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Removal of Metal Ions Using Dyed Cellulosic Materials

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ABSTRACT

Cellulosic substrates, namely sawdust, jute fibres and bamboo pulp, which had been dyed with reactive dye, were subjected to semi-continuous adsorption of different metal ions using packed columns. On passing relatively high concentrations (1200–1300 mg litre^{-1}) of the metal ions Pb^{2+}, Hg^{2+}, Cu^{2+}, Fe^{3+}, Zn^{2+}, Ni^{2+} and Fe^{2+} through the column at a rapid flow rate, it was found that the adsorbent columns were as effective in giving high adsorption levels as single batch experiments. The columns could be regenerated and used repeatedly for adsorbing different metal cations for a number of times without any apparent bleeding out of the dye from the substrate or any degradation of the substrate.

1 INTRODUCTION

With current interest in environmental pollution, the removal of toxic and polluting metal ions from effluents is important in eliminating one of the major causes of water pollution. A number of unconventional substrates in their natural or modified forms have been used in this context.[1–5]

In a previous communication,[6] results on the adsorption of different metal ions on undyed and reactive dye-dyed bamboo pulp and sawdust using batch experiments were reported. In order to make the process of metal cation adsorption more continuous, adsorbent columns made up of undyed and dyed sawdust, jute fibres and bamboo pulp were used, and the results on the adsorption–desorption studies of the metal ions are reported in this paper.

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2 EXPERIMENTAL

2.1 Materials

2.1.1 Substrates
Sawdust and bamboo pulp were purified prior to the adsorption studies as previously described.[6] Jute fibres were purified by boiling for 4 h in a solution containing soap and soda ash, followed by thorough rinsing with water and drying in an oven at 45°C.

2.1.2 Metal salts
Salts of copper, $Cu(COOCH_3)_2 . H_2O$ and $Cu(NO_3)_2 . 3H_2O$, lead, $Pb(COOCH_3)_2 . 3H_2O$ and $Pb(NO_3)_2$, mercury, $Hg(NO_3)_2$ and $HgCl_2$, iron (ferric), $Fe(NO_3)_2 . 9H_2O$ and $FeCl_3$, zinc, $Zn(COOCH_3)_2 . 2H_2O$, nickel, $NiSO_4 . 5H_2O$, and iron (ferrous), $FeSO_4 . 7H_2O$, were of 'Analytical Reagent' grade. All other chemicals were of 'Laboratory Reagent' grade.

2.1.3 Dyestuff
A monochlorotriazine reactive dye, CI Reactive Red 31, was used.[6]

2.2 Dyeing of substrates

The method of dyeing sawdust and bamboo pulp was the same as described previously.[6] The dyeing of jute was also carried out in a similar manner, using trisodium phosphate for fixation of the reactive dye.

2.3 Preparation of columns

The adsorbent columns of undyed and dyed sawdust, jute fibres and bamboo pulp were prepared using glass tubes of 40 mm internal diameter and 600 mm height. Fifty grams of the dry substrate was introduced into the tube (glass-wool plug at the bottom) and the column was tapped gently to promote even distribution of the substrate. The height of the column varied according to the density of the substrate used. Glass wool was also inserted at the top of the column to avoid floating of the substrate particles. Before starting the adsorption studies, the column was wetted by a flow of water, and then allowed to drain.

2.4 Adsorption of metal ions on columns

Solutions of the metal salts (1200–1300 mg litre^{-1} concentration) were prepared by dissolving the requisite amounts in distilled water. This solution

was then passed through the column, maintaining a flow rate of 12·5 ml min^{-1}. The solution eluting was collected and analyzed to give the amount of metal cation adsorbed.

2.5 Determination of adsorbed metal ions

Pb^{2+}, Hg^{2+}, Fe^{3+}, Zn^{2+} and Ni^{2+} were estimated by EDTA methods,[7] Fe^{2+} by the redox method and Cu^{2+} by the iodometric method.

2.6 Regeneration of columns

The columns were regenerated using 1 litre of 1 M strength of different acids, depending upon the anionic part of the metal salts adsorbed. Thus,

TABLE 1
Adsorption of Different Metal Salts by Sawdust Column Packing (Density: 0·114 g cm^{-3})

Salt	*Concentration of metal cation (mg litre^{-1})*		*Metal cation adsorbed*		*Metal cation desorbed*	
	Initial	*Final*	*(mg g^{-1})*	*(%)*	*Eluting acid*	*(%)*
Undyed sawdust						
Lead acetate	1 300	975	6·5	25·0	Acetic	100·0
Lead nitrate	1 300	904	7·3	30·5	Nitric	99·6
Mercuric chloride	1 300	875	8·5	32·7	Hydrochloric	100·0
Mercuric nitrate	1 300	910	7·8	30·0	Nitric	99·3
Copper acetate	1 300	920	7·6	29·2	Acetic	100·0
Copper nitrate	1 300	910	7·8	30·0	Nitric	99·3
Ferric nitrate	1 200	860	6·8	28·3	Nitric	99·3
Ferric chloride	1 200	850	7·0	29·2	Hydrochloric	98·4
Zinc acetate	1 200	845	7·1	29·6	Acetic	99·3
Nickel sulphate	1 300	1 075	4·5	17·3	Sulphuric	98·5
Ferrous sulphate	1 200	950	5·0	20·8	Sulphuric	100·0
Dyed sawdust (CI Reactive Red 31)						
Lead acetate	1 300	103	23·9	92·0	Acetic	100·0
Lead nitrate	1 300	100	24·0	92·3	Nitric	99·8
Mercuric chloride	1 300	350	19·0	73·0	Hydrochloric	100·0
Mercuric nitrate	1 300	320	19·6	75·4	Nitric	99·8
Copper acetate	1 300	60	24·8	95·4	Acetic	100·0
Copper nitrate	1 300	260	20·8	80·0	Nitric	99·8
Ferric nitrate	1 200	350	17·0	70·8	Nitric	99·4
Ferric chloride	1 200	400	16·0	66·7	Hydrochloric	98·6
Zinc acetate	1 200	575	12·5	52·1	Acetic	99·0
Nickel sulphate	1 300	900	8·0	30·8	Sulphuric	98·8
Ferrous sulphate	1 200	800	8·0	33·3	Sulphuric	100·0

hydrochloric acid was used as eluent for chlorides, acetic acid for acetates, nitric acid for nitrates and sulphuric acid for sulphates, making the eluted salts water-soluble. The elution was carried out rapidly maintaining a flow rate of 25 ml min^{-1}, so that the substrate was not in contact with the acid for a prolonged period. The eluent was collected and analyzed for the amount of metal ion desorbed. The column was then repeatedly washed with distilled water to remove all traces of the acid.

2.7 Reuse of regenerated columns

A freshly prepared 1-litre solution of the appropriate metal salt was passed through the regenerated column at a flow rate of 12·5 ml min^{-1}. After

TABLE 2
Adsorption of Different Metal Salts by Jute Column (Packing Density: 0·083 g cm^{-3})

Salt	*Concentration of metal cation (mg litre^{-1})*		*Metal cation adsorbed*		*Metal cation desorbed*	
	Initial	*Final*	*(mg g^{-1})*	*(%)*	*Eluting acid*	*(%)*
Undyed jute						
Lead acetate	1 300	903	7·9	30·5	Acetic	99·8
Lead nitrate	1 300	812	9·8	37·5	Nitric	100·0
Mercuric chloride	1 300	920	7·6	29·2	Hydrochloric	100·0
Mercuric nitrate	1 300	942	7·2	27·6	Nitric	99·4
Copper acetate	1 300	698	12·0	46·3	Acetic	100·0
Copper nitrate	1 300	975	6·5	25·0	Nitric	100·0
Ferric nitrate	1 200	686	10·3	42·9	Nitric	99·7
Ferric chloride	1 200	854	6·9	28·8	Hydrochloric	98·4
Zinc acetate	1 200	798	8·0	33·5	Acetic	99·2
Nickel sulphate	1 300	1 072	4·6	17·5	Sulphuric	99·8
Ferrous sulphate	1 200	960	4·8	20·0	Sulphuric	99·8
Dyed jute (CI Reactive Red 31)						
Lead acetate	1 300	400	18·0	69·2	Acetic	100·0
Lead nitrate	1 300	445	17·1	65·8	Nitric	100·0
Mercuric chloride	1 300	620	13·6	52·3	Hydrochloric	99·6
Mercuric nitrate	1 300	410	17·8	68·5	Nitric	99·5
Copper acetate	1 300	480	16·4	63·0	Acetic	100·0
Copper nitrate	1 300	470	16·6	63·8	Nitric	100·0
Ferric nitrate	1 200	460	14·8	61·7	Nitric	99·8
Ferric chloride	1 200	580	12·4	51·7	Hydrochloric	98·6
Zinc acetate	1 200	600	12·0	50·0	Acetic	99·6
Nickel sulphate	1 300	900	8·0	30·8	Sulphuric	100·0
Ferrous sulphate	1 200	600	12·0	50·0	Sulphuric	100·0

adsorption, the column was again regenerated using dilute acid (1M) and then subjected to further adsorption. This cycle of adsorption–desorption was repeated several times. In another set of experiments, different metal salts were adsorbed at random following similar adsorption–desorption cycles.

3 RESULTS AND DISCUSSION

It has been reported previously[6] that cellulose substrates such as sawdust and bamboo pulp, on dyeing with monochlorotriazine reactive dyes, showed considerable enhancement in the adsorption of metal ions. These

TABLE 3
Adsorption of Different Metal Salts by Bamboo-Pulp Column (Packing Density: 0·095 g cm^{-3})

Salt	*Concentration of metal cation (mg litre^{-1})*		*Metal cation adsorbed*		*Metal cation desorbed*	
	Initial	*Final*	*(mg g^{-1})*	*(%)*	*Eluting acid*	*(%)*
Undyed bamboo pulp						
Lead acetate	1 300	890	8·2	31·5	Acetic	99·8
Lead nitrate	1 300	880	8·4	32·3	Nitric	100·0
Mercuric chloride	1 300	842	9·2	35·2	Hydrochloric	98·8
Mercuric nitrate	1 300	860	8·8	33·8	Nitric	100·0
Copper acetate	1 300	870	8·6	33·0	Acetic	100·0
Copper nitrate	1 300	875	8·5	32·7	Nitric	100·0
Ferric nitrate	1 200	850	7·0	29·2	Nitric	98·6
Ferric chloride	1 200	875	6·5	27·0	Hydrochloric	100·0
Zinc acetate	1 200	890	6·2	25·8	Acetic	98·6
Nickel sulphate	1 300	1 075	4·5	17·3	Sulphuric	99·8
Ferrous sulphate	1 200	940	5·2	21·7	Sulphuric	98·5
Dyed bamboo pulp (CI Reactive Red 31)						
Lead acetate	1 300	400	18·0	69·2	Acetic	100·0
Lead nitrate	1 300	445	17·1	65·8	Nitric	98·6
Mercuric chloride	1 300	520	15·6	60·0	Hydrochloric	99·5
Mercuric nitrate	1 300	510	15·8	60·8	Nitric	99·6
Copper acetate	1 300	310	19·8	76·2	Acetic	100·0
Copper nitrate	1 300	400	18·0	69·2	Nitric	100·0
Ferric nitrate	1 200	460	14·8	61·7	Nitric	99·7
Ferric chloride	1 200	525	13·5	56·3	Hydrochloric	98·6
Zinc acetate	1 200	600	12·0	50·0	Acetic	99·5
Nickel sulphate	1 300	900	8·0	30·8	Sulphuric	100·0
Ferrous sulphate	1 200	700	10·0	41·7	Sulphuric	99·0

TABLE 4
Repeated Adsorption–Desorption of Copper Acetate on Dyed-Sawdust Column (dye, CI Reactive Red 31; eluent, 1M acetic acid)

Adsorption–desorption cycle no.	*Cation concentration (mg litre^{-1})*		*Metal cation adsorbed*		*Metal cation desorbed (%)*
	Initial	*Final*	*(mg g^{-1})*	*(%)*	
1	1 300	60	24·8	95·4	99·8
2	1 300	56	24·9	95·7	100·0
3	1 300	65	24·7	95·0	99·9
4	1 300	65	24·7	95·0	100·0
5	1 300	85	24·3	93·5	100·0
6	1 300	60	24·8	95·4	98·6
7	1 300	62	24·8	95·2	100·0
8	1 300	65	24·7	95·0	96·5
9	1 300	60	24·8	95·4	97·8
10	1 300	67	24·6	94·8	100·0

experiments were carried out in a batchwise manner using stoppered flasks. The glass columns, uniformly packed with the adsorbent materials, provide useful tools for a more continuous process, making it more economical. The results of such adsorptions, using columns of undyed and dyed sawdust, jute and bamboo pulp, are given in Tables 1, 2 and 3, respectively.

Fifty grams of the substrate were packed in a glass column and the rate of flow of the metal salt solution was kept at 12·5 ml min^{-1}. The results shown

TABLE 5
Repeated Adsorption–Desorption of Lead Acetate on Dyed-Jute Column (dye, CI Reactive Red 31; eluent, 1M acetic acid)

Adsorption–desorption cycle no.	*Cation concentration (mg litre^{-1})*		*Metal cation adsorbed*		*Metal cation desorbed (%)*
	Initial	*Final*	*(mg g^{-1})*	*(%)*	
1	1 300	450	17·0	65·4	100·0
2	1 300	452	16·9	65·2	100·0
3	1 300	445	17·1	65·8	98·8
4	1 300	400	18·0	69·2	98·8
5	1 300	400	18·0	69·2	100·0
6	1 300	500	16·0	61·5	98·8
7	1 300	480	16·4	63·0	98·9
8	1 300	400	18·0	69·2	100·0
9	1 300	452	16·9	65·2	100·0
10	1 300	460	16·8	64·6	100·0

TABLE 6
Repeated Adsorption–Desorption of Copper Nitrate on Dyed-Bamboo-Pulp Column (dye, CI Reactive Red 31; eluent, 1M nitric acid)

Adsorption–desorption cycle no.	*Cation concentration (mg litre^{-1})*		*Metal cation adsorbed*		*Metal cation desorbed (%)*
	Initial	*Final*	*(mg g^{-1})*	*(%)*	
1	1 300	400	18·0	69·2	100·0
2	1 300	400	18·0	69·2	100·0
3	1 300	390	18·2	70·0	98·9
4	1 300	405	17·9	68·8	98·8
5	1 300	395	18·1	69·6	100·0
6	1 300	425	17·5	67·3	100·0
7	1 300	415	17·7	68·0	97·8
8	1 300	420	17·6	67·7	98·5
9	1 300	410	17·8	68·5	100·0
10	1 300	430	17·4	66·9	98·5

in the Tables indicate that the adsorption capacity of these substrates greatly increased on dyeing with CI Reactive Red 31. Moreover, the adsorption of the different metal ions studied increased to about 60–70%, except for Cu^{2+} and Pb^{2+}, which gave values as high as 80–90%.

One of the interesting aspects of the column studies is the possibility of the repeated use of the substrate columns for adsorption. The tables also give the results on desorption of the columns using 1 litre 1M acid as eluent. The results indicate almost complete desorption of each of the cations adsorbed in the case of all three adsorbent columns. Therefore, the columns can easily be subjected to reuse.

The results on repeated adsorption–desorption of Cu^{2+} on the dyed-sawdust, of Pb^{2+} on the dyed-jute and of Cu^{2+} on the dyed-bamboo-pulp column are given in Tables 4, 5 and 6, respectively. Such adsorption–desorption cycles were carried out ten times for the same type of salt, and it was observed that in all cases, even after the tenth cycle, the adsorption capacity of the column was not affected. After about 10–14 such cycles, slight bleeding of the colour from the dyed adsorbent columns was noticed. Since the eluting acids may cause hydrolysis of the dye on repetitive contact with the dyed substrate, and since the hydrolyzed dye has no substantivity for the cellulosic material, it is likely to bleed out. It is possible that with increasing amounts of dye bleeding out of the substrate the adsorption capacity of the dyed column will also continue to decrease, ultimately reaching that of the undyed substrate. This conclusion was found to be valid when 30 cycles of adsorption–desorption of Cu^{2+} ion from copper-acetate solution on dyed

TABLE 7
Adsorption–Desorption of Various Metal Salts at Random on Dyed-Sawdust Column (dye, CI Reactive Red 31)

Adsorption–desorption cycle no.	*Salt*	*Cation concentration (mg litre^{-1})*		*Metal cation adsorbed*		*Eluting acid*	*Metal cation desorbed (%)*
		Initial	*Final*	(*mg g^{-1}*)	(%)		
1	Lead acetate	1 300	110	23·8	91·5	Acetic	100·0
2	Copper nitrate	1 300	245	21·1	81·2	Nitric	100·0
3	Ferric chloride	1 200	360	16·8	70·0	Hydrochloric	98·5
4	Zinc acetate	1 200	570	12·6	52·5	Acetic	99·0
5	Copper acetate	1 300	75	24·5	94·2	Acetic	100·0
6	Ferric nitrate	1 200	320	17·6	73·3	Nitric	99·6
7	Mercuric chloride	1 300	350	19·0	73·1	Hydrochloric	100·0
8	Copper nitrate	1 300	230	21·4	82·3	Nitric	99·8
9	Lead acetate	1 300	120	23·6	90·8	Acetic	100·0
10	Lead nitrate	1 300	110	23·8	91·5	Nitric	100·0

TABLE 8

Adsorption–Desorption of Various Metal Salts at Random on Dyed-Jute Column (dye, CI Reactive Red 31)

Adsorption–desorption cycle no.	*Salt*	*Cation concentration (mg litre^{-1})*		*Metal cation adsorbed*		*Eluting acid*	*Metal cation desorbed (%)*
		Initial	*Final*	(*mg g^{-1}*)	(%)		
1	Copper acetate	1 300	460	16·8	64·6	Acetic	100·0
2	Lead nitrate	1 300	445	17·1	65·8	Nitric	100·0
3	Copper nitrate	1 300	470	16·6	63·8	Nitric	100·0
4	Ferric nitrate	1 200	450	15·0	62·5	Nitric	99·8
5	Copper acetate	1 300	450	17·0	65·3	Acetic	100·0
6	Zinc acetate	1 200	610	11·8	49·2	Acetic	99·6
7	Nickel sulphate	1 300	890	8·2	31·5	Sulphuric	100·0
8	Ferric chloride	1 200	570	12·6	52·5	Hydrochloric	98·4
9	Copper nitrate	1 300	470	16·6	63·8	Nitric	100·0
10	Lead acetate	1 300	400	18·0	69·2	Acetic	100·0

TABLE 9
Adsorption–Desorption of Various Metal Salts at Random on Dyed-Bamboo-Pulp Column (dye, C.I. Reactive Red 31)

Adsorption–desorption cycle no.	*Salt*	*Cation concentration (mg litre^{-1})*		*Metal cation adsorbed*		*Eluting acid*	*Metal cation desorbed (%)*
		Initial	*Final*	*(mg g^{-1})*	*(%)*		
1	Copper acetate	1 300	320	19·6	75·4	Acetic	100·0
2	Lead nitrate	1 300	430	17·4	66·9	Nitric	99·6
3	Ferric nitrate	1 200	450	15·0	62·5	Nitric	99·7
4	Zinc acetate	1 200	590	12·2	50·8	Acetic	99·9
5	Copper nitrate	1 300	400	18·0	69·2	Nitric	100·0
6	Nickel sulphate	1 300	890	8·2	31·5	Sulphuric	100·0
7	Mercuric chloride	1 300	510	15·8	60·8	Hydrochloric	99·6
8	Lead acetate	1 300	405	17·9	68·8	Acetic	100·0
9	Mercuric nitrate	1 300	500	16·0	61·5	Nitric	99·0
10	Ferric chloride	1 200	520	13·6	56·7	Hydrochloric	98·5

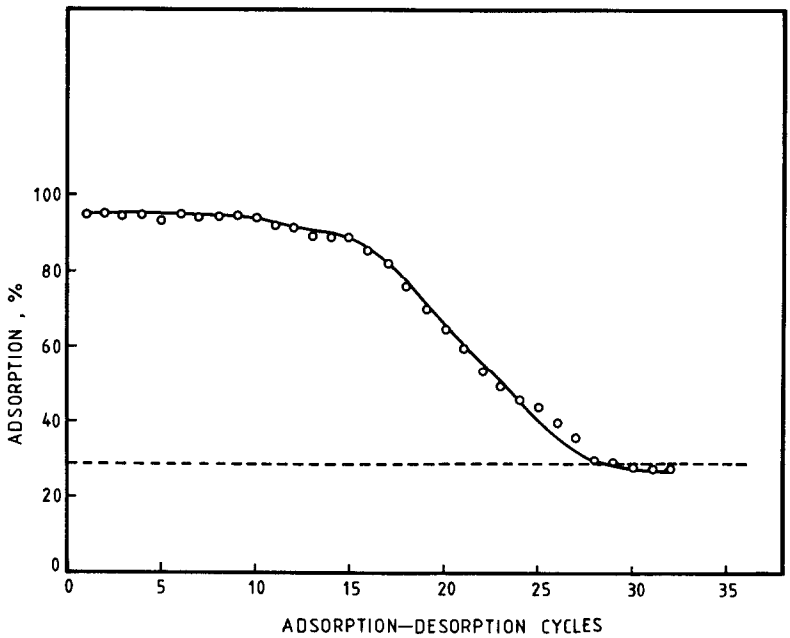

Fig. 1. Plot of repeated adsorption–desorption cycles of copper acetate on a sawdust column dyed with CI Reactive Red 31 versus percentage adsorption; (- - - -) undyed, (——) dyed.

sawdust were carried out (Fig. 1). As the concentration of the eluting acid was not very high (1 M), and as the adsorbent columns were not allowed to dry in the presence of acid, there was virtually no degradation of the substrates.

In addition to adsorbing–desorbing cycles using the same metal ion over a large number of cycles, different metal ions were used for adsorption successively on dyed sawdust, jute and bamboo-pulp columns, and the results are given in Tables 7, 8 and 9, respectively. It can be observed that even in these cases the adsorption levels of each particular metal ion, as well as its desorption level, were the same as if with a fresh column.

It can therefore be concluded that, in order to make the process of heavy metal ion removal more continuous, columns of the adsorbent materials are as efficient as in the case of batch experiments. Moreover, regenerating the columns repeatedly and using them randomly does not deteriorate the adsorption level of the columns, making the process quite economical.

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