

The Use of Dyestuff-treated Rice Hulls for Removal of Heavy Metals from Waste Water

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Synopsis

Rice hulls, when coated with the reactive dye of Procion Red or Procion Yellow, was found to be highly effective for removal of many metal ions from aqueous solutions both in batch and column method. When 120–130 ppm solutions were used, quantitative removal could be achieved with Pb^{2+} , Cd^{2+} , and Hg^{2+} . After the adsorption of metal ions, the substrate could be recovered almost completely by treating with dilute hydrochloric or nitric acid solution, and used repeatedly.

INTRODUCTION

From the problems of environmental pollution, the removal of toxic and sometimes valuable heavy metals from sewage and industrial and mining streams has become an indispensable need and a keen attention has been paid in recent years. Though synthetic ion exchanger resins are effective, they are often unsuitable for the mass removal of heavy metals because their costs are rather expensive. Then, the need for effective and economical removal of these ions resulted in a search for unconventional methods and materials that might be useful in this field.

Many reports using agricultural by products, such as peanut and onion skin and rice-straw, etc., instead of ion exchanger resins have been documented. Of these reports, there are two kinds of methods, namely, the one using natural polymer itself^{1,2} and the other using natural polymer polymerized by formaldehyde.³⁻⁵

Rice hulls, a kind of an agricultural waste by product, are not used as fodder, because they have hard tissue containing a lot of silica, carbohydrates, and lignin. The estimated rice hulls production in Japan, however, amounts to about 3.2 million tons/year, and approximately 37% of the production is disposed by burning. We tested rice hulls modified by treatment with dyestuff as potential adsorbents for heavy metals. For this purpose Procion Red H-3B and Procion Yellow H-5G were chosen (Fig. 1). The cell walls of rice hulls consist mainly of cellulose and lignin, having a lot of hydroxyl groups in their structures, and hydroxyl groups in them are supposed to react with the synthetic dyes and rice hulls coated with reactive dye are obtained. As can be seen in the structures of two dyestuffs, many lone pair electrons of N and O atoms capable of forming coordinate bond to metal ions, metal chelates. Moreover, SO_3Na groups in their structures pay a role of strong acidic ion exchanger. For these reasons two dyestuffs mentioned above were expected to bind heavy metal ions. Then, in this

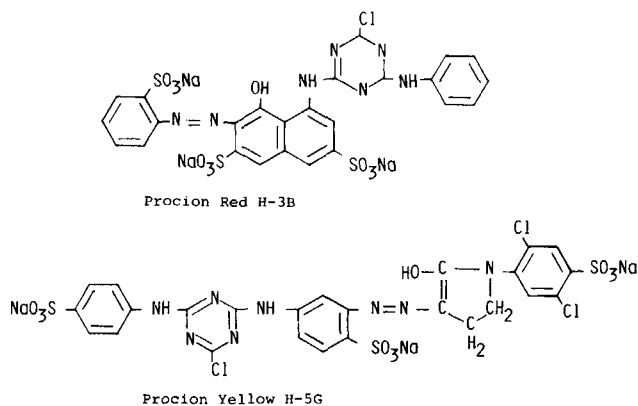


Fig. 1. Structures of procion red H-3B and procion yellow H-5G.

experiment, the adsorption abilities of dyestuff-treated rice hulls against some heavy metals were investigated.

EXPERIMENTAL

Adsorption

Rice hulls (RH) were washed with an excess of water, dried at room temperature, and ground with the mill to pass through the 2-mm screen to increase surface area and to reduce wall effects in a small packed column. A mixture of 1 part of substrate, 20–30 parts of 5% Na_2CO_3 was added to 1% aqueous solution, stirred well, and allowed to stand for 1 h at 80°C . The product was filtered and washed with an excess of water and detergent (cation type) until filtrate became clear. The residue was dried at room temperature. Rice hulls treated with Procion Red H-3B and Procion Yellow H-5G were represented to DTRRH and DTYRH, respectively, as abbreviation.

Capacity experiments were carried out by agitating 0.5 g of the substrates with 50 mL of each solution containing heavy metal ions for 2 h in stoppered Erlenmeyer flasks. The mixture was then filtered, and the filtrate was analyzed by atomic absorption spectrophotometry.

Column experiments were conducted in glass tubes (30×600 mm), using 10 g of the dry substrate in the column. Glass wool was inserted at the top to prevent the substrate from floating. Water was then slowly added to wet the packing. For column experiments, the heavy metal solution having a known concentration of heavy metal ions was passed through the column. The initial and final concentrations of heavy metal ions were determined. After the adsorption was completed, the adsorbed metal ions were eluted with acid and washed thoroughly with water. The bed used could be reused.

Analysis

A mercuric sample was analyzed with a Hiranuma HG-1 Atomic Absorption Spectrophotometer, while other samples were analyzed with a Shimadzu AA-640-01 Atomic Absorption Spectrometer. The quantity of the

heavy metal ions adsorbed on the substrate was calculated by the difference between the initial and final concentration of the solution.

RESULTS AND DISCUSSION

Capacity Experiments (Batch Methods)

The results obtained with capacity experiments (Batch methods) of RH, DTRRH and DTYRH are listed in Tables I–III. As shown, dyestuff-treated substrates were more efficient than untreated material in removing heavy metals from solutions. The removal percentage for different metal ions ranged from 39.7 to 99.8% and 39.1–100% with DTRRH and DTYRH, respectively. Especially, Hg^{2+} , Pb^{2+} , and Cd^{2+} were remarkably adsorbed. However, no effective removal of Cr^{2+} was obtained with either untreated or dyestuff-treated substrates. The reason for this remains unclear. It was also found that final pH values in all cases were always less than initial ones, suggesting that heavy metal ions are bound on the substrate, and hydrogen ions are released into the solutions, with the substrates acting as acid-form ion exchangers.

Effect of pH

It is well known that adsorption of heavy metal ions by solid substrates depends on pH values of the solution. Then, the adsorption of Hg^{2+} in different pH values was examined by using RH, DTRRH, and DTYRH. The results are shown in Figure 2. As can be seen in Figure 2, the amounts of Hg^{2+} taken up by the adsorbents reached a maximum at pH 4 and the effect of adsorption continued to alkaline range, showing that Hg–chelate formed is stable at the range of pH to alkaline side. Meanwhile, at the range of pH 3 and 2, adsorption of Hg^{2+} was inferior to those at the range of pH 4 to alkaline side, showing that the formation of Hg–chelate was influenced at those low acidic pH ranges.

Effects of Temperature

The adsorption of Hg^{2+} was tested at the temperature range from 10 to 60°C. The results in Figure 3 show that temperature did not significantly affect the adsorption.

TABLE I
Removal of Heavy Metal Ions from Solution with Rice Hulls (RH) by Batch Experiments

Compound salts	Concentration (ppm)		Solution (pH)		Cation sorbed (mg/g)	Percentage removal
	Initial	Final	Initial	Final		
CuCl_2	100.0	64.2	5.6	5.0	3.58	35.8
$\text{Pb}(\text{NO}_3)_2$	120.0	31.0	5.5	4.8	8.90	74.2
ZnCl_2	100.0	55.4	6.3	5.9	4.46	44.6
CdCl_2	130.0	58.2	6.5	5.9	7.18	55.2
$\text{K}_2\text{Cr}_2\text{O}_7$	150.0	90.1	5.1	5.7	5.99	39.9
HgCl_2	130.0	43.3	6.4	4.4	8.67	66.7
$\text{Ni}(\text{CH}_3\text{COO})_2$	100.0	44.2	6.7	6.2	5.58	55.8

TABLE II
Removal of Heavy Metal Ions from Solution with Dyestuff-Treated (Red) Rice Hulls by Batch Experiments

Compound salts	Concentration (ppm)		Solution (pH)		Cation sorbed (mg/g)	Percentage removal
	Initial	Final	Initial	Final		
CuCl ₂	100.0	21.2	5.6	4.6	7.88	78.8
Pb(NO ₃) ₂	120.0	0.24	5.5	4.1	11.98	99.8
ZnCl ₂	100.0	24.9	6.3	5.1	7.51	75.1
CdCl ₂	130.0	1.04	6.5	5.2	13.00	99.2
K ₂ Cr ₂ O ₇	150.0	90.5	5.1	5.0	5.95	39.7
HgCl ₂	130.0	9.55	6.4	3.8	12.05	92.7
Ni(CH ₃ COO) ₂	100.0	38.4	6.7	5.0	6.16	61.6

TABLE III
Removal of Heavy Metal Ions from Solution with Dyestuff-Treated (Yellow) Rice Hulls by Batch Experiments

Compound salts	Concentration (ppm)		Solution (pH)		Cation sorbed (mg/g)	Percentage removal
	Initial	Final	Initial	Final		
CuCl ₂	100.0	30.0	5.6	4.6	7.0	70.0
Pb(NO ₃) ₂	120.0	0	5.5	4.2	12.0	100.0
ZnCl ₂	100.0	38.7	6.3	5.2	6.13	61.3
CdCl ₂	130.0	21.71	6.5	5.3	10.83	83.3
K ₂ Cr ₂ O ₇	150.0	91.35	5.1	5.1	5.87	39.1
HgCl ₂	130.0	8.9	6.4	3.7	12.13	93.3
Ni(CH ₃ COO) ₂	100.0	39.2	6.7	5.2	6.08	60.8

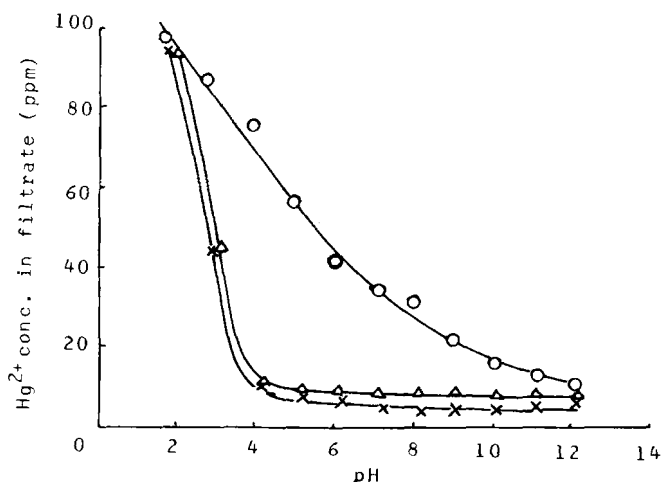


Fig. 2. Effect of pH on the uptake of Hg²⁺ from HgCl₂ (130 ppm) using 0.5 g RH ○, DTRRH △, and DTYRH (X).

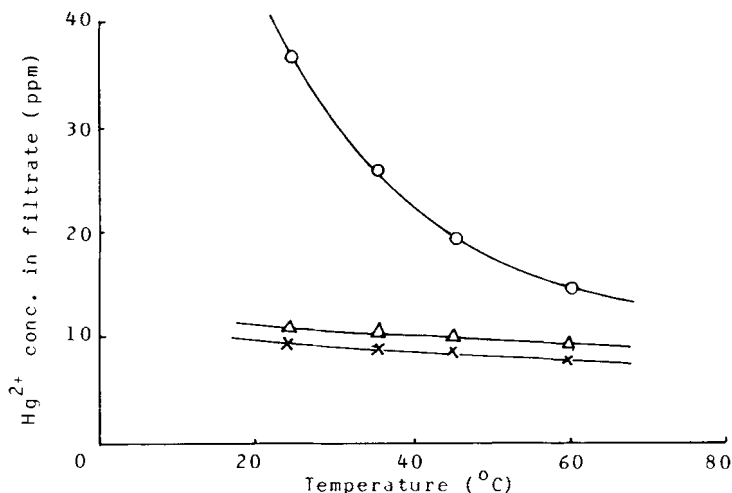


Fig. 3. Effect of temperature on the uptake of Hg^{2+} from HgCl_2 (130 ppm) using 0.5 g RH \circ , DTRRH \triangle , and DTYRH (X).

Removal of Hg^{2+} from 150 ppm Solutions

Table IV gives results for the several experiments of removal of Hg^{2+} from 150 ppm solutions by using the packed column of RH, DTRRH, and DTYRH. As can be seen from Table IV, all of Hg^{2+} were completely removed for the short time by RH, DTRRH, and DTYRH and 150 ppm of initial concentration changed to 1.25, 0.06, and 0.05 ppm in the final effluents.

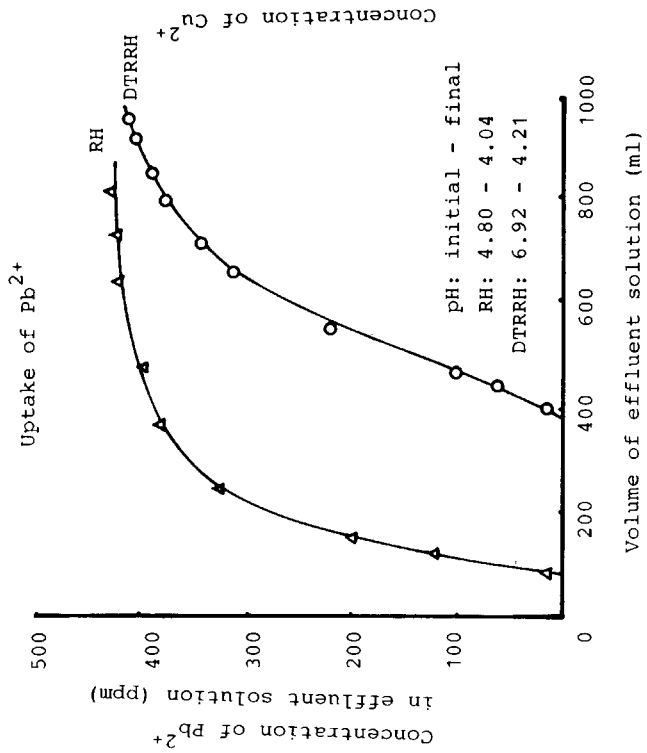
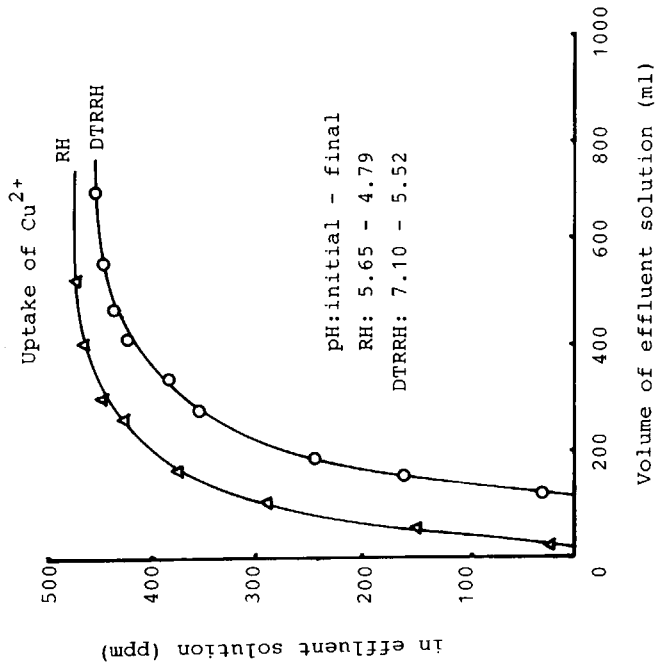
Several experimental results of the removal of other heavy metals (Pb, Cu, Cd, and Ni) from effluents on packed column are shown in Figure 4. When about 500 ppm metal solutions passed through columns packed with 10 g of each adsorbents, all of the heavy metals tested were completely removed (to 0.01 ppm) from the first 50–400 mL of the effluents.

In order to determine the degree of competitive adsorption among various heavy metal ions for the adsorbent, DTRRH was packed in column and treated with a solution which contained 75 ppm each of the following cations: Pb^{2+} , Cu^{2+} , Cd^{2+} , and Ni^{2+} . The results in Figure 5 show that the selective order of metal adsorption by DTRRH, based on mg adsorbed per g substrate, is Pb, Cu, Cd, and Ni. These results are as same as those of Larsen and Schierup.⁶ On the molar basis, however, the selective adsorption

TABLE IV
Removal of Hg^{2+} from Solution on a Packed Column of Substrate^a

	RH	DTRRH	DTYRH
Cation conc in feed (ppm)	150	150	150
Conc of cation in effluent (ppm)	1.25	0.06	0.05
Initial pH	6.4	6.4	6.4
Final pH	4.4	3.9	3.8

^a Hg^{2+} as aqueous HgCl_2 ; columns were packed with 10 g substrate to a height of 16 cm. Flow rate was 2–3 mL/min.



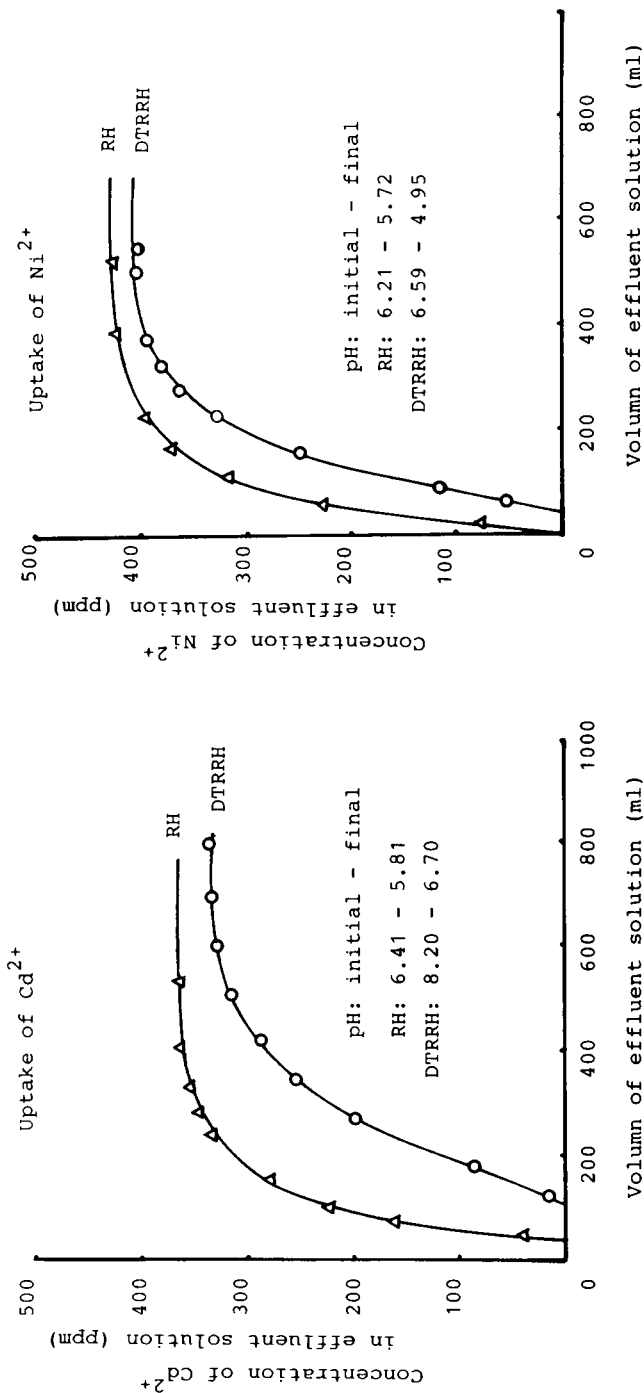


Fig. 4. The uptake of Pb²⁺, Cu²⁺, Cd²⁺, and Ni²⁺ on packed column. Flow rate: 5 mL/min. Cation concentrations in feed, RH, DTRRH (ppm): (Pb²⁺) 410, 420; (Cu²⁺) 4.60, 4.50; (Cd²⁺) 370, 340; (Ni²⁺) 415, 400.

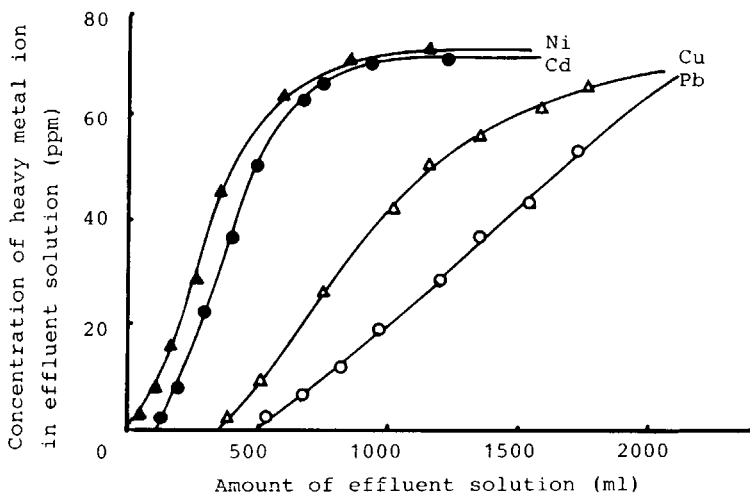


Fig. 5. Competitive adsorption curves of a mixture of all metals in column method: column size 30×600 mm; flow rate 5 mL/min; cation conc in feed 75 ppm; substrate 10 g DTRRH

sequences of Cu, Pb, Ni, and Cd are comparable to those reported for the order of stability of organometallic chelates.⁷⁻¹⁰

Regeneration Experiments

The recovery of heavy metals from the adsorbent used is a significant problem from the viewpoint of the environmental pollution. Then, we examined the recovery of Hg^{2+} and Pb^{2+} from loaded DTRRH and DTYRH by column method. The experimental results are given in Tables V. A packed columns of DTYRH and DTRRH were contacted with HgCl_2 or $\text{Pb}(\text{NO}_3)_2$ solution ($\text{Hg}^{2+}, \text{Pb}^{2+}$: 150 ppm), stripped with 1N HCl (100 mL) and washed with an excess of water to regenerate the hydrogen-form ion ex-

TABLE V
Removal of Hg^{2+} and Pb^{2+} on a Packed Column,^a Regeneration of Substrate and Second Use

Column	F		R		S	
	Hg^{2+}	Pb^{2+}	Hg^{2+}	Pb^{2+}	Hg^{2+}	Pb^{2+}
Cation conc in feed (ppm)	150	150			150	150
Total cation bond (mg Hg^{2+} or Pb^{2+} / g substrate)	29.99	22.27			29.98	20.34
Eluent			1N HCl	1N HNO ₃		
Total eluent (mL)			100	100		
Max conc of Hg^{2+} or Pb^{2+} in eluent (ppm)			5200	6060		

^a Hg^{2+} and Pb^{2+} as aqueous HgCl_2 and $\text{Pb}(\text{NO}_3)_2$, columns (20×400 mm) were packed with 5 g substrate. Flow rate: 2-3 mL/min. F=first adsorption experiment; R=regeneration experiment; S=second adsorption experiment

changer. The column was contacted again with HgCl_2 or $\text{Pb}(\text{NO}_3)_2$ solution in second adsorption experiment. As can be seen in Table V, both experimental results of first and second column adsorption tests were similar. The packings were thus about as active in taken-up Hg^{2+} and Pb^{2+} after they were regenerated as they had been when fresh.

In the regenerative experiments. 1N HCl (100 mL) and 1N HNO_3 (100 mL) were used as eluent. In these experiments the concentration of Hg^{2+} and Pb^{2+} were found to go up to 5200 and 6060 ppm in the effluent, respectively. These results indicate that almost complete recovery of heavy metal ions was achieved.

CONCLUSION

Summarizing the results obtained concerning the capacity, column, and regenerative experiments with dyestuff-treated rice hulls, DTRRH and DTYRH were found to be efficient adsorbents in batch or column experiments using known salt solutions. The adsorption appears to be pH-dependent. Throughout the adsorption experiments mentioned above, any leakage of dyestuff from the substrate was not observed, proving that binding of dyestuff with the rice hulls was remarkably strong not only at neutral to alkaline side but also at low pH's. This point counts among merits of dyestuff-treated rice hulls. These treated hulls may be potentially useful for treating waste water.

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