

# Cupric Ion Removal by Dyed Cellulosic Materials

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## Synopsis

Four different cellulosic materials namely cotton fibers, bamboo pulp, jute fibers, and saw dust were dyed with monochlorotriazine type reactive dyes. The cupric salts, viz., copper nitrate, copper sulphate, copper chloride, and copper acetate were adsorbed from their aqueous solutions of about 250 ppm strength by both undyed and dyed substrates. It was observed that although the undyed substrates do adsorb the metal salts significantly, their capacity increases greatly on dyeing with reactive dyes. Thus, in many cases, the different dyed substrates show an adsorption level of above 90%. Since the substrates chosen differ from each other in a number of ways, the actual adsorption values show wide variation.

## INTRODUCTION

A number of metal ions are known to contaminate the industrial effluents, water supplies, as well as mine waters. Such metal ions include mercury, lead, copper, cadmium, nickel, cobalt, iron, zinc, manganese, gold, silver, platinum, etc. which are toxic and/or precious. The effective and economic removal of such heavy metal ions from sewage and industrial wastes has been the need of the day. Many methods have been proposed and are being used for removal of heavy metal ions from industrial effluents. Conventionally, precipitation of metal ions from solutions as well as the ion-exchange technique are the popular methods. However, synthetic ion-exchange resins are very expensive. Many unconventional methods are, therefore, being thought of for this purpose.<sup>1-3</sup> The agricultural waste products/byproducts of cellulosic origin such as tree bark, peanut skins, walnut expeller, rice straw, paddy husks, sugarcane bagasse, wheat flour waste, etc. are available at a little or no cost. Also, proteins such as wool and other animal keratins, natural and synthetic polyamine polymers like chitosan and the tannin-rich agricultural byproducts are shown to be effective in removal of mercuric and methyl-mercuric salts from water.<sup>2,4</sup> This wool-bound mercury was easily recovered by using aqueous citrate or ethylenediamine tetraacetate solutions at pH 6. The onion skins which contain compounds of polyphenolic groups have been successfully used for binding of the metal ions.<sup>5</sup>

Cupric ion from industrial and mining effluents is also an equally important toxic contaminant which can eliminate all fish and marine plants from the streams for miles downstream from the source.<sup>3</sup> Cupric acetate is also used in the textile industry, to some extent, to get a white print effect by the discharge-resist style of printing, in which the chelateable disperse dye applied onto the surface of polyester fabric is destroyed through formation of chelate between copper ion and the dye. Although advanced countries have stopped using this

process due to the high toxicity in the effluents, others are still making use of this technique due to its simplicity and excellent results.

Randall, Reuter, and Waiss<sup>3</sup> effectively removed cupric ion from aqueous waste solutions using peanut skin, a tannin-containing agricultural waste product. Later on, the use of formaldehyde-polymerized peanut skins in the form of a packed column was found efficient in binding a number of metal ions.<sup>6</sup> They also observed that the process of removal of metal ions is pH-dependent, with a maximum between pH 5 and 7. They further noted that the substrate column can be regenerated by elusion with 1 *N* HCl so that it can be used repeatedly to remove metal ion from the aqueous solutions.

Suemitsu et al.<sup>7</sup> made use of rice hulls by coating them with reactive dye and observed that the adsorption of lead, cadmium, and mercury ions from about 100 ppm solutions increased significantly compared to original substrate. The increase in adsorption was also observed in the cases of other metal ions, although to a lesser extent. Since in all the cases the final pH values were lower than the initial ones, it was suggested that the dye-treated rice hulls act as an acid-form ion exchanger.

The present work reports results on adsorption of cupric salts, namely cupric nitrate, cupric chloride, cupric sulphate, and cupric acetate by different cellulosic substrates. The substrates chosen, cotton, bamboo pulp, jute and sawdust, differ widely in their chemical and physical characteristics, apart from being cellulosic in nature. Different monochlorotriazine-types of reactive dyes were actually dyed onto these substrates to a very light shade and used in the adsorption studies. Iodometric titration method was employed to determine the amount of metal salt taken up by the undyed and dyed substrates.

## EXPERIMENTAL

### Materials

The cotton fibers and jute fibers were purified by boiling for 4 h in a solution containing soap and soda ash, followed by washing with an excess of water and air-drying. The bamboo pulp and the locally available teakwood saw dust were sieved to an approximately uniform size, washed thoroughly with an excess of water and air dried.

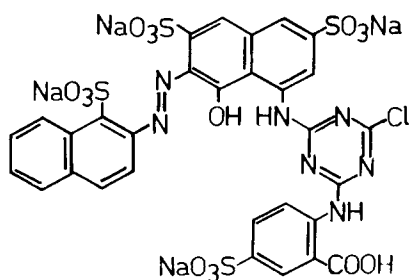
The cupric salts  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , and  $\text{Cu}(\text{COOCH}_3)_2 \cdot \text{H}_2\text{O}$  were all of "analytical reagent" grade.

The following dyestuffs of reactive class were used: (1) C.I. Reactive Red 31, (2) C.I. Reactive Orange 13, (3) C.I. Reactive Yellow 18, and (4) C.I. Reactive Blue 25.

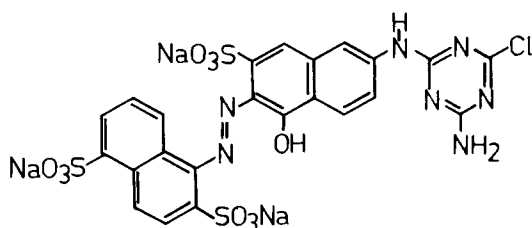
The structures of these dyestuffs are given in Figures 1 and 2. All other chemicals used in the present investigation were of "laboratory reagent" grade.

### Dyeing of Substrates

The dye powder was pasted with cold water followed by dilution with hot water at about 70°C. The cotton fibers were entered at 60°C in a dye bath with liquor ratio 50, prepared for 1% shade to be dyed. After working the material for about 10 min, 70 g/L Glauber's salt was added and dyeing continued at 80°C for another 20 min. Fifteen grams per liter of trisodium phosphate was



C. I. Reactive Red 31



C. I. Reactive Orange 13

Fig. 1. Structures of C.I. Reactive Red 31 and C.I. Reactive Orange 13.

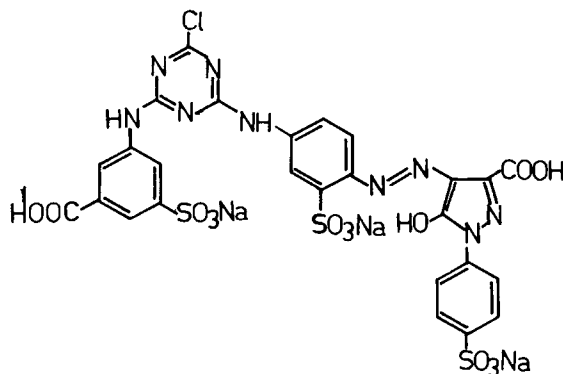
then added, and dyeing was continued for 30 min more. After the dyeing was over, the cotton fibers were removed from the dye bath, squeezed, washed thoroughly with water, soaped at boil using 2 g/L nonionic detergent, washed again with water, and air-dried. The dyeings with other dyestuffs of reactive class were carried out in an identical manner. Bamboo pulp, jute fibers, and sawdust were also dyed by all these dyes in the same way.

### Adsorption of Cupric Ions

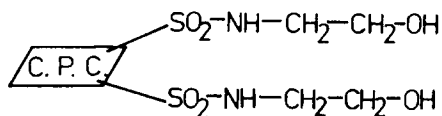
The aqueous solutions of the metal salts were prepared in distilled water. A sample of 1 g substrate was placed in 50 mL of an aqueous solution of about 250 ppm concentration of a cupric salt placed in an 100 mL stoppered Erlenmyer flask and maintained at a constant temperature. The flask was shaken constantly for a period of 2 h. The substrate was then filtered using sintered glass crucible and the filtrate analyzed for the amount of metal salt remaining after adsorption on the substrate.

### Determination of Adsorbed Cupric Ions

The amount of adsorbed cupric ions was estimated as follows: 100 mL of the solution to be analyzed were taken in quick-fit iodometric flask. Twenty-five milliliters of 10% acetic acid and 1 g potassium iodide were added to the flask, stoppered, and kept in darkness for 15 min with intermittent shaking. The liberated iodine was titrated against 0.005 *N* sodium thiosulfate using



C.I. Reactive Yellow 18



(C.P.C. = COPPER PHTHALOCYANINE)

C.I. Reactive Blue 25

Fig. 2. Structures of C.I. Reactive Yellow 18 and C.I. Reactive Blue 25.

starch solution as an indicator after the titration solution gets converted to a pale yellow color. The results were obtained as ppm of a cupric salt.

## RESULTS AND DISCUSSION

The results on adsorption of copper nitrate from its solution by various undyed and dyed cellulosic substrates, in terms of mg salt adsorbed/g substrate and the percentage adsorption values, have been given in Table I. It may be observed that all the undyed substrates adsorb copper nitrate, although the extents of adsorption differ significantly. These adsorption values are found to lie in the range of about 30–75%. Cotton fibers show least adsorption, whereas sawdust shows the maximum. The bamboo pulp and jute fibers give intermediate values of adsorption. Similar results have been obtained in the case of other copper salts, namely copper chloride, copper sulfate, and copper acetate, which are given in Tables II, III, and IV, respectively. Thus, in the case of adsorption of copper nitrate, the cotton fibers adsorbed 40.7%, bamboo pulp adsorbed 66.7%, and jute fibers adsorbed 53.8%, whereas sawdust adsorbed 71.5%. When these substrates were dyed using different monochlorotriazine-types of reactive dyestuffs, the overall adsorption of copper salts from their aqueous solutions increased remarkably, showing adsorption of nearly 90% in many cases. The exact values, however, showed a variation depending upon various substrate-dyestuff-metal salt combination (Tables I, II, III, and IV).

TABLE I  
Adsorption of Copper Nitrate from Solution by Substrates Dyed with Reactive Dyes

Substrate	Solution pH		Concentration of salt solution (mg/L)		Salt adsorbed	
	Initial	Final	Initial	Final	Substrate (mg/g)	%
Cotton fibers	5.20	4.99	253	150	25.75	40.7
Cotton dyed red <sup>a</sup>	5.20	4.20	253	43	52.50	83.0
Cotton dyed orange	5.20	4.72	253	79	43.50	68.7
Cotton dyed yellow	5.20	4.82	253	117	34.00	54.0
Bamboo pulp	5.20	4.95	253	84	42.30	66.7
Pulp dyed red	5.20	4.30	253	7	61.50	97.2
Pulp dyed orange	5.20	4.20	253	21	58.00	91.6
Pulp dyed yellow	5.20	3.90	253	32	55.25	87.4
Pulp dyed blue	5.20	5.00	253	199	13.5	21.2
Jute fibers	5.20	3.97	253	117	34.25	53.8
Jute dyed red	5.20	3.97	253	4	62.50	98.3
Jute dyed orange	5.20	3.35	253	12	60.50	95.2
Jute dyed yellow	5.20	3.38	253	34	55.00	86.6
Sawdust	5.20	4.30	253	72	45.25	71.5
Sawdust dyed red	5.20	4.30	253	16	59.25	93.7
Sawdust dyed orange	5.20	4.25	253	8	61.30	96.8
Sawdust dyed yellow	5.20	4.25	253	42	52.75	83.4

<sup>a</sup> Red = C. I. Reactive Red 31; Orange = C. I. Reactive Orange 13; Yellow = C. I. Reactive Yellow 18; and Blue = C. I. Reactive Blue 25.

The differences in the adsorption levels of a particular copper salt by the different cellulosic substrates may be attributed to the differences in their physical characteristics as well as chemical compositions. It can be clearly seen from Table V that although the 4 substrates under consideration are basically cellulosic in nature, their cellulose contents differ widely. Also, components other than cellulosic and/or functional groups are present which are capable of adsorbing the copper salt. Thus, cotton contains a very high amount of cellulose (85%) with primary and secondary hydroxyl groups present in it that combine with the metal ions. In the case of bamboo pulp, the cellulose content is also high enough (about 92%) and the sites for metal ion adsorption are hydroxyl, carboxyl, as well as carbonyl groups present in the chemical structure due to the process of pulp preparation. The cellulose contents of jute and sawdust are relatively low, approximately 72 and 52%, respectively. These two substrates, however, contain lignin as another major constituent in their structure (about 13% in jute and 31% in sawdust), which has a good capacity for adsorption of metal ions.<sup>2</sup> Lignin possesses a network type of structure having a major portion of methoxyl content (20–23%) of the plant. It also contains about 10% of the free hydroxyl groups.

The values on moisture regain indicate the accessibility of a substrate. A look at the moisture regain values for the four substrates given in Table V suggests that only cotton fibers possess significantly low moisture regain value.

TABLE II  
Adsorption of Cupric Chloride from Solution with Substrates Dyed with Reactive Dyes

Substrate	Solution pH		Concentration of salt solution (mg/L)		Salt adsorbed	
	Initial	Final	Initial	Final	Substrate (mg/g)	%
Cotton fibers	5.86	5.53	260	182	19.50	30.0
Cotton dyed red*	5.86	5.59	260	145	28.75	44.2
Cotton dyed orange	5.86	5.59	260	145	28.75	44.2
Cotton dyed yellow	5.86	5.75	260	170	22.50	34.6
Bamboo pulp	5.86	5.82	260	133	31.75	48.9
Pulp dyed red	5.86	4.46	260	78	45.50	70.0
Pulp dyed orange	5.86	5.55	260	82	44.50	68.5
Pulp dyed yellow	5.86	5.78	260	85	43.80	67.3
Jute fibers	5.86	3.61	260	123	34.30	52.6
Jute dyed red	5.86	3.58	260	57	50.80	78.0
Jute dyed orange	5.86	4.95	260	60	50.00	76.9
Jute dyed yellow	5.86	4.03	260	80	45.00	69.2
Sawdust	5.86	4.95	260	73	46.80	72.0
Sawdust dyed red	5.86	4.45	260	17	60.80	93.5
Sawdust dyed orange	5.86	4.39	260	25	58.80	90.4
Sawdust dyed yellow	5.86	4.36	260	51	52.30	80.4

\* Red = C. I. Reactive Red 31; Orange = C. I. Reactive Orange 13; and Yellow = C. I. Reactive Yellow 18.

The other three substrates exhibit marginal differences in their values. These moisture regain values, therefore, indicate that the cotton fibers have a comparatively compact physical structure which hinders the adsorption of copper ions. A comparison of cotton fibers and bamboo pulp which possess predominantly high cellulose contents leads to the conclusion that more accessibility as well as presence of functional groups other than hydroxyl makes the latter adsorb more copper ions. Among the bamboo pulp, jute fibers, and sawdust, however, the physical structure does not seem to play any major role, but the presence of various types of functional groups affects the adsorption significantly.

It was observed that the initial pH of a copper salt solution drops to different levels during the process of adsorption of the copper ion by any substrate. Suemitsu et al.<sup>7</sup> have suggested that the metal ions bind to the substrate and the hydrogen ions are released in the solution. This decreases the pH of the solution and the substrate acts as an acid-form type of ion exchanger. All the four substrates studied obeyed this concept. Moreover, the drop in pH was observed in the case of all the copper salts studied. Earlier, it has been reported that formaldehyde-treated peanut skins and onion skins adsorbed metal acetates better than other salts and the pH drop is less.<sup>5,6</sup> In the present studies, no such differences in the adsorption of the four copper salts were observed. Perhaps this is due to the different nature of the substrates used in the present study. Peanut skins contain tannins and the onion skins contain polyphenolic groups

TABLE III  
Adsorption of Copper Sulfate from Solution by Substrates Dyed with Reactive Dyes

Substrate	Solution pH		Concentration of salt solution (mg/L)		Salt adsorbed	
	Initial	Final	Initial	Final	Substrate (mg/g)	%
Cotton fibers	5.33	5.23	255	160	23.80	37.2
Cotton dyed red <sup>a</sup>	5.33	4.95	255	40	53.80	84.3
Cotton dyed orange	5.33	4.85	255	70	46.30	72.5
Cotton dyed yellow	5.33	5.02	255	125	32.50	51.0
Bamboo pulp	5.33	5.22	255	90	41.25	64.7
Pulp dyed red	5.33	4.61	255	10	61.30	96.0
Pulp dyed orange	5.33	4.60	255	22	58.30	91.4
Pulp dyed yellow	5.33	4.75	255	32	55.80	87.5
Pulp dyed blue	5.33	5.12	255	199	14.00	22.0
Jute fibers	5.33	4.70	255	120	33.75	53.0
Jute dyed red	5.33	3.90	255	16	59.80	93.7
Jute dyed orange	5.33	4.45	255	25	57.50	90.2
Jute dyed yellow	5.33	4.70	255	35	55.00	86.3
Sawdust	5.33	4.25	255	170	46.25	72.5
Sawdust dyed red	5.33	3.95	255	6	62.30	97.6
Sawdust dyed orange	5.33	4.66	255	8	61.80	96.9
Sawdust dyed yellow	5.33	4.41	255	44	52.80	82.7

<sup>a</sup> Red = C. I. Reactive Red 31; Orange = C. I. Reactive Orange 13; Yellow = C. I. Reactive Yellow 18; and Blue = C. I. Reactive Blue 25.

and hence, they may behave differently than the cellulose or lignin-containing substrates in their capacity to act as an acid-form type of ion exchanger.

The reactive dyes selected for dyeing the various substrates were of the monochlorotriazine type. It may be seen that the presence of azo linkages as well as the presence of groups like  $-\text{COOH}$ ,  $-\text{OH}$ , etc. in the favorable positions ( $O$ ,  $O'$ ) to the azo linkage make it possible to obtain stable five-membered ring chelates with the metal cations. During the process of dyeing, the  $-\text{Cl}$  group of the triazine system reacts with the primary hydroxyl group of the cellulosic chain molecule and forms a covalent bond. Thus, the dyestuff molecule is firmly attached to the cellulosic chain of the substrate and it cannot be detached easily under normal conditions of washing. It was observed that even a treatment with 0.1  $N$   $\text{HCl}$  solution at room temperature for 2 h could not break this bond. Similar treatment was given to various substrates which had adsorbed different copper salts. It was found that in the case of undyed substrates, the adsorbed copper ions could be removed to almost fullest extent, whereas, the removal was only up to about 50% in the case of the dyed substrates. For complete removal of the adsorbed copper ions from the dyed substrates, higher concentration of the acid was required. These results suggest that when the undyed substrates are used, the metal cations get adsorbed on various groups present in the substrate, either from cellulose component or from lignin component. This adsorption is mainly ionic in nature and hence weak, and can be leached

TABLE IV  
Adsorption of Cupric Acetate from Solution by Substrates Dyed with Reactive Dyes

Substrate	Solution pH		Concentration of salt solution (mg/L)		Salt adsorbed	
	Initial	Final	Initial	Final	Substrate (mg/g)	%
Cotton fibers	5.72	5.61	250	160	23.80	38.0
Cotton dyed red*	5.72	5.51	250	133	29.30	46.8
Cotton dyed orange	5.72	5.38	250	138	28.00	44.8
Cotton dyed yellow	5.72	5.54	250	150	25.00	40.0
Bamboo pulp	5.72	4.41	250	115	33.80	54.0
Pulp dyed red	5.72	4.85	250	60	47.80	76.0
Pulp dyed orange	5.72	4.42	250	55	48.80	78.0
Pulp dyed yellow	5.72	4.42	250	55	48.80	78.0
Jute fibers	5.72	4.43	250	140	27.50	44.0
Jute dyed red	5.72	4.26	250	36	53.50	85.6
Jute dyed orange	5.72	5.68	250	30	55.00	88.0
Jute dyed yellow	5.72	4.57	250	37	53.30	85.2
Sawdust	5.72	4.47	250	63	46.80	74.8
Sawdust dyed red	5.72	4.95	250	20	57.50	92.0
Sawdust dyed orange	5.72	4.95	250	28	55.50	88.8
Sawdust dyed yellow	5.72	4.81	250	31	54.80	87.6

\* Red = C. I. Reactive Red 31; Orange = C. I. Reactive Orange 13; and Yellow = C. I. Reactive Yellow 18.

out with the dilute acid. In the case of dyed substrates, only a few hydroxyl groups are utilized in forming dye-cellulose bond, which are then not available for the metal cation adsorption. However, a greater number of groups of varied nature from the dyestuff molecule are now available for the metal cation to combine with the dyed substrate. A comparatively more stable chelate is formed with the groups present in the dye molecules, which explains the difficulty in removal of the adsorbed copper ions from the dyed substrate. The portion of adsorbed copper ions which is held ionically can be removed with this dilute acid, but the remaining portion, which is expected to form metal complexes with the dyestuff molecules cannot be leached out.

TABLE V  
Characteristics of the Substrates

Substrate	Moisture regain (%)	Major constituents (%)
Cotton fibers	5.97	Cellulose 85
Bamboo pulp	7.64	Cellulose 92
Jute fibers	8.19	Cellulose 72 Lignin 13
Sawdust	7.86	Cellulose 52 Lignin 31



The three dyes used were actually dyed using a very low amount (0.01% solution) onto the substrates. Earlier, Suemitsu et al.<sup>7</sup> have treated rice hulls with reactive dyes in such a manner that the amount of dye taken for treatment was very high (1.0% solution). In the present study, therefore, the enhancement of the adsorption of copper ions due to a dye is a very distinct feature. Thus, a very small amount of the reactive dye onto the substrate can bind copper ion very effectively, making the process more economical. It is also possible that other dyestuffs which are cheaper and/or applicable to cellulosic materials more easily can show similar behavior as far as the adsorption of metal cation is concerned. It may be noted here that it is not necessary to have the dyestuff covalently bonded to the cellulosic substrate, but it should be held in the material sufficiently firmly, so that the overall subsequent adsorption of the metal cations increases. Such studies are already under way and we have observed that a direct dye, C.I. Direct Red 23 also increases metal adsorption when dyed on cotton fibers. Although, in general, it was observed that the copper ion adsorption reached a 90% level in many dyed substrates, it should be possible to attain a level of almost 100% either in a particular substrate-dye-metal salt combination or by increasing the time of contact between the dyed substrate and the metal salt solution, or by increasing the amount of dye marginally onto the substrate.

In order to support the fact that the copper ion adsorption increases only in the presence of particular dyes which can form metal complexes with the copper ion, dyeing was carried out onto bamboo pulp using a reactive dye (C.I. Reactive Blue 25) which does not possess any sites for such a metal complex formation. These results are reported in Tables I and II. In this case, it may be observed that the copper ion adsorption from the solutions of copper nitrate and copper sulfate does not improve at all above the levels of those obtained by the undyed bamboo pulp. In fact, it reduces drastically, which is perhaps due to nonavailability of —OH groups for adsorption. This confirms the view expressed earlier that the additional metal cation adsorption has taken place through the formation of chelates between the chelatable dye and the metal ion. Further investigations using different types of metal salts and dyestuffs are being carried out.

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