

STUDIES ON THE DYEING OF CHITIN AND CHITOSAN WITH PRE-METALLISED DYES AT NEUTRAL pH

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Abstract

Both 1:1 pre-metallised acid dyes and pre-coppered direct dyes, but not 1:2 pre-metallised acid dyes, have been shown to readily dye chitin and chitosan from neutral dyebaths. With the 1:1 pre-metallised acid dyes the addition of neutral electrolyte increases the uptake of dye, indicating that electrostatic forces of attraction are not involved in the adsorption process. A mechanism of dyeing is proposed involving complex formation between the metal ion of the pre-metallised dye and the amine groups of the substrate. The wet fastness properties of the 1:1 pre-metallised acid dyeings carried out at neutral pH are at least equal to, and in many cases greater than, those obtained by the conventional dyeing process at pH values of 4.5 - 5. In the case of pre-coppered direct dyes a rigorous washing-off process is required in order to remove dye adsorbed on the substrate, but not complexed with the amine groups, if the maximum wet fastness is to be achieved.

Key words: *chitin; chitosan; pre-metallised dyes; neutral dyeing.*

1. Introduction

There are several types of pre-metallised dyes (pre-mets) currently used in textile dyeing:

- 1:1 pre-metallised acid dyes containing 1 Cr⁺³ ion complexed with 1 dye molecule;
- 1:2 pre-metallised acid dyes containing 1 Cr⁺³ or Co⁺³ ion complexed with 2 dye molecules;
- 1:1 pre-metallised direct dyes containing 1 Cu⁺² ion complexed with 1 dye molecule;
- 2:1 pre-metallised direct dyes containing 2 Cu⁺² ions complexed with 1 dye molecule.

They are produced from dyes containing *o,o'*-dihydroxyazo, *o*-carboxy-*o'*-hydroxyazo, *o*-amino-*o'*-hydroxyazo or *o*-hydroxy-*o'*-methoxyazo structures (in this latter case demethylation occurs during formation of the metal:dye complex so that the product is identical with that from the corresponding *o,o'*-dihydroxyazo dye). These structures function as tridentate ligands so that in the case of the 1:2 pre-metallised acid dyes all six co-ordination sites of the Cr⁺³ or Co⁺³ ions are occupied by ligands that are part of the dye molecules. With the other three types of pre-metallised dyes either 3 (Cr⁺³) or 1 (Cu⁺²) co-ordination sites are occupied by labile ligands such as water molecules in acid or neutral conditions, or hydroxyl groups in alkaline conditions [1].

In view of the well established ability of chitosan to form complexes with transition metal ions the authors previously proposed that 1:1 pre-metallised acid dyes should dye chitin and chitosan under neutral conditions. In a brief paper [2] it was confirmed that this class of dyes does indeed readily dye chitin and chitosan under neutral conditions as well as from acid dye baths. The differences in the effect of added Na₂SO₄ on dye uptake at neutral and acid pH values, and the observed differences in the resultant shades of the dyed substrates depending on whether applied by a neutral or an acid dyeing processes, led to a proposed dyeing mechanism for neutral dyeing. This involves complex formation between the Cr⁺³ ions of the 1:1 pre-metallised acid dyes and unprotonated amine groups of the substrate through displacement of one of the labile ligands occupying a co-ordination site of the Cr⁺³ ion. Since then, further research has been carried out on the neutral dyeing behaviour of the 1:1 acid pre-metallised dyes, and the study has also been extended to include the pre-metallised direct dyes.

2. Materials and methods

2.1. Materials

The chitin was crab chitin obtained from India and ball milled to give a powder having a particle size between 300-500 µm and an F_A value of 0.975. The chitosan used was prepared in the laboratory from this chitin and had an F_A value of 0.38 and <M_v> value of 9.05 × 10⁵ [2]. The chemicals used were GPR grade and the dyes were commercial samples, purified by recrystallisation from aqueous ethanol if required.

Deamination was carried out by stirring chitin powder (30 g) at room temperature in 0.1 M acetic acid (500 ml) to which three portions of NaNO₂ (2.5 g) in distilled water (25 ml) were added at intervals of 3 hours. The deaminated chitin was filtered off, neutralised, rinsed several times in distilled water, and dried.

2.2. Methods

Chitin and deaminated chitin samples were dyed in sealed glass tubes at 90 °C and a liquor ratio of 40:1. Dyeing was carried out for 2 hours, after which the powdered substrate was filtered off and the filtrate analysed by uv-visible spectroscopy to determine the concentration of dye remaining in solution and hence the percentage uptake of dye.

Desorption was also carried out in sealed glass tubes at 90 °C and a liquor ratio of 40:1. After a desorption time of 2 hours the mixture was filtered and the filtrate analysed to determine the percentage desorbed. More severe desorption was carried out by Soxhlet-extraction with water.

Equilibrium dye adsorption values were measured after dyeing at 80 °C for 12 hours, and the dye adsorbed determined as described above.

Diffusion concentration profiles were obtained as described previously [3].

Wet fastness ratings were determined by standard methods using SDC “Multifabric” for the adjacent fabrics.

3 Results and discussion

3.1. 1:1 Pre-metallised acid dyes

3.1.1. Preliminary adsorption studies

Four 1:1 pre-metallised acid dyes were dyed on both chitin and deaminated chitin at neutral pH, a 4% shade (based on weight of chitin) being applied in each case. The results are shown in **Table 1**. Dyeings were also carried out at pH 4.5 (results not shown).

These results strongly suggest that the small percentage of deacetylated residues customarily found in chitin is responsible for the uptake of these metal complexed dyes under neutral conditions. Although an F_A of 0.975 shows that on average there are only 2.5 **D**-glucosamine units per 100 monosaccharide units, this is a sufficiently high concentration to allow reasonably heavy depths of shade to be produced. Such a level of deacetylation gives an amine group concentration of 125 m.equiv.kg⁻¹, which is considerably greater than that found in commercial nylon fibres where values of 40 - 50 m-equiv.kg⁻¹ are typical. Such concentrations are perfectly adequate to allow good depths of shade to be obtained on nylon using acid dyes at pH 4.5 - 5.5, and under these conditions it is well established that the protonated amine groups are the sites at which dyeing occurs. However

Table 1. Uptake of 1:1 pre-metallised acid dyes on chitin and deaminated chitin at neutral pH.

Dye	Percentage uptake of dye	
	Chitin	Deaminated chitin
C.I. Acid Yellow 99	80.7	49.8
C.I. Acid Orange 74	86.4	51.6
C.I. Acid Blue 158	73.1	27.4
C.I. Acid Green 12	84.6	51.2

these low amine group concentrations required for normal dye uptake mean that unless the deamination treatment is 100% effective there could still be appreciable dye uptake through interaction with the remaining amine groups.

The dyeings carried out at neutral pH showed a higher degree of exhaustion and, in some cases, a noticeable difference in hue, compared with those carried out at acid pH. This was very pronounced with C.I. Acid Green 12 which produced a very flat, weak dyeing at acid pH but gave a very strong, bright dyeing when dyed under neutral conditions. This strongly suggests that the mode of interaction between dye and substrate is different when dyed under acid and neutral conditions.

3.1.2. Effect of neutral electrolyte

In the general methods for dyeing wool, silk and nylon with acid dyes at acid pH, neutral electrolytes such as Na_2SO_4 are used to slow the rate of dye uptake in order to improve the levelling properties of the dyes. This retarding effect is due to competition between the dye anions and the electrolyte anions for the positively charged dye sites in the fibre. However, in dyeing cellulose with any of the usual dye classes, where any electrical interaction between the negatively charged substrate and the anionic dye ion is one of repulsion, the addition of neutral electrolyte increases the amount of dye taken up through a combination of reducing electrical repulsion to a minimum and of "salting out" the dye from the aqueous phase to the fibre phase. The effect of increasing amounts of Na_2SO_4 on the uptake on chitin of the 1:1 pre-metallised dye, C.I. Acid Blue 158, at neutral pH was studied. The plot (*Figure 1*) shows that the dye absorbance increases with increase in Na_2SO_4 concentration, indicating the absence of any competitive effect between dye ions and SO_4^{2-} ions, thereby ruling out attractive ionic interaction. This agrees with the previous study [2] covering three 1:1 pre-metallised acid dyes at a single dye concentration (1% o.w.g) in which it was found that at acid pH the addition of Na_2SO_4 decreased dye uptake whereas when dyeing at neutral pH it increased uptake.

3.1.3. Equilibrium adsorption isotherm

The previously proposed dyeing mechanism [2] involves amine groups from the chitin or chitosan replacing labile ligands in the co-ordination sphere of the metal-dye complex:



If this is the mechanism then the equilibrium adsorption should follow a Langmuir plot. To test this, a series of dyeings to equilibrium with C.I. Acid Blue 158 were carried out at neutral pH and the results are plotted in *Figure 2*.

Extrapolation back to $(1/[D]_{s,\infty}) = 0$ gives an intercept of 0.0136 kg.g^{-1} therefore:

- maximum dye uptake = 73.53 g.kg^{-1}
- which is $\equiv 0.127 \text{ mols.kg}^{-1}$ dye (molecular weight of CI AB 158 = 580).

In a chitin sample having $F_A = 0.975$, the equivalent weight of the amine group is 8078, giving an amine group concentration of $0.124 \text{ mols.kg}^{-1}$. This value correlates well with the maximum molar uptake of dye calculated above.

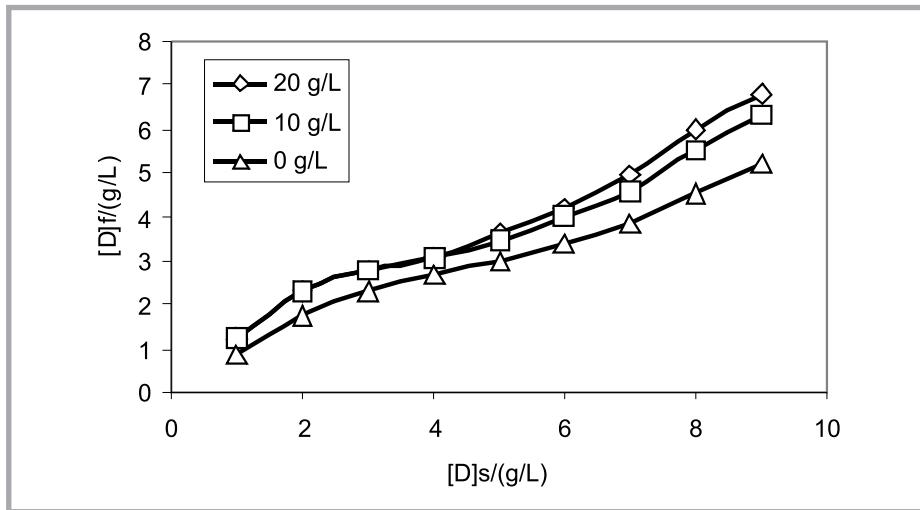


Figure 1. Effect of increasing Na_2SO_4 concentration on uptake of C.I. Acid Blue 158 on chitin at neutral pH.

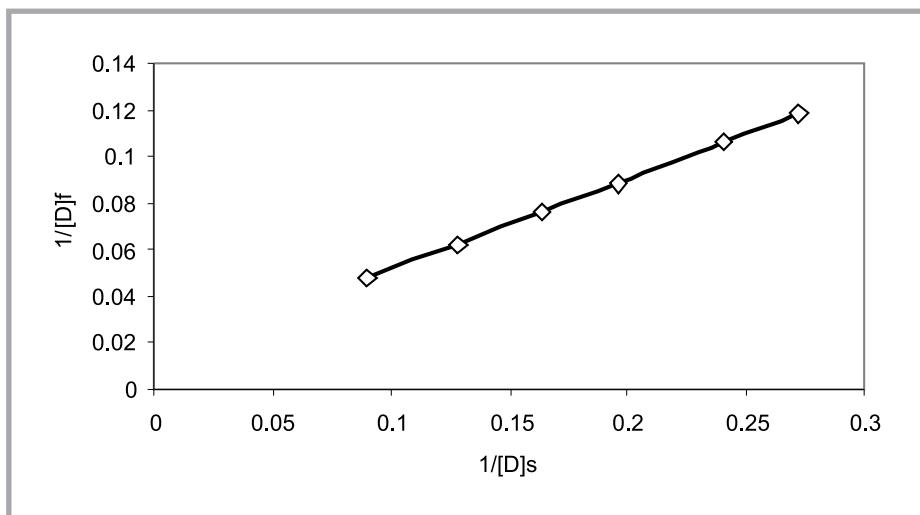


Figure 2. Plot of $1/[D]_{f,\infty}$ versus $1/[D]_{s,\infty}$ for C.I. Acid Blue 158 on chitin at neutral pH.

Adherence to the Langmuir plot, and the very good agreement between the moles of amine groups available and the maximum adsorption of dye that can be achieved at neutral pH, strongly support the suggestion that dye adsorption occurs by a specific site mechanism. This in turn supports the dyeing mechanism proposed earlier [2] and which is given above.

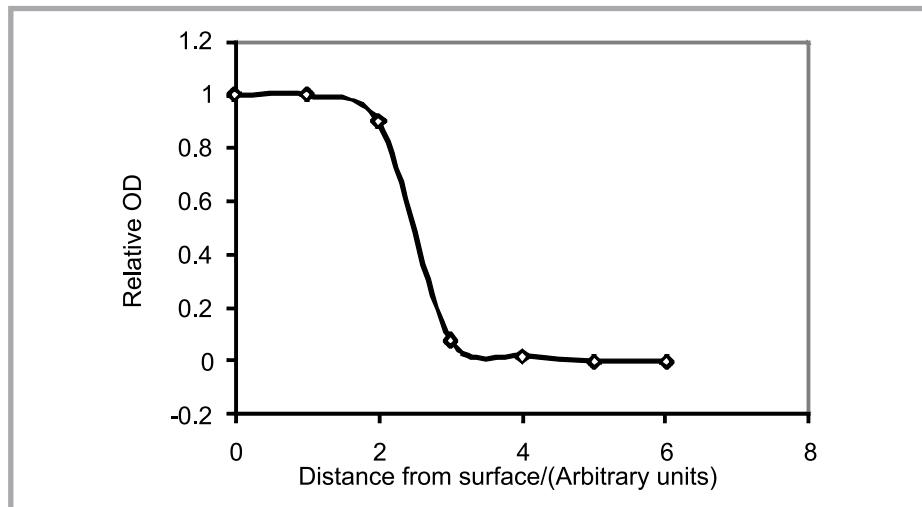


Figure 3. Concentration profile of CI Acid Blue 158 in chitosan film at 80 °C and neutral pH.

3.1.4. Diffusion behaviour

The diffusion behaviour of a 1:1 pre-metallised dye at neutral pH was investigated using the Sekido technique as described previously [3]. The concentration profile is shown in **Figure 3**.

The concentration profile is similar to that obtained previously for acid dyes on nylon at acid pH and is typical for systems where adsorption occurs by a specific site mechanism [4]. However both the nature of the site and the mechanism of interaction between dye ion and site are different in this case, and ionic forces of attraction are not involved.

3.2. 1:1/2:1 pre-metallised direct dyes

Unlike unmetallised acid dyes, which are not adsorbed by chitin and chitosan under neutral conditions, unmetallised direct dyes readily adsorb onto chitin and chitosan in the same manner as they do onto cellulose [3]. Thus it is not as straightforward as it is in the case of pre-metallised acid dyes to determine how the presence of the complexed Cu⁺² ion affects the dyeing mechanism of pre-metallised direct dyes.

3.2.1. Adsorption/desorption behaviour on chitin.

A series of pre-metallised direct dyes and conventional direct dyes i.e. uncoppered, were applied to chitin powder at 80 °C by the normal process for direct dyes on cellulose. The pre-coppered dyes used were Indosol ® dyes, which are a range of copper-complexed direct dyes introduced by Clariant and designed to be used with an aftertreatment with Indosol E-50, a proprietary polybasic condensate of diethylenetriamine and an amide such as cyanamide, dicyandiamide, guanidine or biguanide. The molecular structures of the dyes have not been disclosed so it is not possible to say whether they are 1:1 or 2:1 pre-metallised dyes. Visual examination indicated that although the uncoppered dyes exhaust to a similar

extent as the copper-complexed direct dyes, the latter appear to adhere much more strongly to the chitin substrate (**Table 2**), suggesting that the pre-coppered direct dyes are adsorbed onto the substrate by a different mechanism, namely by formation of a dye≡Cu⁺²-substrate complex..

The effects of the chelated Cu⁺² ion on uptake and resistance to removal was quantified for both chitin and deaminated chitin for four of the Indosol dyes listed above in **Table 3**. Also included is C.I. Direct Blue 218, which is a 2:1 pre-metallised copper complex of C.I. Direct Blue 15, whose structure is known. The latter dye is included for comparison. The dyed samples were not Soxhlet extracted but were desorbed by heating in distilled water at 80 °C, at a liquor ratio of 40:1, for 2 hours.

Like the 1:1 pre-metallised acid dyes (Table 1) the percentages of pre-metallised direct dyes adsorbed on deaminated chitin are less than on chitin itself, but the extent of the decrease is less with the direct dyes, an average decrease of 17.6% for the pre-coppered direct dyes compared with 36.2 for the 1:1 pre-metallised acid dyes. This is to be expected as direct dyes are designed to show good diffuse adsorption on cellulose chains, which have a similar overall molecular shape to chitin and chitosan chains. However the differences in desorption from the chitin and the deaminated chitin substrates are very pronounced for the pre-coppered direct dyes, the average for the five dyes being 2.9% from the chitin substrate and 35.7% for the deaminated chitin substrate.

It is obviously possible that two mechanisms of adsorption occur with Indosol and other copper-complexed direct dyes, the first involving the formation of a complex of the

Table 2. Visual assessment of relative resistance of pre-coppered and non-coppered direct dyes to removal by Soxhlet extraction with water.

Dye	Comments
Indosol Yellow SF-2RL	No observable change
Indosol Rubinole SF-R	No observable change
Indosol Blue SF-GL	No observable change
Indosol Green SF-GLN	No observable change
Indosol Brown SF-BR	No observable change
Indosol Violet SF-B	No observable change
C.I. Direct Blue 29	Severe loss of colour
C.I. Direct Red 79	Significant loss of colour (less severe than DB29)
C.I. Direct Green 59	Significant loss of colour (less severe than DB29)

Table 3. Adsorption/desorption figures for pre-metallised direct dyes on chitin and deaminated chitin.

Dye	Percentage uptake of dye		Percentage desorbed	
	Chitin	Deaminated chitin	Chitin	Deaminated chitin
Indosol Yellow SF-2RL	83.8	68.7	3.8	42.3
Indosol Rubinole SF-R	89.2	71.5	4.2	38.6
Indosol Blue SF-GL	86.5	71.8	2.7	37.0
Indosol Violet SF-B	92.3	75.6	2.2	33.2
C.I. Direct Blue 218	96.3	72.6	1.6	27.2
[C.I. Direct Blue 15]	97.8	94.9	11.2	18.7]

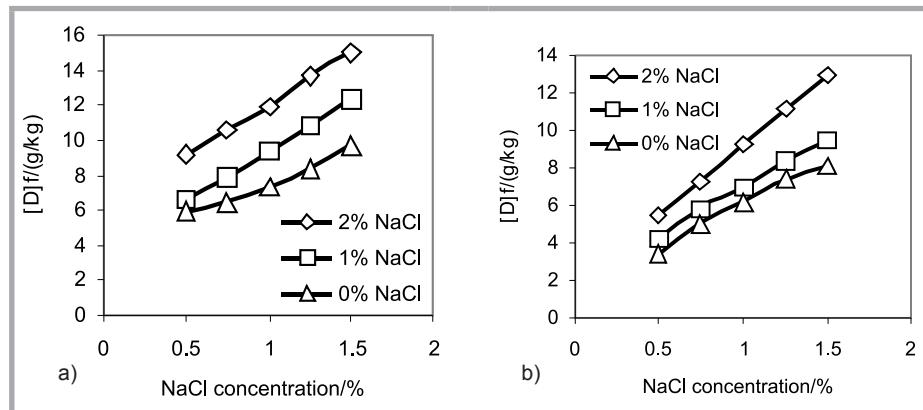


Figure 4. Effect of added neutral electrolyte on adsorption of: a) C.I. Direct Blue 15 (un-coppered direct dye) and b) C.I. Direct Blue 218 (2:1 coppered direct dye), on chitin.

dye with the substrate through the amine groups of chitin acting as ligands for the fourth co-ordination site of the copper ion in the dye-copper ion complex.. The second mechanism is the same as that for the adsorption of normal, uncoppered direct dyes. In this context it is of interest that uptake on the two substrates is less for CI Direct Blue 15 than for its 2:1 copper complex, while its desorption is greater from chitin and less from deaminated chitin. This suggests that although the complexed Cu^{+2} ions improve the affinity of the dye for amine-containing substrates, their presence disrupts and weakens the normal non-specific forces of attraction that would operate between cellulose, chitin or chitosan and a conventional direct dye.

3.2.2. Effect of neutral electrolyte on adsorption on chitin

In dyeing chitin the effect of addition of neutral electrolyte to the dyebath is the same for normal direct dyes (**Figure 4.a**) and for pre-coppered direct dyes (**Figure 4.b**). This indicates the absence of any ionic forces of attraction between the latter type of dye and the substrate and indicates that the role of added neutral electrolyte is to reduce ionic repulsion between dye ion and substrate and to gradually “salt out” the dye ion from the aqueous phase to the substrate phase, as is the case with both direct dyes and pre-coppered direct dyes on cellulose.

3.2.3. Comparison of adsorption/desorption on chitosan and cellulose

For this study samples of woven cotton were padded with a solution of chitosan, dried, neutralised, rinsed and dried. Samples of treated and untreated cotton fabric were then dyed with either Indosol Blue SF-GL or one of two uncoppered direct dyes, and the uptake assessed instrumentally by measuring the K/S values at λ_{\max} using a Datacolour spectro-flash spectro-photometer (**Table 4**). The samples were then Soxhlet-extracted with water and the K/S values re-measured after extraction for 20 minutes and 4 hours (**Table 5**).

All three dyes show an increase in uptake on the chitosan-treated cotton, but the increase is very much greater for the Indosol dye (~ 600% increase for Indosol Blue SF-GL

Table 4. Dye uptake, measured by reflectance spectroscopy, on cotton fabric and chitosan-coated fabric.

Dye	K/S values at λ_{\max}	
	Untreated cotton	Chitosan-treated cotton
C.I. Direct Red 79	2.32	4.79
C.I. Direct Blue 29	2.54	3.63
Indosol Blue SF-GL	1.05	6.19

Table 5. Loss of conventional and pre-metallised direct dyes from cotton and chitosan on Soxhlet extraction.

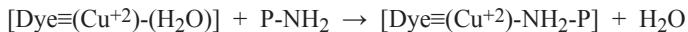
Dye	Decrease in K/S value after extraction/%			
	Untreated cotton		Chitosan-treated cotton	
Extraction time	20 min.	4 hours	20 min.	4 hours
C.I. Direct Red 79	56.9	77.3	62.6	81.2
C.I. Direct Blue 29	57.5	73.4	57.9	71.4
Indosol Blue SF-GL	43.0	65.8	18.3	19.0

compared with ~ 200% for DR 79 and ~ 150% for DB 29). The increase in uptake for the latter two dyes may be attributed to the greater accessibility to dyes of the amorphous chitosan coating compared with the crystalline cotton, but for the Indosol dye there is the added possibility of complex formation with the amine groups of the chitosan through the Cu²⁺ ions of the metal-complexed dye.

The presence of the chitosan coating makes very little difference to the resistance to extraction with near-boiling water shown by the uncoppered dyes at either 20 minutes or 4 hours extraction time (**Table 5**). However the presence of the chitosan coating results in a considerable drop in the amount of the Indosol dye extracted, reducing it from 65.8% after 4 hours (untreated cotton) to 19% (chitosan-treated cotton). There appears to be a more significant loss of Indosol Blue SF-GL here than was observed with chitin as substrate (**Table 2**). This may be due to the much deeper shade obtained here (the wet fastness of a dye decreases with increase in depth of shade), or to a larger proportion of the dye adsorbing as a normal direct dye (diffuse adsorption) in addition to that adsorbed through complex formation, due to the more amorphous structure of the coating compared with particulate chitin.

3.2.4. Diffusion behaviour

The concentration profile for CI Direct Blue 218 at neutral pH was very similar to that obtained (**Figure 3**) for CI Acid Blue 158, a 1:1 pre-metallised acid dye, also at neutral pH, and is indicative of specific site adsorption of the dye ions [4].



3.3. Wet fastness properties of neutral dyed 1:1 pre-metallised acid dyes and 1:1/2:1 pre-metallised direct dyes

The 1:1 pre-metallised acid dyes applied at neutral pH show wet fastness ratings at least equal to, or 1 point greater than, the same dyes applied from a 4% (o.w.f.) H₂SO₄ dye bath. The 1:1 and/or 2:1 pre-metallised direct dyes generally show considerably higher wet

fastness ratings than do the conventional unmetallised direct dyes. However there is always the possibility that some of the dye may be adsorbed by a diffuse adsorption mechanism typical of direct dyes on cellulose, chitin and chitosan [3] and this would lower the wet fastness rating. Hence development of maximum wet would require a vigorous washing-off process after dyeing.

4. Conclusions

The results show that the adsorption of 1:1 pre-metallised acid dyes on chitin and chitosan at neutral pH occurs by a different mechanism than is involved when these dyes are applied at acid pH in the conventional dyeing process.

At neutral pH the mechanism involves interaction between the substrate and the complexed Cr⁺³ ions of the dye leading to replacement of a labile ligand in the Cr⁺³ ion/dye molecule complex by an amine group of the substrate and formation of a dye/Cr⁺³/substrate complex.



The pre-coppered direct dyes, both 1:1 and 2:1, can also interact with amine groups on the substrate by a similar mechanism:



but normal diffuse adsorption may also occur simultaneously. The fact that no acid or electrolyte is needed in the dye bath to obtain very high levels of dye adsorption means that the use of these dyes could be both an environmentally beneficial and a cost effective technique for dyeing chitin and chitosan.

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