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# Coagulation and flocculation of dye-containing solutions using a biopolymer (Chitosan)

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## Abstract

Chitosan, dissolved in acetic acid, was used for the coagulation–flocculation of an anionic dye (Reactive Black 5). In acidic solutions protonated amine groups of chitosan attract dye sulfonic groups. Increasing chitosan dosage increases dye removal up to a concentration resulting in complete neutralization of anionic charges; above, the excess of cationic charges leads to suspension re-stabilization. Process efficiency increases with decreasing the initial pH of dye solution: the molar ratio between dye molecules and amine groups ( $[n]$ ) respects the stoichiometry between sulfonic functions and protonated amine groups at initial pH 5; at initial pH 3 a possible dye aggregation phenomenon results in higher molar ratio  $[n]$ . The coefficient  $[n]$  depends on both the pH and the molecular weight of chitosan. The main mechanism for dye coagulation with chitosan sounds to be charge neutralization at acidic pH.

*Keywords:* Chitosan; Reactive Black 5; Coagulation flocculation; pH effect; Charge neutralization; Effect of molecular weight

## 1. Introduction

Chitosan is an aminopolysaccharide produced by the deacetylation of chitin, one of the most abundant biopolymers (Fig. 1). The physico-chemical properties of chitosan related to the presence of amine functions (acid–base properties, solubility, cationicity) make it very efficient for binding metal cations in near neutral solutions [1–3], and for interacting with anionic solutes in acidic solutions [3–6]. This electrostatic attraction mechanism is responsible for the strong interaction existing between chito-

san and anionic dyes such as Reactive Black 5 (RB 5) [7,8]. Protonated amine groups react with sulfonic functions of the dye in acidic solutions. Indeed, though the intrinsic  $pK$  of amine groups of chitosan strongly depends on both the deacetylation degree (DA) and the degree of dissociation ( $\alpha$ ), for chitosan with a degree of deacetylation above 70%, the  $pK_a$  can be approximately fixed to 6.3–6.4 [9]. Hence, at pH below 5, most of amine groups are protonated and they can attract metal anions (molybdate, vanadate, palladate, chromate, ...) [10–17]. This property has been widely used for the sorption of a number of dyes in solution [5,18–21], as an alternative to conventional sorbents: activated carbons [22–24], agriculture waste materials [25–27]. A much less abundant literature

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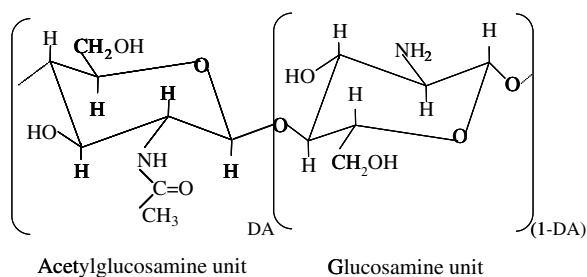


Fig. 1. Structure of chitosan (DA: degree of acetylation).

exists on the use of chitosan in the dissolved-state for the removal of dyes [28,29]. Chitosan has been widely used for the coagulation–floculation of mineral colloids [30–34], in food industry [35,36], bacterial suspensions [37–39]... These processes mainly focused on the recovery of suspended matters and colloid; in the case of dissolved contaminants there are much less studies.

The coagulation and the floculation of suspended particles and colloids result from different mechanisms including electrostatic attraction, sorption (related to protonated amine groups), bridging (related to polymer high molecular weight). In some cases, the amount of protonated amine groups added to the solution is far below the number of charges necessary for the neutralization of the anionic charges held by the colloids; the removal of particles can be explained in this case by a combination of distinct mechanisms such as electrostatic patch and bridging. For these reasons the efficiency of chitosan for the treatment of anionic dyes is suspected to depend on its deacetylation degree and its molecular weight (among structural parameters) and its concentration, additionally to solution parameters (dye concentration, pH, ionic strength of the solution).

The present work focuses on the coagulation–floculation of Reactive Black 5 using chitosan. Experiments have been performed at two initial pHs (pH 3 and 5), with two chitosan samples characterized by the same deacetylation degree but with different molecular weights. The concentration of

chitosan added to dye solution was varied in order to determine the optimum molar ratio between sulfonic groups of the dye and amine groups of chitosan for maximum dye removal. This molar ratio served to calculate the ratio dye/amine groups on the polymer at saturation, i.e. the stoichiometric ratio for the reaction between chitosan and the dye. This maximum binding capacity can be compared to the maximum sorption capacity obtained in sorption isotherms with similar materials (RB 5 dye and chitosan, used in the solid state) [8]. The comparison of solid-state application (sorption) and dissolved-state application (coagulation–floculation) will allow identifying the significant contribution of diffusion properties (accessibility to internal sites) and site availability on the control of sorption properties (versus coagulation–floculation). The influence of a filtration step before analysis was also investigated.

## 2. Material and methods

### 2.1. Chitosan samples

Chitosan samples were kindly donated by Mahatani Chitosan Pvt., Ltd. (Veraval, India). They were characterized by FT-IR analysis for the determination of deacetylation degree (DA) and by size exclusion chromatography for molecular weight measurements. The molecular weight were measured using a IsoChrom LC pump (Spectra-Physics) connected with a protein pack glass 200 SW column and a TSK gel 6000 PW, coupled with multi-angle laser light scattering detector (Wyatt-Dawn DSP) and a differential refractometer (Waters 410). The characteristics of these samples are given in Table 1. The mean value for water content in chitosan samples was close to 10%. This percentage of water was taken into account for the calculation of true concentrations.

The polymers were ground and sieved; the smallest size fraction (0–125  $\mu\text{m}$ ) of each polymer was collected and used for the preparation of coagulant

Table 1  
Characteristics of chitosan samples

Sample	Chitosan comm. ref.	Degree of deacetylation (%)	Viscosity (25 °C) (cps)	$MW_w^a$ ( $\text{g mol}^{-1}$ )	$MW_n^a$ ( $\text{g mol}^{-1}$ )	Polydispersity <sup>a</sup>
B1	222	89.5	740	308,300	144,800	2.1
B6	242 b6	89.5	18	80,100	26,100	3.1

<sup>a</sup> Analyses performed by the Laboratoire des Matériaux Polymères et des Biomatériaux, Université Claude Bernard, Lyon I, France.

solutions. The powder was dissolved in an acetic acid solution. To facilitate the preparation of the polymer solutions, chitosan (2 g) was hydrated overnight in de-mineralized water (98 mL) before 2 g of acetic acid (80% w/w) were added under agitation. The solution was left to stand overnight before being used. The final pH of the solution was close to 4–5.

## 2.2. Dye

The dye (RB 5) was supplied by Aldrich (USA). This dye is characterized as a di-azo compound bearing four sulfonic groups (Fig. 2). The molecular weight of the dye is  $991.82 \text{ g mol}^{-1}$ . The commercial salt was supplied as a mixture of the active material and an inert product: the true dye content was 55%. This must be taken into account for the evaluation of true molar ratio and true sorption capacities. The residual concentration was measured by UV–Visible spectrophotometry for dye concentration at the wavelength of 598 nm (UV–VIS spectrophotometer Shimadzu UV-160 A) after pH control. The dye spectrum may be affected by the pH of the solution, for analytical purpose, a drop of  $3 \text{ mol L}^{-1}$  NaOH solution was systematically added to the samples to maintain a constant pH for the different samples.

## 2.3. Coagulation–flocculation experiments

Experiments on dye coagulation and flocculation were performed using Jar-Test equipment. The dye solution, which pH was controlled using either  $0.1 \text{ mol L}^{-1}$  or  $1 \text{ mol L}^{-1}$  HCl solutions, was mixed after the addition of polymer solution under strong agitation ( $\approx 200 \text{ rpm}$ ) for 3 min and then under slow agitation ( $\approx 40 \text{ rpm}$ ) for 20 min. Samples were col-

lected after a 30-min settling-time at the top of the settling beaker (top 1 cm of water surface) using a syringe and analyzed for dye content in the supernatant, directly or after filtration. Samples collected in the syringe were filtered through a  $1.2 \mu\text{m}$  Whatman filtration membrane (hold on a filter support cartridge). The amount of dye retained on the membrane was negligible (below 2%). Experiments were performed at room temperature (i.e.  $21 \text{ }^\circ\text{C} \pm 1.5 \text{ }^\circ\text{C}$ ). The experimental conditions (agitation time and velocity) have been selected according to conventional values for coagulation–flocculation processes. Kinetic aspects have not been considered in this work. Though increasing the contact time could increase the efficiency of the process, the fast reaction of the dye with chitosan dispersed in the solution is expected to limit the impact of kinetic criteria on the residual concentration. The kinetic parameter is expected to play a more significant effect at higher concentrations of chitosan and dye. Preliminary tests showed that changing the stirring time for both fast and slow agitation velocities did not significantly affect the residual concentration. Some samples were also collected after 2-h settling-time, and the variation of the residual concentration of the dye was less than 15% (compared to standard 30-min settling-time).

The amount of dye on the polymer was calculated by a mass balance equation assuming that the amount of dye that was removed from the solution was bound to the total amount of polymer present in the solution. The dye/polymer molar ratio was varied in order to determine the optimum relationship between dye functional groups and amine groups of chitosan for maximum recovery of the dye.

## 3. Results and discussion

### 3.1. Approach of coagulation–flocculation mechanism

Fig. 3 shows the coagulation–flocculation of RB5 at pH 5 (initial pH subject to change due to the addition of chitosan dissolved in acidic solution) for different initial concentrations. The concentration of chitosan was varied in order to determine the best dosage of coagulant for each dye concentration. Two series have been performed with chitosan B1 (high molecular weight) and chitosan B6 (low molecular weight). Varying chitosan concentration, the residual concentration of the dye in the settled solution systematically reached a minimum before

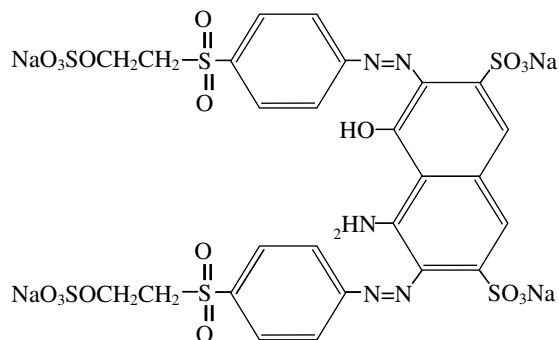


Fig. 2. Structure of Reactive Black 5.

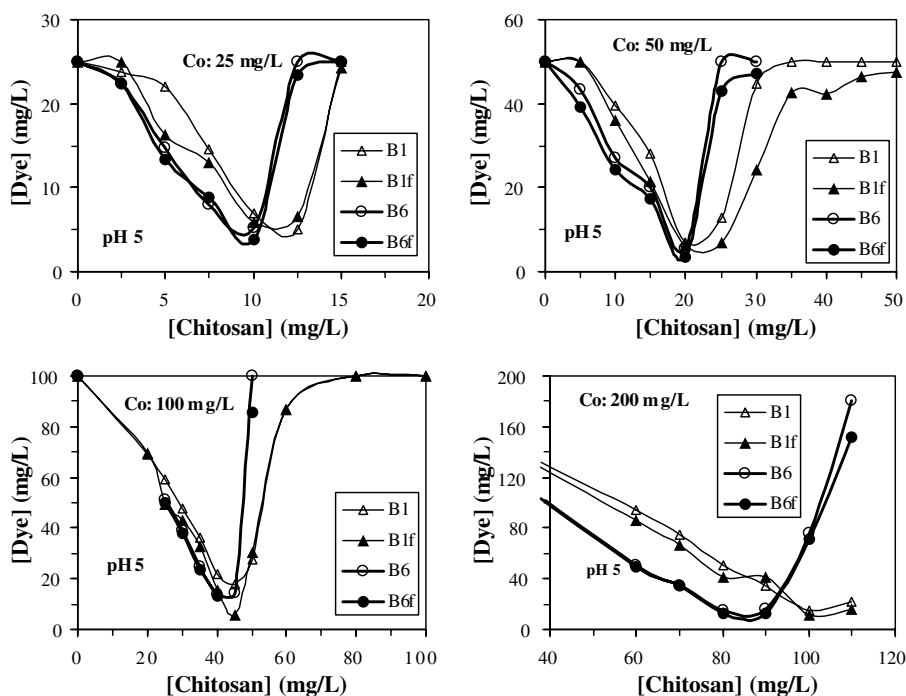


Fig. 3. Influence of filtration step on the optimum chitosan concentration for coagulation–flocculation of RB 5 at initial pH 5 (chitosans B1 and B6) at different initial concentrations of dye.

increasing again. This is the typical curve of a coagulation–flocculation system controlled by charge neutralization mechanism. The anionic dye, bearing sulfonic groups, is electrostatically attracted by protonated amine groups: this reaction allows neutralizing the anionic charges of dyes that can bind together and settle. When the amount of protonated amine groups reached the complete neutralization of anionic charges, the removal of the dye reached a maximum. When increasing the amount of chitosan added to the solution the presence of an excess of protonated amine groups (cationic charges) induced a re-stabilization of the suspension and a decrease in the efficiency of the process. The slopes of the two segments of the curves were significantly different: the segment corresponding to the re-stabilization of the suspension was systematically steeper than that of the charge neutralization segment. The bridging mechanism is enhanced by the flocculating effect of chitosan (due to its high molecular weight) and the interactions of the different anionic groups (sulfonic) on the dye with different protonated amine groups (inter- and intra-chain associations). Chitosan is involved in a dual mechanism including coagulation by charge neutralization and flocculation by bridging mechanism.

### 3.2. Influence of filtration step and chitosan molecular weight on dye removal by coagulation–flocculation

Fig. 3 also shows that the filtration step hardly influenced the optimum dosage of chitosan: the concentration of coagulant required for optimum abatement of dye and the shape of the curves were not significantly changed. The only differences that can be detected between the filtered and non-filtered series were observed on chitosan B1: in the case of high molecular weight chitosan, the filtration step allowed slightly decreasing the residual concentration of the dye. This is indicative that bridging mechanism, which is enhanced for polymers of high molecular weights, contributed to the coagulation–flocculation of the dye. The bridging effect is expected to contribute more to coagulation–flocculation at higher pH (i.e. close to neutral pH). However, these differences were not very marked.

Fig. 3 shows that in most cases chitosan B6 required slightly lower dosages than chitosan B1. Surprisingly the chitosan of highest molecular weight that holds better possibilities for bridging gave slightly worst results than low molecular sample. Yan et al. [40] used poly(acrylic acid) polymers of different molecular weights for the flocculation of

colloidal alumina suspensions and they also found that high molecular weight samples required higher amounts of polymer for maintaining good flocculation performance. They explain this difference in the behavior of the different flocculants by a change in the flocculation mechanism: with low molecular weight polymers, the charge neutralization mechanism is the main mechanism while at increasing the molecular weight of the polymer an increasing part of the flocculation effect is due to bridging mechanism, which usually requires highest dosage of coagulant–flocculant. Das and Somasundaran [41] found more contrasted results for the same system: they observed that for molecular weights lower than  $250,000 \text{ g mol}^{-1}$  decreasing the molecular weight of the coagulant required higher polymer dosages for efficient coagulation, while above  $250,000 \text{ g mol}^{-1}$  increasing the molecular weight of the coagulant required higher polymer dosage. For molecular weights between  $2000$  and  $50,000 \text{ g mol}^{-1}$ , they define the concentration ranges in which the polyelectrolyte behaved as a flocculant and above which it behaved as a dispersant.

At low dye concentration, B1 and B6 required similar chitosan dosage for the optimum abatement of dye (Fig. 4). The correlation of the optimum dosage with initial concentration of the dye indicates that there was a stoichiometric reaction between the dye and chitosan. The slope of this curve slightly increased when the molecular weight of the polymer increased.

### 3.3. Interpretation of the influence of chitosan MW on coagulation–flocculation mechanism

Schatz et al. [42,43] described chitosan as a wormlike molecule with a persistence length increasing from  $4.5$  to  $8.8 \text{ nm}$  when increasing the molecu-

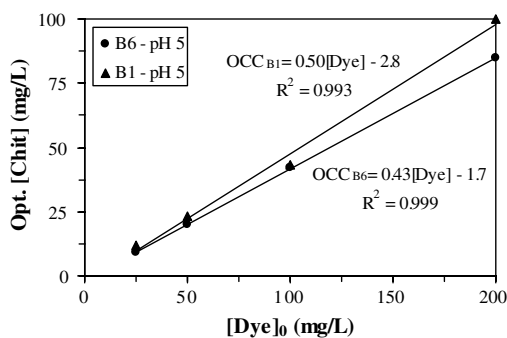


Fig. 4. Correlation between optimum chitosan dosage and initial dye concentration at pH 5.

lar weight of the polymer. This structure was attributed to the intrinsic rigidity of the  $\beta$ -(1  $\rightarrow$  4) glycosidic bond and the possibility of intramolecular hydrogen bonds. Mixing dextran sulfate of smaller chain length than chitosan resulted in premature flocculation for low molecular weight dextran sulfate, followed by a poor stability of the colloids for intermediary molecular weight dextran sulfate. Small molecules of anionic species facilitated the complete ion-pairing with chitosan without enough unpaired sulfate functions to ensure the stabilization of particles. When increasing the molecular weight of dextran sulfate the conformational adaptation of the anionic polyelectrolyte was less favorable and let a number of unpaired sulfate functions that contribute to the stabilization of colloidal particles. Low molecular weight chitosan resulted in the formation of lower size particles, in relation with different charge neutralization behavior and different charge density.

The critical concentration of chain entanglement ( $C^*$ ) increases with decreasing the molecular weight. This may contribute to explain that high molecular weight chitosan can be slightly less efficient due to possible interactions between the polymer chains, at least in the coagulant preparation. These interactions contribute to decrease the mobility of polymer chains and the statistical probability for cationic sites to encounter anionic charges. The change in the stiffness of the chain may also affect the possibility for sulfonic groups of the dye to interact with protonated amine groups of different glucosamine units (steric hindrance and conformation adaptation). Ashmore et al. [44] also commented the influence of the rigidity of chitosan backbone chains on the flocculation of latex particles. They observed that for chitosans of medium molecular weight increasing the degree of acetylation increased the rigidity of the chain, which in turn made difficult for the polymer to match the template of charges set by the latex particle surfaces. They observed that this negative effect was less significant with high molecular weight chitosan due to greater density of the charge patch attainable with the longer chain length molecule.

### 3.4. Influence of pH on the optimization of coagulation–flocculation of RB5

Experiments have been performed using chitosan B1 for different concentrations of dyes at initial pH 3 and pH 5. Fig. 5 shows the relative residual



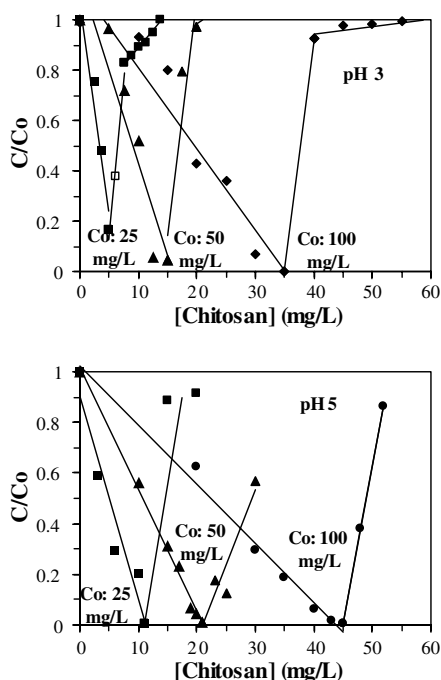


Fig. 5. Influence of initial RB 5 concentration on the efficiency of dye removal at in initial pH 3 and 5 with chitosan B1 – determination of optimum chitosan dose.

concentration of dye in function of chitosan concentration. The optimum concentration of chitosan (OCC, mg/L) linearly increased with dye concentration (mg/L) as it was observed in Fig. 4:

$$\text{At pH 5: } \text{OCC} = 0.41[\text{Dye}] + 2$$

$$\text{At pH 3: } \text{OCC} = 0.40[\text{Dye}] - 5$$

These values obtained only with three different initial dye concentrations (25, 50 and  $100 \text{ mg L}^{-1}$ , versus  $25\text{--}200 \text{ mg L}^{-1}$  in Fig. 4 for pH 5) have to be taken as an indication of the magnitude order of the parameters. The slopes of the curves were comparable in this range of concentration for pH 3 and pH 5. However, at pH 3 the amount of chitosan to be added for an efficient coagulation–flocculation of RB 5 was lower than that needed at pH 5. This may be explained by the acid–base properties of chitosan. The  $pK_a$  of amine groups strongly depends on the deacetylation degree of chitosan and the dissociation degree of the polyelectrolyte [9]. The  $pK_a$  of amine groups is close to 6.3–6.4 for fully dissociated chitosan (with deacetylation degree close to 90%). This means that at pH 5, or below, more than 90% of amine groups were protonated. The initial pH 3 obviously led to a more protonated form

of chitosan. However, it is important to observe that the addition of significant amounts of chitosan (dissolved in acetic acid solution) in the dye solution (at the initial pH 5) involved a significant change of the pH of the final solution. At pH 3, the pH hardly changed (by less than 0.2 pH unit), while at pH 5 the pH of the solution decreased to 3.5–4.0. This means that the final pHs were of the same order of magnitude for pH 3 and pH 5 experiments. Changing the initial pH of the solution involved a weak but significant difference in the performance of the system, i.e. requiring lower quantities of chitosan. However, the relative residual concentration of the dye after coagulation–flocculation and filtration was much lower, especially at low dye concentration, when the initial pH of the solution was set at pH 5. It seems that decreasing the initial pH of the solution had a positive impact on the amount of chitosan to be added to the solution for efficient dye removal, but a negative influence on the residual dye concentration. Increasing the initial concentration decreased the differences in the residual concentrations of the dye, probably due to the cross-linking effect of this poly-anionic dye: the dye can interact with several glucosamine units (inter- and intra-chain bonds). The interaction of chitosan with poly-anionic ions was used for the ionotropic gelation of chitosan using tri-polyphosphate [45] or heptamolybdate ions [46,47]: the control of the pH in slightly acidic experimental conditions (i.e. close to pH 5) revealed favorable.

The slope of the first section of the curves (coagulation–flocculation segment) decreased with increasing the initial concentration for both pH 3 and pH 5 (Fig. 5), while the slope of the second section of the curve (re-stabilization segment) was roughly the same. This means that when increasing the initial concentration of the dye the selection of the optimum dosage will be easier.

Fig. 6 compares the coagulation–flocculation profiles for  $50 \text{ mg L}^{-1}$  concentration solutions of RB 5 at initial pH 3, 5 and 7. This confirms the trends observed in Fig. 5: increasing the initial pH increased the amount of chitosan to be added to dye solution for optimum removal efficiency. Though the difference was not very marked between pH 3 and pH 5 (from 15 to  $22 \text{ mg L}^{-1}$ ); the optimum dosage dramatically increased at pH 7 (about  $50 \text{ mg L}^{-1}$ ). The final pHs of the suspension at the optimum dosage of chitosan were not very different: close to pH 2.9, pH 3.7 and pH 4.3 for initial values 3, 5 and 7, respectively. The addition of increasing

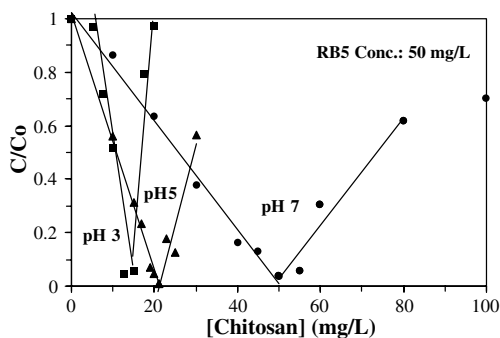


Fig. 6. Influence of initial pH on the coagulation–flocculation of RB5 (dye concentration  $50 \text{ mg L}^{-1}$ ), using chitosan B1.

amounts of acidic chitosan solutions led to greater pH change. The key parameter for an efficient use of chitosan seems not being the final pH but the initial pH (under selected experimental procedure). Additionally, this figure shows that the slopes of both the first section of the curves (corresponding to neutralization segment) and the second section (corresponding to re-stabilization of the suspension) decreased with increasing the pH. The short range of concentrations for optimum coagulation–flocculation increased with the initial pH, rendering the process easier to control at large scale.

### 3.5. Optimum molar ratio dye/amine groups

The residual concentrations found in the supernatant of the suspensions can be considered for the calculation of a virtual binding capacity (in  $\text{mg dye g}^{-1}$  chitosan or  $\text{mmol dye g}^{-1}$  chitosan) using the mass balance equation, and assuming that the total amount of polyelectrolyte added to the solution is available for interacting with the dye. It is also possible to calculate a conversion ratio between g of chitosan and mmol of amine groups: it is necessary to take into account the water content of chitosan flakes used for the preparation of chitosan solutions (i.e. approximately 10%) and the deacetylation degree (i.e. 89.5%). These different conversion ratios have been used for the calculation of the coefficient  $[n]$  ( $[n]$ : mol dye/mol amine groups) representing the molar ratio at optimum chitosan dosage. Fig. 7 shows the coefficient  $[n]$  at initial pH 5 for different initial concentrations. This coefficient varied between 0.2 and 0.3 mol dye/mol amine groups depending on experimental conditions (filtration step, molecular weight of chitosan for B1 and B6 samples). The mean value for  $[n]$  was around 0.25 mol dye/mol amine groups. This ratio corresponds to a stoichiometry 4:1 between chitosan

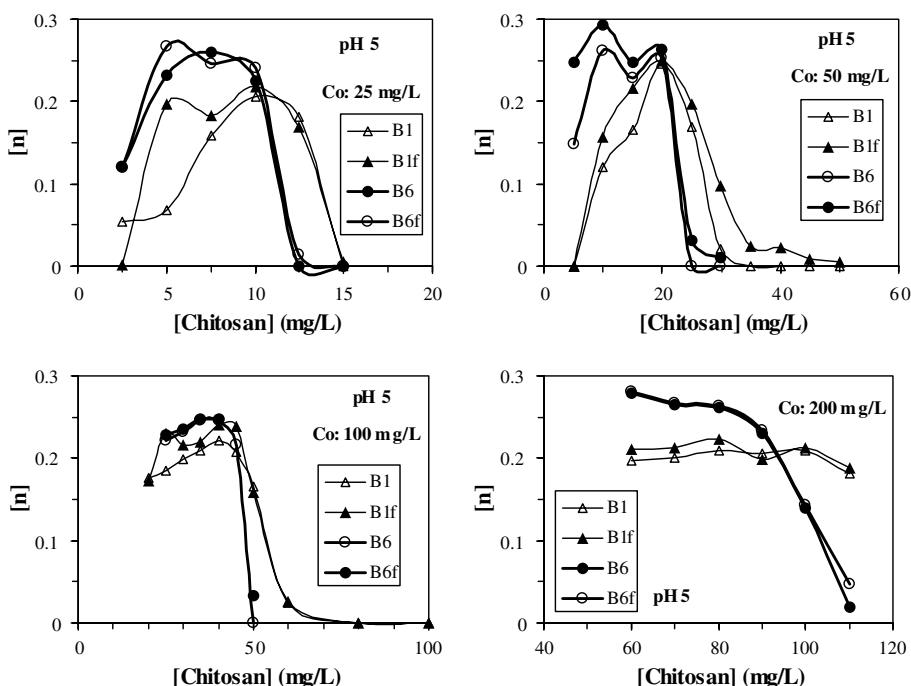


Fig. 7. Determination of the maximum molar ratio dye/amine groups ( $[n]$ , mol dye/mol amine groups) in the coagulation–flocculation of RB 5 using chitosans B1 and B6 at initial pH 5.



and dye that correlates well with the stoichiometry of active groups on both the polymer and the dye. Indeed, the dye bears four sulfonic groups per dye unit. The molar ratio dye/chitosan has been used for quantification of chitosan in solution by Roberts [18,48].

The filtration step hardly influenced the value of  $[n]$  whatever the chitosan sample (B1 or B6) and the concentration of the dye. Increasing the molecular weight decreased  $[n]$ . The molar ratio  $[n]$  varied between 0.2 and 0.25 for high molecular weight chitosan, while it varied between 0.25 and 0.3 for low molecular weight chitosan. At optimum chitosan dosage, a greater number of amine groups were required for the neutralization of sulfonic functions of the dyes with high molecular weight chitosan (in the range 4–5 for B1 against 3–4 for B6). This means that not all amine groups of B1 chitosan sample were available for interactions with dye anionic sites (i.e. for the neutralization of anionic charges of the dyes). The lower efficiency of amine groups in high molecular weight chitosan can be due to decreased availability of amine functions: intra- and inter-chain hydrogen bonds between OH groups and amine groups make them less available for reacting with sulfonic functions. This effect is especially significant when polymer concentration exceeds the critical concentration of entanglement ( $C^*$ ), which is proportional to the reciprocal of molecular weight. When the molecular weight increases, this causes more linkages between the chains and then less availability of reactive groups. It is noteworthy that the bridging effect, which is usually increased for high molecular weight polymer, was not sufficient to compensate the lack of availability of amine groups. This confirms that the main mechanism involved in the coagulation–flocculation of RB5 with chitosan is charge neutralization. This contrasts with the case of coagulation of bentonite suspension for which the amount of chitosan required for efficient abatement of turbidity was much lower than the amount required for charge neutralization and for which using high molecular weight slightly increased the efficiency of the process [49]. In the case of bentonite suspensions, the mechanism involved a series of process including bridging and charge patch neutralization.

It is interesting to compare these stoichiometric ratios between the dye and amine groups obtained by the coagulation–flocculation process to the values obtained at saturation of chitosan in the solid form in the sorption process. Previous investiga-

tions on the sorption of RB 5 using another chitosan sample (deacetylation degree 87%) have shown that the maximum sorption capacity was close to 1000 mg dye complex  $\text{g}^{-1}$  chitosan at pH 3. Taking into account the purity of the dye, this maximum sorption capacity was 550 mg dye  $\text{g}^{-1}$  (i.e. 0.56 mmol dye  $\text{g}^{-1}$  chitosan) and maximum sorption capacity can be converted to 0.12 mol dye/mol amine groups. This is two times lower than the optimum ratio found in the coagulation–flocculation process at pH 5 (final pH close to pH 3). This means that the solid-state process (i.e. adsorption) is less favorable than the dissolved-state process (i.e. coagulation–flocculation) for the optimum use of amine functions of chitosan. The conformation of the polymer in the solid-state is clearly less favorable due to inter and intra-bonds between the polymer chains. These linkages make some of the reactive groups less available for electrostatic interactions. Additionally the poor diffusivity of chitosan controls the diffusion to internal sites: the conformation (and stiffness) and the diffusion characteristics of chitosan in the solid-state limit the reactivity of amine groups.

Fig. 8 shows  $[n]$  for different experiments carried out at initial pH 3. In this case,  $[n]$  was significantly greater than at initial pH 5, especially for low initial dye concentrations: it was closed to 0.5 mol dye/mol amine groups. This means that at initial pH 3 the interaction of sulfonic groups of the dye with amine groups of chitosan did not respect the stoichiometry: only two amine groups were required for binding one dye molecule. There are several reasons that could explain this difference in the coagulation–flocculation mechanism, related to (a) acid–base properties of the dye (lower dissociation of the dye) and/or (b) aggregation mechanism. Aggregation

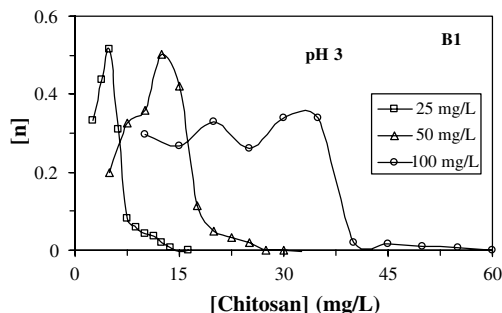


Fig. 8. Determination of the maximum molar ratio dye/amine groups ( $[n]$ , mol dye/mol amine groups) in the coagulation–flocculation of RB 5 using chitosan B1 at initial pH 3.

mechanism has been cited to interfere in the sorption of some dyes on activated carbon [50]. Here the partial aggregation of the dye may result in greater number of dye molecules bound to amine groups. In the case of heptamolybdate binding to chitosan the Mo/NH<sub>2</sub> molar ratio largely exceeds 1/1 (i.e. 1.5–1.7 mol Mo/mole NH<sub>2</sub> groups) [13]: the binding of one heptamolybdate resulted in the binding of seven Mo. The same interpretation can be used for dye–dye association: the binding of one dye aggregate causes the binding of two or more dye units.

#### 4. Conclusion

Chitosan dissolved in acetic acid was very efficient for the coagulation–flocculation of Reactive Black 5. In acidic solutions, the charge neutralization (associated to bridging effect) was responsible for dye removal. An excess of cationic charge contributed to re-stabilizing the suspension and reducing the efficiency of the process. For a given initial pH the optimum dosage correlated well with the initial concentration of the dye indicating that the addition of the polyelectrolyte can be easily monitored by the determination of dye concentration in the feed solution (using for example on-line spectrophotometric measurements).

Using high molecular weight chitosan slightly decreased process efficiency due to a reduced availability of amine groups and a less flexible structure that is suspected to avoid the adaptation of the conformation of the polyelectrolyte to the distribution of anionic charges on the dye. Decreasing the initial pH resulted in a decrease of the dosage of chitosan required for an efficient coagulation–flocculation. At saturation of the polymer (corresponding to optimum dosage) and at initial pH 5 the molar ratio between dye and amine groups (i.e. 1:4) respected the stoichiometry between sulfonic functions and amine groups (i.e. 1:1). At pH 3 lower amounts of chitosan were required, probably due to dye aggregation phenomenon. Dissolving chitosan allows increasing its reactivity for dye binding, due to higher accessibility and better availability of amine groups, compared to solid-state use of chitosan.

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