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Dyestuffs for Improved Metal Adsorption from Effluents

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ABSTRACT

Reactive dyestuffs, widely used for dyeing cellulosic textiles, have been subjected to a novel use. Cheap cellulose-containing materials, such as bamboo pulp and sawdust, have the capacity to adsorb heavy metal ions, and this is enhanced further on dyeing these substrates with reactive dyes of the monochlorotriazine type. Almost complete removal of metal ions such as Cu^{2+}, Pb^{2+}, Hg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, *and* Ni^{2+} *from their aqueous solutions has been achieved. The role of the dyestuff in improving the metal ion adsorption is discussed.*

1 INTRODUCTION

Contamination of streams and rivers by industrial effluents containing different metal salts is a serious environmental problem. Many methods have been proposed for the removal of these metal ions, of which ion-exchange is a convenient one; however, the synthetic ion-exchange resins are expensive. Many agricultural waste products and by-products, mainly of cellulosic origin, have been tried by different workers.[1–4] These materials include tree bark, rice straw, paddy husk, sugarcane bagasse and wheat flour waste. Proteins such as wool[5] and other animal keratins,[6] natural and synthetic polyamine polymers like chitosan,[7] as well as tannin-rich agricultural by-products, have also been found to be effective in the removal or mercury salts from polluted water.[8] Many reactive dyes contain the azo chromophore and substituents such as hydroxyl, sulphonic acid, amino and

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carboxyl, and when present in the o—o′ positions to the azo group, can provide opportunities for chelating a metal ion. In addition, such favourable conditions may also be created when the dye reacts with the cellulosic chain.

Results on the improved capacity of two cellulosic substrates, namely bleached bamboo pulp and sawdust, on dyeing with a number of reactive dyes of the monochlorotriazine type are reported here.

2 EXPERIMENTAL

2.1 Materials

2.1.1 Substrates

The bamboo pulp and sawdust used in this study were purified. The pulp was soaked in boiling water for about 30 min and further boiled with intermittent stirring for 20 min. It was then washed several times with hot water. After final washings with cold deionized water, the material was oven-dried at about 45°C.

Locally available teak-wood sawdust was soaked overnight in water. Floating wood chippings and other contaminants were removed and the sawdust was washed four to five times with boiling water, then with cold water and finally with deionized water. The mass was then dried at about 45°C. The dried mass was seived to an approximately uniform size.

2.1.2 Metal salts

The following 'Analytical Reagent' grade salts were used: copper acetate, lead acetate, mercuric chloride, ferric nitrate, ferrous sulphate, zinc acetate, and nickel sulphate. All the other chemicals used in the study were 'Laboratory Reagent' grade.

2.1.3 Dyestuffs

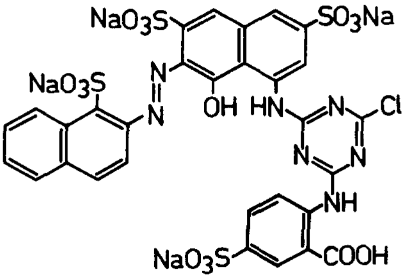
The following reactive dyestuffs were used:

CI Reactive Yellow 18
CI Reactive Orange 13
CI Reactive Red 31
CI Reactive Blue 25

The structures of these dyestuffs are given in Figs 1 and 2. A direct dye, CI Direct Red 23, was also used (Fig. 3).

2.2 Dyeing of substrates

The reactive dye powder was dissolved by pasting with cold water, and the solution was diluted to the requisite amount with hot water at about 70°C.



(a)

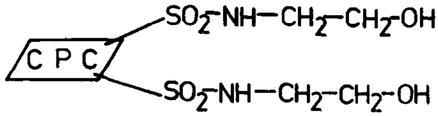


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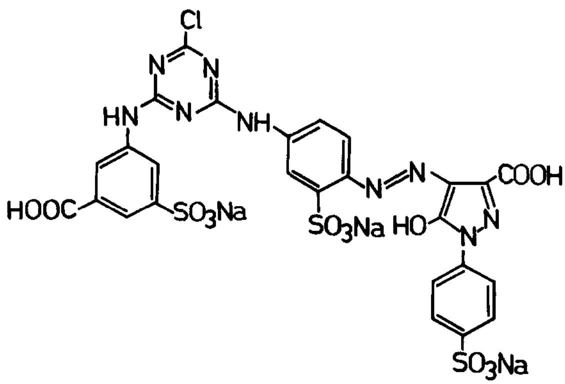
Fig. 1. Structures of (a) CI Reactive Red 31 and (b) CI Reactive Blue 25. (CPC = copper phthalocyanine.)



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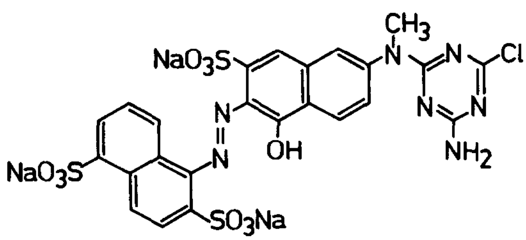

(b)

Fig. 2. Structures of (a) CI Reactive Yellow 18 and (b) CI Reactive Orange 13.

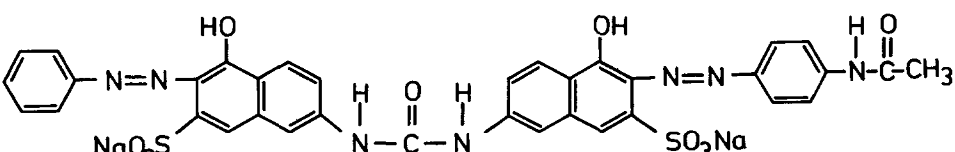

Fig. 3. Structure of CI Direct Red 23.

The bamboo pulp was entered at 60°C in a dyebath of liquor ratio 1:50, prepared for 2% shade. After about 15 min, 70 g $litre^{-1}$ Glauber's salt was added in two portions at intervals of 15 min. After dyeing for another 20 min, 15 g $litre^{-1}$ trisodium phosphate was added in two portions over 15 min and dyeing was continued at 80°C for 60 min. The substrate was then filtered, washed thoroughly with water, soaped at the boil for 20 min using 2 g $litre^{-1}$ of non-ionic detergent, filtered and again washed with hot and then cold water. Care was taken to ensure that the final washings were colourless. The substrate was then dried at 45°C.

A similar dyeing procedure was used for the sawdust, but the dye fixation was achieved using 15 g $litre^{-1}$ Na_2CO_3. The dyed pulp was then cut to uniform size.

2.3 Adsorption of different metal ions

Four grams of the substrate in a stoppered Erlenmyer flask was shaken for 2 h with the metal salt solution of 120–130 ppm cation concentration prepared in distilled water. The material-to-liquor ratio was maintained at 1:50. After completion of the equilibrium, the substrate was filtered using a sintered glass funnel and the filtrate analyzed. From the amount of cation remaining in the filtrate, the percentage of cation adsorbed was calculated.

2.4 Determination of adsorbed metal ions

EDTA[9] methods for the purpose of analysis of different metal cations like Pb^{2+}, Hg^{2+}, Fe^{3+}, Zn^{2+}, and Ni^{2+} were extensively used. The methods used were either direct methods or standard replacement methods.

Iron, in its ferrous state, was estimated by redox titration in acidic medium employing a standard solution of potassium permanganate in dilute sulphuric acid (10%), the potassium permanganate itself acting as the indicator.

Cupric ion was estimated by the iodometric method. By addition of potassium iodide to an acidic solution of the cupric salt, an equivalent amount of iodine was liberated, which was then titrated against standard thiosulphate solution, using starch indicator near the end-point. The results obtained, as milligrammes per litre for the salt, were expressed as percentage adsorption and were compared with the undyed substrates.

3 RESULTS AND DISCUSSION

The bamboo pulp and sawdust were dyed with three monochlorotriazine reactive dyes—CI Reactive Yellow 18, CI Reactive Orange 13 and

TABLE 1
Metal Ion Adsorption by Dyed Bamboo Pulp

Metal ion	*Metal ion adsorbed (%)*			
	Undyed	*Dyed with CI Reactive*		
		Yellow 18	*Orange 13*	*Red 31*
Cu^{2+}	50·0	80·0	86·0	82·0
Pb^{2+}	8·6	52·0	53·0	56·0
Hg^{2+}	8·0	51·0	53·8	56·8
Fe^{3+}	60·0	82·8	84·0	85·2
Fe^{2+}	30·3	51·5	39·4	42·4
Zn^{2+}	22·5	40·0	42·0	40·0
Ni^{2+}	27·6	40·6	46·2	44·5

CI Reactive Red 31. These were then subjected to equilibrium adsorption of various metal cations from their aqueous solutions. Tables 1 and 2 give the results of these studies. It may be noted that the substrates used do possess adsorption capacity even in the undyed form, and this is greatly enhanced after dyeing them.

Both the substrates are basically cellulosic in nature, although the cellulose content of bamboo pulp is as high as 92%, while that of sawdust is 52%. Due to the process of pulp preparation, carbonyl groups are also present in the structure of bamboo pulp, in addition to hydroxyl and carboxyl groups. Sawdust, on the other hand, contains about 31% lignin, which is also known to adsorb metal ions.[10] Lignin possesses a network type of structure in which methoxyl and hydroxyl groups are present. The

TABLE 2
Metal Ion Adsorption by Dyed Sawdust

Metal ion	*Metal ion adsorbed (%)*			
	Undyed	*Dyed with CI Reactive*		
		Yellow 18	*Orange 13*	*Red 31*
Cu^{2+}	61·5	95·1	94·0	96·1
Pb^{2+}	10·0	80·0	93·0	84·2
Hg^{2+}	9·2	61·4	82·2	75·4
Fe^{3+}	60·2	90·0	96·6	94·3
Fe^{2+}	18·8	65·6	68·8	72·0
Zn^{2+}	33·4	45·0	51·8	54·0
Ni^{2+}	27·6	48·6	55·3	50·0

presence of these various groups in the two structures is responsible for the metal cation adsorption and their presence makes possible the formation of chelates with metal ions when the groups are in favourable positions.

When these substrates were dyed with a reactive dye of the monochlorotriazine type, the chloride group of the triazine ring system reacts with the primary hydroxyl group of the cellulosic chain molecule, forming a covalent bond. The dyestuffs selected are azo dyes containing substituents such as —OH and —SO_3H in the o—o′ positions to the azo linkage.

The data shown in Tables 1 and 2 appears to show that a particular dye is better than the other two in its capacity for metal adsorption. Experiments using other cellulosic materials like cotton and jute fibres dyed with these three reactive dyes have also been conducted; in general, the conclusion is that the adsorption is dependent on three factors—the substrate, the dye and the particular metal salt. Thus, it cannot be said that a particular dye shows greater capability than the other two. It may be noted that, in the case of Fe^{2+} ion adsorption by the dyed bamboo pulp, CI Reactive Yellow 18 shows higher values than that for the other two dyes. Also, in many cases, there is very little difference in the percentage of metal adsorbed in the presence of the three dyes in a substrate. About 2–4% variation in the adsorption values is likely, since the results are obtained through calculations using titration readings. Thus, the three dyestuffs possess more or less similar adsorption capacity for a particular metal cation. The capacities, however, differ depending on the nature of metal cation, namely charge and size of the metal ion.[11]

In previous studies,[10] it is shown that cotton and jute fibres adsorb cupric ions effectively and that the physical structure of different substrates also plays a significant role in metal ion adsorption. In work reported by Suemitsu *et al.*,[12] reactive-dye-coated rice hulls have been shown to adsorb different metal ions. This present work emphasizes more clearly the role of a particular dyestuff in enhancing the adsorption capacity. The dyeing is carried out from a very low concentration of the dye solution (0·01% solution) and, hence, the amount of dyestuff required is low.

The nature of dyestuff is of prime importance, since the presence of suitable groups in appropriate orientations is necessary for a stable chelate formation. The three triazinyl dyes used in the present work form chelates with the metal ions. When high concentrations of dye and metal salt were mixed in their aqueous solution forms, turbidity was observed; at low concentrations it was difficult to observe any turbidity with Cu^{2+} ions, but with Pb^{2+} ions, however, substantial precipitation occurred even at low concentrations. Also, on combination of dye and metal in solution, there was a shift in absorption maxima. For example, with the dye CI Reactive Orange 13 and Pb^{2+} ion, the absorption maxima shifted from 510 to 490 nm; a similar shift was observed with Cu^{2+} ions. On adsorption of metal ions on the dyed substrates, strong acids were required to elute the metal ions, which can be taken as further evidence for chelate formation.

On dyeing bamboo pulp with CI Reactive Blue 25 (*N*-*β*-hydroxyethylsulphone type) it was observed, in the case of Cu^{2+} ion adsorption from copper acetate solution (130 ppm cation concentration), that 56% adsorption by the undyed bamboo pulp decreased to 30%. The reason for this is that the dye reacts with the hydroxyl groups of the cellulosic chain molecules and decreases the availability of —OH groups of the substrate for metal adsorption. Similar results were obtained for zinc acetate (130 ppm cation concentration): the value of 22·5% for the control sample decreased to 2·5% for the dyed sample.

The prerequisite for metal chelate formation by the dye is not restricted to reactive dyes. Any dye capable of chelating could be used. Thus, CI Direct Red 23 (Fig. 3) is an azo dye which can form chelates and it also enhances the metal ion adsorption capacity. Thus, when dyed on bamboo pulp at 2% shade and subjected to Cu^{2+} ion adsorption (from copper acetate solution), the percent adsorption values were as follows for a 130-ppm concentration: undyed bamboo pulp showed adsorption of 55·0%, which enhanced to 87·0% on direct dye dyeing.

It can, therefore, be concluded that a cheap and effective method of removing various heavy metal ions which are detrimental to water quality has been obtained, and many such dyestuffs dyeable on different types of substrates, including cellulosic and protein, can be used for this purpose.

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