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Chitosan/acid dye interactions in wool dyeing system

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Abstract

This study assesses the interactions that could occur during dyeing of the chitosan treated wool fibres on basis of the spectrophotometric study, by measuring the absorbance values of the solutions containing dye and chitosan. It has been shown that there is a 1:1 stoichiometry between protonated amino groups and sulfonate acid groups on the dye ions in low concentrated chitosan solutions. This interaction forms an insoluble chitosan/dye product. With the excess of chitosan in the solution, the dye can be distributed between the different chitosan molecules and the soluble chitosan/dye products remain in the solution. The mechanism of the interaction is suggested, that involves the possibility of adsorbed dye molecules to be desorbed and redistributed between other components present in the system, depending on system parameters (pH, temperature and electrolyte presence). This fact is important in explanation of dyeing behaviour of chitosan treated wool and enables the assessment of the mechanism of dyeing of accordingly modified textile fibres.

Keywords: Acid dye; Chitosan; Interaction; Spectrophotometry; Dyeing

1. Introduction

Nowadays, the surface modification of textile fibres is considered as the best route to obtain modern textile treatments (Jocic et al., 2002). It enables the required level of beneficial effect by the modification of fibre surface only, thus minimising whole fibre attack, and hence the deterioration in fibre quality could be easily avoided. As one of the most promising treatments, we recognize and suggest the hydrogen peroxide or low-temperature plasma (LTP) pre-treatment combined with biopolymer post-treatment (Erra et al., 1999; Julià et al., 1998). Among various available biopolymers, the polysaccharide chitosan (CHT) is highly recommendable, since it shows unique chemical and biological properties and its solubility in acidic solutions makes it easily available for industrial purposes.

The polysaccharide-based cationic biopolymer chitosan is poly(1,4)-2-amino-2-deoxy-β-D-glucan, usually obtained by deacetylation of chitin that is widely present in the nature as a component of some fungi, exoskeleton of insects and marine invertebrates (crabs and shrimp). The chemistry of chitosan is similar to that of cellulose, but it reflects also the fact that the 2-hydroxyl group of the cellulose has been replaced with a primary aliphatic amino group. Among many other uses, it has been recently shown that chitosan improves the dye coverage of immature fibres in cotton dyeing (Mehta & Combs, 1997) and that it could be successfully used as a thickener and binder in pigment printing of cotton (Bahmani, East, & Holme, 2000).

In wool finishing, chitosan has been used as a shrink-resist agent (Julià, Pascual, & Erra, 2000; Masri, Randal, & Pittman, 1978) and as an agent for improving the dyeability of wool (Davidson & Xue, 1994; Filipowska, Walawska, & Rybicki, 2000; Jocic, Julià, & Erra, 1997; Yen, 2001). The modified fibre always shows somewhat different dyeing behaviour, so the influence of the biopolymer to the fibre dyeability has to be examined in detail (Jocic et al., 2000;

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Vilchez, Navarro, Jocic, & Erra, 2001) and the best way to achieve this is to investigate the interaction between chitosan and dye in the solution (Jocic et al., 2001, 2002).

This study attempts to clarify the interactions that occur during dyeing of the modified wool fibres on basis of the spectrophotometric study by measuring the absorbance values of the solutions containing dye and chitosan. In order to mimic the realistic dyeing conditions, the behaviour of the solutions after adding electrolyte and increasing the temperature is followed. To get explanations about the dyeing behaviour of chitosan treated wool, various factors, mainly pH and temperature, are considered in detail. Based on the model proposed, the mechanism of the interaction is suggested.

2. Experimental

Three different acid dyes were selected for the experiment (Table 1). AR88 is a rather hydrophobic classical monosulfonated levelling acid dye of the lowest r.m.m. (400.4). AR27 is a rather hydrophilic three-fold sulfonated monoazo levelling dye of r.m.m. 604.5. AB113 is disulfonated milling acid dye of higher r.m.m. (681). It is a slow-dyeing molecule with poor migration properties. Chitosan (Vanson, USA) (viscosity 369 cps and deacetylation degree 84.9%) has been used as obtained, without further purification.

For the measurement of binding of dye by chitosan, a series of 14 buffered (pH 4.2 and 6.5) chitosan solutions were prepared having different chitosan contents between 1×10^{-4} and 6×10^{-2} g/l, each containing the 2.5×10^{-2} g/l of dye (Table 2), which corresponded exactly to the dye concentration used for the dyeing of wool samples (Jocic et al., 2000, 2001, 2002; Vilchez et al., 2001). The chitosan/dye solutions were buffered with a sodium acetate/acetic acid buffer (pH 4.2) or potassium dihydrogen phosphate/disodium hydrogen phosphate buffer (pH 6.5). After standing for 24 h at room temperature, the solutions were centrifuged for 20 min at 3000 rpm to precipitate the insoluble components and the sample was carefully taken from the rest of the solution. In some cases the centrifugation had to be repeated and even the centrifuge speed had to be increased in order to obtain clear solution. The absorbance values of the solutions were measured at λ_{max} (room temperature; 10 mm path length cell) by a UV-VIS spectrophotometer UV-265FW (Shimadzu, Japan) and plotted against chitosan concentration (C_{CHT}) and the mole ratio of chitosan amino group to dye ion (*P*/*D* ratio). The same measurements were repeated with the solutions to which electrolyte (1 g/l Na_2SO_4) has been added. In order to follow the influence of temperature the solutions with and without electrolyte were heated at 85 °C, maintained at that temperature for 2 h, then cooled again to room temperature and the changes in absorbance monitored.

P/*D* ratio has been calculated as the ratio of mean chitosan residues (chitosan monomer molecular weight, $M_{eq(P)}$) to dye molecules (dye equivalent mass, $M_{eq(D)}$), considering that one amino group of chitosan monomer unit binds with one sulfonate group of acid dye (1:1 stoichiometry). Empirical equation for the calculation of the mean polymer residue weight of chitosan is

$$M_{eq(P)} = \left(\frac{S_{deAC}}{100}\right)M_{deAC} + \left(\frac{100 - S_{deAC}}{100}\right)M_{AC}$$

where

S_{deAC} deacetylation degree (%);
M_{deAC} molar mass of deacetylated glucoside unit (g/mol);
M_{AC} molar mass of acetylated glucoside unit (g/mol).

Table 2 gives the data about *P*/*D* ratio for all three dyes and corresponding solutions. The calculated chitosan monomer molecular weight $M_{eq(P)}$ of 167.34 g/mol corresponds to the polymer unit that has one amino group. The dye equivalent mass $M_{eq(D)}$ corresponds the dye molecule with one sulfonate group (monovalent) and it has been

Table 1
The characteristics of dyestuffs used in the experiment

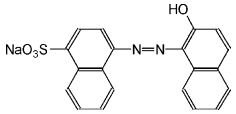
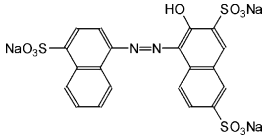
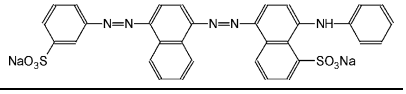
Dye abbrev	Commercial name	Manufacturer	CI name	r.m.m.	λ_{max} (nm)	Purity (%)	Molecular structure
AR88		Sigma Chem. Co.	Acid red 88 (CI 15620)	400.4	505	90	
AR27	Amaranth/ azorubin S	Aldrich Chem. Co.	Acid red 27 (CI 16185)	604.5	521	80	
AB113	Erionyl marine R 180	CIBA	Acid blue 113 (CI 26360)	681	566	100	

Table 2
P/D ratio in solutions used for measuring dye/chitosan interaction

Solution	Chitosan conc. (g/l)	Conc. of mean chitosan residues (*P*), mol/l	*P/D* ratio		
			AR27 (0.025 g/l)	AR88 (0.015 g/l)	AB113 (0.025 g/l)
1	1×10^{-4}	5.98×10^{-7}	6.45×10^{-3}	1.77×10^{-2}	8.14×10^{-3}
2	2×10^{-4}	1.19×10^{-6}	1.29×10^{-2}	3.55×10^{-2}	1.63×10^{-2}
3	4×10^{-4}	2.39×10^{-6}	2.58×10^{-2}	7.09×10^{-2}	3.26×10^{-2}
4	8×10^{-4}	4.78×10^{-6}	5.16×10^{-2}	1.42×10^{-1}	6.51×10^{-2}
5	1.4×10^{-3}	8.37×10^{-6}	9.04×10^{-2}	2.48×10^{-1}	1.14×10^{-1}
6	2×10^{-3}	1.19×10^{-5}	1.29×10^{-1}	3.55×10^{-1}	1.63×10^{-1}
7	3×10^{-3}	1.79×10^{-5}	1.94×10^{-1}	5.32×10^{-1}	2.44×10^{-1}
8	4×10^{-3}	2.39×10^{-5}	2.58×10^{-1}	7.09×10^{-1}	3.26×10^{-1}
9	6×10^{-3}	3.59×10^{-5}	3.87×10^{-1}	1.06	4.88×10^{-1}
10	1×10^{-2}	5.98×10^{-5}	6.45×10^{-1}	1.77	8.14×10^{-1}
11	1.5×10^{-2}	8.96×10^{-5}	9.68×10^{-1}	2.66	1.22
12	2×10^{-2}	1.19×10^{-4}	1.29	3.55	1.63
13	4×10^{-2}	2.39×10^{-4}	2.58	7.09	3.26
14	6×10^{-2}	3.58×10^{-4}	3.87	10.6	4.88

calculated knowing the dye purity (%), the dye molecular mass (g/mol) and the number of sulfonate groups of the dye.

3. Results and discussion

3.1. Wool/chitosan/dye interaction

It is known that the binding of chitosan to wool is due to ionic interactions, such as carboxyl groups in wool forming salts with the free amino groups in chitosan, and hydrogen bonding interactions between hydroxyl and amide groups of the wool with the hydroxyl groups of the chitosan (Davidson & Xue, 1994). Furthermore, since chitosan is polyamino-carbohydrate, it is expected to have some of the interaction characteristics of both polysaccharides and proteins, since it contains a polymer chain of substituted glucosidic residues together with a high proportion of amino residues (Yamamoto, 1984).

Below the iso-electric point of wool (pH 4.2), wool is positively charged mainly because of the presence of basic groups in lysine and arginine, whereas above that point carboxyl groups confer a net negative charge on the fibre. When $pH<6$, the amino groups within the wool, either at the ends of protein chains or in amino acid side chains, will be always present in protonated form. At the $pH>6$ almost all carboxylate groups in wool will be present as anions (Vickerstaff, 1954). In acid solutions chitosan behaves as a cationic polyelectrolyte due to protonation of the amino groups. Since the pK value of the amino groups of the chitosan is 6.3 and pK value of the monomer is close to 7.7, above the pH value 6.5 the amino groups ($-NH_2$) should be only partly (about 20% at pH 6.9) protonated into $-NH_3^+$. Therefore, the amino groups of the chitosan are at pH 4.2 protonated to form cationic amino groups, but at pH 6.5 chitosan should have very low positive charge (Muzzarelli, 1977).

As the pH is increased to 6.5 the electrostatic forces of attraction would progressively decrease because of decreasing positive charge on the wool and chitosan. This would inhibit dye adsorption. Therefore, in absence of electrostatic attraction, van der Waals forces and hydrophobic interaction would provide attraction between dye and wool. At pH 6.5 it is expected that the rate of dyeing would be independent of electrostatic forces and that it would be diffusion controlled (Davidson & Xue, 1994). All these facts are reflected in scheme (Table 3) that gives information about active species present in an aqueous solution at different pH.

Knowing these facts about wool and chitosan, two different pH values are chosen (pH 4.2 and 6.5) for chitosan/dye interaction assessment and for dyeing experiment (Jocic et al., 2000, 2001, 2002; Vilchez et al., 2001). Anyhow, even though both chitosan and wool are capable to adsorb acid dye, there is a lot difference between two substrates in the adsorption of acid dye. In acidic solutions, acid dye anions are adsorbed at the cationic acetamido and amino groups of chitosan, presumably rather as by wool fibres. The differences between wool and chitosan may be also a result of differences in accessibility of sites to the anions (Giles & Hassan, 1958; Giles, Hassan, Laidlaw, & Subramanian, 1958; Giles, Hassan, & Subramanian, 1958).

3.2. Chitosan/dye interaction

The most probable mechanism of the interaction between chitosan and dye is likely to be ionic interaction of the dye ions with the amino groups of chitosan. As it can be seen in Table 3, at pH 4.2 the sulfonate groups of the dye dissociate and are converted to dye anions ($D–SO_3^-$). At pH 6.5 this process is scarcely possible, thus dye mostly exists in the solution in the form of undissociated molecules ($D–SO_3Na$). Therefore, the interaction mechanism is not based solely on the formation of the $CHT–NH_3^+\ {}^-O_3S–D$ product on a one to one basis (one protonated amino group reacts with one

Table 3
Simplified scheme of ionic state and the possible interactions between wool (W), chitosan (CHT), chitosan treated wool (CHT + W) and dye (D) in aqueous solution at pH 4.2 and 6.5

Components present in aqueous solution	pH of aqueous solution	
	4.2	6.5
Wool (W)	(1) $^{+}H_3N$-W-COO^{-} (2) $^{+}H_3N$-W-COOH	(1) H_2N-W-COO^{-} *(2) $^{+}H_3N$-W-COO^{-}
Chitosan (CHT)	(1) $^{+}H_3N$-$(CHT)_x$-$(CHT)_y$-NH_3^{+} (fully protonated) (2) $(CHT)_z$-NH-CO-CH_3 (acetoamido group)	(1) H_2N-$(CHT)_x$-$(CHT)_y$–NH_2 (nonprotonated) (2) $^{+}H_3N$-$(CHT)_x$-$(CHT)_y$–NH_2 (partly protonated) (3) $(CHT)_z$-NH-CO-CH_3 (acetoamido group)
Wool (W) + Chitosan (CHT)	(1) $^{+}H_3N$-W-COO^{-} $^{+}H_3N$-$(CHT)_x$-$(CHT)_y$-NH_3^{+} (2) hydrogen bonding e.g. $^{+}H_3N$-W-C(=O)-OH····· O=C(-CH$_3$)-HN-$(CHT)_z$-$(CHT)_{x+y}$-NH_3^{+} (3) van der Waals and hydrophobic interaction (adsorbed CHT): W/CHT	(1) van der Waals and hydrophobic interaction (adsorbed CHT): W/CHT *(2) H_2N-W-COO^{-} $^{+}H_3N$-$(CHT)_x$-$(CHT)_y$–NH_2
Chitosan treated wool (W+CHT)	(1) $^{+}H_3N$-W-COO^{-} $^{+}H_3N$-$(CHT)_x$-$(CHT)_y$-NH_3^{+} (2) hydrogen bonded i.e adsorbed CHT: $^{+}H_3N$-W-C(=O)-OH····· O=C(-CH$_3$)-HN-$(CHT)_z$-$(CHT)_{x+y}$-NH_3^{+}	(1) H_2N-W-COO^{-} $^{+}H_3N$-$(CHT)_x$-$(CHT)_y$-NH_2 (2) H_2N-W-C(=O)-OH····· O=C(-CH$_3$)-HN-$(CHT)_z$-$(CHT)_{x+y}$-NH_2 *(or $-NH_3^{+}$) *(3) $^{+}H_3N$-W-COO^{-} $^{+}H_3N$-$(CHT)_x$-$(CHT)_y$-NH_2 *(4) $^{+}H_3N$-W-C(=O)-OH····· O=C(-CH$_3$)-HN-$(CHT)_z$-$(CHT)_{x+y}$-NH_2 *(or $-NH_3^{+}$)
Dye (D)	(1) D-SO_3^{-} *(2) D-SO_3Na	(1) D-SO_3Na *(2) D-SO_3^{-}
Wool (W) + Dye (D)	(1) HOOC-W-NH_3^{+} $^{-}O_3S$-D (2) van der Waals and hydrophobic interaction: W/D	(1) van der Waals and hydrophobic interaction: W/D *(2) $^{-}$OOC-W-NH_3^{+} $^{-}O_3S$-D
Chitosan (CHT) + Dye (D)	(1) insoluble product CHT/D for CHT/D<1 (i.e. P/D<1) D-SO_3^{-} $^{+}H_3N$-$(CHT)_x$-$(CHT)_y$-NH_3^{+} $^{-}O_3S$-D (2) soluble product CHT/D for CHT/D>1 (i.e. P/D>1) $^{+}H_3N$-$(CHT)_x$-$(CHT)_y$-NH_3^{+} $^{-}O_3S$-D	(1) van der Waals and hydrophobic interaction: CHT/D (2) hydrogen bonding: CHT/D (3) insoluble product CHT/D for CHT/D<1 (i.e. P/D<1) (4) soluble product CHT/D for CHT/D>1 (i.e. P/D>1) *(5) D-SO_3^{-} $^{+}H_3N$-$(CHT)_x$-$(CHT)_y$-NH_2
Chitosan treated wool (W+CHT) + Dye (D)	At the fibre surface: (1) D-SO_3^{-} $^{+}H_3N$-W-COO^{-} $^{+}H_3N$-$(CHT)_x$-$(CHT)_y$-NH_3^{+} $^{-}O_3S$-D (2) D-SO_3^{-} $^{+}H_3N$-W-C(=O)-OH····· O=C(-CH$_3$)-HN-$(CHT)_z$-$(CHT)_{x+y}$-NH_3^{+} $^{-}O_3S$-D (3) HOOC-W-NH_3^{+} $^{-}O_3S$-D (4) van der Waals and hydrophobic interaction: W/D In the dyeing solution: *(5) $^{+}H_3N$-$(CHT)_x$-$(CHT)_y$-NH_3^{+} $^{-}O_3S$-D (possible chitosan desorption)	At the fibre surface: (1) van der Waals and hydrophobic interaction: W/D (2) van der Waals and hydrophobic interaction: CHT/D (3) hydrogen bonding: CHT/D

*, less probable; CHT, chitosan glucoside unit; $x+y$, total number of deacetylated chitosan glucoside units, both protonated and nonprotonated; z, number of acetylated chitosan glucoside units.

sulfonate group), and some other combinations are possible depending on the solution pH, affecting the degree of protonation of amino groups, as well as on chemical groups present in the dye.

Wong, Szeto, Cheung, and McKay (2003) confirmed that the dye molecules, when adsorbed on chitosan, are more or less attached to chitosan molecules in a flat or layered manner, that is, covering long chitosan molecules with benzene rings oriented paralelly (as far as possible) to the polysaccharide chain of chitosan. If the attachment of the dye were at one point only (electrostatic reaction between amino and sulfonate groups), it would be expected that the dye molecule is more spatially oriented. This result confirms that, in addition to electrostatic bonding, there is a strong possibility of hydrogen bonding between chitosan and dye molecules.

When aliquots of dye solution of constant concentration were mixed with various volumes of chitosan solution and diluted to a standard volume with the buffer, the series of spectra were obtained. The main peak at λ_{max} generally was not shifted by increasing chitosan concentration on binding with chitosan, but for the most concentrated solutions of chitosan a shift in the absorbance maximum has been observed, this being

followed visually as a change in the colour of the solution.

The absorbance values at λ_{max} were plotted against the mole ratio of chitosan amino group to dye ion (*P*/*D* ratio) and presented in Figs. 1–3. Fig. 1 shows the results obtained for AR88. At pH 4.2 it could be clearly seen that a product with the stoichiometry 1:1 is forming, independently of the temperature (at both 20 and 85 °C) and electrolyte content. The behaviour above *P*/*D* ratio 1 is two-fold:

- when solution contains electrolyte, the absorbance remains constant;
- when solution does not contain electrolyte, the absorbance increases being followed with a batochromic shift in the absorbance spectra.

At pH 6.5 the stoichiometry of the interaction product formation seems to be dependent on the temperature. Hence, at 20 °C the product with stoichiometry 1:1 is forming, which by increasing the temperature to 85 °C becomes 3:1. The behaviour above the stoichiometric *P*/*D* ratio is similar to the behaviour observed at pH 4.2.

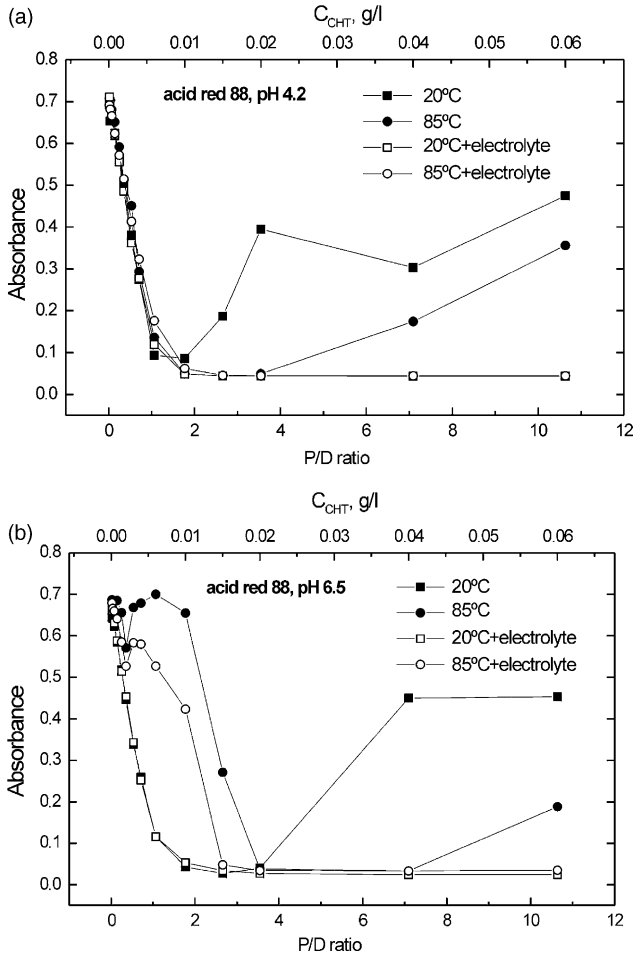


Fig. 1. Change in absorbance of AR88 at pH 4.2 (a) and pH 6.5 (b) as a function of chitosan concentration (g/l) i.e. *P*/*D* ratio.

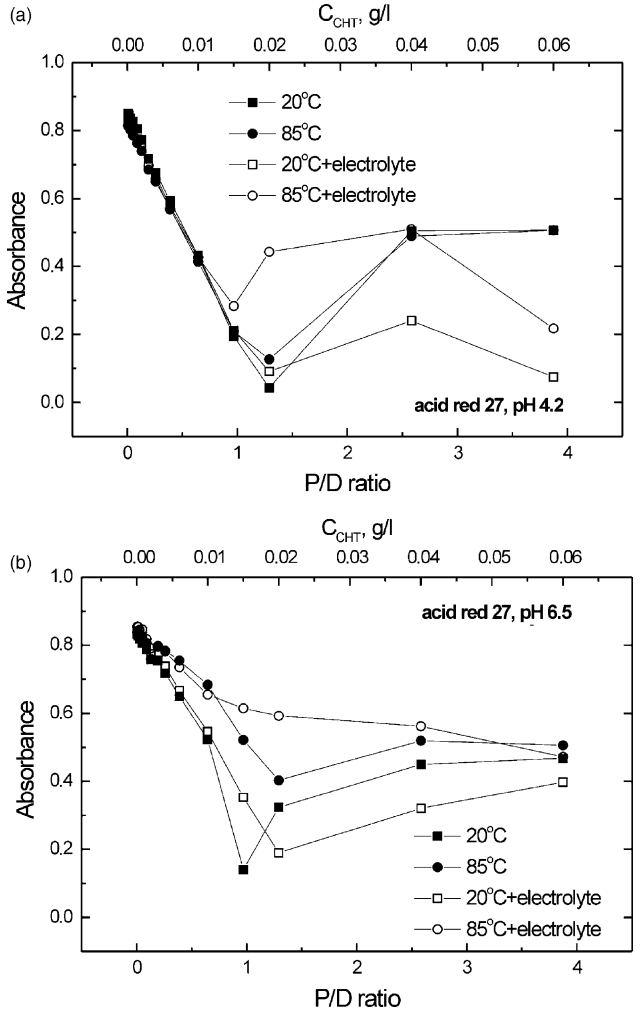


Fig. 2. Change in absorbance of AR27 at pH 4.2 (a) and pH 6.5 (b) as a function of chitosan concentration (g/l) i.e. *P*/*D* ratio.

Fig. 2 shows the results obtained for AR27. AR27 shows completely different behaviour when compared to AR88 and AB113. It is interesting to note that for every chitosan concentration, the solution always contains the dye that did not interact with chitosan, which is the consequence of very good water solubility of AR27. Thus, above the *P*/*D* ratio 3 solubility effect is predominant over the effects being produced by temperature increase and electrolyte presence. At pH 4.2 the stoichiometry of interaction product formation is near *P*/*D* ratio 1 in all cases. For *P*/*D* ratio above 1, the absorbance increase is obvious. For solutions without electrolyte, there is no obvious influence of temperature increase. By adding electrolyte, the behaviour of the solutions changes, mainly above a *P*/*D* ratio 1, where the temperature influence becomes considerable. These solutions mainly show lower absorbance values compared to the corresponding solutions without electrolyte, thus meaning the improved chitosan/dye binding or stabilizing of the product formed. By heating to 85 °C this behaviour is not anymore clearly recognizable. At pH 6.5, the behaviour is similar to pH 4.2, but the dye binding to chitosan seems to

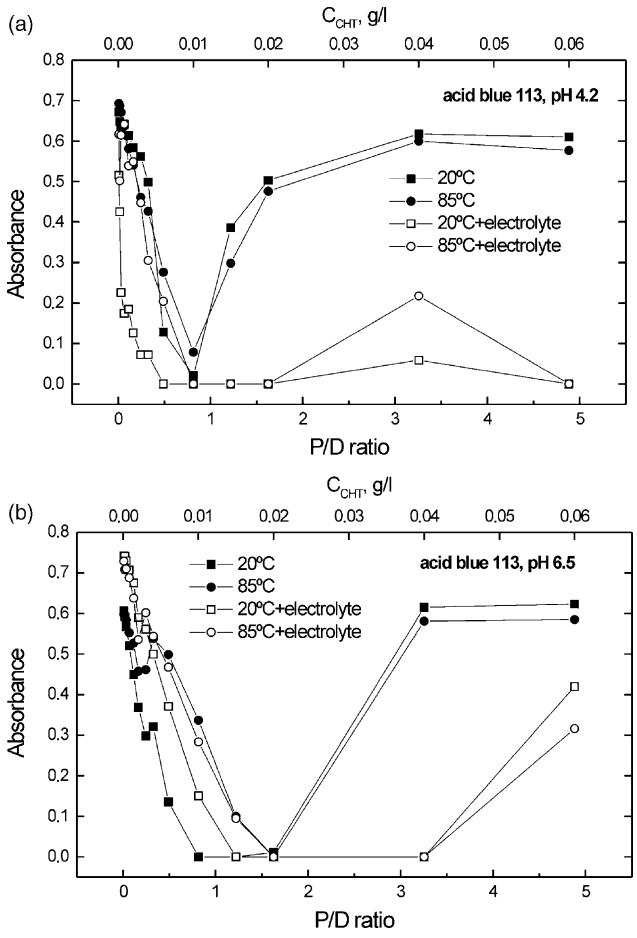


Fig. 3. Change in absorbance of AB 113 at pH 4.2 (a) and pH 6.5 (b) as a function of chitosan concentration (g/l) i.e. *P*/*D* ratio.

be less pronounced. The heating of the solutions to 85 °C generally produces higher absorbance values, even before reaching *P*/*D* ratio 1. By adding electrolyte, the same trend could be observed, but with the differences much more pronounced.

Fig. 3 shows the results obtained for AB113. At pH 4.2, chitosan/dye product with the stoichiometry 0.5:1 or 1:1 is formed and absorbance gradually increases when no electrolyte is present. By adding electrolyte to the solutions, the absorbance remains constant. At pH 6.5, the stoichiometry of the interaction product formation is shifted to major *P*/*D* ratios, between 1 and 2, and the behaviour is similar to the behaviour observed at pH 4.2. In general, this dye (AB113) shows behaviour very similar to the behaviour of AR88, except for the fact that the solutions containing electrolyte at *P*/*D* ratio above 3 show the absorbance increase. This could be probably due to better solubility of this dye (two sulfonate groups).

Hence, the graphs presented at Figs. 1–3 generally show that by increasing the chitosan concentration there is a steady decrease in absorbance (i.e. chitosan/dye binding occurs) up to approximately *P*/*D* ratio 1 when the formation of an insoluble product is observed. These solutions show absorbance values almost zero, which means that all available dye interacts with chitosan (which is mostly precipitated).

Above this value, even though on the basis of 1:1 stoichiometry it could be expected that absorbance reaches a constant value, this was not the fact in our investigation. With the excess of chitosan above that necessary for the stoichiometric balance between protonated amino groups on the chitosan and dye ions, two phenomena occur:

- the low absorbance value of the solution does not change significantly, this behaviour being always observed for solutions containing electrolyte;
- the absorbance values begin to increase.

According to the Beer's law, the increase of absorbance has to be interpreted as an increase of the number of coloured particles in the solution, probably due to the formation of a new soluble chitosan/dye product as the consequence of the dye distribution between different chitosan molecules (Fig. 4).

Big differences in the behaviour at pH 4.2 and 6.5, according to our opinion are attributable to chitosan properties, which is at pH 4.2 almost completely protonated and thus the ionic interaction between chitosan and dye is much pronounced. When considering generally the effect of pH on the stoichiometry of the chitosan/dye insoluble product formation, AR88 and AB113 show similar behaviour as they both increase the *P*/*D* ratio corresponding to the stoichiometry of the chitosan/dye insoluble product formation, when pH changes from 4.2 to 6.5. This could be attributed to somewhat limited solubility of both dyes (AR88 and AB113) compared to AR27. It is interesting to note that AR27 at pH 4.2 reaches the minimum absorbance of almost zero, which is not the case at pH 6.5. At pH 6.5, in the presence of electrolyte, by increasing the temperature to 85 °C, chitosan/dye interaction products are mostly soluble in the solution, independently of increasing chitosan concentration. Thus, since AR27 is rather hydrophilic dye, the increase of pH and adding electrolyte affect the chitosan/dye interaction in the way that the most of the formed chitosan/dye interaction product remains soluble. The dye most sensitive to temperature increase is AR88.

The results we obtained could be supported with some literature considerations. Stefancich, Delben, and Muzzarelli (1994) studied different polysaccharide/dye systems and showed that the chitosan is able to modify the spectra of acid dyes. The thermodynamic data of the same systems showed that the dyes are extensively bound onto the polysaccharides studied, but that the hydration spheres of the interacting species are not destroyed by the interaction (Delben, Gabrielli, Muzzarelli, & Stefancich, 1994). Maghami and Roberts (1988) measured equilibrium dye adsorption of AR27 on chitosan and clearly demonstrated a 1:1 stoichiometry between protonated amino groups in the chitosan and sulfonate acid groups on the dye ions.

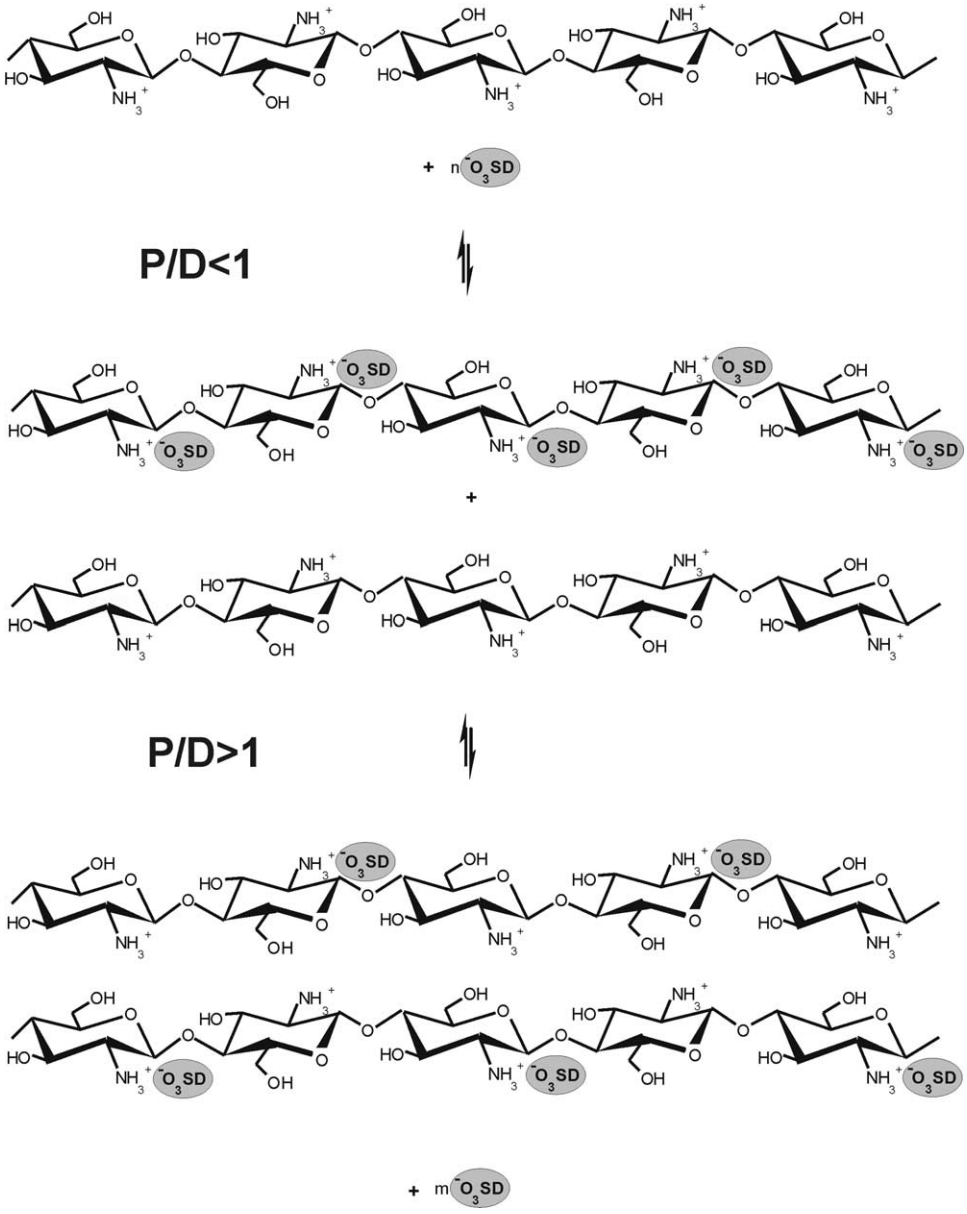


Fig. 4. Schematic presentation of the model proposed for the interaction between chitosan and dye.

As the salt affects both ionic and hydrophobic interactions between acid dye and wool fibre (Yang, 1998), it will affect extensively the interaction between chitosan and dye. Therefore, the increase in absorbance by adding the electrolyte could be attributed to the destruction of the electrostatic bonds between chitosan and dye ions. Gummow and Roberts (1985) found that there is a steady increase in the free dye fraction with increase in sodium chloride concentration up to approximately 0.1 mol/dm^3 at which concentration there is a complete reversal of metachromacy with 100% free dye. These authors claim that there is also the effect of the order the addition of the electrolyte. If it is added to the dye solution before the chitosan, the extent of reversal for a given electrolyte concentration is slightly greater than if the chitosan is added before the electrolyte. This suggests that it is easier to prevent the chitosan/dye binding than to break down the product once formed.

Due to the presence of protonated amino groups chitosan exhibits polyelectrolyte character in dilute acid aqueous solution at low pH (below pH 6.5) and its hydrodynamic behaviour in the solution is intricate. Wu, Zou, and Wang (1995) found that the intramolecular hydrogen bonds between chitosan macromolecules are probably maintained in solution. Polyelectrolyte effect is responsible for the fact that chitosan chain is slightly extended in aqueous solution and even in dilute solution chitosan still forms a small number of large-sized aggregates. In dilute solutions,

chitosan molecules follow the structure of wormlike chains. The chain conformation is strongly induced by ionic strength and deacetylation degree. The lower the ionic strength, the more extended the molecule. Forming of the large sized aggregates and a gel is related to the formation of local hydrophobic contacts, or hydrogen bonding, responsible for a more or less important physical reticulation of chitosan chains. It seems that the addition of low-molecular weight electrolytes is not able to completely eliminate the polyelectrolyte effect and hydrogen bonding between different chitosan chains, but nevertheless promotes aggregation (Pedroni, Schulz, Gschaider de Ferreira, & Morini, 2000).

Moreover, since interaction between chitosan and dye is ionic or some other type (van der Waals or hydrophobic), the sodium sulphate presence in the solution diminishes the solubility of dye, which is decreasing the ionic interaction with chitosan, and maintaining the other type of interaction.

Fig. 4 gives the possible explanation of unusual behaviour observed for *P*/*D* ratio above 1. We suggest that the increase in absorbance at *P*/*D* ratio above 1 could be attributed to the formation of a new soluble chitosan/dye product as the consequence of the dye distribution on different chitosan molecules.

As explained earlier, in acid solutions, protonated amino groups along the chitosan chain can act as dye sites for anionic dyes. Therefore, chitosan adsorbs dye anion strongly by ionic interaction between CHT–NH_3^+ and D–SO_3^-. Thus, the adsorption of anionic aromatic solutes (acid dyes) by chitosan is supposed to be largely an ion-exchange process, assisted by van der Waals attraction between the aromatic nuclei and the glucosidic residues of the chitosan molecular chains.

If we suppose that pH and temperature are constant, then at $P/D \leq 1$ basically we have dye molecules (or ions) in 'free' form, some soluble dye/chitosan product particles and insoluble dye/chitosan product in the form of precipitate. Insoluble product particles have all chitosan active sites (available for binding) saturated with dye. By increasing the chitosan concentration over *P*/*D* ratio 1, while maintaining the dye concentration constant, the redistribution of dye between chitosan macromolecules occurs, so they are not saturated anymore with dye and thus remain soluble, which reflects in an absorbance increase. It is important to notice that there are not 'privileged' chitosan macromolecules within the solution (there are no macromolecules that can interact with more dye compared to the other) and the mean number of molecules of dye which interact with chitosan macromolecule is maintained constant or it could be understood as a kind of normal distribution.

4. Conclusions

The absorption spectrometry measurements proved the occurrence of interaction between the chitosan and acid dye in an aqueous solution.

By assessment of chitosan/dye interaction it was possible to show that there is a 1:1 stoichiometry between protonated amino groups and sulfonate acid groups on the dye ions in low concentrated chitosan solutions. This interaction between chitosan and dye forms an insoluble product.

With the excess of chitosan in the solution, the dye can be distributed between the different chitosan molecules and the chitosan/dye soluble products remain in the solution.

Dye binding to chitosan involves mostly the adsorption on the active sites on chitosan macromolecule. Thus adsorbed dye molecules could be desorbed and redistributed between other components present in the system, depending on system parameters (mainly pH, temperature and electrolyte presence). This fact is important in explanation of dyeing behaviour of chitosan treated wool and should help to assess the mechanism of dyeing of accordingly modified textile fibres.

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