Metal Ion Removal by Dyed Cellulosic Materials

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SYNOPSIS

Further studies on adsorption of different metal ions by the four dyed and undyed cellulosic substrates namely cotton fibers, bleached bamboo pulp, jute fibers, and sawdust were carried out. Different metal ions adsorbed were Fe^{2+}, Fe^{3+}, Pb^{2+}, and Hg^{2+}. The equilibrium metal adsorption was studied by EDTA method. The control and dyed substrates adsorbed these metal ions to a significant extent, thus providing an effective and cheap method for adsorption of costly but polluting and toxic metals like Pb^{2+} and Hg^{2+}. The adsorption levels varied up to 95% for various substrate–dye–metal ion combinations.

INTRODUCTION

A number of heavy metal ions contaminate water of which mercury and lead in particular play a significant role in contaminating streams and rivers. These metals are toxic, but are industrially important. The effective and economic removal of these, therefore, is an important task. Ion exchange and precipitation are efficient techniques for this, however, they are costly. The manufacturing of ion exchange resins in itself involves hazards and pollution. On the other hand, natural materials which are abundantly and cheaply available can perform the same task.

Many agricultural waste products/byproducts of cellulosic origin are available at very little or no cost, and have been successfully utilized for metal ion adsorption by many workers.[1-3] Also, wool is known to bind mercury and methyl mercuric salts from water which can be easily recovered by citrate or EDTA in aqueous form.[4]

The present paper reports the further results on adsorption of salts of other metals like ferrous sulphate, ferric chloride, ferric nitrate, lead acetate, lead nitrate, mercuric nitrate, and mercuric chloride. The substrates and the monochlorotriazine dyestuffs were same as those used in our earlier studies which described the adsorption of different copper salts.[5] The EDTA method was employed to determine the amount of metal salt remaining in the solution after adsorption by the dyed and undyed substrates.

EXPERIMENTAL

Materials

Substrate

The cellulosic substrates (viz. cotton fibers, bleached bamboo pulp, jute fibers, and sawdust) were purified by methods described in our earlier paper.[5]

Metal Salts

The salts of iron namely $FeSO_4 \cdot 7H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $FeCl_3$; the salts of lead namely $(CH_3-COO)_2Pb \cdot 3H_2O$, $Pb(NO_3)_2$; and the salts of mercury namely $Hg(NO_3)_2$ and $HgCl_2$ were all of "analytical reagent" grade.

Dyestuffs

The dyestuffs namely CI Reactive Red 31, CI Reactive Orange 13, and CI Reactive Yellow 18, used were same as in the earlier work and their structures have been given in our earlier paper.[5] All the other chemicals used were of "laboratory reagent" grade.

Dyeing of Substrates

The method of dyeing these substrates with reactive dyes has been described earlier.[5]

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Adsorption of Different Metal Ions

The aqueous solutions of the metal salts were prepared in distilled water. A sample of 4 g substrate was placed in 200 mL of an aqueous solution of 120–130 ppm metal cation concentration in a 500 mL stoppered Erlenmyer flask and maintained at a constant temperature. The flask was shaken constantly for a period of 2 h. The substrate was then filtered using a sintered glass crucible and the filtrate analyzed for the amount of metal cation remaining after adsorption on the substrate.

Determination of Adsorbed Metal Ions

The concentration of various metal ions used in this study was determined by standard EDTA methods.[6] A .005 *M* solution of EDTA was prepared in distilled water and standardized against .005 *M* zinc sulphate solution. The pH 10 buffer and the ERIO-T indicator used in these titrations were prepared by the standard methods. The Mg/EDTA complex used for the replacement method of titration was also prepared in the usual manner. The methods used for estimation of different metal salts have been given by Flaschka.[6]

For estimation of the Fe^{2+} cation, a standard solution of 0.005 *N* $KMnO_4$ in acidic medium was used and the redox method of titration was followed.

Estimation of the Fe^{3+} ion was done by the sodium acetate–potassium thiocyanate method in acidic conditions (pH = 2–3), at 45–50°C. In this method, the red color of the iron–thiocyanate complex changed to pale yellow on addition of EDTA at the end point of reaction.

The salts of lead were estimated by the direct method, using tartaric acid to keep the lead ion in solution as tartarate. A buffer of pH 10 was used with ERIO-T as an indicator. The color change was from blood red to green.

Titration of mercury was done by the standard replacement method using Mg/EDTA complex and pH 10 buffer. The equivalent-liberated Mg^{2+} was then titrated with standard EDTA using ERIO-T as an indicator. The color change was from red to bluish-green.

RESULTS AND DISCUSSION

The results on adsorption of different metal salts of iron, lead, and mercury by the cellulosic substrates, both undyed and dyed with different monochloro-

Table I Adsorption of Ferrous Sulfate From Solution by Substrates Dyed With Reactive Dyes

Substrate	Concentration of Salt Solution (mg/L)		Concentration of Metal Cation (mg/L)		Metal Cation Adsorbed	
	Initial	Final	Initial	Final	mg/g Substrate	%
Cotton fibers	596	484	120	96.8	5.80	18.8
Cotton dyed red*	596	391	120	78.2	10.45	34.4
Cotton dyed orange	596	391	120	78.2	10.45	34.4
Cotton dyed yellow	596	410	120	82.0	9.50	31.2
Bamboo pulp	596	414	120	82.8	9.30	30.3
Pulp dyed red	596	342	120	68.4	12.90	42.4
Pulp dyed orange	596	362	120	72.4	11.90	39.4
Pulp dyed yellow	596	287	120	57.4	15.65	51.5
Jute fibers	596	398	120	79.6	10.10	33.0
Jute dyed red	596	287	120	57.4	15.65	51.5
Jute dyed orange	596	287	120	57.4	15.65	51.5
Jute dyed yellow	596	295	120	59.0	15.25	50.3
Sawdust	596	484	120	96.8	5.80	18.8
Sawdust dyed red	596	164	120	32.8	21.80	72.0
Sawdust dyed orange	596	183	120	36.6	20.85	68.8
Sawdust dyed yellow	596	203	120	40.6	19.85	65.6

* Red: CI Reactive Red 31; Orange: CI Reactive Orange 13; and Yellow: CI Reactive Yellow 18.

Table II Adsorption of Ferric Chloride From Solution by Substrates Dyed With Reactive Dyes

Substrate	Concentration of Salt Solution (mg/L)		Concentration of Metal Cation (mg/L)		Metal Cation Adsorbed	
	Initial	Final	Initial	Final	mg/g Substrate	%
Cotton fibers	350	227	120	77.9	10.52	35.2
Cotton dyed red*	350	162	120	55.6	16.10	54.0
Cotton dyed orange	350	48	120	16.5	25.88	86.3
Cotton dyed yellow	350	162	120	55.6	16.10	54.0
Bamboo pulp	350	138	120	47.3	18.18	60.4
Pulp dyed red	350	48	120	16.5	25.88	86.3
Pulp dyed orange	350	48	120	16.5	25.88	86.3
Pulp dyed yellow	350	36	120	12.3	26.93	89.7
Jute fibers	350	132	120	45.0	18.75	62.3
Jute dyed red	350	48	120	16.5	25.88	86.3
Jute dyed orange	350	36	120	12.3	26.93	89.7
Jute dyed yellow	350	53	120	18.2	25.45	84.9
Sawdust	350	138	120	47.3	18.18	60.6
Sawdust dyed red	350	12	120	4.1	28.98	96.6
Sawdust dyed orange	350	8	120	2.7	29.33	97.8
Sawdust dyed yellow	350	35	120	12.0	27.00	90.0

* Red: CI Reactive Red 31; Orange: CI Reactive Orange 13; and Yellow: CI Reactive Yellow 18.

triazine types of reactive dyes have been reported in Tables I–VII. We have already reported such studies on different copper salts.[5] In the present study it may also be observed that the undyed substrates adsorb various metal ions to different extents. Surprisingly, the adsorption of the salts of lead and mercury takes place, to a very small extent, on the control substrates as compared to the adsorption of the salts of copper[5] and iron.

Tables I–III show the results on adsorption of iron salts. For the three salts, ferrous sulfate, ferric chloride, and ferric nitrate, the adsorption of ferrous sulfate by the control substrates was not very high. A maximum value of 33% adsorption by jute fibers was obtained as compared to over 60% by the same substrate in the case of ferric salts. In the present study, we have increased the initial metal cation concentration to a high level of 120–130 mg/L as compared to only about 50–55 mg/L in earlier studies. Also, the dyeings of the various substrates by the reactive dyes were at a higher level of 2% instead of 1%. As expected, the dyed substrates drastically improved in their capacity to adsorb iron salts although the ferrous ions could be adsorbed only to a maximum of 72% in the case of sawdust dyed with CI Reactive Red 31. On the other hand, the ferric ions were adsorbed to a level nearing 100% in the case of sawdust dyed with CI Reactive Orange 13. The differences in adsorption levels exhibited by sawdust dyed with CI Reactive Red 31 and with CI Reactive Orange 13 are marginal as observed in our earlier studies on copper ion adsorption. This may be due to the similarities in the structures of the two dyes as far as the capabilities of chelation with metal ion are concerned.

The results on adsorption of lead acetate and lead nitrate are given in Tables IV and V, respectively. In general, the different undyed substrates adsorb lead ions to an extremely low level, the maximum adsorption being about 15% in the case of jute fibers. On dyeing with different reactive dyes, the adsorption can be enhanced depending upon the substrate used. Thus, in case of cotton fibers, the adsorption increased to about 24% on dyeing, whereas, it increased to above 80% in case of dyed sawdust. The jute fibers showed a maximum level of adsorption of about 60% when dyed, although the control fibers had shown higher adsorption than that by other undyed substrates.

The adsorption of mercuric nitrate and mercuric chloride has also been studied and the results are given in Tables VI and VII, respectively. As in the case of lead salts, the mercuric salts also exhibited poor adsorption by the undyed substrates which im-

Table III Adsorption of Ferric Nitrate From Solution by Substrates Dyed With Reactive Dyes

Substrate	Concentration of Salt Solution (mg/L)		Concentration of Metal Cation (mg/L)		Metal Cation Adsorbed	
	Initial	Final	Initial	Final	mg/g Substrate	%
Cotton fibers	884	453	120	61.4	14.65	48.8
Cotton dyed red*	884	242	120	32.7	21.83	72.6
Cotton dyed orange	884	242	120	32.7	21.83	72.6
Cotton dyed yellow	884	283	120	38.2	20.45	68.0
Bamboo pulp	884	354	120	48.0	18.00	60.0
Pulp dyed red	884	121	120	16.3	25.93	85.2
Pulp dyed orange	884	142	120	19.2	25.20	84.0
Pulp dyed yellow	884	152	120	20.5	24.88	82.8
Jute fibers	884	352	120	47.8	18.05	60.2
Jute dyed red	884	61	120	8.2	27.95	93.1
Jute dyed orange	884	50	120	6.8	28.30	94.3
Jute dyed yellow	884	101	120	19.0	25.25	88.6
Sawdust	884	352	120	47.8	18.05	60.2
Sawdust dyed red	884	50	120	6.8	28.30	94.3
Sawdust dyed orange	884	30	120	4.0	29.00	96.6
Sawdust dyed yellow	884	88	120	11.9	27.03	90.0

* Red: CI Reactive Red 31; Orange: CI Reactive Orange 13; and Yellow: CI Reactive Yellow 18.

Table IV Adsorption of Lead Acetate From Solution by Substrates Dyed With Reactive Dyes

Substrate	Concentration of Salt Solution (mg/L)		Concentration of Metal Cation (mg/L)		Metal Cation Adsorbed	
	Initial	Final	Initial	Final	mg/g Substrate	%
Cotton fibers	240	224	130	121.0	2.25	6.6
Cotton dyed red*	240	182	130	98.6	7.85	24.0
Cotton dyed orange	240	185	130	100.0	7.50	23.0
Cotton dyed yellow	240	187	130	101.0	7.25	22.0
Bamboo pulp	240	219	130	118.6	2.85	8.6
Pulp dyed red	240	106	130	57.4	18.15	56.0
Pulp dyed orange	240	113	130	61.2	17.20	53.0
Pulp dyed yellow	240	115	130	62.3	16.93	52.0
Jute fibers	240	203	130	110.0	5.00	15.4
Jute dyed red	240	102	130	55.0	18.75	57.7
Jute dyed orange	240	96	130	52.0	19.50	60.0
Jute dyed yellow	240	111	130	60.0	17.50	53.8
Sawdust	240	216	130	117.0	3.25	10.0
Sawdust dyed red	240	38	130	20.6	27.35	84.2
Sawdust dyed orange	240	17	130	9.2	30.20	93.0
Sawdust dyed yellow	240	48	130	26.0	26.00	80.0

* Red: CI Reactive Red 31; Orange: CI Reactive Orange 13; and Yellow: CI Reactive Yellow 18.

Table V Adsorption of Lead Nitrate From Solution by Substrates Dyed With Reactive Dyes

Substrate	Concentration of Salt Solution (mg/L)		Concentration of Metal Cation (mg/L)		Metal Cation Adsorbed	
	Initial	Final	Initial	Final	mg/g Substrate	%
Cotton fibers	210	196	130	121.0	2.25	6.5
Cotton dyed red*	210	158	130	97.8	8.05	24.6
Cotton dyed orange	210	161	130	99.7	7.58	23.2
Cotton dyed yellow	210	166	130	102.8	6.80	21.0
Bamboo pulp	210	192	130	118.9	2.78	8.6
Pulp dyed red	210	94	130	58.2	17.95	55.0
Pulp dyed orange	210	99	130	61.3	17.18	53.0
Pulp dyed yellow	210	103	130	63.8	16.55	51.0
Jute fibers	210	180	130	111.4	4.65	14.3
Jute dyed red	210	95	130	58.8	17.80	54.8
Jute dyed orange	210	90	130	55.7	18.60	57.1
Jute dyed yellow	210	110	130	68.0	15.50	47.6
Sawdust	210	192	130	118.8	2.80	8.6
Sawdust dyed red	210	42	130	26.0	26.00	80.0
Sawdust dyed orange	210	33	130	20.4	27.40	84.3
Sawdust dyed yellow	210	50	130	31.0	24.75	76.2

* Red: CI Reactive Red 31; Orange: CI Reactive Orange 13; and Yellow: CI Reactive Yellow 18.

Table VI Adsorption of Mercuric Nitrate From Solution by Substrates Dyed With Reactive Dyes

Substrate	Concentration of Salt Solution (mg/L)		Concentration of Metal Cation (mg/L)		Metal Cation Adsorbed	
	Initial	Final	Initial	Final	mg/g Substrate	%
Cotton fibers	210	196	130	121.0	2.25	6.7
Cotton dyed red*	210	157	130	97.2	8.20	25.2
Cotton dyed orange	210	159	130	98.4	7.90	24.2
Cotton dyed yellow	210	161	130	99.7	7.58	23.5
Bamboo pulp	210	192	130	119.0	2.75	8.6
Pulp dyed red	210	86	130	53.2	19.20	59.0
Pulp dyed orange	210	105	130	65.0	16.25	50.0
Pulp dyed yellow	210	107	130	66.0	16.00	49.0
Jute fibers	210	188	130	116.0	3.31	10.2
Jute dyed red	210	76	130	47.0	20.75	63.8
Jute dyed orange	210	84	130	52.0	19.50	60.0
Jute dyed yellow	210	88	130	54.0	19.00	58.0
Sawdust	210	185	130	115.0	3.75	11.9
Sawdust dyed red	210	32	130	20.0	27.50	84.6
Sawdust dyed orange	210	19	130	12.0	29.50	91.0
Sawdust dyed yellow	210	40	130	25.0	26.30	80.9

* Red: CI Reactive Red 31; Orange: CI Reactive Orange 13; and Yellow: CI Reactive Yellow 18.

Table VII Adsorption of Mercuric Chloride From Solution by Substrates Dyed With Reactive Dyes

Substrate	Concentration of Salt Solution (mg/L)		Concentration of Metal Cation (mg/L)		Metal Cation Adsorbed	
	Initial	Final	Initial	Final	mg/g Substrate	%
Cotton fibers	176	164	130	121.0	2.25	6.5
Cotton dyed red*	176	133	130	98.2	7.95	24.2
Cotton dyed orange	176	135	130	99.7	7.58	23.1
Cotton dyed yellow	176	137	130	101.0	7.25	22.2
Bamboo pulp	176	162	130	120.0	2.50	8.0
Pulp dyed red	176	76	130	56.0	18.50	56.8
Pulp dyed orange	176	81	130	60.0	17.50	53.8
Pulp dyed yellow	176	86	130	63.5	16.62	51.0
Jute fibers	176	158	130	117.0	3.25	10.0
Jute dyed red	176	73	130	54.0	19.00	58.5
Jute dyed orange	176	77	130	57.0	18.25	56.0
Jute dyed yellow	176	83	130	61.0	17.25	53.0
Sawdust	176	160	130	118.0	3.00	9.2
Sawdust dyed red	176	43	130	32.0	24.50	75.4
Sawdust dyed orange	176	31	130	20.4	27.40	82.2
Sawdust dyed yellow	176	68	130	50.2	19.95	61.4

* Red: CI Reactive Red 31; Orange: CI Reactive Orange 13; and Yellow: CI Reactive Yellow 18.

proved considerably upon dyeing them. Here again, the cotton fibers, dyed or undyed, performed poorly. The dyed sawdust proved to be a good adsorbent as in other cases, improving the level of adsorption above 80%.

During these studies on different metal salt adsorption, the substrates acted as acidic ion exchangers as is evident from the drop in pH in each metal salt solution after adsorption. If we compare the results of the present communication with the earlier ones on copper ion adsorption,[5] it may be observed that for similar substrate types, the adsorption levels of cupric and ferric ions are nearly the same, whereas those of ferrous ions are much less. The adsorption levels of lead and mercury cations are very low as compared to those of iron and copper cations. These observations may be explained on the basis of the ionic radii of the various metal cations as given in Table VIII. It may be seen that the ionic radii of lead and mercury ions are much higher than those of the iron and copper ions. The ionic radii is related to the bulkiness of the metal cation, hence, we observe lower adsorption of lead and mercury ions by the undyed substrates. The ionic radii of cupric, ferric, and ferrous ions are close to each other. However, the ferrous ion gets adsorbed less by the undyed substrate as compared to the ferric ion due to its lower electro-negativity.

Among the different undyed substrates, cotton fibers adsorb the least amount of any metal salt which, perhaps, relates to the lower accessibility of this substrate as indicated by its moisture-regain value as well as the different chemical composition in relation to other substrates.[5] On dyeing, however, all the substrates showed higher metal adsorption even in the case of heavy metals like lead and mercury. This shows that at least for heavy metal cations, the adsorbent should have a stronger capacity to form a chelate—and from that point of view it may be concluded that the dyestuff has a major role to play. Further studies on adsorption of a few more important cations using dyestuffs other than mono-

Table VIII Ionic Radii of the Metals

Metal Cation	Ionic Radius (Å)
Cu^{2+}	0.72
Fe^{2+}	0.74
Fe^{3+}	0.64
Pb^{2+}	1.20
Hg^{2+}	1.10

chlorotriazine class as well as using noncellulosic and synthetic fiber waste like polyamide, silk, etc., are underway. It may be worth mentioning here that we have obtained encouraging results using nylon fibers. Moreover, results on the kinetics of metal ion adsorption by different substrates, as well as the results on column studies to make the process of adsorption continuous and economically feasible, will also be reported later.

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