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Effects of adsorption interferents on removal of Reactive Red 195 dye in wastewater by chitosan

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Abstract: Reactive Red 195, which is an azoic anionic dye characterized by the presence of five sulfonic groups and one azoic group, is efficiently removed using chitosan. The increasing chitosan dose had a dramatic positive impact on the achieved color removal, there was approximately a linear relationship between chitosan dose and color removal of dye before color removal reach maximum. Also, the increase of dye concentration led to the increase of chitosan dosage in order to get the same color removal. 92 mg/L of chitosan dosage was sufficient to achieve complete remove of dye at initial concentration of dye at 200 mg/L. For the higher concentrations of dye, high dosages were necessary to reach complete color removal. On the other hand, the use of adsorption interferents(Fe^{2+}, Na^+, HCO_3^- and others) can be interesting, addition of ions had effect on the color removal of Reactive Red 195. Comparing with blank, addition of chemical species approximately decreased the color removal except Na^+ and combination of Fe^{2+} + HCO_3^-. However, comparing with Fe^{2+} alone and HCO_3^- alone, combination of Fe^{2+} + HCO_3^- increased the color removal.

Keywords: chitosan; Reactive Red 195; dye; coagulation; color removal

Introduction

Wastewater discharged from dyeing processes can be one of the biggest contributors to textile effluent; this comprises mainly residual dyes and auxiliary chemicals. Over 50000 ton of dyes is discharged into effluent annually, with the proportion of this total varying according to dye, fiber of application, and relative degree of dye fixation(Blackburn, 2004). As many other industrial sectors, growing concern about environmental issues has prompted the textile industry to investigate more appropriate and environmentally friendly treatment technologies to meet the discharge consents becoming stricter every day. Textile preparation, dyeing and finishing plants are currently being forced to treat their effluents at least partially prior to discharge to publicly owned treatment works due to the high organic load, strong and resistant color as well as high dissolved solids content of the discharged wastewater(Arslan, 2001).

Chitosan (2-acetamido-2-deoxy-β-D-glucose) is a cationic, deacetylated derivative of chitin in which the acetyl group has been chemically or enzymatically excised to form a molecule having one amino group and two free hydroxyl groups on each glucose ring(Fig.1). The cationic nature of chitosan and the consumer preference for "natural processes" make it an ideal candidate for applications such as wastewater treatment(Anjos, 2002; Chen, 2000), purification of water (Divakaran, 2001; Zeng, 2002), food wastes processing (Savant, 2000). It was shown that detailed information on conditions of wastes processing and the interactions of dye molecules need to be investigated for controlling their properties and optimization of the further applications.

The present study focused on the removal of Reactive Red 195 in water by chitosan. This dye is azoic anionic dye characterized by the presence of five sulfonic groups and one azoic group(Fig.2). It has good solubility in water, which cause to be removed difficultly. The objectives were to give a detailed information on conditions of wastes processing and the interactions of dye molecules.

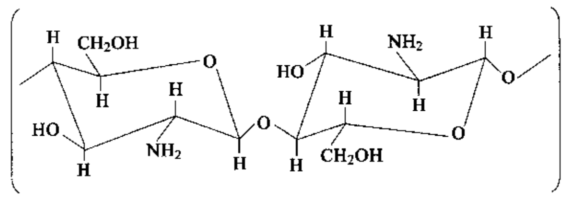

Fig.1 Structure of chitosan

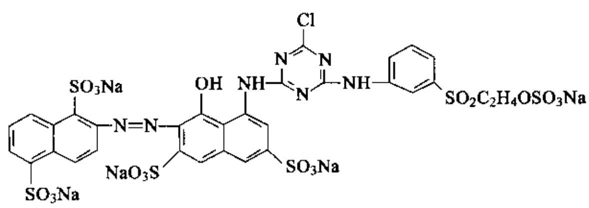

Fig.2 Chemical structure of Reactive Red 195

1 Experimental

1.1 Materials

Chitosan was supplied by Zhejiang Yuhuan Ocean Biochemical Company(the degree of deacetylation is 90%). Protonation was achieved by contact of chitosan with a HCl solution maintained at ca. pH 3 overnigh. 1 g of chitosan was dissolved in 100 ml water at ca. pH 3 for coagulation exemperiments. Reactive Red 195(Fig.2) was supplied by Zhejiang Runtu Dye Company, the dye was used as supplied without purification. Reactive Red 195 was directly diluted in water and the solubility of the dye was checked over the experimental pH range(ca. pH 1—10).

1.2 Procedures

The study of the influence of pH on dye removal was performed by mixing chitosan solution containing 2 mg of chitosan with 50 ml of dye solution (at the concentration of 100 mg/L). One series of experiments was performed keeping the pH constant with 0.1 mol/L HCl acid or 0.1 mol/L sodium hydroxide solutions. After 0.5 h, spectroscopic analysis of sample was carried out in a 1 cm quartz cell using a UV-2401PC Shimadzu Spectrophotometer(Kyoto, Japan).

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The wavelength of maximum absorption (λ_{max}) (542 nm) of Reactive Red 195 was determined and a calibration graph of absorbance versus dye concentration formulated at λ_{max} .

1.3 FTIR measurements

The samples of the chitosan, Reactive Red 195 and floc from chitosan and Reactive Red 195 were mixed with KBr and examined with 8900-FTIR, Shimadzu.

2 Results and discussion

2.1 Effect of pH on the flocculation of Reactive Red 195 using chitosan

Tests were conducted as described above, initially at pH values of 4, 5, 6, 7, 8, 9 using a chitosan concentration of 40 mg/L. The results presented in Fig. 3 show that the low color removal were found between pH 6—9, and the color removal ranked from 4.5% to 8.5%. However, about 90% removal of color is achieved between 4 and 5. This showed that pH strongly influenced removal of Reactive Red 195. This may be attributed to the degree of the protonation of the amine groups of chitosan. Because the dye is characterized by the presence of sulfonic groups, these anionic functions are attracted by protonated amine groups of chitosan. Thus, the protonation of the amine groups were necessary for the attraction of sulfonic groups, which led to the color removal. Between 6 and 9, the protonation of the amine groups were low, so the color removal is very low. However, at pH 4 and 5, the protonation increase, thus, the color removals greatly increase. It confirmed that for Reactive Red 195, the key mechanism is electrostatic attraction. For optimum removal of Reactive Red 195, it appeared necessary to maintain pH at 5. So, below 5, most of the amine groups were protonated.

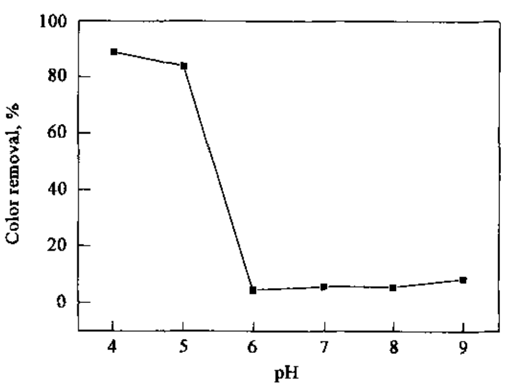

Fig.3 Effect of pH on the flocculation of Reactive Red 195 using chitosan

2.2 Effect of varying chitosan dosage on dye removal

As maximum efficiency of color removal was seen at pH 4, all further tests were conducted at pH 4. Tests were conducted using 32, 36, 40, 44, 48 mg/L of chitosan to study the effect of chitosan dosages. Fig.4 shows the effect of chitosan dosages on color removal of Reactive Red 195 at pH 4. As expected, the increasing chitosan dose had a dramatic positive impact on the achieved color removal, there was approximately a linear relationship between chitosan dose and color removal of dye. Also, low color removal efficiencies were obtained for varying chitosan doses between 0 and 32 mg/L at pH 4. It may be attributed to the following reasons: (1) the increase of electrostatic attraction duo to increase of amine groups of chitosan as reported above; (2) the formation of chitosan and Reactive Red 195 complexes by electrostatic interaction (Schatz, 2004). The complexes led to an enhancement of color removal, which was used as coagulating agents for treatment of cheddar cheese whey (Savant, 2000).

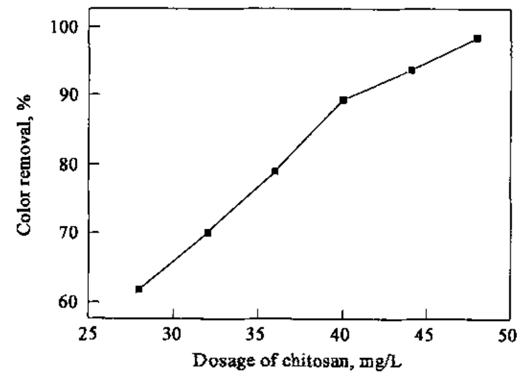

Fig.4 Effect of various chitosan dosage on dye removal at pH 4

2.3 Effect of dye concentration

A series of experiments were conducted to investigate the dependence of color removal on dye concentration at pH 4. The concentrations of reactive red 195 varied from 200 mg/L to 500 mg/L. Fig.5 shows the effect of dye concentration on color removal at pH 4. As can be observed, the increase of dye concentration led to the increase of chitosan dosage in order to reach the same color removal. 92 mg/L of chitosan dosage was sufficient to achieve the complete remove of dye at initial concentration of dye 200 mg/L, for the higher concentrations (400 mg/L, 500 mg/L), 160 mg/L or 200 mg/L of chitosan dosage, respectively, was necessary to reach the complete color removal. According to molar calculation of chitosan (in chitosan monomeric weight) and Reactive Red 195, the molar ratio of chitosan and Reactive Red 195 was 3 in 200 mg/L Reactive Red 195, however the molar ratios decreased to 2.6 in both 400 mg/L and 500 mg/L Reactive Red 195. Maybe the formation of chitosan and Reactive Red 195 complexes by electrostatic interaction led to an enhancement of color removal for higher concentration of dye.

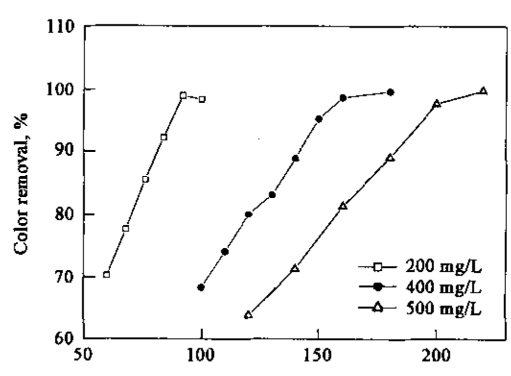

Fig.5 Effect of dye concentration on color removal at pH 4

2.4 Effect of chemical species in water on dye removal

Actually, the natural water contain cations and anions, and it was reported the flocculation difference between tap water and distilled water using chitosan (Divakaran, 2001). Thus, the present of cations and anions maybe have effect on color removal. Table 1 shows the effect of chemical species on color removal at pH 4 (dye concentration: 100 mg/L). These species, which are suspected to be present in natural water in minute quantities (Divakaran, 2001), were tested, alone or in combination. The water also had no significant UV absorption in the range 200—800 nm, indicating the absence of any significant inorganic content.

Table 1 Effect of chemical species in water on dye removal at pH 4

Species	Concentration, mol/L	Color removal, %	Species	Concentration, mol/(L·each)	Color removal, %
Blank		78.2	Combinations		
Cations			Ca^{2+} + HCO_3	10^{-4}	66.1
Ca^{2+}	10^{-4}—10^{-3}	70	Fe^{2+} + HCO_3^-	10^{-7}—10^{-4}	82.9
Na^+	10^{-3}—10^{-2}	84.8	Mg^{2+} + HCO_3^-	10^{-4}	68.0
Mg^{2+}	10^{-4}	70	Cl^- + HCO_3^-	10^{-4}	71.4
Fe^{2+}	10^{-7}—10^{-4}	66.7	SO_4^{2-} + HCO_3^-	10^{-7}—10^{-4}	68.0
Anions			Ca^{2+} + Mg^{2+}	10^{-4}	64.6
Cl^-	10^{-4}—10^{-2}	70			
SO_4^{2-}	10^{-7}—10^{-4}	70			
HCO_3^-	10^{-4}	69.8			
$H_2PO_4^-$	10^{-5}—10^{-3}	68.5			

These results indicated that addition of ions had effect on the color removal of Reactive Red 195. Comparing with blank, addition of chemical species approximately decrease the color removal except Na^+ and combination of Fe^{2+} + HCO_3^-. As for cations, it may be attributed to chelation between cations and chitosan, which decreased electrostatic interaction between chitosan and dye. On the other hand, the additions of anions can lead to the formation of electrostatic interaction between anions and chitosan, which decreased the electrostatic interaction between chitosan and dye. Thus, the color removal decreased. However, comparing with Fe^{2+} alone and HCO_3^- alone, the combination of Fe^{2+} + HCO_3^- increased the color removal. On the other hands, comparing with Mg^{2+} alone and HCO_3^- alone, combination of Mg^{2+} + HCO_3^- decreased the color removal. So, the mechanism of combination needs to be explored.

2.5 FTIR spectroscopic analysis

The FTIR spectra of chitosan, Reactive Red 195 and floc from chitosan and Reactive Red 195 are shown in Fig.6 (a, b, c), respectively. The characteristic absorptions of the chitosan (Fig.6a) are located at 3450 cm^{-1} (—OH), 1597 cm^{-1} (—NH_2), 1648 cm^{-1} (amide I band) and 1550 cm^{-1} (amide II band) (Tian, 2003). The characteristic absorptions of sulfonic groups of dye are located at 1213 cm^{-1}, 1048 cm^{-1} (Fig. 6c). Also, the characteristic absorptions of sulfonic groups of dye are present in floc (Fig. 6b), but become smaller. This maybe shows that the complex has been formed. On the other hand, the peak shown at 1550 cm^{-1} (Fig. 6b) in floc is assigned as a symmetric deformation of NH_2^+. Thus, it can be concluded that positively charged NH_2^+ exists in floc from chitosan and dye.

2.6 Interaction between chitosan and Reactive Red 195

Blackbum studied the interaction between dye and starch and thought that the interaction between dye and polysaccharide would based on (1) dipole-dipole hydrogen bonding interations between chitosan hydroxy groups and

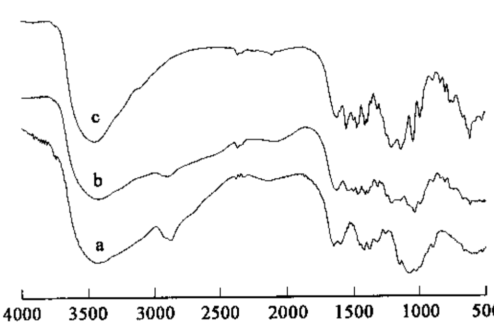

Fig.6 FTIR spectra of chitosan, Reactive Red 195 and floc
a. chitosan; b. floc from chitosan and Reactive Red 195; c. Reactive Red 195

azoic group in the dye molecules; (2) Yoshida H-bonding between chitosan hydroxy groups and aromatic residues in dye (Blackburn, 2004). Comparing with starch and cellulose, chotisan consists of one amino group and two free hydroxyl groups on each glucose ring, the protonation of the amine groups were necessary for the attraction of sulfonic groups. According to the report above, the electrostatic attraction (Fig.7) between chitosan and dye was very important for the formation of chitosan and Reactive Red 195 complexes, which led to color removal. The use of adsorption interferents (Fe^{2+}, HCO_3^-, SO_4^{2-} + HCO_3^- and others) decreased the electrostatic attraction, thus, color removal of dye also decreased.

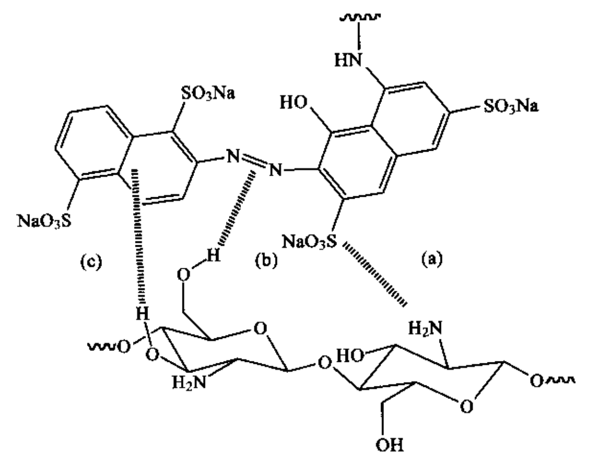

Fig.7 Interaction of chitosan and Reactive Red 195
a. electrostatic attraction; b. dipole-dipole hydrogen bonding interations between chitosan hydroxy groups and azoic group in the dye molecules; c. Yoshida H-bonding between chitosan hydroxy groups and aromatic residues in dye

3 Conclusions

Reactive Red 195, which is an azoic anionic dye characterized by the presence of five sulfonic groups and one azoic group, is efficiently removed using chitosan. The protonation of chitosan may explain the electrostatic attration of this anionin dye and its optimium pH is close to 4. The increasing chitosan dose had a dramatic positive impact on the achieved color removal, there was approximately a linear relationship between chitosan dose and color removal of dye. Also, the increase of dye concentration led to the increase of chitosan dosage in order to get the same color removal. 92 mg/L of chitosan dosage was sufficient to achieve the complete remove of dye at initial concentration of dye at 200 mg/L, for the higher concentrations(400 mg/L, 500 mg/L), 160 mg/L or 200 mg/L, respectively, was necessary to reach the complete color removal. On the other hand, addition of ions had effect on the color removal of Reactive Red 195. Comparing with blank, addition of chemical species approximately decreased the color removal except Na^{+} and combination of Fe^{2+} + HCO_3^-. However, comparing with Fe^{2+} alone and HCO_3^- alone, combination of Fe^{2+} + HCO_3^- increased the color removal. Future studies are needed to explore the detailed information and mechanism of interaction of combination of chemical species with chitosan.

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