits and vegetables. We tried to determine the phytic acid content in rice bran using the colorimet-

Table 1. Removal Efficiency of Rice Bran without Phytic Acid or Phytic Acid for Fe^{3+}

Sample	Fe^{3+} (mg/l)		
	Before treatment	After treatment	Removal efficiency (%)
Rice bran without phytic acid	5	4.9–5.0	$0.1 \pm 0.05^{a)}$
Phytic acid	5	0.42–0.56	$90.3 \pm 1.1^{a)}$

a) Data represent the mean ± S.D. of three separate samples. Reaction time, 90 min; rice bran without phytic acid, 10 g/l. Phytic acid, 50% phytic acid solution 0.1 ml.

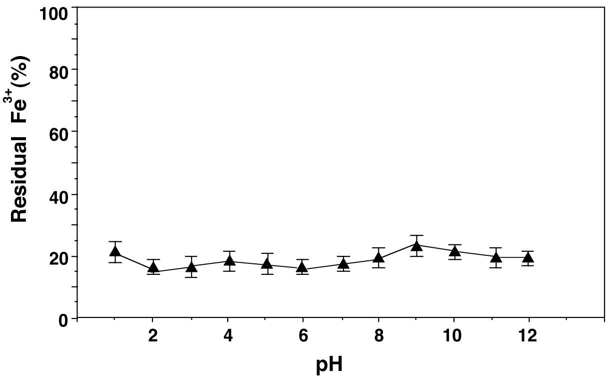

Fig. 3. Effects of pH on the Removal of Fe^{3+} by Phytic Acid

Data represent the mean ± S.D. of three separate determinations. Phytic acid, 50% phytic acid solution 0.1 ml ; Fe^{3+}, 5 mg/l. Fe^{3+} (1 g/l) standard solution was diluted 200-fold with buffer solution, and 100.0 ml was used for the experiment. Each solution of HCl, citric acid phosphate buffer, carbonate buffer, and calcium hydroxide buffer was used for the preparation of pH 1–2, 3–7, 8–11, and 12 solutions, respectively.

ric method[8] and found 3–4% phytic acid.

Kennedy and Sehelstraete[12] reported that phytic acid was primarily found in the outer layers of rice bran. De Boland *et al.*[9] reported that brown rice contained 0.89% phytic acid, whereas the germ had 3.48% and the pericap 3.37%. Our result is similar to that of de Boland *et al.* From this information, research into the removal mechanism of Fe^{3+} by rice bran has focused on the chelating properties of phytic acid. Table 1 shows the removal efficiency of Fe^{3+} by rice bran without phytic acid; no removal effect was observed. Fe^{3+} was removed from water samples with an average removal efficiency of 90.3% after 90 min when 0.1 ml of 50% phytic acid solution was added to water samples containing 5 mg/l Fe^{3+} (Table 1).

Figure 3 shows the effects of pH on the removal of Fe^{3+} by phytic acid using buffer solution with a reaction time of 90 min. The reaction was observed over the range of pH 1–12, and the removal rate by phytic acid was similar to that of rice bran. These results indicate that the removal of Fe^{3+} by rice bran can be attributed to the phytic acid contained in rice bran.

Rice bran is a by-product from polishing brown rice. Rice bran is inexpensive, costing 1/100–1/200 the price of phytic acid. Additionally, the use of rice bran is significant from the aspect of the effective utilization of waste material.

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