Treatment of ink-containing wastewater by coagulation/ flocculation using biopolymers

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Abstract

A coagulation/flocculation process using a selection of biopolymers (chitosan and tannin) was used to treat an ink-containing effluent generated in the processing of packaging. The efficiency of the process was investigated in terms of the influence of pH, coagulant and flocculant concentrations, as well as chitosan characteristics (especially the molecular weight). The process was particularly efficient under acidic solutions: the amount of coagulant and flocculant to be used were significantly reduced by limiting the pH to 5. Optimum conditions for colour abatement (measured at 528 nm) were obtained at pH 5 using the most viscous chitosan (highest molecular weight) at a concentration close to 20 $mg \cdot \ell^{-1}$ and a concentration of tannin close to 70-100 $mg \cdot \ell^{-1}$.

Keywords: chitosan, polymer concentration, molecular weight, poly-tannin, ink, coagulation, flocculation

Introduction

The packaging industry frequently uses dyes, pigments and inks for the conditioning of cardboard boxes and the printing of advertisements. The process generates highly coloured effluents that cannot be discharged without treatment due to the:

- Direct toxicity of these effluents
- Colour they impart is very undesirable to the water user (Chua and Loh, 2004).

Adsorption is the process which is most frequently employed for the treatment of coloured effluents, using for example activated carbon (McKay, 1983; Walker and Weatherley, 1999; Wu et al., 2001a; Yang and Al-Duri, 2001), resins (Karcher et al., 2002), agricultural wastes (Annadurai et al., 2002; Morais et al., 2000; Robinson et al., 2002), micro-organisms (Fu and Viraraghavan, 2003) and biopolymers (Chiou and Li, 2002; McCarrick et al., 2003; Wu et al., 2001b). However, this process usually comprises a simple transfer of pollutant from a dispersed phase to a concentrated phase. The use of expensive materials and the necessity to control the discharge of these loaded materials sometimes makes the process non-cost -effective. Biological processes are commonly cited for the treatment of coloured effluents alone (Bell and Buckley, 2003; Fu et al., 2001), or in combination with sorption processes (Walker and Weatherley, 1999). Some other processes such as photochemical (Arslan and Balcioglu, 2001; Genç, 2004) and catalytic degradation processes also exist. These oxidation processes may cause pollution hazards since in some cases the products generated during the oxidation are more hazardous for the environment than original contaminants. Membrane processes using nanofiltration techniques have recently received great attention (Chabot et al., 1999; Diaper et al., 1996; Koyuncu et al., 2004). However, processes such as coagulation and flocculation are shown to be simpler and more cost-effective (Choi et al., 2001; Chu, 2001; Kacha et al., 2003; Kim et al., 2004; Metes et al., 2000; Zemaitaitiene et al., 2003). The use of some conventional materials for coagulation/flocculation is frequently discussed due to changes in environmental regulations (Divakaran and Pillai, 2001; Özacar and Sengil, 2003). For example, the use of inorganic salts (frequently used as coagulants) such as aluminium chloride or sulphate is now controversial due to the possible impact of aluminium on Alzheimer disease. Polyacrylamide is the basis of many flocculants and its discharge in the environment is now considered hazardous due to the possible release of monomers that could enter in the food chain, with potential impact on health (carcinogenic effect). For these reasons, the research recently focused on the use of bio-coagulants and bio-flocculants (Chen et al., 2003; Strand et al., 2003; Tripathy et al., 2001). Among these natural products, chitosan has received a great deal of attention for the past 20 years for many applications in wastewater treatment, including sorption of metal ions (Guibal, 2004), dyes (Gibbs et al., 2003; McCarrick et al., 2003), but also coagulation/flocculation (Ashmore and Hearn, 2000; Bratskaya et al., 2002; Divakaran and Pillai, 2002; Huang et al., 2000; Roussy et al., 2004; Strand et al., 2002). Chitosan is a polymer constituted of glucosamine and acetylglucosamine units. The presence of amine groups confers to this polymer interesting cationic properties in acidic solutions. The protonation of amine groups is also responsible for polymer dissolving. Tannins (polyphenolic products of plant origin) have also recently received attention for their potential application in coagulation and flocculation due to their anionic behaviour in solution (Özacar and Sengil, 2000; 2003). These polymers are divided into two groups, namely, the condensed tannins which are derivatives of flavanols, and the hydrolysable tannins, which are esters of a sugar, usually glucose (Özacar and Sengil, 2003). They carry carboxyl and hydroxyl groups.

The objective of the present study was to investigate the use of both chitosan and tannins (in combination) for the coagula-

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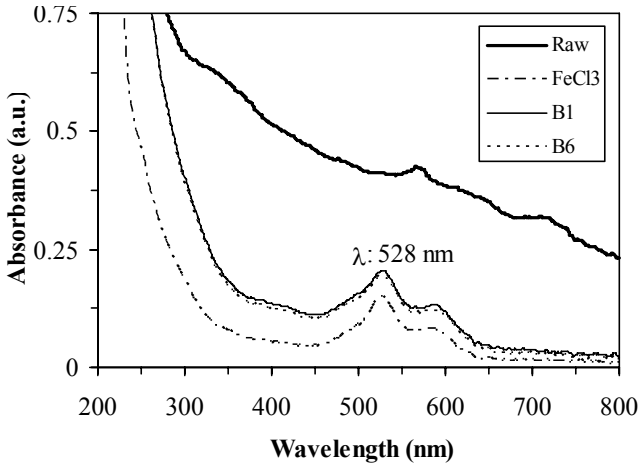

Figure 1
UV-spectra of raw industrial ink-containing solution (after 100-times dilution), and solution treated with $FeCl_3$, and chitosan-tannin (B1 and B6 chitosan samples, used in optimum experimental conditions) after filtration (treated solutions have been analyzed without dilution)

tion and the flocculation of industrial solutions containing dark violet ink. The effluent emanated from a cardboard box-making company. Chitosan was used in a first step for the coagulation and tannin was used in a second step for promoting the final flocculation of the solution. Experiments were performed at pH 5 and natural pH (i.e. pH 8). Several crossed experiments varying chitosan and tannin concentrations were performed in order to optimise the process at both acidic and alkaline pH. The influence of the molecular weight of chitosan was also tested using two different chitosan samples.

Material and methods

Materials

Chitosan was supplied by Mahtani Chitosan Pvt. Ltd. (India). Two samples (B1 and B6) were tested: One with a deacetylation degree of 89.5% (determined by IRTF measurements) and the other with a viscosity of 740 and 18 cps (measured at 25°C, using a Brookfield viscosimeter and a paddle N° 1 at the speed of 60 r·min^{-1}), respectively. The molecular weight was determined by gel permeation chromatography coupled with laser light scattering and refractometry measurements: molecular weight in weight and number, MW_w/MW_n, were 308300/144800 g·mol^{-1} and 80100/26100 g·mol^{-1}, for B1 and B6, respectively. Chitosan was dissolved in acetic acid: The final concentration of the chitosan was 10 g·ℓ$^{-1}$ (final acetic acid concentration was10 g·ℓ$^{-1}$, prepared from acetic acid at 80% (m/m). Tannins were supplied by Diagonal (France). The content of tannin solution was 33% (m/m).

Ink-containing effluent was supplied by a cardboard box-making company. The initial pH was measured at pH 7.5. The solution was characterised by chemical oxygen demand (COD) measurements and dry extract. The spectrum of the effluent was obtained using a Secomam Anthelie Junior spectrophotometer (Secomam, France). The spectrum is shown in Fig. 1.

Experimental procedure

The jar-test method was used for the study of coagulation flocculation. The homogeneous solution was fractionated in several beakers containing 250 mℓ of solution. A sample was also collected to measure the initial absorbance. The initial pH of the solution was measured and then controlled to a fixed value (depending on the experiments) using a dilute HCl solution (0.01 to 0.1 M) or a sodium hydroxide solution (0.01 to 0.1 M).

Fixed volumes of chitosan solution were then added to the beakers maintained under agitation in the Jar-Test (10409 Flocculator, Fisher Bioblock Scientific) equipped with 6 rectangular pales (75x25 mm). The beakers were agitated at high velocity (200 rotations·min^{-1}) for 3 min. At the end of this strong agitation phase a fixed volume of the solution of tannin was added to the solution. Therefore the velocity of agitation was decreased to 40 rotations·min^{-1}. This slow agitation was maintained for 15 min. The agitation was then stopped. Samples were collected after 10 min of settling in the upper part of the beaker for filtration using filter membranes (pore size: 1.2 to 1.4 µm). Filtered samples were analyzed by UV-visible spectrophotometry (Shimadzu UV 160-A) at the wavelength of 528 nm, shown to be the maximum absorbance peak of treated effluents (Fig. 1). The absorbance of filtered samples was used for the comparison of coagulation/flocculation efficiency. A blank experiment was performed in the absence of chitosan to evaluate the stability of the solution at pH 7.5 and pH 5.

Additionally, the aspect of the suspension was observed in the course of the slow agitation phase and after 5 and 10 min of settling. The volume of sludge formed during the settling phase was roughly measured at 5 and 10 min (after being transferred into a graduated cylinder), when possible (piston settling instead of diffuse settling).

To compare the coagulation/flocculation performance of biopolymers to conventional processes, a series of experiments was performed using $FeCl_3$ prepared from an acidic $FeCl_3$ solution (concentration 600 g·ℓ$^{-1}$). The coagulant was added directly to the industrial effluent during the phase of high velocity of agitation and the pH was controlled at pH 7.5 using NaOH. Other experimental procedures were the same as for biopolymer systems.

Additionally a complementary experiment was performed on solutions treated with chitosan B1 and B6 associated with tannin (under selected experimental conditions corresponding to maximum efficiency). In this experiment, 1 ℓ of solution was treated with chitosan and tannin and the suspension, at the end of the slow agitation phase, was carefully transferred to a graduated cylinder and the volume of the sludge was regularly measured (piston settling rather than diffuse settling).

As a complementary analysis, COD measurements were performed using the potassium dichromate method with a Hach DR 2000 spectrophotometer under optimum coagulation/ flocculation experimental conditions.

TABLE 1
Influence of the tannin concentration (TC) added to the solution on the coagulation/flocculation efficiency at pH 7.5 (chitosan concentration 100 mg·ℓ$^{-1}$)

	Chitosan B1			Chitosan B6		
TC (mg·ℓ$^{-1}$)	990	1 320	1 630	990	1 320	1 630
Aspect of flocs under agitation	NS	Large	Small numerous	Few	Large	Small numerous
Solution aspect after 5 min	NS	Turbid	Clear	NS	Dark coloured	Dark coloured
Sludge volume (mℓ) at 5 min	NS	50	80	NS	50	80
Solution aspect after 10 min	Weak decantation	Clear	Clear	Weak decantation	Clear	Clear
Sludge volume (mℓ) at 10 min	NS	40	80	NS	40	70
Absorbance (A_{528}) after filtr.	NS	0.271	0.180	NS	0.156	0.176

T.C.: Tannin concentration
NS: non-significant

TABLE 2
Influence of the chitosan concentration (CC) added to the solution on the coagulation/flocculation efficiency at pH 7.5 (tannin concentration 1 630 mg·ℓ$^{-1}$)

	Chitosan B1			Chitosan B6		
CC (mg·ℓ$^{-1}$)	40	60	80	40	60	80
Aspect of flocs under agitation	Small	Large and dispersed	Large and dispersed	Small	Numerous	Numerous
Solution aspect after 5 min	Slow decantation	Clear	Clear	Weak decantation	Turbid	Clear
Sludge volume (mℓ) at 5 min	60	70	70	NS	80	80
Solution aspect after 10 min	Slow decantation	Clear	Clear	Weak decantation	Clear	Clear
Sludge volume (mℓ) at 10 min	60	40	40	Turbid	70	70
Absorbance (A_{528}) after filtr.	0.121	0.129	0.258	0.344	0.226	0.136

CC: Chitosan concentration
NS: non-significant

Results

Neutral pH

The optimisation of the process combining the successive additions of chitosan and tannin to the solution was performed varying first the concentration of tannin (with a fixed concentration of chitosan: 100 mg·ℓ$^{-1}$) and then varying the concentration of chitosan for a fixed amount of tannin (i.e. 1 630 mg·ℓ$^{-1}$). The results obtained on chitosans B1 and B6 are summarised on Tables 1 and 2. Table 1 shows that chitosan B1 and B6 had completely different behaviours regarding the coagulation/flocculation efficiency. While an increase of tannin concentration improved the efficiency of the process for chitosan B1 (decrease of the residual optical density measured at 528 nm), the optimum efficiency was obtained at an intermediary concentration of tannins for chitosan B6 (i.e. 1 320 mg·ℓ$^{-1}$). Regardless of the characteristics of chitosan, the volume of sludge increased with increasing tannin dosage. Under selected experimental conditions (chitosan concentration: 100 mg·ℓ$^{-1}$) chitosan B6 was more efficient than sample B1. In these conditions, low molecular weight of chitosan was preferred. The low molecular weight may bring about a better dispersion of the polymer and a greater availability of amine groups. In high molecular weight chitosan at neutral pH amine groups may be involved in hydrogen bonds that cause polymer coiling and reduce the availability of amino groups.

The optical density of the solution after filtration was around 0.16 to 0.18 a.u.; this is far below the optical density of the initial solution. Due to the loading of the solution it was necessary to strongly dilute the effluent to reach a measurable optical density. After diluting the effluent 100 times, the optical density was 0.42 a.u.; this means that the coagulation/flocculation process allowed decreasing the absorbance by a factor 250. Colour removal exceeded 99.5%.

Setting tannin concentration to 1 630 mg·ℓ$^{-1}$, the efficiency of the process was tested using variable amounts of chitosan. Significant differences were also observed between chitosans B1 and B6. Increasing the amount of chitosan resulted in a decrease of treatment efficiency for B1 sample (increase of the residual turbidity), while the efficiency was improved at increasing concentration for sample B6. Chitosan B1 was globally better than chitosan B6: residual optical densities were lower at low polymer dosage and the volumes of sludge was significantly decreased. The residual optical density was again far below that of the initial solution: under optimum experimental conditions, the optical density after filtration was below 0.13 a.u. This means a yield greater than 99.7% for colour removal.

Tables 1 and 2 show that the molecular weight of chitosan had globally a limited impact on the potential of the process. Under optimum experimental conditions for each chitosan the residual optical densities were comparable for low and high molecular weight biopolymer. The only significant change was in the doses of chitosan and tannin. The chitosan with the highest molecular weight required slightly lower amounts of coagulant and flocculant, certainly due to enhanced bridging effect.

At pH 7.5 large amounts of chitosan and tannin were required to reach a substantial abatement of the optical density of treated solution. Chitosan can behave as a coagulant (charge neutralisation) and as a flocculant (bridging), depending on the nature of the colloids, the pH of the suspension and the experimental conditions (concentrations). The respective contributions of these mechanisms also depend on the experimental conditions and the characteristics of chitosan (its molecular weight, its degree of deacetylation). Decreasing the pH frequently results in a diminution of the concentration of chitosan required for optimum coagulation/flocculation. For example in the case of mineral suspensions (bentonite) the amount of polymer to be used was decreased by a factor 10 to 50 when decreasing the pH to 5, com-

TABLE 3
Influence of the tannin concentration (TC) added to the solution on the coagulation/flocculation efficiency at pH 5 (CC 60 mg·ℓ$^{-1}$)

	Chitosan B1					
TC (mg·ℓ$^{-1}$)	330	660	990	1 320	1 560	1 980
Aspect of flocs under agitation	Small numerous	Small numerous	Small	Small	Very small	NS
Solution aspect after 5 min	Coloured	Coloured	Very coloured	Coloured & turbid	NS	NS
Sludge volume (mℓ) at 5 min	50	65	100	90	NS	NS
Solution aspect after 10 min	Coloured	Coloured	Very coloured	Coloured & turbid	No decantation	No decantation
Sludge volume (mℓ) at 10 min	50	65	100	90	NS	NS
Absorbance (A_{528}) after filtr.	0.146	0.149	0.184	0.261	NS	NS

TC: Tannin concentration
NS: non-significant

TABLE 4
Influence of the tannin concentration (TC) added to the solution on the coagulation/flocculation efficiency at pH 5 (CC 20 mg·ℓ$^{-1}$)

	Chitosan B1					
TC (mg·ℓ$^{-1}$)	46	59	66	192	726	990
Aspect of flocs under agitation	Very small	Large & numerous	Large & numerous	Large & numerous	Large & numerous	NS
Solution aspect after 5 min	NS	Coloured Slow decantation	Coloured Slow decantation	Coloured Fast decantation	Coloured Slow decantation	Coloured & turbid
Sludge volume (mℓ) at 5 min	Weak decantation	50	50	50	100	Slow decantation
Solution aspect after 10 min	NS	Dark coloured	Coloured	Coloured	Coloured	Coloured & turbid
Sludge volume (mℓ) at 10 min	Weak decantation	40	40	50	60	75
Absorbance (A_{528}) after filtr.	0.871	0.205	0.132	0.198	0.212	0.281

TC: Tannin concentration
NS: non-significant

TABLE 5
Influence of the of the chitosan concentration (CC) added to the solution on the coagulation/flocculation efficiency at pH 5 (tannin concentration 66 mg·ℓ$^{-1}$)

	Chitosan B1				
CC (mg·ℓ$^{-1}$)	4	8	12	16	20
Aspect of flocs under agitation	Very small numerous	Small	Small	Large	Large
Solution aspect after 5 min	Diffuse decantation	Weak decantation	Fast decantation	Fast decantation	Fast decantation
Sludge volume (mℓ) at 5 min	NS	50 mℓ	50 mℓ	50 mℓ	100 mℓ
Solution aspect after 10 min	Very weak decantation	Very coloured	Coloured	Coloured	Coloured
Sludge volume (mℓ) at 10 min	NS	50	45	40	40
Absorbance (A_{528}) after filtr.	NS	0.314	0.141	0.143	0.138

CC: Chitosan concentration
NS: non-significant

pared to neutral pH. Indeed, due to the intrinsic pK_a (which is close to 6.4) at pH 5, most of amine groups of chitosan are protonated and can be engaged in charge neutralisation with anionic groups of dyes and pigments. Similar experiments have been performed at pH 5 in order to evaluate the improvement of coagulation/flocculation performance with experimental conditions more favourable to charge neutralisation mechanism.

Acidic pH

A first series of experiments was performed with chitosan B1 at a concentration of chitosan of 60 mg·ℓ$^{-1}$ with variable amounts of tannins (Table 3). The best results were obtained at the lowest amount of tannins: tannin concentration should not exceed 700 mg·ℓ$^{-1}$. The volume of sludge logically increased with increasing amounts of tannin. This first series shows that the amounts of chitosan and tannin were in excess though significantly lower than the doses required at neutral pH. This confirms that when the experimental conditions facilitate the charge neutralisation mechanism (i.e. acidic pH) the efficiency of the process is improved and the concentration of coagulant and flocculant can be reduced. Similar conclusions were found by Papic et al. (2000) using a synthetic cationic flocculant for the removal of reactive dyes from wastewater. The second series of experiments was performed with lower amounts of chitosan B1 and tannins (Table 4). Chitosan concentration was set at 20 mg·ℓ$^{-1}$, and the amount of tannin was varied between 46 and 990 mg·ℓ$^{-1}$. A minimum optical density was obtained at a concentration of tannin close to 70 mg·ℓ$^{-1}$. The residual optical density after filtration was close to 0.13, also corresponding to a minimum volume of sludge (about 40 mℓ after 10 min of decantation). It is interesting to observe that the efficiency of the process was very sensitive to the amount of tannin at low concentration while an

TABLE 6
Influence of the tannin concentration (TC) added to the solution on the coagulation/flocculation efficiency at pH 5 (chitosan concentration 20 mg·ℓ$^{-1}$)

	Chitosan B6				
TC (mg·ℓ$^{-1}$)	66	79	106	132	158
Aspect of flocs under agitation	Very small & numerous	Small	Small	Large	Large
Solution aspect after 5 min	Weak decantation	Fast decantation	Fast decantation	Fast decantation	Weak decantation
Sludge volume (mℓ) at 5 min	40	20	20	20	30
Solution aspect after 10 min	Coloured	Weakly coloured	Coloured	Coloured	Coloured
Sludge volume (mℓ) at 10 min	40	20	20	20	30
Absorbance (A_{528}) after filtr.	0.217	0.152	0.188	0.227	0.242
T.C.: Chitosan concentration NS: non-significant					

TABLE 7
Influence of the concentration of $FeCl_3$ added to the solution on the coagulation/flocculation efficiency at pH 7.1 to 7.6

	$FeCl_3$ (mg·ℓ$^{-1}$)					
	600	**700**	**800**	**1 000**	**1 100**	**1 200**
Aspect of flocs under agitation	Very small	Large & numerous	Large & numerous	Large & numerous	Large & numerous	NS
Solution aspect after 10 min	Very turbid	Very turbid	Weak decantation	Fast decantation	Fast decantation	Slow decantation
Sludge volume (mℓ) at 10 min	Weak decantation	Weak decantation	50	50	50	Weak decantation
Absorbance (A_{528}) after filtr.	0.909	0.551	0.237	0.141	0.107	0.400
NS: non-significant						

excess of tannin had a lower impact on the coagulation/flocculation performance.

The tannin concentration was set at 66 mg·ℓ$^{-1}$ and the concentration of chitosan (B1) was varied between 4 and 20 mg·ℓ$^{-1}$ (Table 5). The efficiency of the process was almost constant in the concentration range 12 to 20 mg·ℓ$^{-1}$. The minimum volume of sludge produced after 10 min of settling was obtained at chitosan concentrations of 16 to 20 mg·ℓ$^{-1}$, while the residual optical density (after filtration) was close to 0.14. These results confirm that the optimum dosage for chitosan B1 and tannin was close to 20 mg·ℓ$^{-1}$of chitosan and 70 mg·ℓ$^{-1}$ of tannin.

The same concentration (i.e. 20 mg·ℓ$^{-1}$) of chitosan B6 was used for a series of experiments performed with increasing concentrations of tannins (Table 6). The best results were obtained with a concentration of tannins close to 80 mg·ℓ$^{-1}$, the residual absorbance was close to 0.15 and the volume of sludge tended to 20 mℓ. Comparing the results obtained with B1 and B6 chitosan, it appears that similar dosages of chitosan and tannin were appropriate for an efficient treatment of this effluent at acidic pH. The differences between B1 and B6 were less marked than at neutral pH. The bridging mechanism (partly controlled by the molecular weight of the polymer) may not be the predominant mechanism for the abatement of colour and turbidity of the ink-containing solution. In acidic solutions, the charge neutralisation is the main active mechanism.

Özacar and Sengil (2000, 2003) compared the effectiveness of tannin and anionic synthetic polyelectrolyte (AN913, a copolymer of acrylamide and acrylic acid synthesised by SNF Floerger, France) for the coagulation of colloidal particles (clay material). They found that the addition of tannin significantly improves the filterability of the flocculated sludge (Özacar and Sengil, 2000). Additionally using tannin allowed decreasing significantly the amount of alum sulphate to be added, compared to conventional anionic coagulant (Özacar and Sengil, 2003). The correlation between turbidity abatement and the variation of the zeta potential that tends to 0 when varying the dosage of alum clearly indicates that the effectiveness of tannin is due to charge neutralisation. However, they pointed out the contribution of several chemical reactions such as:

- Al complexation reactions with tannins
- Al hydrolysis reactions
- Direct precipitation of Al-tannate particles
- Adsorption of tannin or complexed Al-tannate species to amorphous aluminium hydroxide

In the case of tannin-chitosan combination it is expected that:

- Chitosan precipitation in near neutral solution
- Tannin adsorption on chitosan macromolecules
- Charge neutralisation could be involved in the improvement of the effectiveness of the colour abatement of ink-containing effluents

Choi et al. (2001) synthesised polyamine flocculants for the treatment of dye wastewater in combination with alum and observed that the addition of polyamine allowed the substantial reduction of the dosage of aluminium sulphate. They observed that the zeta potential of the polyamine solution decreases (tending to 0 mV) as the molecular weight increases. They attributed this result to the charge density of the polyelectrolyte that is increasing together with its molecular weight. High charge density favours the adsorption of suspended particles onto the polyamine flocculant. This can be transposed to chitosan behaviour that can be obviously assimilated to polyamine. They observe that polyamines with higher charge density have lower zeta potential and increasing adsorption capacity with the alum/polyamine treatment. For this reason, high molecular weight samples are preferred.

Zemaitaitiene et al. (2003) investigated the role of anionic substances present in industrial effluents on the removal of textile dyes from solutions using cationic flocculant. They suggest the formation of triple complexes. Electrostatic interactions are

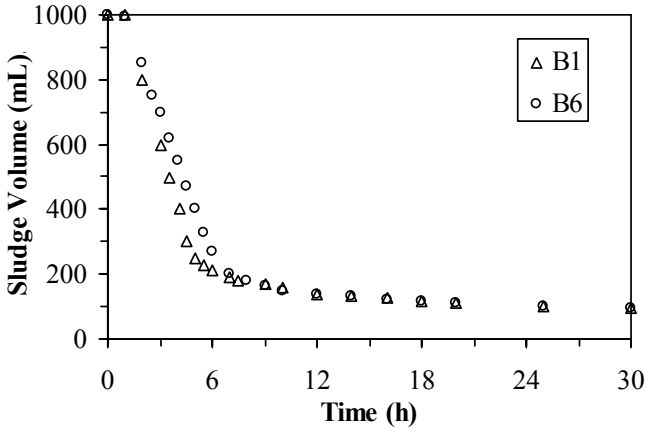

Figure 2
Settling curves for the suspension produced in the coagulation/flocculation of industrial ink-containing solution with chitosan B1 and B6 under optimum selected conditions

responsible for transferring dye particles from the water environment to the polymer chain, while the incorporation of dye ions or molecules intro triple complexes occurs probably due to Coulombic and non-polar forces. Chemicals with a-polar highly hydrophobic sites (presumably aromatic rings, hydrocarbon chains) which preserve their negative charge during interaction with dye ions or molecules, facilitate their transfer from water environment to the polymer. The role of anionic polysaccharide derivatives often used as textile printing thickeners probably consists in inserting new easily adaptable non-polar moieties for dye binding and reducing the stability of the total system. Interpolymeric complex formation, competitive reactions between polysaccharides and dye anions and thus the flocculation efficiency, can be easily controlled by varying the pH and the ionic strength of the solutions. In the present case, tannins also act as anionic substances that may form triple-complexes with chitosan macromolecules and dye molecules.

Treatment with $FeCl_3$

Kim et al. (2004) have investigated the effectiveness of $FeCl_3$ for the treatment of dye-containing effluents. They showed that $FeCl_3$ efficiency is strictly controlled by the structure and chemical properties of the dyes and observed that the coagulation of disperse dyes using $FeCl_3$ is much more efficient than that of reactive dye, in relation with lower solubility of disperse dye, final floc formation and settling quality.

Table 7 summarises the results obtained for the treatment of the industrial ink-containing solution with $FeCl_3$. This coagulating agent was very efficient for the abatement of colour and turbidity. The optimum dosage was found at a concentration of $FeCl_3$ of 1 100 mg·ℓ$^{-1}$. Settling was relatively fast and the flocs were large compared to chitosan/tannin flocs. The minimum optical density (after filtration) was close to 0.11, slightly below the lowest values obtained with the biopolymer system. The volume of sludge was obviously higher than that obtained with biopolymers.

To be able to compare the efficiency of the different processes, the COD was measured for the initial industrial solution, the effluent treated with chitosans B1 and B6 at acidic pH with optimum concentrations of chitosan (20 mg·ℓ$^{-1}$) and tannin (70 mg·ℓ$^{-1}$ for chitosan B1; and 80 to 100 mg·ℓ$^{-1}$ for chitosan B6). The initial COD of the solution was 5 150 mg·ℓ$^{-1}$, after treatment with ferric chloride the residual COD felt down to 680 mg·ℓ$^{-1}$ and to 720 and 710 mg·ℓ$^{-1}$ after treatment with chitosan B1 and chitosan B6, respectively. The treatments gave comparable COD abatements, corresponding to 84% efficiency. The volume of sludge after a settling time of 1 day was doubled for ferric chloride treatment compared to chitosan/tannin treatment. The dissolved matter was also measured on the initial solution at a value of 4.75 g·ℓ$^{-1}$, while after being treated with chitosan B1 (using optimum experimental conditions) the dissolved matter decreased down to 1.34 g·ℓ$^{-1}$. This means that the dissolved matter removed by the coagulation process did not exceed 3.4 g·ℓ$^{-1}$. The sludge produced may thus contain less than 4 g·ℓ$^{-1}$.

These results confirm that chitosan, associated with tannin has comparable efficiency to a conventional coagulation process using mineral coagulant ($FeCl_3$) with a reduced volume of loaded sludge and a lower environmental impact.

Sludge settling

Figure 2 shows the settling curves for chitosans B1 and B6 performed using the industrial solution with optimum experimental conditions for each of these chitosan samples. Though a slightly faster settling of the sludge was observed in the first hours of decantation for chitosan B1 (the highest molecular weight), the settling profiles were very similar. The settling time should be 16 to 24 h for reaching the equilibrium of decantation (without filtration): this is a very long contact time that suggests that a static decantation (batch decantation) should be more appropriate than a dynamic settling tank. Indeed with a so slow settling (corresponding to a velocity of 70 mm·h^{-1}, in the linear section of the settling curve), the surface area of the settling time would be very large. A static settling strategy is preferred to a dynamic settling.

COD abatement

Under optimum experimental conditions, i.e. pH controlled to pH 5, chitosan concentration close to 20 mg·ℓ$^{-1}$ and tannin concentration in the range 70 to 100 mg·ℓ$^{-1}$, the COD of the industrial ink solutions was decreased by 80 to 85%. The initial COD of the solution was around 8 000 to 9 000 mg O_2·ℓ$^{-1}$ and it decreased to 1 800 to 2 000 mg O_2·ℓ$^{-1}$. This means that after coagulation/flocculation treatment the effluent can be discharged into the city wastewater collector. Indeed, the local regulations authorise the discharge to the city wastewater collector for effluents with a COD of lower than 2 000 mg O_2·ℓ$^{-1}$.

Conclusion

The association of chitosan and tannin used respectively as a coagulant and a flocculant allowed a significant reduction in the absorbance of industrial effluents containing soluble inks. The optimum experimental conditions were found in

acidic solutions (i.e. pH 5) where the charge neutralisation mechanism induced by the cationic properties of chitosan contributes to the high efficiency of the process. Working at pH 5 substantially reduced the amounts of reagents to be added. Hence, at this pH a concentration of chitosan of close to 20 mg·ℓ$^{-1}$ was sufficient after the addition of 70 to 100 mg·ℓ$^{-1}$ of tannin for reducing the absorbance of the solution to 0.12 to 0.15. This was equivalent to a 300-times reduction of absorbance of the industrial solution. Colour removal exceeded 99% considering the absorbance of the solution at 528 nm. This treatment allowed 84% reduction of COD, which was comparable to the abatement obtained by coagulation with $FeCl_3$ (at the concentration of 1 100 mg·ℓ$^{-1}$). Though the process slightly improved with a high molecular weight chitosan, this parameter did not show a great effect on coagulation/flocculation performance, as a confirmation of the predominance of charge neutralisation mechanism (vs. bridging mechanism).

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