Column Studies on Metal Ion Removal by Dyed Cellulosic Materials

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SYNOPSIS

Cellulosic materials, namely bleached bamboo pulp, jute fibers, and sawdust dyed with a reactive dye of monochlorotriazine type were used in the column studies for removal of different metal ions. The use of an adsorption column makes the process continuous, so that it is economically viable on an industrial scale. After the adsorption of metal ions such as Cu^{2+}, Pb^{2+}, Hg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+} and Ni^{2+}, the adsorbents were successfully regenerated by using dilute acids. These columns were then used repeatedly for adsorption either of the same salt for more than ten times or of different salts in succession. No loss in adsorption power was observed.

INTRODUCTION

Keen attention has been paid in recent years to environmental pollution and its abatement. The removal of toxic and polluting metal ions from effluents by ion exchange techniques has become standard practice. Reports indicate that unconventional substrates[1,2] like sugarcane bagasse, rice hulls, unmodified and modified peanut skins[3] and onion skins[4] have been used as adsorbents for this purpose. These being very cheap, can compete well with the synthetic ion exchange resins.

Chemical modification of natural substrates like wood to make them effective as metal ion adsorbents has been reported.[5] Suemitsu et al.[6] used rice hulls coated with Procion type reactive dyes as an efficient ion exchanger in packed columns to remove lead and mercury ions.

We have successfully carried out work on almost complete removal of different metal ions from their dilute aqueous solutions using various cellulosic substrates dyed with reactive dyes of the monochlorotriazine type.[7,8] These studies were based on batch experiments leading to equilibrium adsorption.

In this paper, we are reporting results on the adsorption of different metal ions like Cu^{2+}, Pb^{2+}, Hg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, and Ni^{2+} using adsorbent columns. The columns were made up of undyed and reactive dye-dyed bamboo pulp, jute, and sawdust. After the adsorption studies, these columns were regenerated by eluting the metal ions by the use of different acids in dilute form to get soluble metal salts. These columns were then subjected to repeated cycles of adsorption of same metal ion for more than 10 times to evaluate the column efficiency. Studies were also conducted on adsorption of different metal ions in a random sequence.

EXPERIMENTAL

Materials

Substrates

The cellulosic substrates, viz. bleached bamboo pulp, jute fibers, and saw dust were purified by methods described in our earlier communication.[7]

Metal Salts

The following materials were all of "Analytical Reagent" grade: the salts of copper, namely $Cu(NO_3)_2 \cdot 3H_2O$ and $Cu(COOCH_3)_2H_2O$; the salts

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of lead, $Pb(NO_3)_2$ and $Pb(COOCH_3)_2 \cdot 3H_2O$; the salts of mercury, $HgCl_2$ and $Hg(NO_3)_2$; the salts of iron in the ferric form, namely $FeCl_3$ and $Fe(NO_3)_3 \cdot 9H_2O$; the salts of iron in the ferrous form as $FeSO_4 \cdot 7H_2O$; the salt of zinc as $Zn(COOCH_3)_2$ and the salt of nickel as $NiSO_4 \cdot 5H_2O$.

Dyestuff

C. I. Reactive Orange 13 was used for dyeing the different substrates.

Chemicals

All the chemicals used in our study were of "Analytical Reagent" grade.

Dyeing of Substrates

The method of dyeing the different substrates with reactive dye has been described earlier.[7]

Preparation of Columns

Glass columns of 40-mm internal diameter and 600-mm height with a stopcock arrangement were used. Glass wool was introduced at the bottom of the column. Fifty grams of uniformly cut bleached bamboo pulp in its dry form was inserted from the top and the column was tapped gently to promote the even distribution. Glass wool was also inserted at the top of the column to prevent the adsorbent particles from floating. Water was slowly added from the top

Table I **Adsorption of Different Metal Salts by Bamboo Pulp Column (Packing Density 0.095 g/cm^3)**

	Concentration of Metal Cation (mg/L)		Metal Cation Adsorbed		Metal Cation Desorbed	
Salt	Initial	Final	mg/g	% Adsorbed	Eluting Acid	% Recovery
			Undyed Bamboo Pulp			
Copper Nitrate	1300	875	8.5	32.7	Nitric	100.0
Copper Acetate	1300	870	8.6	33.0	Acetic	100.0
Copper Chloride	1300	910	7.8	30.0	Hydrochloric	99.5
Lead Acetate	1300	890	8.2	31.5	Acetic	99.8
Lead Nitrate	1300	880	8.4	32.3	Nitric	100.0
Mercuric Chloride	1300	842	9.2	35.2	Hydrochloric	98.8
Mercuric Nitrate	1300	860	8.8	33.8	Nitric	100.0
Ferric Chloride	1200	875	6.5	27.0	Hydrochloric	100.0
Ferric Nitrate	1200	850	7.0	29.2	Nitric	98.6
Ferrous Sulfate	1200	940	5.2	21.7	Sulfuric	98.5
Zinc Acetate	1200	890	6.2	25.8	Acetic	98.6
Nickel Sulfate	1300	1075	4.5	17.3	Sulfuric	99.8
			Dyed Bamboo Pulp (C. I. Reactive Orange 13)			
Copper Nitrate	1300	450	17.0	65.4	Nitric	100.0
Copper Acetate	1300	300	20.0	76.9	Acetic	100.0
Copper Chloride	1300	500	16.0	61.5	Hydrochloric	99.0
Lead Acetate	1300	475	16.5	63.5	Acetic	99.8
Lead Nitrate	1300	550	15.0	57.7	Nitric	100.0
Mercuric Chloride	1300	520	15.6	60.0	Hydrochloric	99.4
Mercuric Nitrate	1300	530	15.4	59.2	Nitric	99.6
Ferric Chloride	1200	525	13.5	56.2	Hydrochloric	98.2
Ferric Nitrate	1200	480	14.4	60.0	Nitric	99.7
Ferrous Sulfate	1200	735	9.3	38.8	Sulfuric	100.0
Zinc Acetate	1200	624	11.5	48.0	Acetic	99.3
Nickel Sulfate	1300	925	7.5	28.8	Sulfuric	100.0

of the column to wet the packing and then allowed to drain away. Similar columns were prepared using jute fibers and sawdust, both in their undyed and dyed forms.

Adsorption of Different Metal Ions on Columns

The requisite amount of a metal salt was dissolved in distilled water to obtain 1 L of fairly concentrated solution. This solution was applied to the top of the column. A flow rate of 12.5 mL/min was maintained for all the experiments. All the liquor coming out of the column at the bottom was collected and subjected to analysis to find the amount of metal ion adsorbed.

Determination of Adsorbed Metal Ions

The method of analysis for different salts of copper, lead, mercury, and iron has been given in our earlier communications.[7,8] For the estimation of Ni^{2+} and Zn^{2+} ions standard EDTA methods[9] were used. The salts of Zn^{2+} were estimated by the direct method using buffer of pH 10 and mixed type of ERIO-T indicator. A standard 0.005 M EDTA solution was added, when the color changed from blood-red to green. The Ni^{2+} ions were estimated by the indirect method. An excess of standard EDTA was added and the unconsumed EDTA was back-titrated by a standard $MgSO_4$ solution using pH 10 buffer and ERIO-T indicator.

Table II Adsorption of Different Metal Salts by Jute Column (Packing Density 0.083 g/cm^3)

	Concentration of Metal Cation (mg/L)		Metal Cation Adsorbed		Metal Cation Desorbed	
Salt	Initial	Final	mg/g	% Adsorbed	Eluting Acid	% Recovery
			Undyed Jute			
Copper Nitrate	1300	975	6.5	25.0	Nitric	100.0
Copper Acetate	1300	698	12.0	46.3	Acetic	100.0
Copper Chloride	1300	665	12.7	48.8	Hydrochloric	99.2
Lead Acetate	1300	903	7.9	30.5	Acetic	99.8
Lead Nitrate	1300	812	7.9	37.5	Nitric	100.0
Mercuric Chloride	1300	920	7.6	29.2	Hydrochloric	100.0
Mercuric Nitrate	1300	942	7.2	27.6	Nitric	99.4
Ferric Chloride	1200	854	6.9	28.8	Hydrochloric	98.4
Ferric Nitrate	1200	686	10.3	42.9	Nitric	99.7
Ferrous Sulfate	1200	960	4.8	20.0	Sulfuric	99.8
Zinc Acetate	1200	798	8.0	33.5	Acetic	99.2
Nickel Sulfate	1300	1072	4.6	17.5	Sulfuric	99.8
			Dyed Jute (C. I. Reactive Orange 13)			
Copper Nitrate	1300	470	16.6	63.8	Nitric	100.0
Copper Acetate	1300	495	16.1	62.0	Acetic	100.0
Copper Chloride	1300	572	14.6	56.0	Hydrochloric	99.2
Lead Acetate	1300	450	17.0	65.4	Acetic	99.8
Lead Nitrate	1300	464	14.1	64.3	Nitric	100.0
Mercuric Chloride	1300	641	13.2	50.7	Hydrochloric	99.6
Mercuric Nitrate	1300	402	17.9	69.0	Nitric	99.6
Ferric Chloride	1200	625	11.5	48.0	Hydrochloric	98.6
Ferric Nitrate	1200	466	14.7	61.2	Nitric	99.7
Ferrous Sulfate	1200	608	11.9	49.3	Sulfuric	100.0
Zinc Acetate	1200	619	11.6	48.4	Acetic	99.3
Nickel Sulfate	1300	933	7.4	28.2	Sulfuric	100.0

Regeneration of Columns

The columns were regenerated by the use of dilute acids. The selection of the acid was based upon the anion in the metal salt solution used in the adsorption study. Thus, for eluting nitrates, nitric acid was used, for eluting acetates, acetic acid was used, for eluting chlorides, hydrochloric acid was used, and for eluting sulfates, sulfuric acid was used. The selection of the acid in this way ensured that the eluted salts were water soluble. One litre of 1 N acid was used as eluent. The elution was carried out rapidly maintaining a flow rate of 25 mL/min, so that the substrate was not in contact with the acid for a long time. The solution was collected at the bottom of the column in order to analyze the amount of metal ion desorbed. The column was then repeatedly washed with distilled water to remove all the traces of the acid.

Reuse of Regenerated Columns

Experiments were carried out by passing 1-L solution of a metal salt through a regenerated column at specific flow rate (12.5 mL/min) to adsorb the metal ion. Upon adsorption, the column was again regenerated using dilute acid and subjected to further adsorption. This cycle of adsorption–desorption was repeated at least 10 times. In another experiment, different metal salts were adsorbed at random, one after another, following similar adsorption–desorption cycles.

Table III Adsorption of Different Metal Salts by Sawdust Column (Packing Density 0.114 g/cm^3)

	Concentration of Metal Cation (mg/L)		Metal Cation Adsorbed		Metal Cation Desorbed	
Salt	Initial	Final	mg/g	% Adsorbed	Eluting Acid	% Recovery
			Undyed Sawdust			
Copper Nitrate	1300	910	7.8	30.0	Nitric	99.3
Copper Acetate	1300	920	7.6	29.2	Acetic	100.0
Copper Chloride	1300	960	6.8	26.2	Hydrochloric	99.0
Lead Acetate	1300	975	6.5	25.0	Acetic	100.0
Lead Nitrate	1300	904	7.3	30.5	Nitric	99.6
Mercuric Chloride	1300	875	8.5	32.7	Hydrochloric	100.0
Mercuric Nitrate	1300	910	7.8	30.0	Nitric	99.3
Ferric Chloride	1200	850	7.0	29.2	Hydrochloric	98.4
Ferric Nitrate	1200	860	6.8	28.3	Nitric	99.3
Ferrous Sulfate	1200	950	5.0	20.8	Sulfuric	100.0
Zinc Acetate	1200	845	7.1	29.6	Acetic	99.3
Nickel Sulfate	1300	1075	4.5	17.3	Sulfuric	98.5
			Dyed Sawdust (C. I. Reactive Orange 13)			
Copper Nitrate	1300	250	21.0	80.8	Nitric	99.5
Copper Acetate	1300	32	25.4	97.5	Acetic	100.0
Copper Chloride	1300	180	22.4	86.2	Hydrochloric	99.2
Lead Acetate	1300	103	24.0	92.0	Acetic	100.0
Lead Nitrate	1300	102	24.0	92.0	Nitric	99.6
Mercuric Chloride	1300	400	18.0	69.2	Hydrochloric	100.0
Mercuric Nitrate	1300	300	20.0	76.9	Nitric	99.3
Ferric Chloride	1200	583	12.3	47.5	Hydrochloric	98.4
Ferric Nitrate	1200	439	15.2	63.4	Nitric	99.4
Ferrous Sulfate	1200	745	9.1	37.9	Sulfuric	100.0
Zinc Acetate	1200	500	14.0	58.3	Acetic	99.3
Nickel Sulfate	1300	850	9.0	34.6	Sulfuric	98.8

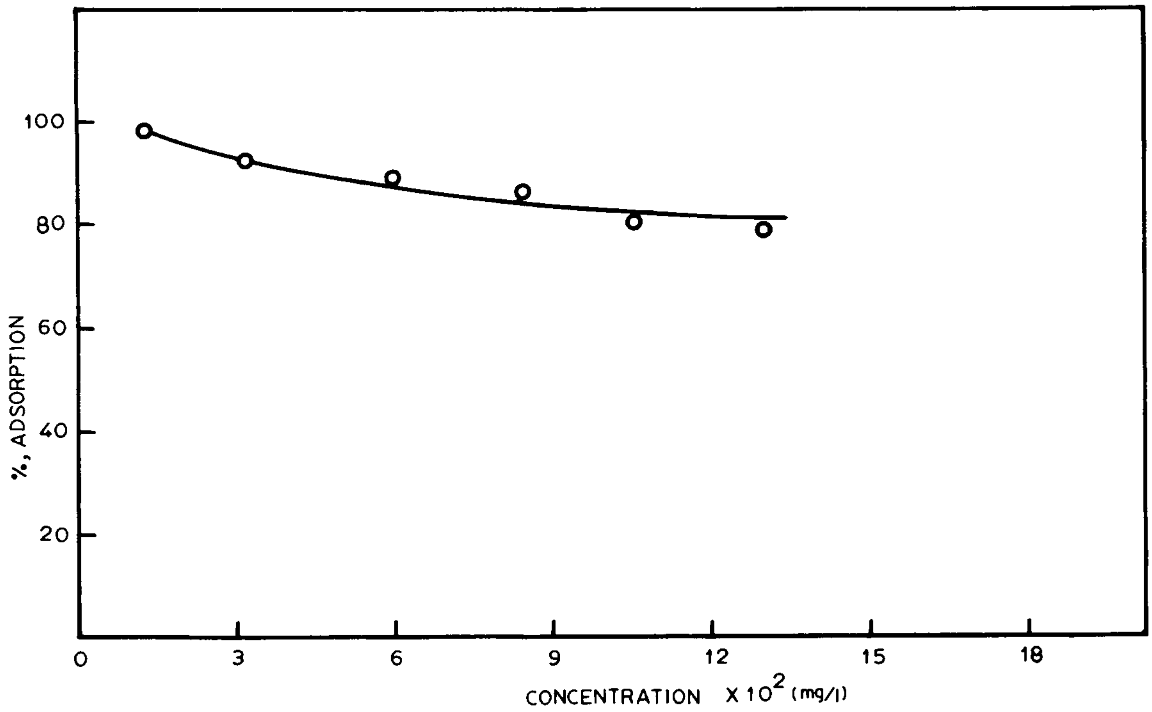

Figure 1 Effect of Cu^{2+} concentration on adsorption (copper acetate adsorbed on dyed bamboo pulp).

RESULTS AND DISCUSSION

The results on adsorption of different metal salts on the columns made up of undyed and dyed bamboo pulp, jute fibers, and sawdust are presented in Tables I, II, and III, respectively. Earlier, we have shown that the batch experiments using these substrates could give adsorption of various metal ions to a considerably high level.[7,8] In the column studies, the adsorbent column was made up of 50 g of substrate, and the total metal salt solution taken was 1 L. Since it was found that the time of 80 min is more than

Table IV Repeated Adsorption–Desorption of Lead Acetate on Dyed Jute Column (Dye—C. I. Reactive Orange 13; Eluent—1 N Acetic Acid)

Adsorption–Desorption Cycle No.	Cation Concentration (mg/L)		Metal Cation Adsorbed		Metal Cation Desorbed
	Initial	Final	mg/g	% Adsorbed	% Recovery
1	1300	450	17.00	65.4	100.0
2	1300	452	16.96	65.2	100.0
3	1300	445	17.10	65.8	98.8
4	1300	500	16.00	61.5	100.0
5	1300	450	17.00	65.4	97.7
6	1300	455	16.90	65.0	98.2
7	1300	450	17.00	65.4	97.7
8	1300	445	17.10	65.8	99.4
9	1300	520	15.60	60.0	100.0
10	1300	480	16.40	63.0	97.6

sufficient for achieving maximum possible adsorption, the rate of flow of solution through the column was maintained at 12.5 mL/min. Also, in theoretical interest, we have increased the cation concentration to a very high level of 1200–1300 ppm for capacity studies. From the results given in these tables, it is clear that even in the column experiments, for any particular cation all the dyed substrates showed higher adsorption compared to that of the undyed substrates.

In another set of column experiments, different concentrations of copper acetate were adsorbed on dyed bamboo pulp. These results are plotted in Figure 1 which shows that as the concentration of the metal cation increases, the adsorption capacity of the substrate decreases. Thus, at a very low concentration of 130 ppm of Cu^{2+} cation, the adsorption was found to be 98.5%; this decreases to 76.9% for a cation concentration of 1300 ppm. In the results given in Tables I, II, and III, usually the percentage adsorption is about 60–70% on dyed substrates. In very few cases like copper and lead ions on dyed sawdust, the values are quite high, about 80–90%.

Tables I, II, and III also provide the results of cation adsorption using 1 L of 1 N acid as eluent. The acid chosen was of the same nature as of the anionic part of the metal salt, so that on desorption, the original completely water-soluble salt is recovered. For example, nitric acid was used for desorption of nitrates, hydrochloric acid for chlorides, etc. It was found that almost complete desorption of each cation was accomplished from all the types of adsorbent columns indicating that all the columns can be easily regenerated.

The columns of dyed jute and dyed sawdust were tested for repeated adsorption of the same metal cation. Table IV gives the results on repeated adsorption–desorption of Pb^{2+} on the columns made up of jute fibers dyed with C. I. Reactive Orange 13, and Table V gives similar results for Cu^{2+} adsorption–desorption on the dyed sawdust column. In each case, 10 adsorption–desorption cycles were carried out. The results indicate that even after completion of the 10th cycle, the adsorption capacity of the column was not affected. After 10 cycles, however, slight bleeding of the color from the dyed substrate was noticed. This was due to the repetitive contact of the dyed substrate with the eluting acid which leads to the hydrolysis of the dye to some extent. The hydrolyzed dye has no affinity for cellulose and hence, it is known to bleed out of the substrate. It is possible that as the dye bleeds out, the adsorption capacity of the substrate will go on decreasing, ultimately reaching that of the undyed substrate. Since the concentrations of the acids used as eluents were quite low (1 N) and the adsorbent columns were not allowed to dry in the presence of acid, virtually no degradation of the substrates was evident.

Further studies were carried out to observe whether the adsorption capacity of a substrate column remains unchanged towards different metal cations. Thus, after desorbing a metal ion, another metal salt, randomly chosen, was adsorbed and desorbed from the column. The results of such studies on dyed jute and dyed sawdust columns are given in Tables VI and VII. It is interesting to note that the results on adsorption as well as desorption of

Table V Repeated Adsorption–Desorption of Copper Acetate on Dyed Sawdust Column (Dye—C. I. Reactive Orange 13; Eluent—1 N Acetic Acid)

Adsorption–Desorption Cycle No.	Cation Concentration (mg/L)		Metal Cation Adsorbed		Metal Cation Desorbed
	Initial	Final	mg/g	% Adsorbed	% Recovery
1	1300	32	25.4	97.5	99.8
2	1300	45	25.1	96.5	97.7
3	1300	50	25.0	96.2	100.0
4	1300	36	25.3	97.2	99.9
5	1300	52	24.9	96.0	100.0
6	1300	100	24.0	92.3	100.0
7	1300	150	23.0	88.5	98.7
8	1300	100	24.0	92.3	100.0
9	1300	56	24.8	95.7	96.5
10	1300	65	24.7	95.0	93.1

Table VI Adsorption–Desorption of Various Metal Salts at Random on Dyed Jute Column (Dye—C. I. Reactive Orange 13)

Adsorption–Desorption Cycle No.	Salt	Cation Concentration (mg/L) Initial	Cation Concentration (mg/L) Final	Metal Cation Adsorbed mg/g	Metal Cation Adsorbed % Adsorbed	Eluting Acid	Metal Cation Desorbed % Recovery
1	Lead Acetate	1300	452	16.9	65.2	Acetic	99.8
2	Copper Acetate	1300	470	16.6	63.9	Acetic	100.0
3	Lead Nitrate	1300	460	16.8	64.6	Nitric	100.0
4	Copper Nitrate	1300	470	16.6	63.9	Nitric	100.0
5	Lead Nitrate	1300	455	16.9	65.0	Nitric	100.0
6	Zinc Acetate	1200	625	11.5	47.9	Acetic	100.0
7	Copper Acetate	1300	490	16.2	62.3	Acetic	100.0
8	Copper Chloride	1300	575	14.5	55.8	Hydrochloric	99.3
9	Nickel Sulfate	1300	920	7.6	29.2	Sulfuric	100.0
10	Ferric Nitrate	1200	470	14.6	60.8	Nitric	99.7
11	Mercuric Chloride	1300	650	13.0	50.0	Hydrochloric	100.0
12	Ferrous Sulfate	1200	600	12.0	50.0	Sulfuric	100.0
13	Ferric Chloride	1200	622	11.6	48.2	Hydrochloric	98.6
14	Mercuric Nitrate	1300	415	17.7	68.1	Nitric	99.4

different metal cations on repeatedly regenerated columns are very similar to those obtained on adsorption–desorption of the cations on a fresh column. Thus, the adsorption capacity of the column remains unchanged even for different metal cations after a number of regeneration cycles.

To conclude, it may be said that the cheap cellulosic materials which have been shown to adsorb different metal cations from the effluents in the batch experiments can be used very efficiently in the form of packed columns to make the process of adsorption continuous. The rate of flow of the solution through the column was also three to four times higher compared to conventional ones. Even

Table VII Adsorption–Desorption of Various Metal Salts at Random on Dyed Sawdust Column (Dye—C. I. Reactive Orange 13)

Adsorption–Desorption Cycle No.	Salt	Cation Concentration (mg/L) Initial	Cation Concentration (mg/L) Final	Metal Cation Adsorbed mg/g	Metal Cation Adsorbed % Adsorbed	Eluting Acid	Metal Cation Desorbed % Recovery
1	Copper Acetate	1300	40	25.2	97.0	Acetic	100.0
2	Copper Nitrate	1300	260	20.8	80.8	Nitric	99.5
3	Zinc Acetate	1200	505	13.9	57.9	Acetic	99.3
4	Ferric Chloride	1200	580	12.4	51.7	Hydrochloric	98.4
5	Ferric Nitrate	1200	430	15.4	64.2	Nitric	99.4
6	Lead Acetate	1300	100	24.0	92.3	Acetic	100.0
7	Lead Nitrate	1300	110	23.8	91.5	Nitric	99.6
8	Ferrous Sulfate	1200	811	7.8	32.4	Sulfuric	100.0
9	Mercuric Chloride	1300	350	19.0	73.1	Hydrochloric	100.0
10	Nickel Sulfate	1300	900	8.0	30.8	Sulfuric	98.8
11	Cupric Chloride	1300	185	22.3	85.7	Hydrochloric	99.7
12	Mercuric Nitrate	1300	300	20.0	76.9	Nitric	99.5

then, the adsorption level was significantly high. The regeneration experiments have proved to be quite encouraging, enhancing further the economy of the process. Studying the kinetics of this adsorption–desorption behavior would be interesting and we are in the process of doing so.

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