

Review

A REVIEW OF THE PHYSICAL CHEMISTRY OF DYEING CHITIN AND CHITOSAN

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Abstract

The literature on the adsorption and diffusion of anionic dyes, including acid, direct, reactive and metal-complexed dyes, on chitin and chitosan is reviewed. The similarity of the overall chain structure of cellulose to both chitin and chitosan, together with the presence of the C(2)-amine groups on the latter two polymers, means that they show considerable similarity in dyeing behaviour to both polysaccharide and protein substrates.

Key words: Chitin; chitosan; dye adsorption; dye diffusion

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1. Introduction

It has been known for over 80 years that chitin, and more especially chitosan, are readily dyed with conventional textile dyes used for dyeing both protein fibres – wool, silk, cashmere and other animal fibres - and cellulosic fibres - cotton, flax viscose rayon etc. [1]. This can be readily understood as both chitin and chitosan possess amine groups that are protonated under acid conditions, and so they may be dyed with the same dye classes as are used on wool, silk and other protein fibres, namely the various sub-groups of acid dyes (equalising, milling, super-milling, 1:1 and 1:2 pre-metallised, and mordant acid dyes). At acid pHs these dyes are adsorbed by a site specific mechanism in which electrostatic interaction between the protonated amine groups on the polymer and anionic groups on the dye ions is the main force of attraction. In these systems the dye structure is relatively unimportant and although some additional diffuse adsorption may occur depending on the size, shape and hydrophilic/hydrophobic balance of the dye ions involved, specific site adsorption involving electrostatic interactions will remain the main mechanism of adsorption [2].

Additionally, both chitin and chitosan have a repeat structure consisting of two β -(1 \rightarrow 4)-linked anhydro-D-glycopyranose units, with each unit rotated around the glycosidic bond by 180° with respect to the preceding unit. This leads to a flat, ribbon-like structure very similar to that of the cellulose chain in fibres such as cotton, flax and viscose rayon and hence chitin and chitosan can be dyed with the same dye classes as are used with cellulose fibres, namely direct, reactive, sulphur and vat dyes. All of these dyes are adsorbed on cellulose by a diffuse adsorption mechanism that requires the dyes to have large planar structures to maximise the van der Waals forces of attraction between the dye ions and the flat polymer chain [2]. This is true even for reactive dyes, for although these dyes subsequently react with the fibre to form a covalent bond between dye and polymer chain, adsorption of the dye onto the polymer chain is a prerequisite if covalent bond formation is to take place.

2. Discussion of specific dye types

2.1. Acid dyes

The first systematic study of this was by Giles *et al.* [3] working with chitin from lobster shell. Isotherms of equilibrium uptake of dye as a function of dyebath pH were obtained for several dyes (Figure 1) and these followed the same pattern as had been previously found by Peters for acid dyes on nylon [4], although Giles *et al.* made no reference to the previous work of Peters. Dyes 1 and 2 show an increase in the equilibrium adsorption with decrease in pH down to about 6, then a plateau down to about pH 2.5, followed by a steep increase as the pH is reduced further. Dye 3 follows roughly the same pattern but at a higher level of equilibrium adsorption at all pH values and with a less sharply defined plateau (Figure 1). The greater adsorption of III at all pH values may be attributed to its greater surface area and hydrophobic character, both of which factors would increase the extent of diffuse adsorption in addition to the specific site adsorption, while both I and II show almost identical adsorptions, as would be expected from their very similar structures. The slightly greater adsorption values for II across the pH range may be due to its ability to form an *o*-hydroxyazo chelate ring, thereby increasing the planar area of II and also reducing any solubilising effect of the naphthol OH group, and so marginally increasing the contribution of diffuse adsorption to the overall uptake.

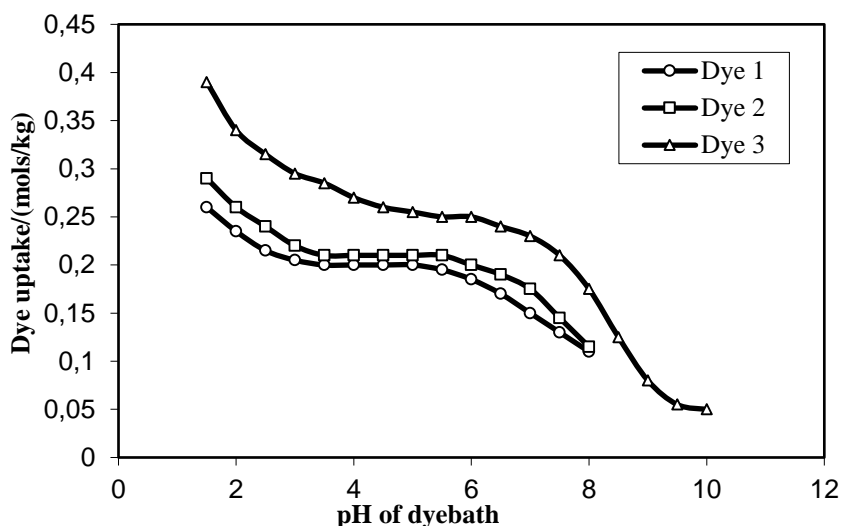


Figure 1. Equilibrium adsorption of acid dyes on chitin as a function of dye bath pH.

Dye 1: Sodium 4-(4-hydroxy-1-naphthylazo)-benzenesulphonate; Dye 2: (C.I. Acid Orange 7) Sodium 4-(2-hydroxy-1-naphthylazo)-benzenesulphonate); Dye 3: (C.I. Acid Red 88) Sodium 4-(2-hydroxy-1-naphthylazo)-1-naphthalenesulphonate.

The plateau marks the pH range where all the amine groups, but no amide groups, are protonated and can act as dye sites. By analogy with Peters' study on nylon substrates [4] the steep rise in dye uptake at pH values below about 2 may be attributed to protonation of amide groups along the chain, possibly with accompanying acid hydrolysis of the amide groups, leading to an increase in positively charged dye sites. This interpretation of the plot immediately suggests a method for determining the F_A value, but surprisingly Giles *et al.* did not use their adsorption results to analyse the chitin, instead basing their determination of F_A values on the much less accurate elemental analysis method. Similar plots down to pH 3 were later reported for the adsorption of Metanil Yellow (MY) and C.I. Reactive Blue 15 (RB15) on crosslinked chitosan beads under acid conditions, when the anionic reactive dye would behave as an acid dye during the adsorption stage [5]. Giles *et al.* [3] also measured the Apparent Heat of Adsorption ($-\Delta H_{app}$) for several dyes at acid pH and found the values to be very low, which is consistent with an ion exchange mechanism, whereas the values determined at neutral pH were considerably larger, indicating that the adsorption process occurs by different mechanisms at acid and neutral pHs.

The equilibrium adsorption of acid dyes on chitosan at acid pH values was studied by Maghami and Roberts using a mono- (C.I. Acid Orange 7), di- (C.I. Acid Red 13), and tri-sulphonic acid dye (C.I. Acid Red 27) and with 0.03 M acetic acid as the dye bath medium [6]. The results (Figure 2) confirm that there is a 1:1 stoichiometry between protonated amine groups and sulphonic acid groups on the dye ions, and multiple repeats of dyeing to equilibrium showed very good reproducibility of dye uptake. This reproducibility, coupled with the stoichiometry, was subsequently made use of in a simple dye adsorption method for determining F_A values of chitin and chitosan [7]. Surprisingly Chiou and Chuang [5] did not connect the much larger molar adsorption of MY relative to that of RB15 with the fact that MY is a mono- sulphonic acid dye, whereas RB 15 has four $-\text{SO}_3\text{Na}$ groups and hence each molecule of the latter will electrically neutralise 4 positively charged sites. Nor did they

consider the relative purity and/or nature of the other components present in the commercial sample of RB 15 used. Instead they argued that the differences in uptake were due to the smaller MY molecules being able to penetrate the chitosan beads more readily.

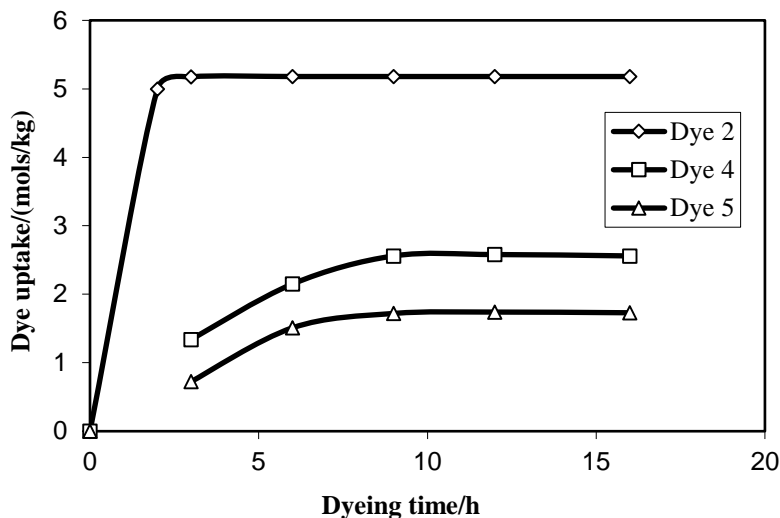


Figure 2. Uptake of dye on chitosan as a function of dyeing time at reflux temperature.

Dye 2: Sodium 4-(2-hydroxy-1-naphthylazo)-benzenesulphonate (C.I. Acid Orange 7);

Dye 4: Disodium 2-hydroxy-1,1'-azonaphthalene-4',6-disulphonate (C.I. Acid Red 13);

Dye 5: Trisodium 2-hydroxy-1,1'-azonaphthalene-3,4',6-trisulphonate (C.I. Acid Red 27).

Although there are many papers in the literature on effluent treatment that report the rates of adsorption of acid dyes on chitin and chitosan, the study of Guthrie *et al.* [8] is the only one to attempt to measure the true diffusion coefficient of an acid dye in chitosan. Using chitosan in film form and the Sekido role technique [9] they obtained diffusion coefficients of the order of $10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$, which are reasonable, but the dependence of the diffusion coefficient (D_c) on dye concentration was very unusual. In all other dye-polymer systems studied to date D_c has been found to either increase with, or to be independent of, increase in dye concentration [10]. It was suggested that the unusual diffusional behaviour noted in the acid dye/chitosan system was due to the $\text{Chit-NH}_3^+ \dots \text{O}_3\text{S-Dye}$ salt forming a more compact, less permeable structure than that of undyed chitosan, making the substrate increasingly less permeable with increase in dye concentration [8].

Several studies of acid dyeing chitosan as a component of a textile fabric have been reported. Davidson and Xue [11] found that a pre-treatment of wool fabric with chitosan largely eliminated 'tippy' dyeing, which is the term for the difference in dyeing behaviour found between damaged and undamaged wool fibres. Also, although C.I. Acid Yellow 17 was taken up levelly at pH 4.4, the rate of uptake at pH 4.0 was sufficiently more rapid to give rise to unlevel uptake. At both pH values the dye exhaustion was $\geq 99\%$ with as little as 0.1% chitosan on weight of wool. Shimizu *et al.* [12] studied the dyeing behaviour of a cellulose/chitin composite fibre, Crabyon[®], with C.I. Acid Orange 7 (Dye 2 above). Crabyon[®] fibres containing 3, 10 and 20% chitin were used and the equilibrium dye uptakes at pH 4 were in the order $\text{CR}(20) > \text{CR}(10) > \text{CR}(3)$. The dyeing rates were $\text{CR}(20) \gg \text{CR}(10) \gg \text{Silk} > \text{CR}(3)$ while the thermodynamic parameters of dyeing for CR(3) were found to be very similar to those for silk. These similarities were considered as supporting

evidence that ionic interaction between Dye-SO₃⁻ and Chit-NH₃⁺ plays a significant role in this dyeing process. Yoshida *et al.* [13] studied the dyeing behaviour of C.I. Acid Orange 7 on three chitosan fibres: ChF (uncrosslinked); ChF-A (crosslinked); and ChF-B (more highly crosslinked), with amine group concentrations as determined by HCl titration of 4.90, 4.51, and 3.30 mols/kg respectively. At pH 3 and 4 the maximum uptake on each fibre was close to the value indicated by the amine group concentration, suggesting an ion exchange adsorption mechanism, but at pH 6.9 the equilibrium uptake values were ChF > ChF-A > ChF-B and the values were increased by the addition of neutral electrolyte, indicating that the adsorption mechanism was not an ion exchange mechanism. Surprisingly the equilibrium values for ChF and ChF-A at pH 6.9 exceeded those obtained at pH 3 or 4, suggesting multilayer adsorption.

Jocić *et al.* [14] studied the effects of low-temperature plasma and chitosan pre-treatments, separately and combined, on the dyeing behaviour of wool fabric at pH 4.2 and 6.5. Although at pH 4.2 all three treatments reduce the 'time of half dyeing' ($t_{1/2}$), which is an inverse measure of the apparent diffusion coefficient, by approximately 90% at pH 6.5 the chitosan on its own has no effect at all, and the LTP treatment reduced $t_{1/2}$ by less than 30%. The authors concluded that at acid pH values the chitosan functions by rapidly adsorbing the dye from the dyebath and subsequently transferring it to the wool fibres. Significantly there is no difference in the saturation dye exhaustion.

2.2. Direct dyes

Although several studies on effluent treatment have examined the uptake of direct dyes on chitosan, usually under acid conditions so that the direct dyes would be expected to behave like large acid dyes, very little research has been carried out on their dyeing mechanism or diffusion behaviour at neutral pH to confirm that dyeing occurs by a similar mechanism to that of direct dyes on cellulose. The main characteristics of the adsorption process of direct dyes on cellulose have been shown [15-17] be:

1. The addition of a neutral electrolyte increases the equilibrium adsorption of dye (in specific site adsorption processes added neutral electrolyte tends to reduce adsorption through competition for the sites);
2. The addition of a neutral electrolyte reduces the rate of diffusion of the dye;
3. The concentration profile, a plot of 'Dye concentration' *versus* Distance from the substrate surface' is rectilinear over most of the plot;
4. The diffusion coefficient is concentration dependent, initially increasing linearly with concentration at the point measured, followed by a gradual decrease in the rate of increase.

Carlough *et al.* [18] measured the diffusion coefficients of four direct dyes at 60°C on chitosan film, using the Dayne's Time Lag method. Values varied from 4.48×10^{-11} – 4.54×10^{-10} cm².s⁻¹, which is within the range shown by direct dyes on cellulose at that temperature, but no investigation of the mechanism of diffusion was carried out.

Mazengarb and Roberts [19] found that the equilibrium adsorption of direct dyes in chitosan film increases with increase in addition of NaCl and, using the Sekido roll technique [9] established that the rate of diffusion decreases with increase in NaCl concentration (Figure 3).

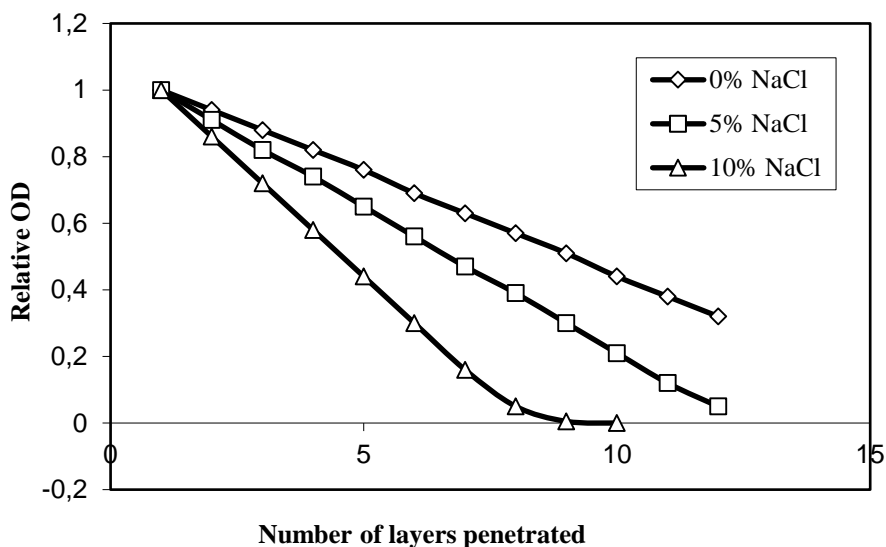


Figure 3. Effect of NaCl concentration (% owg) on rate of diffusion.

In the same paper they determined the concentration profile for a direct dye diffusing in chitosan film (Figure 4), which is identical to that for a direct dye on cellulose [17], and analysed it to determine the concentration dependence of the diffusion coefficient D_C . This analysis (Figure 5) shows that D_C for a direct dye on chitosan shows similar behaviour to that for a direct dye on cellulose:

$$D_C = D_0(1 + \beta C) \dots\dots\dots(1)$$

although the values of the constants differ somewhat for the two substrates (Table 1).

The value of D_0 for the dye in chitosan film is approximately four times greater than in cellulose film. This difference can be attributed to the difference in physical structure, the cellulose film having been subjected to stretching during extrusion and processing whereas the chitosan film was used ‘as cast’. Hence the polymer chains in the former would be more orientated and offer more physical resistance to diffusion.

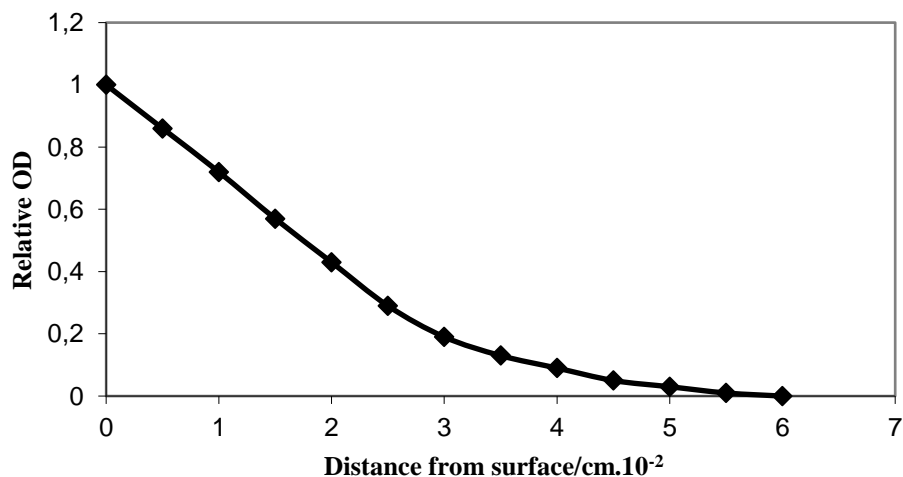


Figure 4. Concentration profile for chitosan film dyed with C.I. Direct Blue 15 under neutral conditions for 120 minutes at 80°C.

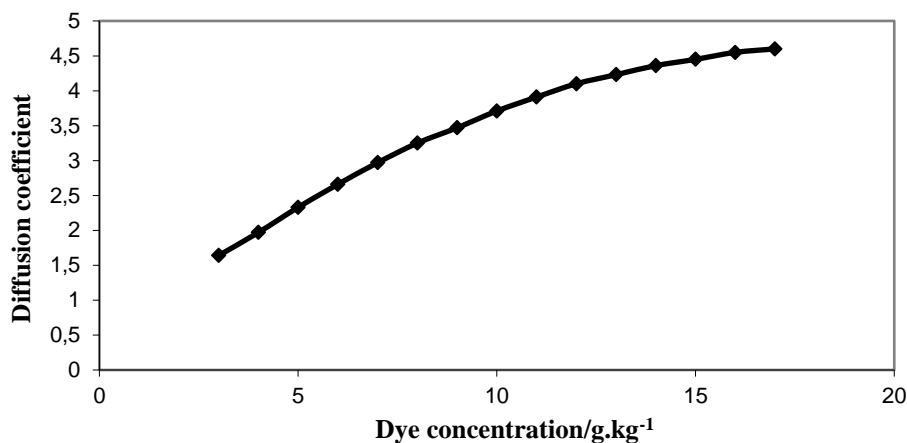


Figure 5. The dependence of D_C on dye concentration for C.I. Direct Blue 15 on chitosan.

The average value of the diffusion coefficient is of the order of $10^{-9} \text{ cm}^2.\text{s}^{-1}$, considerably greater than those reported by Carlough [18]. This is presumably due to the difference in the temperatures at which the diffusion measurements were carried out; 60°C [18] and 90°C [19] respectively.

Table 1. Values of the constants in Eqⁿ 1 for diffusion of a direct dye in cellulose and chitosan films.

Substrate:	D_0	β
Cellulose film	$1.5 \times 10^{-9} \text{ cm}^2.\text{s}^{-1}$	$1.6 \text{ cm}^2.\text{s}^{-1}$
Chitosan film	$6.5 \times 10^{-9} \text{ cm}^2.\text{s}^{-1}$	$0.51 \text{ cm}^2.\text{s}^{-1}$

In application studies Rippon has shown that a chitosan pre-treatment of cotton fabric improves the dye coverage of thin-walled immature cotton fibres [20]. These tend to form entangled clumps (neps) during processing and often appear as white or pale spots against the background colour in dyed fabrics. Rippon reported that the most effective method of applying chitosan to cotton was by a pad-dry-rinse process, with approximately 90% of the chitosan applied being retained after drying, but all the application methods used gave an increase in dye uptake. Although significant increase in dye uptake was obtained with chitosan contents as low as 0.02% (o.w.f.) a chitosan content of 0.1% (o.w.f.) was required to produce dyeings completely devoid of neps. Rippon concluded a possible explanation for the preferential improvement in the colour yield of neps is that chitosan is preferentially sorbed by the immature cotton fibres. However he also suggested that even if both mature and immature fibres absorb similar concentrations of chitosan, the proportional increase in depth of shade resulting from the uptake of chitosan would be greater for the pale-dyeing immature cotton than for the deeper-dyeing mature cotton fibres. Subsequently Mehta and Combs [21] reported that chitosan could be used as an after-treatment to cover undyed neps in the dyed fabric, followed by a re-dyeing step. They concluded that the optimum chitosan concentration uptake was 0.8% chitosan (o.w.f.), considerably greater than required when the chitosan was applied as a pre-treatment [20] and that 0.1-0.3% dye (o.w.f.) was the optimum concentration for the re-dye bath, which could indeed be the original exhausted dyebath.

2.3. Metal complex dyes on chitin and chitosan

There are several types of pre-metallised dyes (pre-mets) used commercially: 1:1 pre-metallised acid dyes; 1:2 pre-metallised acid dyes; 1:1 and 2:1 pre-metallised direct dyes. In each type the dye molecules act as tri-dentate ligands. Thus in the 1:2 pre-mets all six co-ordination sites of the Cr^{+3} or Co^{+3} metal ions are occupied by dye ligands, whereas in the 1:1 pre-metallised acid dyes only 3 of the 6 co-ordination sites of the Cr^{+3} are occupied by dye ligands, the remaining 3 being occupied by water molecules. The pre-metallised direct dyes are complexes involving Cu^{+2} and again 3 of the co-ordination sites are occupied by the dye molecule and the remaining site by a water molecule. The 2:1 pre-met direct dyes contain two tridentate sites so each dye molecule can complex with two Cu^{+2} ions, each ion having one co-ordination site occupied by a water molecule [22].

Although non-metallised and 1:2 pre-metallised acid dyes readily dye chitin and chitosan under acid conditions, they only stain both substrates when applied from a neutral bath. In contrast to this pH-dependent behaviour, 1:1 pre-metallised acid dyes have been shown to dye chitin and chitosan under both acid and neutral conditions [23, 24], although there is a visually perceptible difference in shade when the same dye is applied under neutral conditions and under acid conditions, suggesting different modes of attachment at the two pHs. Also the effect of the addition of a neutral electrolyte (Na_2SO_4) to the dyebath differed: at acid pH there was a decrease in depth of shade while at neutral pH there was an increase. The former behaviour is typical of electrostatic dye/fibre interactions and the decrease may be attributed to competition between dye anions and the SO_4^{-2} ion for the protonated amine dyesites. No such interactions occur in neutral conditions, instead the Na_2SO_4 functions by 'salting out' the dye ion onto the un-ionised substrate [23].

The importance of the amine groups in the neutral dyeing process was further supported by comparing the dye uptake on chitin powder before and after partial deamination by reaction with nitrous acid, where deamination was found to reduce the dye uptake by 38-63% depending on the dye. Furthermore, although the average uptake of 5 pre-metallised direct dyes on deaminated chitin was 72.1%, compared to 89.5% on unmodified chitin, the average desorption from the dyed deaminated chitin samples was 35.7% compared to only 2.9% from the dyed unmodified chitins [24]

Finally a series of dyeings to equilibrium on chitin powder ($F_A = 0,975 \equiv [-NH_2] = 0.124$ mols.kg⁻¹) were carried out at neutral pH with C.I. Acid Blue 158 and the results found to follow a Langmuir Equilibrium Adsorption plot (Figure 6).

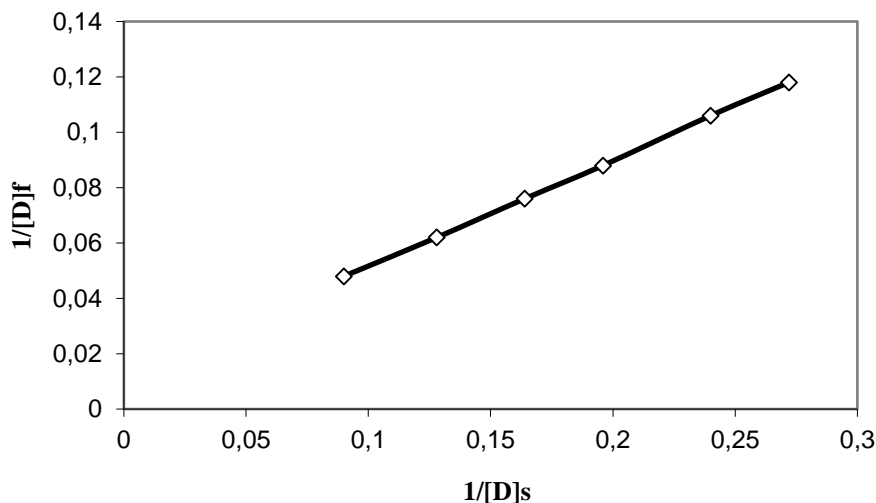
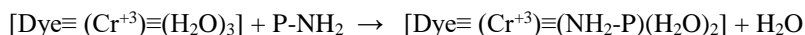


Figure 6. Plot of $1/[D]_{f,\infty}$ versus $1/[D]_{s,\infty}$ for C.I. Acid Blue 158 on chitin at neutral pH

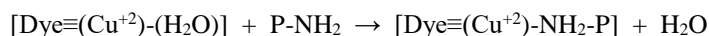
Extrapolation back to $(1/[D]_{s,\infty}) = 0$ gives an intercept of 0.0136 kg.g⁻¹ therefore:

1. maximum dye uptake = 73.53 g.kg⁻¹
2. which is $\equiv 0.127$ mols.kg⁻¹ dye (molecular weight of CI AB 158 = 580).

This confirms that there is a 1:1 correlation between the number of amine groups in the substrate and the maximum uptake of a metal-complexed dye [24] and strongly supports the proposed dyeing mechanism [23,24] in which amine groups from the chitin or chitosan replace labile ligands, presumably H₂O molecules, in the co-ordination sphere of the metal-dye complex:



for chromium-complexed acid dyes and:



for copper-complexed direct dyes:

2.4. Reactive dyes

Although reactive dyes are unique in that they form a covalent bond with the substrate, formation of this covalent bond can only occur after the dye molecules have been adsorbed onto the substrate. Also for all the reactive groups used to date the covalent bond is formed either by a nucleophilic substitution, or a nucleophilic addition reaction. This means that in dyeing chitin and chitosan with this class of dye there is a conflict between the pH required for maximum adsorption and that required for maximum fixation of the adsorbed dye. This is shown, Figure 7, for C.I. Reactive Blue 5, a monochlorotriazinyl dye [25]. The

exhaustion/fixation dependence on pH will depend on the nature of the reactive group and ideally the rate of adsorption should be greater than the rate of reaction with the substrate in order to avoid uneven dyeing. However the dye should not react too slowly or else it will require a prolonged time at the boil to ensure adequate fixation.

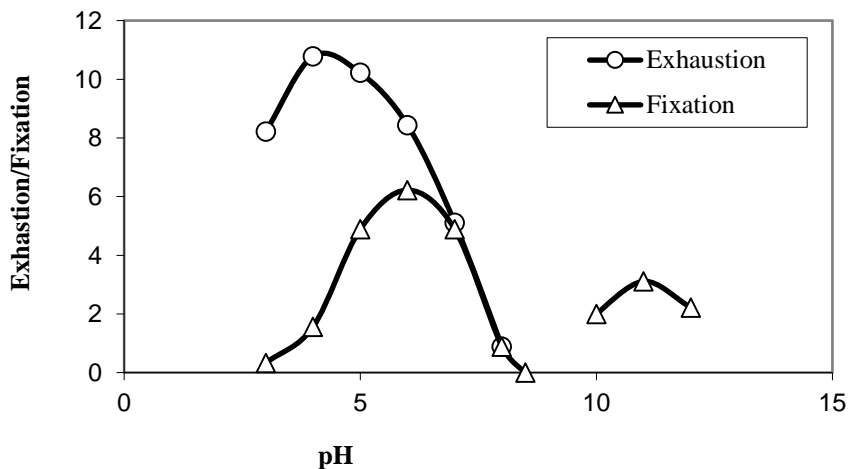


Figure 7. pH dependence of exhaustion and fixation of C.I. Reactive Blue 5 on Crabyon® CR20.

Another dye studied by Shimizu *et al.* [25] is C.I. Reactive Blue 19, which has a sodium sulphatoethylsulphonyl reactive group. Here the dependence is more balanced and maximum exhaustion and fixation occur at the same pH (Figure 8)

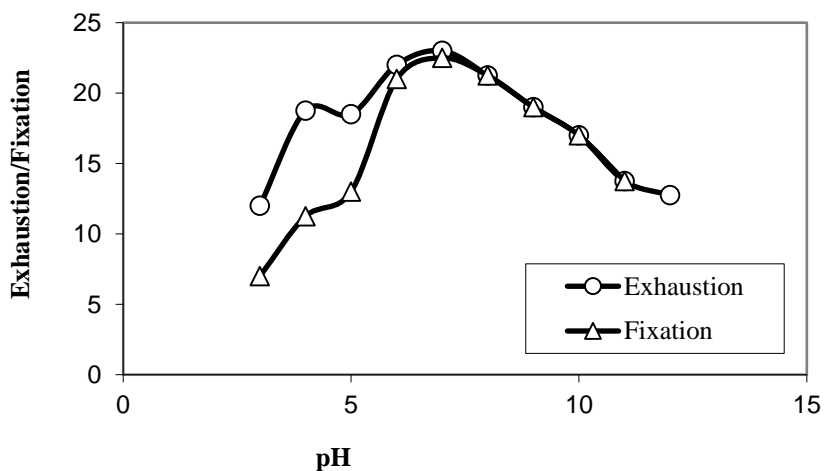


Figure 8. pH dependence of exhaustion and fixation of C.I. Reactive Blue 19 on Crabyon® CR20.

Davidson and Xue [12] reported that the rate of reactive dye uptake onto chitosan-treated wool was greater than on untreated wool, and that at the early stage of dyeing the exhaustion increased in proportion to the amount of chitosan applied to the wool. No difference was found in the reflectance spectra or in the colour fastness when the final bath temperature was 100°C, but there was a reduction in the fastness properties when a lower temperature (60°C) was used. The authors concluded that at the lower dyeing temperature the presence of the chitosan helps the initial dye uptake but does not affect the migration properties. The more uniform penetration induced by the chitosan pre-treatment was shown by photomicrographs after dyeing with an FBA at 80°C.

Jocić *et al.* studied the effect on dyeing behaviour of pre-treating the wool with a chitosan/non-ionic surfactant mixture [26]. The rate of dye uptake was increased in all cases, compared to that of wool that had not been pre-treated, and the effect was particularly striking in the case of the higher concentrations of the surfactant. For the chitosan/non-ionic mixture to be effective it was necessary to age it for 5 days, by which time the viscosity of the solution had decreased noticeably indicating some interaction between chitosan and surfactant. A fresh chitosan/non-ionic surfactant solution was no more effective than a pre-treatment with chitosan itself. Also, at the same concentration of dye taken up, the measured depth of shade increased with increase in surfactant in the pre-treatment solution, suggesting a method for obtaining deeper shades without increasing the amount of dye used. As part of a study of the effectiveness of a chitosan pre-treatment to prevent wool fabric felting Julià *et al.* [27] examined the possible effect of the molecular weight of the chitosan on the dyeing properties, using a reactive dye. They found that there was a marked difference in dyeing behaviour between untreated and chitosan-treated wool, but that there was no noticeable difference in the effect of chitosans with molecular weights covering the range of $\sim 7 \times 10^4$ to $\sim 7.5 \times 10^5$.

The above studies involved using reactive dyes designed for application to wool and applied at acid pHs, but another paper [28] reports on the effect of a chitosan pre-treatment on cotton fabric on the subsequent dyeing using a typical dyeing process for reactives on cellulosic fibres; exhaustion from a neutral bath by NaCl or Na₂SO₄ and fixation by reaction with Cell-O⁻ ions generated by addition of Na₂CO₃ or NaOH. In all cases the dye uptake was significantly greater than for the untreated cotton, while the method of pre-treatment had very little effect. The “Increase of dyeability”, however, varied with the dye used from 13% up to 91%. The authors attempted to relate this variation to the reactive groups involved but the argument is not convincing, being based on one example of each of the four reactive groups examined so that other aspects of each dye’s structure could not be taken into account. One interesting observation is that the dye uptake was greater if the samples were dyed directly after the pre-treatment step, rather than if stored for 48 hours before dyeing. Presumably the “never dried” chitosan coating is more accessible to the dye, hence can absorb more dye.

3. References

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