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Influence of Chitosan Characteristics on Coagulation and Flocculation of Organic Suspensions

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ABSTRACT: Several samples of chitosan with different degrees of deacetylation and of different molecular weights were tested for the coagulation–flocculation of organic suspensions. Organic suspensions were prepared by mixing mushroom powder with tap water. Experiments were carried out at pH 5, pH 7, and pH 9. Because decreasing the pH reduced the amount of chitosan required to reach the required turbidity, at pH 9, a high concentration of chitosan was required to achieve the required treatment levels, whereas the difference was less significant between pH 7 and pH 5 (the required concentration of chitosan was halved). Though viscosity, correlated to the molecular weight of chitosan, affected treatment performance, its influence on the efficiency of coagulation–flocculation could

be substantially reduced by slightly increasing the concentration of the polymer. This is of importance in the processing of industrial effluents: the aging of a chitosan solution, which may cause partial depolymerization, and loss of viscosity, will have a limited impact on process efficiency. The degree of deacetylation also has a limited effect on treatment performance, especially when the degree of deacetylation exceeds 90%.

Key words: chitosan; organic colloids; coagulation–flocculation; impact of polymer characteristics; concentration effect; degree of deacetylation; molecular weight

INTRODUCTION

Chitosan is an amino-polysaccharide that has been widely studied for the sorption of inorganic^{1,2} and organic contaminants.^{3–9} Metal cations are adsorbed on the amine groups of the biopolymer by chelation on the free electron doublet of the nitrogen atom.¹⁰ The protonation of amine groups in acidic solutions gives the polymer interesting ion exchange properties.¹¹ Indeed, with an intrinsic pK_a close to 6.5,¹² the polymer is fully protonated at a pH of close to 5, and this protonation gives it the possibility of attracting metal anions,¹³ dyes,⁴ and organic compounds.⁸ The protonation of amine groups also is responsible for the polymer dissolving in acidic solutions, with the notable exception of sulfuric acid solutions. Chitosan dissolved in acetic acid or hydrochloric acid can be used for the uptake of metal cations using polymer-enhanced ultrafiltration^{14,15} These interactions of dissolved chitosan with solutes also may be used for the coagulation and flocculation of dissolved contaminants¹⁶ and suspended colloids.¹⁷

Several studies have focused on the use of chitosan for fish processing,¹⁸ in the food industry,^{19,20} and in river silt water,²¹ latex particles,^{22,23} microorganisms,^{24,25} and suspensions containing mineral colloids.^{17,26–28} The properties of chitosan, including its cationic behavior and molecular weight, may be used both for charge neutralization (coagulating effect for anionic compounds) and for particle entrapment (flocculating effect). Actually, the coagulating and the flocculating mechanisms may be used either simultaneously or alternately for the settling of suspended particles.¹⁷ The contribution of each mechanism depends on the pH of the suspension. Only a few studies have focused on the impact of chitosan properties on the performance of the coagulation and flocculation of suspended particles.^{24,29} A previous study showed that the degree of deacetylation of chitosan has a limited impact on the coagulation–flocculation of suspended mineral colloids.¹⁷ The aging of a chitosan solution may cause a decrease in the molecular weight of the polymer. For this reason, it is important to verify the polymer's impact in order to determine how the aging of the chitosan solution will affect the efficiency of the process. Increasing the molecular weight of a chitosan increases the efficiency of the treatment. However, this variation in performance can easily be compensated for by slightly increasing the concentration of the biopolymer.¹⁷ For suspended mineral col-

TABLE I
Characteristics of Chitosan Samples

Sample	Chitosan commercial reference	Degree of deacetylation (%)	Viscosity at 25°C (cps)	MW _w (g/mol)	MW _n (g/mol)	Polydispersity
A	221	78	1500	230,700	110,000	2.1
B1	222	89.5	740	308,300	144,800	2.1
B2	232 b2	89.5	262	235,200	101,300	2.3
B3	232 b3	89.5	186	222,000	85,400	2.6
B4	242 b4	89.5	72	155,000	68,700	2.3
B5	242 b5	89.5	28	94,300	41,300	2.3
B6	242 b6	89.5	18	80,100	26,100	3.1
C1	233	95	110	182,300	84,750	2.2
C2	243	95	60	97,700	8400	11.6
C3	253	95	12	45,100	7300	6.2

loids, it was found that very little chitosan was needed, especially when working in acidic media (in this case, a concentration as low as 0.2 mg/L was sufficient to reach the required level of turbidity).

The objective of the present work was to evaluate the impact of the characteristics of chitosan on the coagulation and flocculation of organic suspensions. To achieve a high level of reproducibility in the characteristics of the organic suspensions, they were prepared by adding dried (and finely ground) mushrooms to tap water. This biomass (*Agaricus bisporus*; common name: button mushroom) was obtained from an industrial producer of food flavors, as a byproduct of mushroom growth and preparation (stems of the mushrooms). The mycelium was dried, ground, and sieved. Coagulation and flocculation of the organic suspension were performed using chitosan with different characteristics (degree of deacetylation and viscosity or molecular weight). Most experiments were performed at pH 5 and pH 7 because preliminary experiments had shown that a high concentration of polymer was required with a pH of 9. Special attention was paid to the influence of polymer concentration on the efficiency of the process.

EXPERIMENTAL

Materials

Chitosan samples were kindly donated by Mahtani Chitosan Pvt. (Veraval, India) and degree of deacetylation (DD) was characterized by FTIR analysis (film-state analysis) and molecular weight (MW) by size-exclusion chromatography using coupled detection units (laser-light scattering measurement and refractometry). The properties of the samples are summarized in Table I. All the samples were prepared from the same stock, referenced as sample A. From this stock, the steps of deacetylation were performed in order to prepare samples B1 and C1. In addition, samples B1 and C1 were each submitted to a supple-

mentary depolymerization procedure to prepare samples with a lower molecular weight.

The polymers were ground and sieved; the smallest size fraction (0–125 μm) was collected and used for the preparation of the coagulant solutions. The powder (2 g of chitosan) was dissolved in 100 mL of an acetic acid solution that was prepared by diluting 2 g of acetic acid (80% w/w) in 100 mL of water. The final pH of the solution was close to 4.

The mushrooms were obtained from an industrial producer of food flavors. The material was ground and sieved. A fraction of less than 250 μm was used to prepare a stock of material for the complete study. Solutions were prepared by mixing known amounts of organic powder with 8 L of tap water in order to prepare suspensions of 3 g/L. Agitation was maintained at 1000 rotations/min for 5 min, and then the solution was left to settle for 20 min to remove large unsuspended particles. The upper part was collected in a tank that was maintained under agitation at 500 rotations/min to prepare homogeneous suspensions.

The electrophoretic mobility of the mushroom suspensions was measured at Penn State University using a Penn Kern Lazer Zee zeta meter, Model 501, to calculate the zeta potential of the mushroom material at different pHs. In the pH range of 3–9 the zeta potential was systematically negative, with a decreasing trend between pH 2.5 (null value) and pH 3.5 (–10 mV), followed above pH 4 by a slightly decreasing trend (to –20 mV).

Jar-test procedure

The jar-test method was used to study coagulation/flocculation. The homogeneous solution was fractionated in several beakers containing 600 mL of suspension. A sample also was collected to measure the initial turbidity. The initial pH of the suspension was measured and then controlled to a fixed value (depending on the experiments) using a dilute HCl

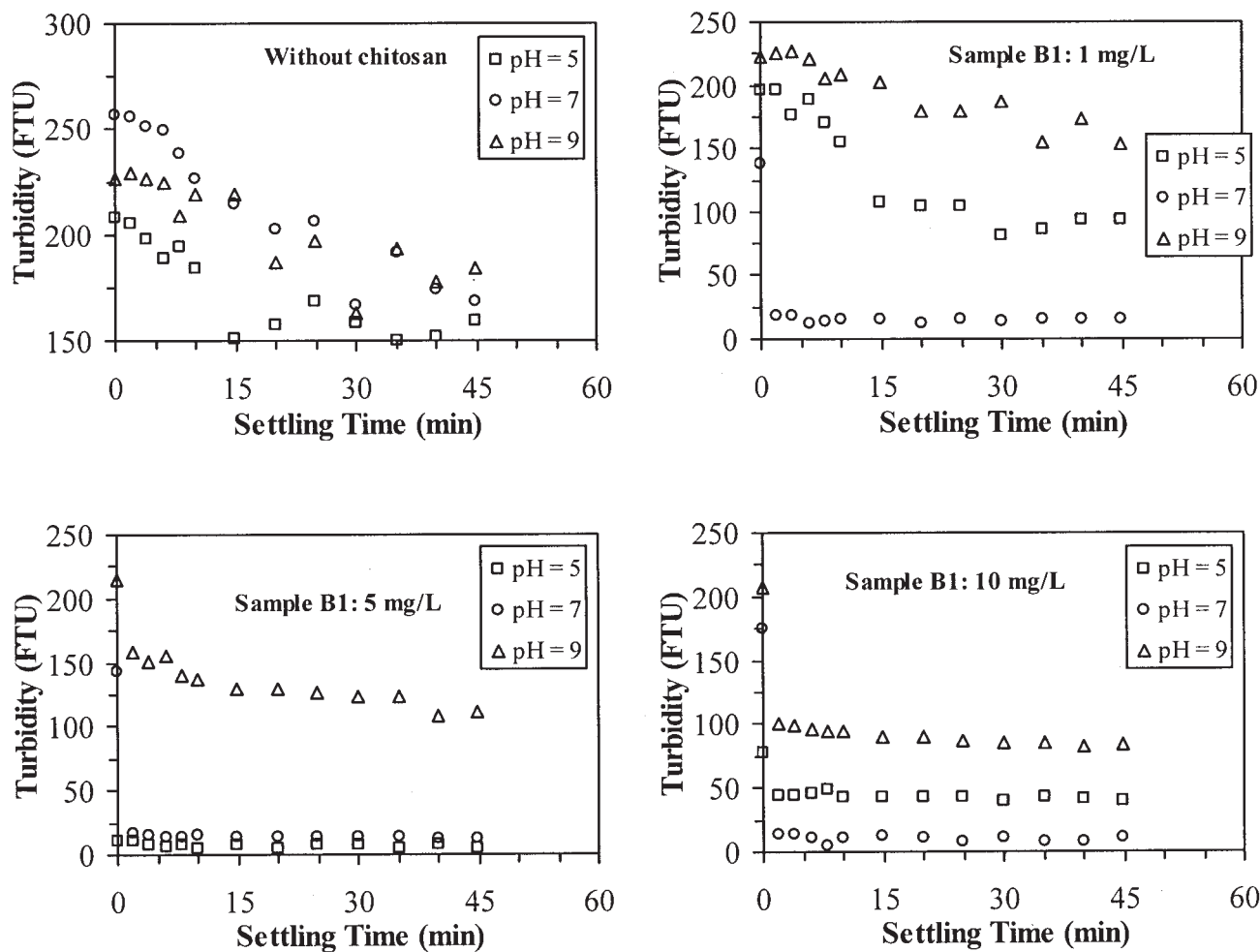


Figure 1 Influence of pH on the coagulation and flocculation of organic suspensions—influence of the addition of chitosan and of polymer concentration (chitosan B1).

(0.01M–0.1M) or sodium hydroxide (0.01M–0.1M) solution.

Different volumes of the chitosan solution were then added to the beakers maintained under agitation in the jar-test (10409 Flocculator, Fisher Bioblock Scientific), equipped with six rectangular pales (75 × 25 mm). After the addition of the chitosan, the beakers were agitated at high velocity (200 rotations/min) for 3 min. Then, in a second step, the velocity of the agitation was decreased to 40 rotations/min, which was maintained for 20 min. The agitation was stopped, and samples were regularly collected in the upper part of the beaker in order to measure the turbidity of the solution. It should be noted that the coagulated/flocculated suspended matter frequently tended to float, and the sampling operations resulted in resuspension of floating material, which in turn introduced artifacts in the measurement of the turbidity of the suspension. A blank experiment was systematically performed in the absence of chitosan to evaluate the “natural” decantation of the suspension un-

der the selected experimental conditions (pH, concentration of suspended matter).

The turbidity was measured in triplicate using a HACH DR/2000 turbidimeter; and the turbidity unit was FTU (formazine turbidity unit). The mean value was used for quantification.

RESULTS AND DISCUSSION

Influence of pH

Figure 1 compares the coagulation–flocculation of organic suspensions in the presence of increasing concentrations of chitosan (sample B1: DD 89.5%, viscosity 740 cps) to their natural decantation at different pHs (i.e., in acidic, neutral, and alkaline media). Without chitosan the natural decantation of the organic suspension was not efficient, and turbidity only decreased by 40%. The residual turbidity did not decrease below 150 FTU, even after 45 min of settling. The suspension was very stable. The addition of chi-

tosan significantly improved decantation efficiency. However, the effect was highly dependent on the pH and on the concentration of chitosan. At low chitosan concentration (i.e., 1 mg/L), coagulation–flocculation was only efficient at pH 7: residual turbidity tended to be 20 FTU, well above the fixed limit (i.e., 10 FTU) but far below the values reached with pH 5 and pH 9. Moreover, turbidity equilibrium was reached within the first minutes of settling, whereas 20–30 min of decantation were necessary to reach the equilibrium at an acidic or an alkaline pH. Increasing the concentration of chitosan to 5 mg/L increased the efficiency of the coagulation–flocculation, especially at pH 5 and pH 7. At pH 9 the turbidity tended to be 100 FTU after 45 min of settling, despite the improved efficiency. Performance was comparable at pH 5 and pH 7 in both equilibrium and kinetics. The final turbidity was close to the fixed limit, regardless of pH. At pH 9, increasing the chitosan concentration to 10 mg/L slightly increased treatment efficiency, but not enough to reach the target turbidity values. Although at pH 7 the efficiency of the process was maintained (residual turbidity around 10 FTU), at pH 5, the excessive number of cationic charges contributed by the protonated amine groups led to restabilization of the suspension and a decrease in coagulation–flocculation efficiency.

These results confirm the double effect of chitosan in the process and, more specifically, the relative contribution of the coagulation (charge neutralization) and flocculation (colloid entrapment) effects at the different pHs. At a neutral pH, both the coagulation and the flocculation mechanisms were involved in the removal of organic colloids, whereas, in acidic suspensions, the contribution of charge neutralization was the principal mechanism. Indeed, whatever the pH of the suspension, zeta-metric measurements showed that, above pH 3, the suspension was anionic (between -10 and -20 mV), whereas chitosan was protonated in acidic solutions. Huang and Chen observed that chitosan maintained a positive range when the pH was below 8.²⁶ The pK_a of chitosan depends on the degree of acetylation, the degree of neutralization of amine groups.¹² However, for the samples of chitosan used in this study, with a degree of acetylation of less than 13%, the pK_a at 50% dissociation was in the range of 6.3–6.7. This means that more than 90% of the chitosan's amine groups were protonated at pH 5 and therefore were available for neutralizing anionic charges in the mushroom suspension. This is consistent with previous results obtained for mineral suspensions.¹⁷ However, this positive effect on coagulation–flocculation efficiency contrasts with the results obtained by Strand et al. concerning the treatment of bacterial suspensions.²⁹ They observed that the pH had a limited effect between pH 4 and pH 7.4.

The very low efficiency of chitosan at alkaline pH also confirmed that, at least partial, protonation of the

biopolymer's amine groups was required to achieve efficient coagulation–flocculation of these organic suspensions. For these reasons, the following experiments only focused on acidic and neutral media.

Influence of degree of deacetylation

It is important to note that the deacetylation procedure resulted in partial and simultaneous depolymerization. Thus, it is difficult to separate the relative contributions of degree of deacetylation and molecular weight on process efficiency.

Acidic pH

Figure 2 compares the kinetic profiles of the decantation of organic suspensions using different concentrations of chitosan for three samples characterized by increasing degree of deacetylation. At low concentration of chitosan (i.e., 1 mg/L), the kinetic profiles of the decantation were only slightly affected by the degree of deacetylation. Surprisingly, the best results were obtained with the least deacetylated sample (Sample A). However, because the molecular weight of this sample was significantly greater than that of the other samples, the decreased number of cationic charges was compensated for by its enhanced flocculating effect. In most cases, equilibrium turbidity was reached within the first 15–20 min of settling, with residual turbidity ranging from 30 to 50 FTU, far above the acceptable limit (i.e., 10 FTU). The number of cationic charges contributed by the polymer was not sufficient to achieve complete coagulation–flocculation of the organic colloids.

Increasing the chitosan concentration to 2.5 or 5 mg/L substantially increased the efficiency of the process: with a chitosan concentration of 2.5 mg/L, residual turbidity tended to be 8–10 FTU, and with a concentration of 5 mg/L, it was as low as 5 FTU. Above a settling time of 10–15 min the differences in the kinetic profiles were smoothed. This shows that the degree of deacetylation of chitosan hardly affected the coagulation–flocculation of organic suspensions made from mushroom waste.

At an acidic pH, the degree of deacetylation had a limited effect that was completely compensated for when the concentration of the polymer was increased to 2.5–5 mg/L. The concentration of chitosan required to reach the limiting turbidity was significantly higher than the dosage required in acidic solutions for the coagulation–flocculation of mineral colloids (bentonite suspensions), for which the optimum concentration has been found to be around 0.2 mg/L¹⁷ with similar concentrations of suspended material.

Ashmore and Hearn compared a series of chitosan samples for flocculation of model latex particles.²² They prepared well-characterized latexes with known

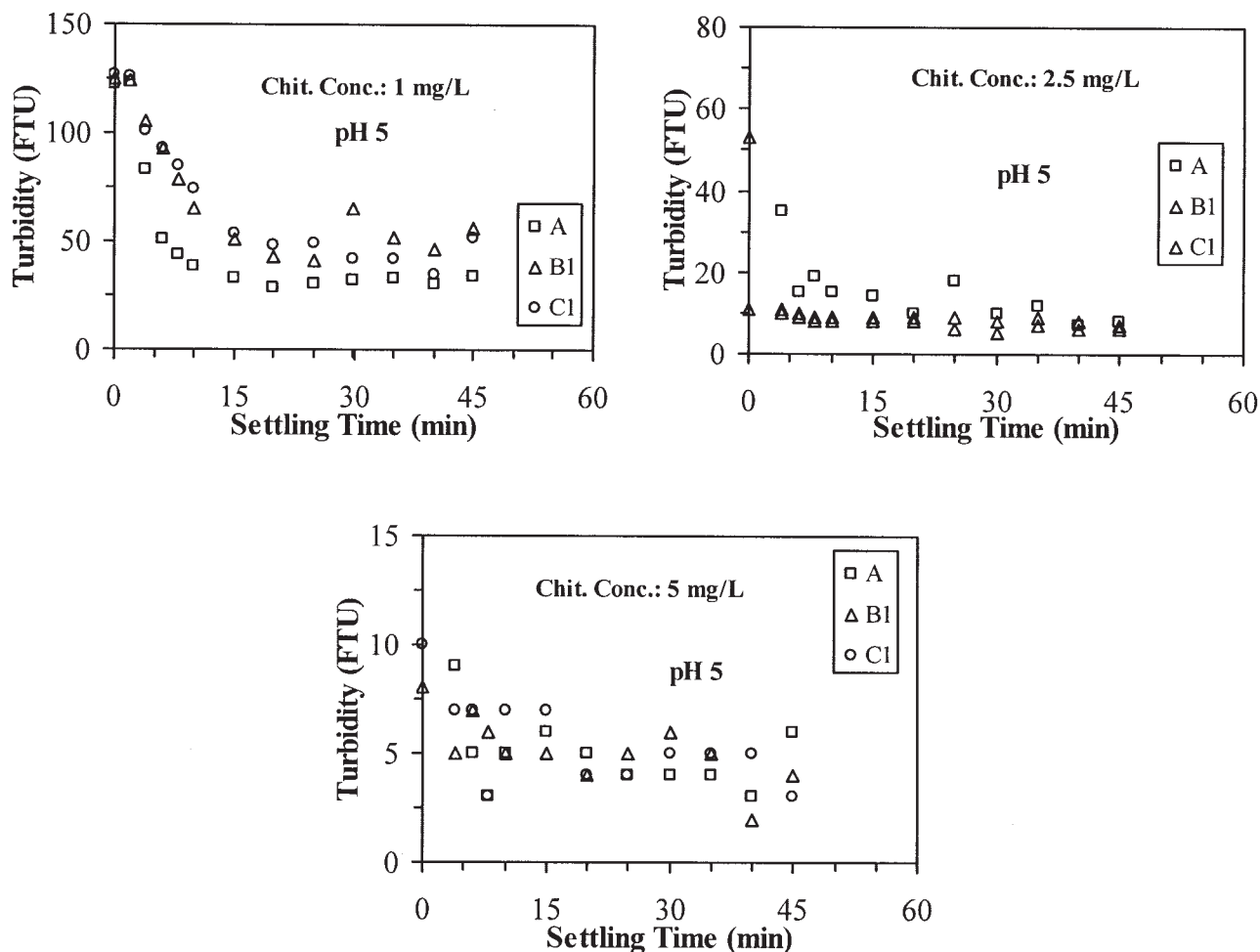


Figure 2 Influence of the degree of chitosan deacetylation on the coagulation and flocculation of organic suspensions at pH 5—influence of polymer concentration.

amounts of sulfate groups on the surface of the latex particles and correlated the ratio of chitosan amine groups to sulfate groups with the flocculation efficiency, taking into account the acid–base properties of the polymer (by varying the pH). They commented that the flocculation mechanism proceeds by charge neutralization with a contribution from a “charge patch mechanism.” The positive charges of the polyelectrolyte chain are usually more closely spaced than the center-to-center distances between negative charges on the particle surface. Thus, when the polymer molecule is adsorbed in a relatively flat configuration on the particle surface to give a “mosaic pattern,” a local excess of positive charges is introduced, whereas the rest of the surface is free of flocculant and carries the original negative charge. At a high degree of deacetylation, corresponding to linear charge densities, the concentration of chitosan for optimum flocculation is independent of molecular weight. As the linear charge density on the molecules decreases, more molecules are involved in the neutralization. In addition, with decreasing deacetylation, the backbone of the molecule becomes stiffer as a

consequence of intramolecular hydrogen bonding between the acetamido ($-\text{NHCOCH}_3$) and hydroxymethyl (HOCH_2-) moieties.

Neutral pH

In a neutral suspension, a greater amount of chitosan was required in order to reach a substantial abatement of the turbidity of the suspension (Fig. 3). At the lowest concentration of chitosan (2.5 mg/L), the efficiency of the process increased with the degree of deacetylation of chitosan, and a wide dispersion in the residual turbidity was observed. With the sample of the highest degree of deacetylation, the turbidity conformed to the limit value fixed for turbidity (i.e., 10 FTU), and the settling time necessary for reaching the equilibrium was very short (about 10–15 min). When the degree of deacetylation was decreased (together with the molecular weight), the residual turbidity increased to 20–25 FTU (for sample B1) and up to 45–50 FTU (for sample C1). This improvement in coagulation–flocculation may be explained by an increase in

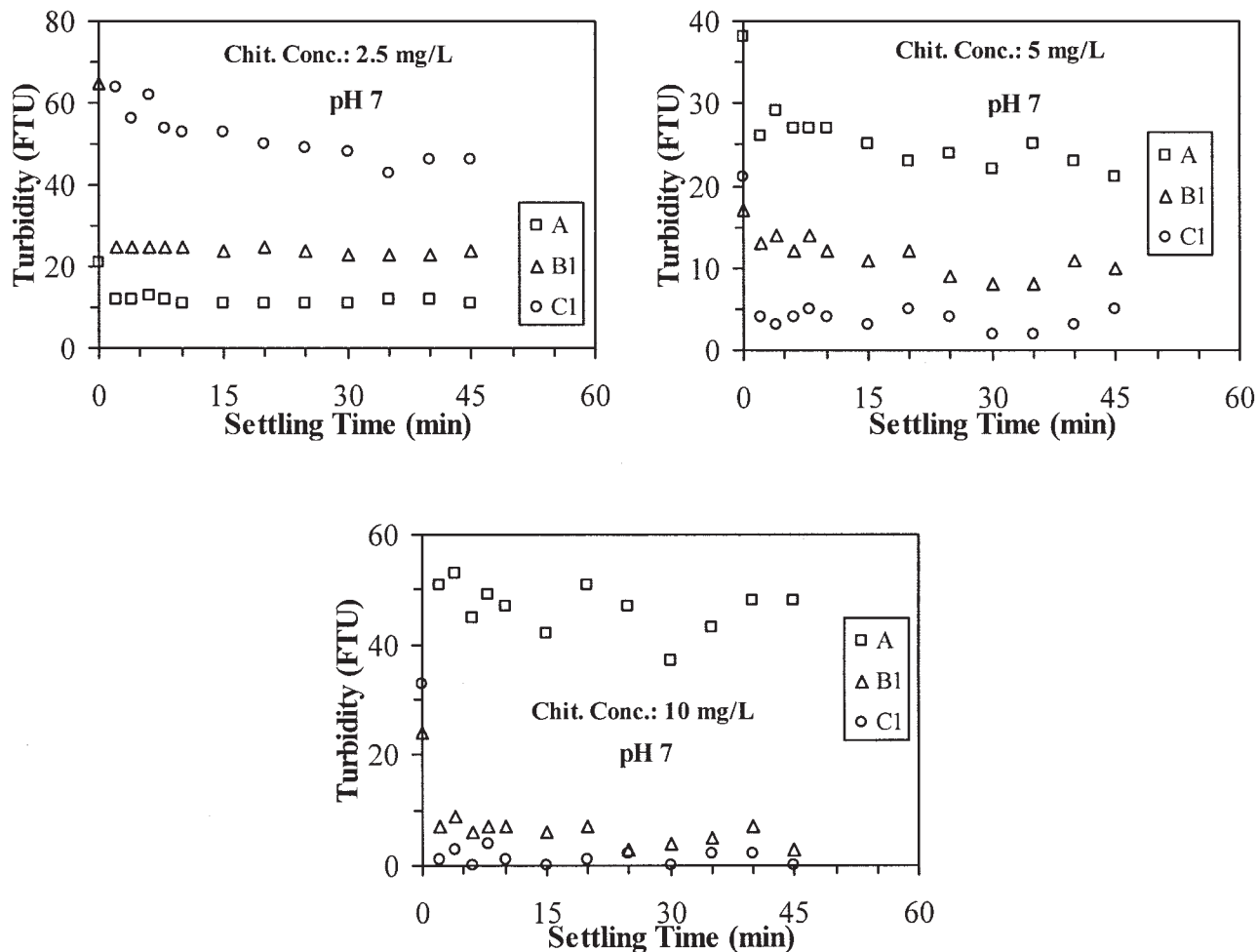


Figure 3 Influence of the degree of chitosan deacetylation on the coagulation and flocculation of organic suspensions at pH 7—influence of polymer concentration.

the number of amine groups, though, at pH 7, only a few of these amine groups were protonated, increasing their number may have contributed to enhancing the coagulation effect.

A reciprocal trend was observed when the concentration of chitosan was increased. With chitosan concentrations of 5 and 10 mg/L, coagulation–flocculation efficiency increased with an increasing degree of deacetylation. Except for sample A (lowest DD and highest MW), the residual turbidity of the suspension conformed to 10 FTU after only 10–20 min of decantation. In most cases, the most deacetylated sample (DD 95%) gave a residual turbidity half that of the intermediate sample (DD 89.5%). With a concentration of chitosan between 5 and 10 mg/L, a deacetylation degree of 90% was sufficient at pH 7 to reach treatment requirements.

Chen et al. investigated the influence of chitosan characteristics on bentonite flocculation using jar-test experiments.³⁰ They correlated the characteristics of chitosan (DD and MW) with the polarization of its microenvironment. They concluded that the amount

of chitosan required for efficient flocculation of a bentonite suspension slightly increased when the degree of deacetylation decreased, but they also observed that the molecular weight had a highly significant effect. They also concluded that the bridging mechanism more significantly influenced the coagulation process than did the degree of deacetylation. An important study by Strand et al. was recently published that was a comparison of the effect of different chitosans (varying the molecular weight and the deacetylation percentage) on the coagulation–flocculation of *Escherichia coli* bacteria.²⁹ Flocculation efficiency increased when (a) the degree of deacetylation was decreased and (b) the molecular weight of the chitosan was increased, independently of polymer concentration. Though the pH had a limited effect on treatment efficiency, Strand et al. showed that a certain amount of charged residue was essential for efficient flocculation by all chitosan types at a pH of 7.4. Above that pH, the chitosan concentration needed to be increased at a high degree of deacetylation in order to maintain flocculation efficiency, and with a low degree of deacetylation, flocculation

culation was completely inhibited. Increasing the ionic strength increased the width of the optimum concentration range. This can be explained by the impact of ionic strength on (a) the conformation of the polymer in solution (the limited segment–segment repulsion gave the polymer a more flexible structure) and (b) the change in the pK_a (as a result of the screening of charged groups). The degree of deacetylation influenced chitosan solubility, charge density, and the conformation of the polymer. Moreover, the presence of acetyl groups made the polymer chain hydrophobic. Although a high degree of deacetylation was expected to increase the charge density, and thus the flocculating efficiency of the polymer, this enhancement in flocculation performance was not observed. At a pH of 6.8, chitosan solubility was expected to decrease (especially at high degree of deacetylation), and, for this reason, higher polymer doses should be required for efficient flocculation. Actually, the same relationship between the degree of deacetylation and the concentration range for chitosan was found at a pH 5 as that found at a pH 6.8. This confirms that the presence of acetyl groups (lower deacetylation degree) improves flocculation efficiency (through an increase in the hydrophobicity of the polymer). Chen et al. concluded that, at low molecular weight, chitosan flocculates *Escherichia coli* bacteria by charge neutralization, whereas at high molecular weight, a bonding mechanism is predominant. At a high degree of deacetylation, the concentration of chitosan required to improve flocculation efficiency increased at pH 7.8. The mechanism included a sweep-out mechanism because of the excess of insoluble chitosan: cells were entrapped in the precipitated mass. However, this mechanism did not occur when the degree of deacetylation was low (for example, 51%) because of the solubility of chitosan at a neutral pH.

More recently, Strand et al. compared the efficiency of different chitosans for the flocculation of eight species of bacteria.²⁴ They observed that it was not possible to establish a correlation between the surface properties of these microorganisms (bacterial surface charge and hydrophobicity) and the characteristics of the chitosan used to flocculate them. They concluded that electrostatic attraction did not really play the predominant role in the flocculation process. Comparing these results with polystyrene–latex particles, they observed that the optimum concentration range for chitosan was enlarged with a decreasing degree of deacetylation.

Obviously, decreasing the degree of deacetylation may enhance the coagulation and flocculation of organic suspensions because of its impact on hydrophobic interactions and chitosan solubility. The positive effect with a decreasing degree of deacetylation is counterbalanced by the negative impact of weaker electrostatic effects. In the present study, all samples

except for sample A (deacetylation degree 78%) were characterized by degrees of deacetylation that were very close together (89.5% and 95% for the B and C series, respectively). For these reasons, it is not surprising that only small variations from the degree of deacetylation were observed between series B and series C.

Influence of molecular weight

Acidic pH

The influence of molecular weight was tested on the two chitosan stocks with the highest degree of deacetylation (i.e., DD 89.5% for series B, and DD 95% for series C).

With samples from series B, the coagulation–flocculation behavior was significantly affected by the concentration of chitosan (Fig. 4). At a low concentration (i.e., 1 mg/L), the molecular weight of the polymer influenced the decantation profiles. With the samples of highest molecular weight (B1 and B3), the settling curves overlapped: they were characterized by a slow decantation of organic colloids and a final turbidity close to 40 FTU, whereas, for the samples of lower molecular weight (B4–B6), equilibrium was reached in the first 15 min of settling with equilibrium turbidity decreasing from 28 to 15 FTU. These unfavorable conditions enable the differences between the various chitosan samples to be clarified. Increasing the concentration to 2.5 mg/L drastically diminished the differences between the samples. In most cases equilibrium turbidity (below 10 FTU) was reached in the first 10 min of settling. Similar trends were obtained at a chitosan concentration of 5 mg/L. However, the data were greatly dispersed, especially for the samples of lower molecular weight. The tendency of coagulated material to float on the surface of the suspension made turbidity difficult to measure. With low-molecular-weight chitosan, a flotation technique would be more appropriate.

This dispersion of the data (because of flotation phenomena) was less significant in samples from series C (not shown). Regardless of chitosan concentration, the three samples showed comparable results. Whatever the sample in series C, a settling time of 15–25 min was required to reach equilibrium. Independent of molecular weight, residual turbidity was between 5 and 10 FTU. These results are consistent with those obtained with less deacetylated chitosan material. Table II shows residual turbidities after a 30-min settling time for two concentrations of chitosan (from the C1–C3 series). These data clearly show that the molecular weight (in this concentration range) did not significantly influence coagulation efficiency.

In the coagulation–flocculation of latex particles, Asmore and Hearn observed that when the degree of

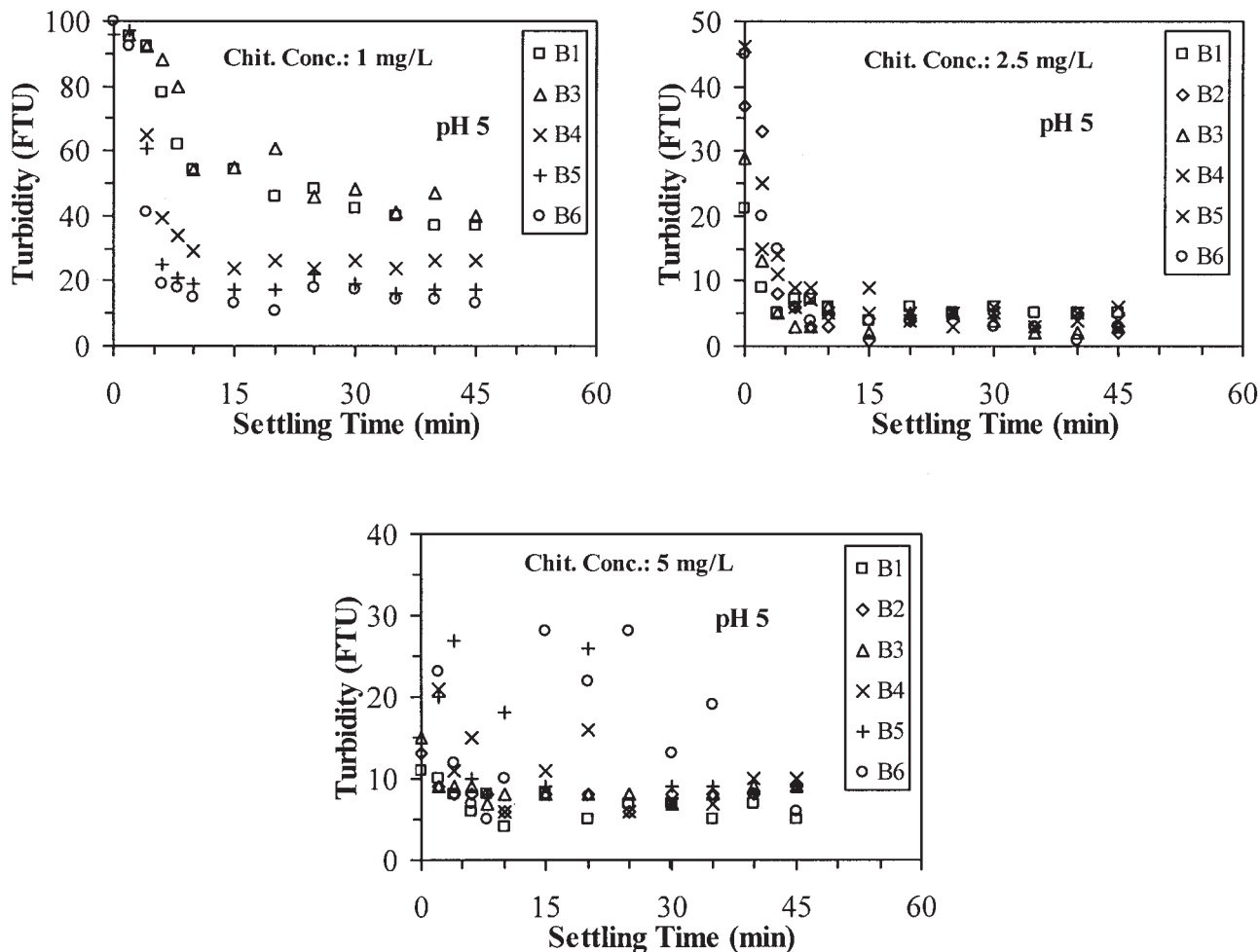


Figure 4 Influence of the molecular weight of chitosan on the coagulation and flocculation of organic suspensions at pH 5—Influence of polymer concentration (DD 89.5%).

deacetylation decreased, the polymer chains became more rigid and that the efficiency of the polymer for flocculation increased with higher molecular weight.²² They also observed that the efficiency of the polymer increased in acid conditions (to maintain cationic be-

havior and solubility). For these reasons, they recommended using a high degree of deacetylation under acid conditions for optimum flocculating efficiency. They reported confirmation of these results in a more recent study of the same parameters with differentsized latex particles.²³ They concluded that molecular weight and degree of deacetylation both had only a small effect on the optimum flocculation concentration and that efficiency improved with increases in both molecular weight and linear charge density. Increasing the ionic strength of the dispersion medium broadened the flocculation concentration range and diminished the rate enhancement produced by the “charge patch” mechanism.

TABLE II

Effect of Chitosan Molecular Weight on Coagulation-Flocculation of Organic Suspensions at pH 5 and pH 7 — Influence of Polymer Concentration on Residual Turbidity

pH	Chitosan (mg/L)	C1	C2	C3
5	2.5	10	8	5
5	5	6	6	6
7	2.5	43	43	31
7	5	1	2	7
7	8	2	2	4
7	10	1	2	7

Measured after a 30-min settling time for samples C1, C2, and C3 (deacetylation degree: 95%).

Neutral pH

At a neutral pH, the first series of experiments (performed with a chitosan with a DD of 89.5%) showed that residual turbidity remained below 10 FTU as long as the concentration remained above 5 mg/L (Fig. 5).

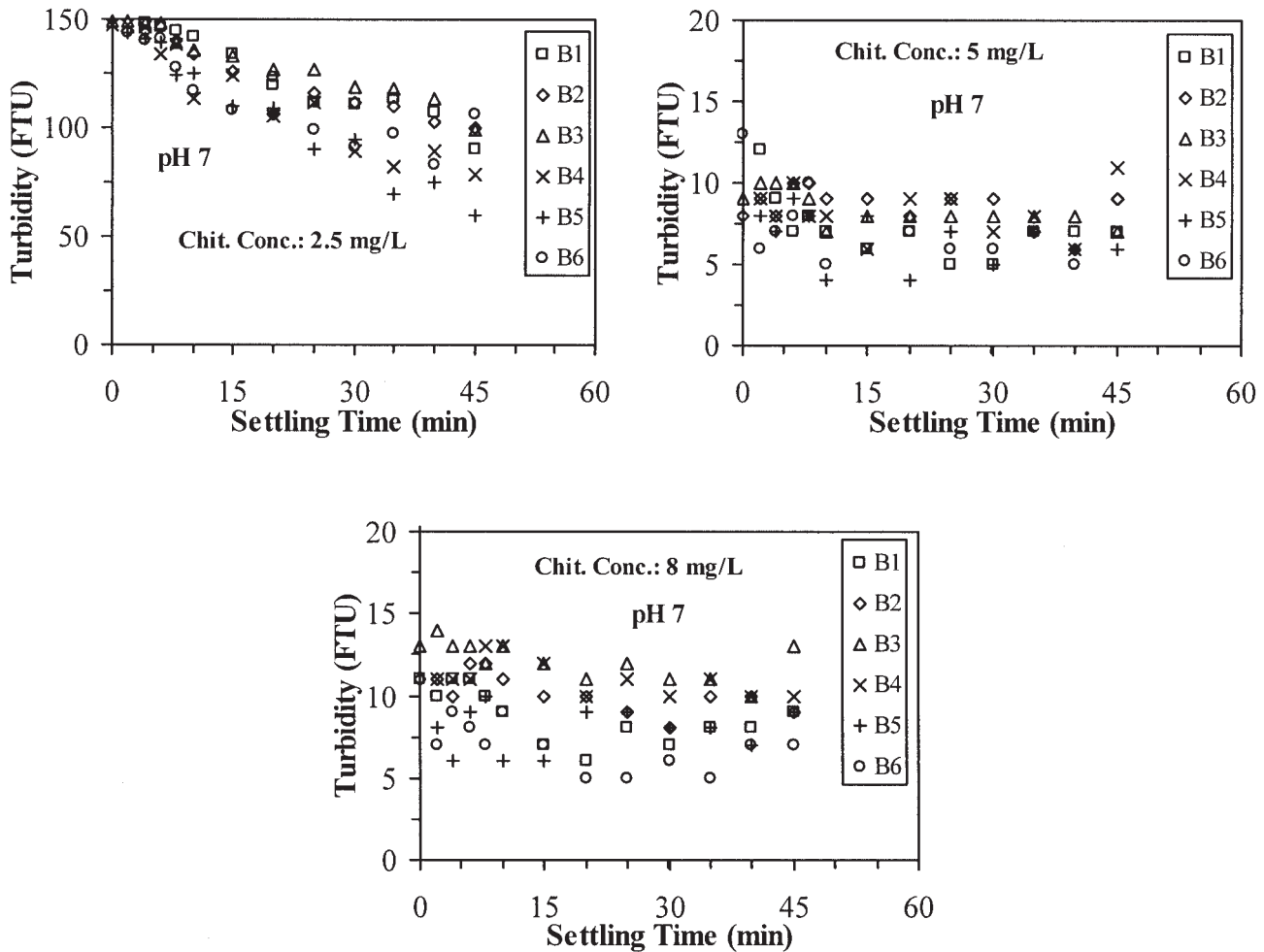


Figure 5 Influence of molecular weight of chitosan on the coagulation and flocculation of organic suspensions at pH 7—influence of polymer concentration (DD 89.5%).

This was consistent with accepted turbidity levels. The kinetic profiles were very close: the dispersion of the turbidity values remained below 5 FTU with varying molecular weight of chitosan (for a chitosan concentration of 5 mg/L). When the amount of chitosan increased to 8 mg/L, the dispersion of the turbidity values was wider, partly because of the flotation of coagulated particles. On the other hand, when chitosan concentrations were decreased to 2.5 mg/L, the experimental conditions were unfavorable, and the abatement of the turbidity was significantly reduced: under the best experimental conditions (with low-molecular-weight chitosan) the turbidity was systematically higher than 50 FTU after 45 min of settling. The variation in kinetic profiles with molecular weight was not significant.

The last series of experiments was performed with chitosan characterized by a high degree of deacetylation (DD 95%). Table II summarizes the residual turbidity obtained after a 30-min settling time with different chitosan concentrations for samples C1–C3. At the lowest concentration (i.e., 2.5 mg/L), the unfavor-

able experimental conditions led to high residual turbidity values (higher than 30 FTU). The higher efficiency was obtained for the less viscous chitosan (lowest molecular weight); however, the largest variation among those in the series did not exceed 20 FTU. At an increasing chitosan concentration, the efficiency of the process significantly increased: in the range of 5–10 mg/L, the residual turbidity was systematically below 10 FTU, with a settling time as low as 15 min. The kinetic profiles, which are not shown, were very close, regardless of concentration and chitosan characteristics (except for the equilibrium value reported in Table II). The best results were obtained with chitosan samples of low molecular weight: the kinetic profiles of series C2 and C3 overlapped and showed little difference with the kinetic profile of series C1, regardless of chitosan concentration (in the range of 5–10 mg/L). High-molecular-weight chitosan seemed slightly less favorable to the coagulation–flocculation of organic suspensions. However, the differences were not very marked: the amount of chitosan added to the suspension tended to smooth the effect of the molecular

weight of the biopolymer. Two other reasons can explain this limited effect of chain length: (1) the polydispersity of the samples (between 2 and 3 for series B, and between 2 and 12 for series C) and (2) the limited range of molecular weights in each series (3–4 between the lowest and highest molecular weights). Thus, the differences between the samples were not large enough to have a great effect. Long-chain fractions are expected to contribute more to the flocculating effect of the polymer than short-chain fractions.

CONCLUSIONS

Chitosan is very efficient (after being diluted in acidic solutions) for the coagulation–flocculation of organic suspensions (3 g/L) prepared from mushroom waste. The process is very sensitive to pH: decreasing the pH to 5 halves the amount of coagulant necessary to reach an efficient abatement of turbidity. In the pH range investigated, the organic suspension was basically anionic (as shown by zeta-meter measurements). At a pH of 5, amine functions were fully protonated and available for charge neutralization, whereas at pH close to neutral, only a small fraction of the amine groups were protonated and able to interact with anionic colloids. This explains the strong contribution of the charge neutralization effect because of electrostatic interactions at an acidic pH. At pH 5, a low concentration of chitosan (i.e., 2.5 mg/L) was sufficient to achieve acceptable abatement of turbidity (below 10 FTU). Under these conditions the degree of deacetylation and the molecular weight had a limited effect. At lower chitosan concentration, the removal efficiency increased with molecular weight. At a pH close to neutral, a higher chitosan concentration (i.e., 5–10 mg/L) was required to reach the target abatement of turbidity, that is, 10 FTU. The coagulation performance was slightly improved by deacetylating the chitosan and decreasing its molecular weight.

A chitosan concentration close to 5 mg/L seemed to be a good compromise that minimized the impact of the characteristics of the polymer, using slightly acidic conditions.

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