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MODIFIED *HARDWICKIA BINATA* BARK FOR ADSORPTION OF MERCURY (II) FROM WATER

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Abstract—*Hardwickia binata* bark was found to have a good sorption capacity for mercury (II). Colour leaching can be prevented and the physical characteristics of the bark can be improved by treatment with formaldehyde in acidic medium. Studies indicated that the sorption of Hg(II) increases as the pH increases and a contact time of 2 h was found to be optimum. The effect of concentration shows that modified bark can remove most of the Hg(II) from water if its concentration is below 20 mg/l and sorption of mercury conformed to the Freundlich adsorption isotherm. The presence of light metal ions interferes with the sorption of mercury. Mg(II) at a concentration of 200 mg/l interferes with sorption to a maximum extent. Among the different anions, it was observed that sorption of mercury was maximum for acetate and nitrate (97%). The break-through sorption capacity determined by conducting a column experiment was observed to be 21 mg/g.

Key words—mercury removal, wastewater treatment, bark, sorption

INTRODUCTION

Although it has been known for many centuries that mercury is poisonous to animals and humans, it was not until the late 1950s that extreme toxicity to humans became evident. The addition of mercury through waste discharges into natural bodies of water poses serious problems because of probable entry of mercury into the food chain. Consequently, removal of mercury in water and wastewater assumes importance. Some of the major industries discharging mercury in their effluents are chlorine manufacturing, switchgear/batteries, paints, fertilizers and pharmaceuticals.

Mercury is commonly removed from wastewaters by the following methods:

- —chemical precipitation
- —conventional coagulation;
- —lime softening;
- —adsorption;
- —ion exchange; and
- —reverse osmosis.

High capital and regeneration costs of activated carbon and ion exchange resins have resulted in a search for a suitable alternative sorbent and to this end bituminous coal was investigated as a sorbent for removing mercury from water (Pande and Chaudhuri, 1981). A limited study (Pande and Chaudhuri, 1982) indicated the potential of coal surface modification through chemical pretreatment in enhancing mercury sorption. Fly ash, an industrial solid waste of thermal power plants, is also one of the least expensive and most unconventional adsorbents. Zinc and organic acids have been removed from aqueous solutions using fly ash (Prabhu *et al.*, 1981; Ahmed *et al.*, 1983). The use of modified tree barks has been investigated for removal of heavy metals by various workers (Ballard *et al.*, 1941; Vaughn, 1967; Randall *et al.*, 1975; Pawan Kumar and Dara, 1980, 1982).

This paper deals with investigations on the use of *Hardwickia binata* bark.

EXPERIMENTAL METHODS

The bark sample was procured locally and dried. It was ground in order to increase the surface area and to reduce the wall effects in the small packed columns. The mean particle size used was 0.18 mm. Two parts of this powder were treated with 20 parts of 0.2 N H_2SO_4 and five parts of 39% HCHO. It was kept in an oven at 50°C for 6 h and occasionally stirred. The product was washed with double distilled water several times, dried at 60°C and then powdered. This powder was used for the study. Formaldehyde (HCHO) polymerized and insolubilized the coloured, water soluble tannins from the bark.

Chemicals and glassware

All chemicals used were of analytical grade. Stock mercury solution (1000 mg/l) was prepared from analytical reagent grade and this was used to prepare a working solution for other experimental work. Distilled water was used in the experiments. All glassware used was properly washed with potassium permanganate, oxalic acid and nitric acid to minimize interference in the mercury estimation.

Batch studies

Batch sorption tests were performed at room temperature and the reaction mixture consisted of a total volume of 100 ml of 100 mg/l of Hg^{2+} and 1 g of sorbent. The reaction mixture was placed in a stoppered glass bottle and agitated

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in a rotary shaker. At the end of the desired contact time, bottles were removed from the shaker, contents were filtered through Whatman No. 1 filter paper and analysed for mercury. pH of the reaction mixture was recorded initially and at the end of the experiment using a digital pH meter (Control Dynamics).

Column studies

Downflow column studies were conducted using a 20 mm i.d. glass column. Ten g of the bark was suspended in distilled water for about 15 min and then transferred to a glass column. Glass wool was kept at the bottom and at the top of the bark powder so that it is not lost with the liquid flow nor will it float.

Mercury was analysed by using a Coleman MAS-50 mercury analyser and other metal ions were estimated by using a Perkin-Elmer 372 atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Effect of pH on uptake of Hg^{2+}

The effect of pH on the equilibrium mercury concentration is presented in Fig. 1. It is observed from this figure that the sorption of mercury increases with increase in pH (5.38 mg/g at pH 2.4 to 9.58 mg/g of bark at pH 12). This increase in the sorption of mercury was also observed by Karthikeyan and Chaudhuri (1986). High sorption of mercury by the bark and high pH values is indicative of chelation or enhanced ion exchange. But for all subsequent experiments, a pH of 6.0 was employed in order to ensure that the mercury is not precipitated as the hydroxide. The final pH of the reaction mixture remained between pH 2.3 and 3.6 during the experiment when the initial pH of the reaction mixture varied from 2.4 to 10.0. But at an initial pH of 12.0, the final pH increased to 9.5 (Fig. 2) which may be due to precipitation of mercuric hydroxide.

Time of equilibrium

The concentration of the mercuric chloride solution used for the experiment was 100 mg/l Hg^{2+}. The initial pH of the solution was adjusted to 6.0. One hundred ml of 100 mg/l Hg^{2+} solution was agitated with 1 g of the bark for different periods of contact time. The effect of contact time on adsorption of mercury (II) is presented in Fig. 3. This figure shows that adsorption increased steadily as the time of contact increased up to 2 h beyond which there was not much difference. Therefore, a contact time of 2 h was used for all subsequent experiments using this bark.

Figure 4 represents a plot of $\ln(C_{A0}/C_A)$ vs t (h) where

C_A = concentration after time t (mg/l)
C_{A0} = initial concentration of reactant (mg/l)

which shows a straight line. This yielded the following relation

$$(C_{A0}/C_A) = 1.57t^{0.25}.$$

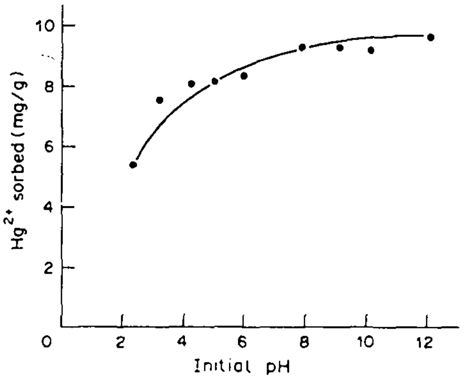

Fig. 1. Effect of pH on the removal of Hg^{2+} by *Hardwickia binata* bark.

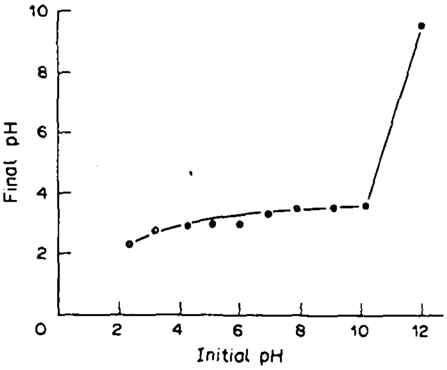

Fig. 2. Relation between initial and final pH.

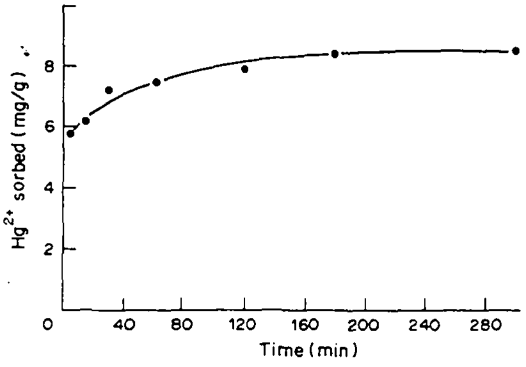

Fig. 3. Effect of contact time on the removal of Hg^{2+} by *Hardwickia binata* bark.

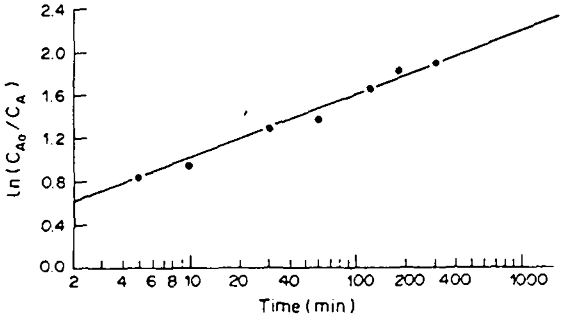

Fig. 4. Effect of contact period on adsorption.

Table 1
Hg²⁺ c
Initial
5.0
10.0
20.0
30.0
50.0
70.0
100.0
200.0
400.0

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Table 1. Effect of concentration on sorption of mercury (Hg^{2+})

Hg^{2+} conc. (mg/l)		Final	Hg^{2+} sorbed	Hg^{2+} removed	
Initial	Final	pH	(mg/g)	(%)	k (h^{-1})
5.0	0.241	3.4	0.48	95.18	1.52
10.0	0.241	3.4	0.98	97.59	1.86
20.0	0.630	3.3	1.94	96.85	1.73
30.0	2.26	3.3	2.77	92.46	1.20
50.0	9.10	3.2	4.09	81.80	0.85
70.0	14.10	3.2	5.39	79.86	0.80
100.0	28.20	3.2	7.18	71.80	0.63
200.0	103.50	3.2	9.65	48.25	0.33
400.0	265.00	3.2	13.50	33.75	0.21

Effect of concentration

One hundred ml of solution with mercury concentrations varying from 5 to 400 mg/l at pH 6.0 was agitated in each case with 1 g of bark powder for 2 h. The results of the experiment are shown in Table 1. From this data the first order reaction rate constant (k) was found using the following relation

$$k = 1/t \ln C_{A0}/C_A$$

and the values of k are also shown. It was found that there was an increase in the sorption of mercury as the initial concentration increased but the % removal of Hg^{2+} decreased (Fig. 5). At low concentrations (below 20 mg/l Hg^{2+}) sorption was 95–97% This suggests that modified *Hardwickia binata* bark can remove most of the Hg^{2+} from water if its concentration is below 20 mg/l. Figure 6 shows a graph of Hg^{2+} sorbed per gram of the bark vs residual concentration of Hg^{2+}. Positive adsorption results in the removal of solutes from solution and their concentration at the surface of the solids, to such time as the concentration of the solute remaining is in dynamic equilibrium with that at the surface (Weber, 1971). The preferred form for depicting this distribution is to express the quantity, q_e, being the amount of solute adsorbed per unit weight of solid adsorbent, and C, the concentration of solute remaining in solution at equilibrium. From the results of this experiment it was observed that adsorption of Hg^{2+} on *Hardwickia binata* bark conformed to the Freundlich adsorption isotherm.

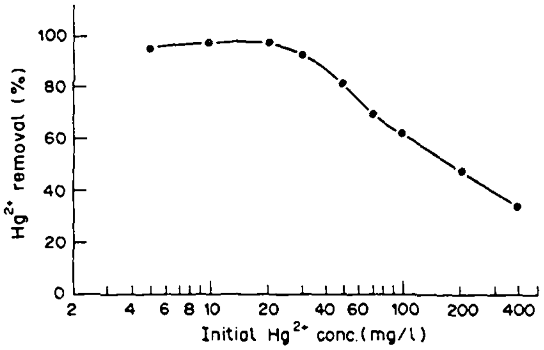

Fig. 5. Effect of concentration on the sorption of Hg^{2+}.

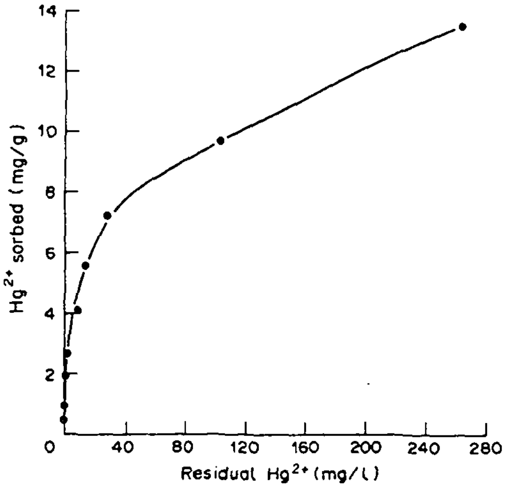

Fig. 6. Adsorption isotherm of Hg^{2+}.

Data are usually fitted in the logarithmic form of the equation by

$$\ln q_e = \ln k_F + 1/n \ln C$$

where K_F and n are constants.

The Freundlich isotherm is presented in Fig. 7 which shows a logarithmic plot of q_e vs C giving a straight line with a slope of $1/n$ and an intercept equal to the value of $\ln k_F$. The intercept $\ln k_F$ is roughly an indicator of sorption capacity and the slope is an

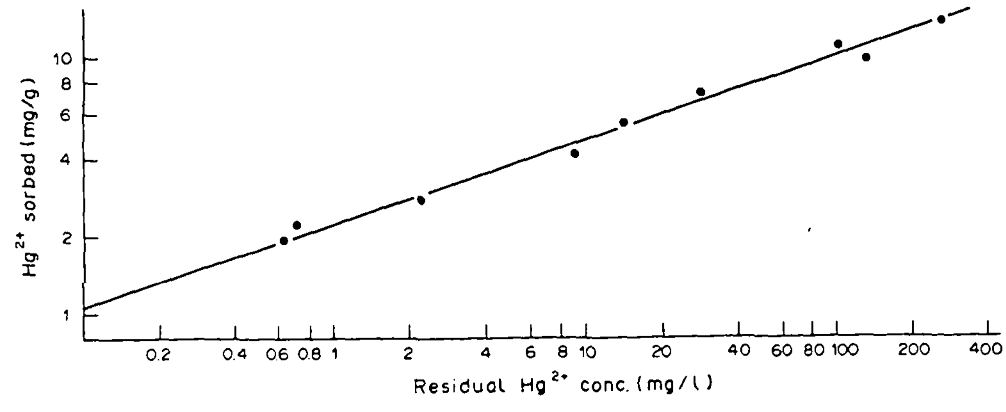

Fig. 7. Freundlich adsorption isotherm.

adsorption intensity (Weber, 1971). This plot yielded the relationship shown below:

$$q_e = 1.07\ (\mathrm{Hg})^{0.3243}.$$

The correlation coefficient obtained for the Freundlich adsorption isotherm was found to be 0.9084. To test the significance of the correlation coefficient, Student's *t*-test was applied. The *t*, calculated, was found to be 5.322 and the critical value from the table for $(n - 2)$ degrees of freedom was 5.208 at 1% level of significance. Figure 8 presents the plot of mercury concentration vs first order reaction rate constant (k). An examination of the effect of mercury concentration on the relative rate constant (k) provides additional information regarding the mercury sorption process. Weber (1967) reported that the relationship between soluble concentration and the rate of sorption helps to describe the mechanism of removal taking place. In cases of strict surface adsorption, a variation of rate should be proportional to the first power of concentration; however, when pore diffusion limits the sorption process, the relationship between concentration and the rate of reaction will not be linear (Knocke *et al.*, 1981). Figure 8 shows that a direct linear relationship does not exist in the case of mercury sorption on *Hardwickia binata* bark. It seems likely that pore diffusion limits the overall rate of mercury sorption.

Effect of light metal ions

The effect of Na^+, K^+, Ca^{2+} and Mg^{2+} on the uptake of Hg^{2+} by the *Hardwickia binata* bark was investigated. Batch experiments were conducted using 100 ml of 100 mg/l Hg^{2+} solution, adding different concentrations of Na^+, K^+, Ca^{2+} and Mg^{2+} (50–200 mg/l) and agitating the contents for 2 h. The results are presented in Fig. 9 which showed that the percentage sorption of Hg^{2+} from solution was 79% in the absence of any light metals studied. This adsorption decreases as the concentrations of light metals increase in all cases which clearly showed that the presence of light metal ions interfered in the removal of mercury from the aqueous systems by the bark. This interference was maximum in the case of Mg^{2+} (Hg^{2+} removal 28%) at a concentration of 200 mg/l. However, this is contrary to the findings of Thiem *et al.* (1976) who observed an increase in mercury sorption on activated carbon with an increasing Ca^{2+} concentration. This reduction in mercury adsorption might be due to a competitive ion effect between light metal ions and mercury for the sorption sites on the bark.

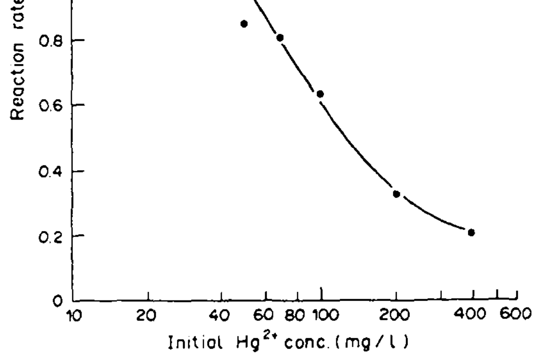

Fig. 8. Effect of Hg^{2+} concentration on the observed rate of sorption.

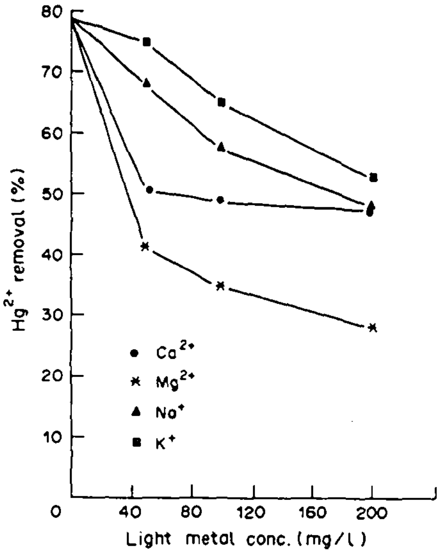

Fig. 9. Effect of metal ions on the removal of Hg^{2+}.

Effect of anions

In order to examine the effects of different anions on mercury sorption by this bark, experiments were conducted with salts such as mercury acetate, mercury nitrate, mercury sulphate and mercury chloride. One hundred ml of 100 mg/l of each Hg^{2+} at pH 6.0 was agitated with 1 g of the bark substrate for 2 h. The results of the experiments are shown in Table 2.

It was observed that the sorption of mercury was maximum for acetate and nitrate (97%) whereas in case of sulphate it was 92%. This sorption was found

Table 2. Effect of anions on sorption of mercury (Hg^{2+})

Anions	Final pH	Final Hg^{2+} (mg/l)	Hg^{2+} sorbed (mg/g)	Hg^{2+} removed (%)
Acetate	5.2	3.0	9.70	97.0
Nitrate	3.4	2.5	9.75	97.5
Sulphate	3.5	8.0	9.20	92.0
Chloride	3.5	24.5	7.55	75.5

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to be minimum for chloride (75.5%). It is interesting to note that Friedman and Masri (1973) concluded, based on their studies on sorption of mercury by modified wools and polyamino acids, that the presence of chloride ions, but not sulphate ions, in aqueous media decreased the extent of binding of mercury to both native and modified wools.

Competition among cations

One hundred ml of solution containing 20 mg/l each of Hg^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+} and Cu^{2+} was shaken with 1 g bark for 2 h. It was observed that sorption of these metals on the bark was found as shown below:

Hg^{2+} = 1.05 mg, Cd^{2+} = 0.82 mg, Pb^{2+} = 0.91 mg,

Zn^{2+} = 0.76 mg and Cu^{2+} = 0.59 mg

COLUMN STUDIES

A continuous process employing a packed bed of substrate is often considered to be more efficient and economical to operate than a batch process. Two litres of mercuric chloride solution (Hg^{2+} = 52.25 mg/l) at pH 6.0 was allowed to flow through the column at a rate of 5 ml/min with a detention period of 6.28 min. The experiment was run for 6 h and 40 min. Mercury in the effluent was reduced to levels of 0.06 mg/l Hg^{2+} with a pH of 3.4. It has been observed that about 60–70% of the retained mercury desorbs when treated with dilute nitric acid and column can be reused.

Adsorption capacity of the bark

Ten g of the bark powder was packed in a glass column. Five litres of solution with a concentration of 100 mg/l of Hg^{2+} was passed through the column at a rate of 5 ml/min. It took 16 h and 40 min for the complete solution to pass through the column. The pH and the mercury concentration in the effluent were observed to be 3.0 and 3.0 mg/l, respectively.

The length of the 10 cm column was divided equally into 5 parts of 2 cm each. Each part was extracted with 4 N HNO_3, filtered through Whatman No. 1 filter paper and the filtrate analysed for Hg^{2+}. Hg^{2+} adsorption by each portion was then calculated. The results are shown in Table 3. It can be seen from the table that the maximum amount of sorption took place in the top segment of the column (0–2 cm). The uptake of Hg^{2+} by this 2 cm (2 g) of substrate is 68.0 mg showing that the maximum sorption of mercury (II) was about 34 mg Hg^{2+}/g of bark. This corresponds to the sorption capacity of 0.34 mequiv Hg^{2+}/g of bark.

Table 3. Sorption capacity of the substrate

Depth of column from the top (cm)	Hg^{2+} (mg)
0–2	68.0
2–4	27.0
4–6	37.0
6–8	5.7
8–10	6.1

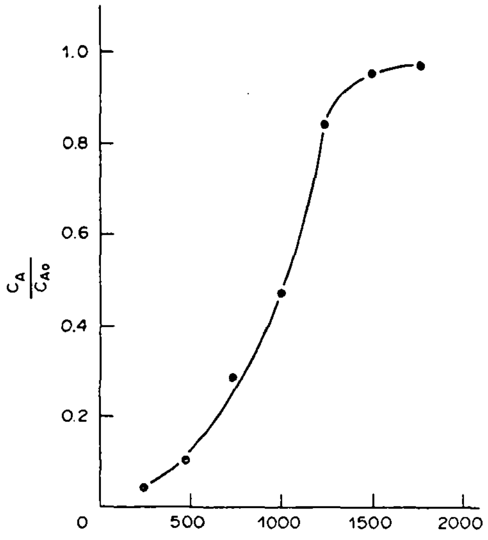

Fig. 10. Break-through curve of Hg^{2+}.

Experiments were also conducted to find the break-through capacity of the column. Two litres of solution with a Hg^{2+} concentration of 200 mg/l was passed through the column at a rate of 5 ml/min. A graph was plotted of C_A/C_{A0} vs volume of eluant (Fig. 10) and the capacity of the column, as determined at $C_A/C_{A0} = 0.5$ (Srivastava *et al.*, 1989), was found to be 21 mg/g.

Competition among cations

Treated bark powder is a complex material that can effectively bind many metal ions at its binding sites by the same or different mechanisms. To determine the competition among various heavy metals ions for the substrate binding sites, 10 g of treated bark was packed in a column and 5 l. of the combined solution containing 20 mg/l each of Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} was allowed to flow through the column at a rate of 5 ml/min. After the feed was discontinued, the column was thoroughly washed with distilled water and then the dry extruded packing was cut into 2 cm sections. The substrate segments were leached with dilute HNO_3 and the metal concentrations were determined. The results are shown in Fig. 11. It was observed that amongst the cations used, sorption of Pb^{2+} is highest followed by Cd^{2+}, Zn^{2+}, Cu^{2+} and Hg^{2+}.

CONCLUSIONS

The following conclusions may be drawn on the basis of the present studies.

Treated *Hardwickia binata* bark can be used for the removal of Hg^{2+} from water and wastewaters. The degree of removal was found to be dependent on the initial pH of the solution and it increased as

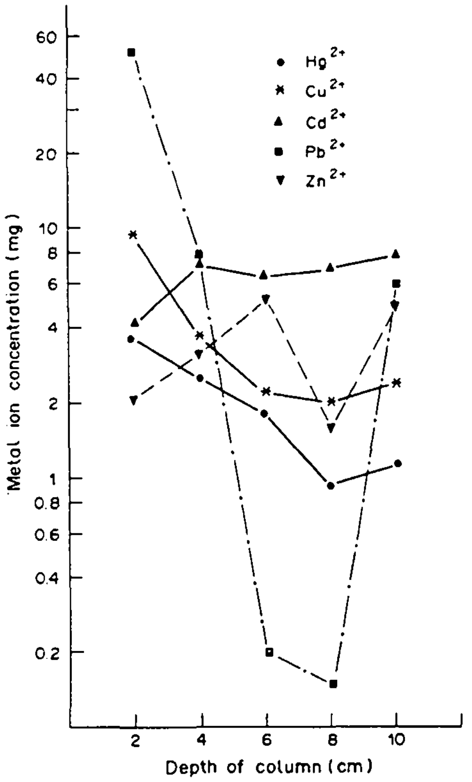

Fig. 11. Effect of metal cations on the sorption of Hg^{2+}.

the pH increased. The optimum contact time was observed to be 2 h. Sorption of Hg^{2+} on this bark was found to proceed in accordance with the Freundlich adsorption equation.

Studies on the effects of light metal ions on mercury removal indicated that the maximum interference in mercury removal was due to the presence of Mg^{2+}. Column studies showed that the capacity of the bark was 0.34 mequiv/g. In the presence of metal cations such as Pb^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+} the sorption of Hg^{2+} was the lowest compared to other cations showing that other cations compete with Hg^{2+} for sorption by the bark.

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