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Enhanced coagulation of bentonite particles in water by a modified chitosan biopolymer

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ABSTRACT

Chitosan, a biodegradable compound, is used as an eco-friendly coagulant in water and wastewater treatment to avoid production of the large amounts of sludge using conventional chemical coagulants. Conditioning of chitosan using four different salts (Na_2SO_4, $NaHSO_4$, $(NH_4)_2SO_4$, and $KHSO_4$) along with H_2SO_4 and treatment condition optimization were investigated to enhance coagulating efficiency for bentonite suspension. Chitosan dissolved in acetic acid was used for coagulation of 5 g/l bentonite suspension. The optimum concentration of chitosan required for maximum coagulation of bentonite suspension was 5 mg/l. Among the five additives used for conditioning, $NaHSO_4$, at all concentrations, was found to be the most effective for enhancing the coagulating efficiency of chitosan and it was at its maximum when conditioned by 0.05 mM $NaHSO_4$. $NaHSO_4$ conditioned chitosan showed better coagulating efficiency than unconditioned chitosan at all pHs (3–8) tested in this study. The coagulation of bentonite by chitosan was found to decrease with increase in pH of the suspension. Using 5 mg/l of $NaHSO_4$ conditioned chitosan at pH 6, the removal percentage of bentonite was increased from 76% to 88 % compared to unconditioned chitosan.

1. Introduction

Water treatment plants face many problems when removing turbidity from raw untreated water in order to produce drinking water that is pure enough for its intended use. Inorganic coagulants such as alum and poly aluminum chloride (PACl) are widely used for the removal of raw water turbidity because they are cost effective and easy to handle. However, the sludge obtained from such treatment poses disposal problems because of its aluminum content and the residual aluminum concentration in the treated water has raised public health concerns [1]. McLachlan [2] reported that extensive intake of alum may cause Alzheimer's disease. The search for a better alternative for conventional coagulants has become an important challenge in the water treatment process, with the aim of minimizing the detrimental effects associated with the use of such coagulants.

In many studies, cationic polyelectrolytes have been highlighted as effective coagulants or flocculants for negatively charged suspended particles found in natural turbid water. Chitosan, a polycationic, biodegradable, non-toxic and high molecular weight linear copolymer of glucosamine and N-acetyl glucosamine, is soluble and positively charged in acidic media and may therefore be used as an eco-friendly coagulant and flocculant [3]. Chitosan can be prepared through the deacetylation of chitin, which is second only to cellulose in terms of abundance in nature, and is found in the shells of crustaceans such as crabs and shrimps. Thus, chitosan can be obtained from a waste product of the crab industry. Chitosan has been widely used as an effective coagulant or flocculant for a wide variety of suspended solids in various food and fish processing industries [4–7], and for suspensions containing mineral colloids in water [8–10]. The biopolymer chitosan has also gained importance in environmental biotechnology due to its very good adsorption capacity for dyes and metal ions [11–13]. Applications of chitosan for coagulation and flocculation of montmorillonite, bentonite and kaolinite suspensions have been reported [14–16]. Chitosan is even more ecological and effective than alum, because it produces less sludge [17]. The reactivity of chitosan for coagulation and flocculation of suspended particles and colloids results from several mechanisms, including electrostatic attraction, sorption (related to protonation of the amine group of chitosan and chelating capacity due to the high content of –OH groups) and bridging (related to the high molecular weight of chitosan). The contribution of each mechanism depends on the pH of the suspension.

In the present study, conditioning of chitosan was carried out using different additives prior to its use as a coagulant for bentonite suspension. The objective of this work was to observe the effects of chitosan conditioning on bentonite coagulation and to select the most effective additive for conditioning. The optimum dosage of

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modified chitosan for maximum removal of suspended bentonite was determined. The influence of pH and bentonite concentration on the coagulation process was also examined in this study.

2. Materials and methods

2.1. Chemicals

Chitosan (CS, >85% deacetylation) and bentonite used in the present investigation were purchased from Sigma Chemical Co., USA. All other chemicals were of analytical grade and were also procured from Sigma Chemical Co., USA.

2.2. Turbid water

Water with desired turbidity was prepared by mixing 5 g/l bentonite in 25 ml deionized water. pH of the bentonite suspension was adjusted by adding 0.1 (N) HCl or NaOH. Bentonite has negative zeta potential in deionized water [18].

2.3. Preparation of chitosan solution as coagulant

Chitosan was dissolved in 1 % acetic acid solution by stirring overnight at 150 rpm to make 0.5 % stock solution. The stock solution was diluted to the desired concentration by adding deionized water prior to each experiment. Concentration of chitosan was varied from 0.1 to 20 mg/l in 25 ml (5 g/l) bentonite suspension at pH 6 to determine its optimum concentration for bentonite coagulation at 30 °C after 30 min. The calibration curve of bentonite in the suspension was carried out by measuring absorbance of different predetermined concentrations of bentonite at 540 nm using a DR5000 spectrophotometer (HACH, USA). Concentration of bentonite in the experimental bentonite suspension before and after coagulation was calculated from the calibration curve. Triplicate runs were performed for each condition of all the experiments.

2.4. Screening of additives for conditioning chitosan solution

Fifty ml of chitosan solution at 25 mg/l was conditioned using different additives viz., ammonium sulfate [$(NH_4)_2SO_4$], sodium sulfate [Na_2SO_4], potassium bisulfate [$KHSO_4$] and sodium bisulfate [$NaHSO_4$] in shaking condition at 150 rpm overnight at 50 °C. Concentration of each additive during conditioning was varied from 0.005 to 0.5 mM). Fifty ml chitosan solution (25 mg/l) was also conditioned using sulfuric acid (H_2SO_4) with the same concentration range. In the case of $NaHSO_4$, a wider range of concentration [0.001–50 mM] was tested. The coagulation of the 25 ml (5 g/l) bentonite suspension at pH 6 was performed using each variety of conditioned chitosan at a concentration of 5 mg/l in order to obtain the most effective additive and its concentration for conditioning chitosan solution.

2.5. Bentonite dosage

The coagulation of the 25 ml bentonite suspension was achieved using 5 mg/l unconditioned and $NaHSO_4$-conditioned chitosan at pH 6. The concentration of bentonite in 25 ml suspension was varied from 1 to 20 g/l.

2.6. Effect of pH

The effect of pH on the coagulation process was studied over a pH range of 3.0–8.0 and at an initial bentonite concentration fixed at 5 g/l. To observe the effect of acid type on the bentonite coagulation, pH adjustment of the bentonite suspension was done using HCl as well as H_2SO_4. Twenty-five ml of pH-adjusted bentonite suspension was coagulated by 5 mg/l chitosan conditioned with $NaHSO_4$ at its optimum concentration for conditioning as described above.

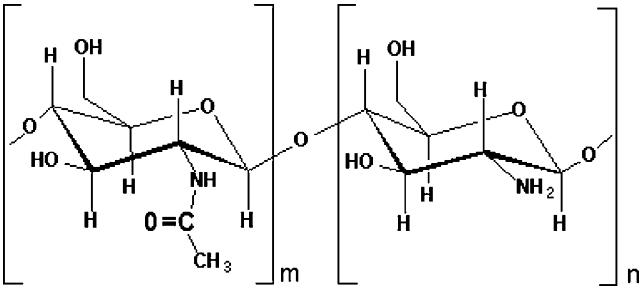

Fig. 1. Chemical structure of chitosan.

Optimum dosage of chitosan was studied over a pH range of 3.0–8.0 with an initial bentonite concentration fixed at 5 g/l. Concentrations of unconditioned and $NaHSO_4$-conditioned chitosan were varied from 0.5 to 20 mg/l in 25 ml of pH-adjusted bentonite suspension.

2.7. Calculation of molar amine content

Fig. 1 shows that chitosan is a co-polymer of N-acetyl glucosamine (GlcNAC) and glucosamine ($GlcNH_2$) and that it contains m mol units of GlcNAC and n mol units of $GlcNH_2$. Here, $m \gg n$ indicates chitin and $m \ll n$ indicates chitosan. The deacetylation ratio of chitosan (f_D) is given by this equation:

$$f_D = \frac{n}{m+n} \tag{1}$$

For 85%-deacetylated chitosan (Sigma, USA), $m = 0.15$, $n = 0.85$ and $f_D = 0.85$ were calculated. The average weight of monomer ($M_{cs,mon}$) in chitosan can be given by this equation:

$$M_{cs,mon} = MW_m \times (1 - f_D) + MW_n \times f_D \tag{2}$$

where MW_m is 191 g/mol unit m and MW_n is 161 g/mol unit n. Then, molar amine content ($\bar{C}_{NH_2}$, mol NH_2/g chitosan) of chitosan can be given by

$$\bar{C}_{NH_2} = \frac{f_D}{M_{cs,mon}} = \frac{f_D}{MW_m \times (1 - f_D) + MW_n \times f_D} \tag{3}$$

For 85%-deacetylated chitosan, the 0.0051 mol/g of molar amine content was calculated.

3. Results and discussion

3.1. Chitosan as a coagulant

Fig. 2 shows sedimentation of bentonite suspension over time with and without chitosan coagulant. While 30% of bentonite was removed within 30 min in control suspension, chitosan at a concentration of 5 mg/l removed 76% bentonite from a 5 g/l suspension. This coagulation process was very fast initially and around 84% bentonite was removed within 1 h of coagulation.

3.2. Screening of additives

Fig. 3A and B show that conditioning of chitosan with different additives improved the coagulating efficiency, but to a different extent. It has been reported that the presence of sulfate ions in bentonite suspension enhanced the coagulating efficiency of coagulant [19]. The additives used in this study for conditioning of chitosan enhanced the coagulating efficiency of chitosan because all of the

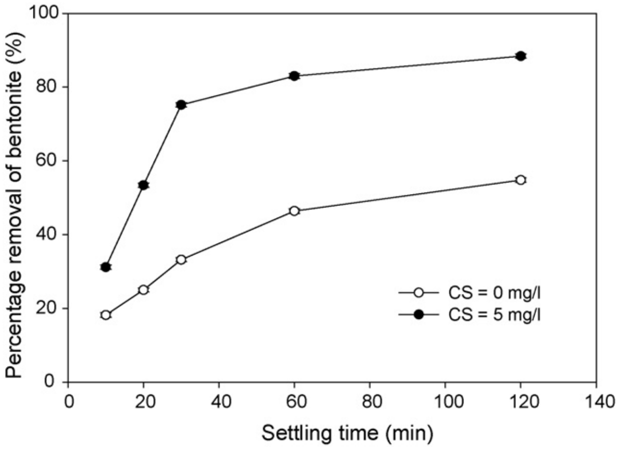

Fig. 2. Effects of chitosan addition on removal percentage of bentonite (%) at pH 6.

additives contain sulfate ions. Van Duin and Hermans [20] hypothesized that chitosan formed larger aggregates in the presence of sulfate ions. Therefore, chitosan appears to have a higher molecular weight, and this might cause enhancement of bentonite coagulation. Among the five additives used for conditioning chitosan, $NaHSO_4$ and $KHSO_4$ were found to be more effective than the others due to protonation of the amine group of chitosan by

$$RNH_2 \xrightarrow{NaHSO_4 \text{ or } KHSO_4 \text{ or } H_2SO_4} RNH_3^+ \quad (4)$$

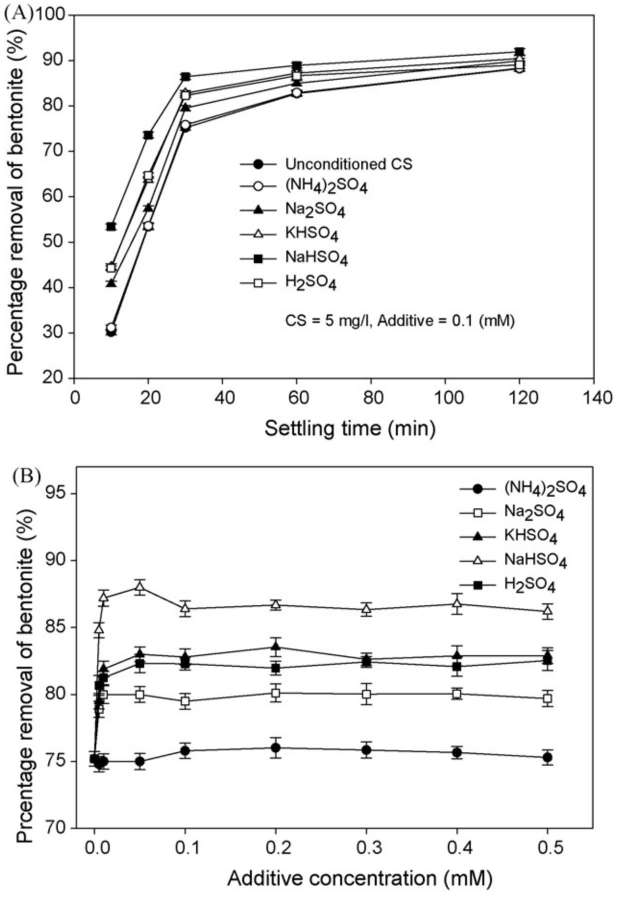

Fig. 3. Effects of chitosan conditioning, using different additives at different concentrations, on the removal of bentonite (%) at pH 6. (A) Removal over time and (B) removal after 30 min settling.

$NaHSO_4$ and $KHSO_4$ have the same pK_a value of 1.9, which indicates an acid strength similar to phosphoric acid. Chitosan has a pK_a value of 6.2, and at pH 6.2 chitosan has zero zeta potential. Overall conditioning of chitosan with $NaHSO_4$ and $KHSO_4$ increased its coagulating capacity because the amine group of chitosan was protonated by H^+ produced from the dissociation of $NaHSO_4$ or $KHSO_4$ in the chitosan solution during conditioning.

Conditioning of chitosan solution with ammonium sulphate would probably form the $R–NH_3{}^+SO_4NH_4{}^-$, as proposed by Muzzarelli and Rocchetti [21], and this would enhance bentonite coagulation.

$$RNH_2 \xrightarrow{(NH_4)_2SO_4} RNH_3^+NH_4SO_4^- \quad (5)$$

However, the enhancement of coagulating capacity of chitosan after conditioning with $(NH_4)_2SO_4$ was found to be much lower than with $NaHSO_4$ and $KHSO_4$, due to very high pK_a value (9.25) for $(NH_4)_2SO_4$.

Conditioning of chitosan with Na_2SO_4 also increased bentonite coagulation because chitosan forms larger aggregates in presence of this salt containing sulfate ions [20] and alkaline cations in this salt can favour delamination of the bentonite particles in the suspension, which thereby displays highly accessible surfaces [22]. However Na_2SO_4 conditioned chitosan was found to show lower coagulating capacity compared to $NaHSO_4$ and $KHSO_4$ conditioned chitosan because Na_2SO_4 is a neutral salt, which is completely dissociated in water.

Fig. 3B shows that at all concentrations, $NaHSO_4$ was the most effective additive for increasing the coagulating efficiency of chitosan. Although $NaHSO_4$ and $KHSO_4$ both have the same pK_a value (1.9), $NaHSO_4$-conditioned chitosan was a much better coagulant than $KHSO_4$-conditioned chitosan. One possible explanation for this observation is that alkaline cations can favour delamination of the bentonite particles in the suspension, which thereby displays highly accessible surfaces [22]. The lower ionic size of Na^+, as compared to K^+, would gain more easily access on the bentonite surfaces. Furthermore, the lower ionic size of Na^+ leads to higher absolute values of enthalpy of hydration. Therefore the difference in the hydration capacity between the cations, and consequently the differences in the sizes of hydrated cations and their interaction with chitosan, would be the possible reason for higher coagulating efficiency of chitosan conditioned by $NaHSO_4$ [22].

Chitosan solution was also protonated by H_2SO_4 (pK_a values of −3 and 1.92) during conditioning [23] and that increased its efficiency for bentonite coagulation. However $NaHSO_4$ conditioned chitosan showed better bentonite removal than H_2SO_4 conditioned chitosan due to presence of alkaline cations, which delaminate the bentonite particles in the suspension [22].

3.3. *Optimal concentration of $NaHSO_4$ during conditioning of chitosan*

Fig. 4 shows that the removal percentage of bentonite suspension with 5 mg/l chitosan was enhanced by increasing the concentration of $NaHSO_4$ up to 0.05 mM during the conditioning. Further increase in concentration of $NaHSO_4$ during the conditioning could not produce any further increment; instead, a slight decrease was found in its coagulating capacity. Calculations of molar amine content using Eqs. (1)–(3) show what percentage of the whole amine groups of chitosan were protonated at optimal concentrations of $NaHSO_4$ during conditioning. The 25 mg/l chitosan solution has 0.128 mM NH_2 for 85%-deacetylated chitosan. Removal percentage values of bentonite around 88% and 86.4% were achieved after conditioning 50 ml chitosan solution with 0.05 and 0.1 mM $NaHSO_4$, respectively, and these concentrations are not enough to completely protonate 25 mg/l chitosan solution. This

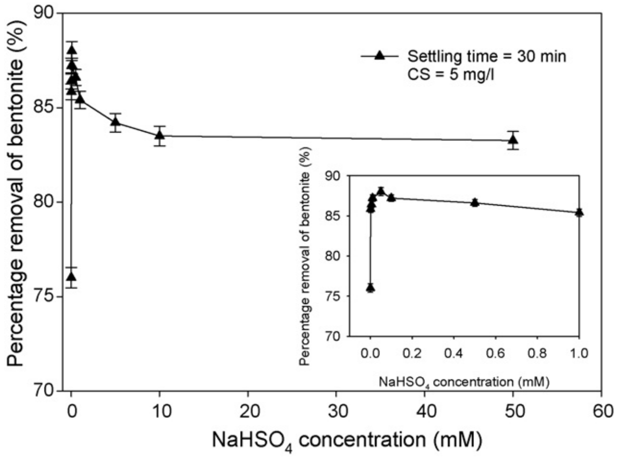

Fig. 4. Effects of $NaHSO_4$ concentration variation during conditioning of chitosan on the removal of bentonite at pH 6.

indicates that complete protonation of amine groups of chitosan by $NaHSO_4$ during conditioning would not be required to achieve its maximum coagulating capacity.

3.4. Effect of chitosan concentration

Fig. 5 shows that the percentage removal of bentonite was enhanced by increasing the chitosan concentration up to 5 mg/l. Further increase in chitosan concentration reduced bentonite coagulation. Concentration variation of chitosan conditioned with $NaHSO_4$ at two concentrations viz., 0.05 and 2 mM, produced a similar pattern of coagulation as obtained with unconditioned chitosan. The optimum concentration of chitosan for coagulation of 25 ml (5 g/l) bentonite suspension was found at 5 mg/l for all three cases. Therefore, very low doses of chitosan (5 mg/l) were required for destabilization and coagulation of concentrated bentonite suspension. The cation exchange capacity (CEC) of bentonite was found to vary between 50 and 100 meq/100 g depending on the mineralogical condition [19]. Therefore, effective coagulation was achieved with much lower doses of chitosan than would be required for complete charge neutralization of bentonite, and this process was guided by the combined effects of electrostatic patch and bridging mechanisms. This coagulation process was fast; around 88% removal of bentonite was achieved within 30 min at pH 6 with 5 mg/l chitosan conditioned with 0.05 mM $NaHSO_4$. Removal percentage values around 76% and 85% were achieved after 30 min with 5 mg/l of unconditioned chitosan and chitosan conditioned with 2 mM $NaHSO_4$, respectively. A possible explanation for the decreased removal percentage of bentonite with increased chitosan concentration (beyond 5 mg/l) is that increased chitosan amounts may favor chitosan–chitosan associations at the expense of chitosan–bentonite interactions.

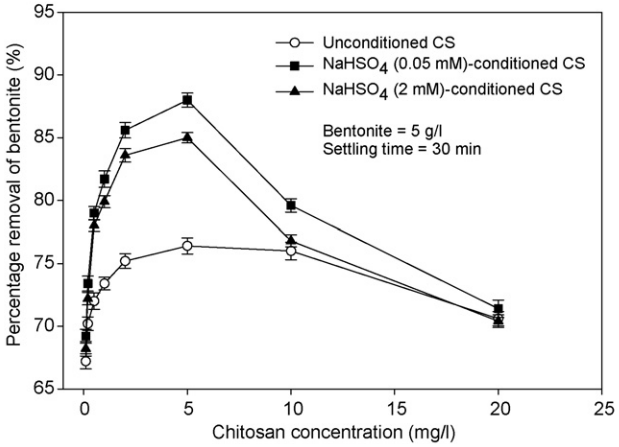

Fig. 5. Effects of chitosan concentration on the removal of bentonite (%) at pH 6.

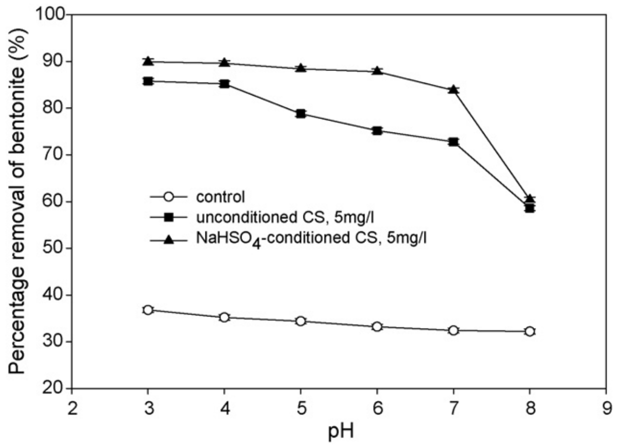

Fig. 6. Effects of pH on the removal of bentonite (%) using unconditioned and $NaHSO_4$ conditioned chitosan at 5 mg/l.

3.5. Effect of pH variation

Fig. 6 indicates that both unconditioned and 0.05 mM $NaHSO_4$-conditioned chitosan at 5 mg/l coagulated 25 ml (5 g/l) bentonite suspension very effectively at pH 3 and 4. This phenomenon can be attributed to a higher degree of protonation of amine groups of chitosan at lower pH. Coagulation of bentonite particles was enhanced by the increase in charged groups of chitosan, which increased electrostatic interaction with anionic surface of bentonite. At pH 3 and 4, removal of bentonite was around 89.9% and 89.6% for 0.05 mM $NaHSO_4$-conditioned chitosan and 85.8% and 85.2% for unconditioned chitosan. 0.05 mM $NaHSO_4$−conditioned chitosan showed slightly higher coagulation efficiency than unconditioned chitosan at pH 3 and 4, probably due to the presence of sulfate ion in the bentonite suspension, which has a positive effect on chitosan during coagulation.

Fig. 6 shows that at pH 5 and 6, the removal of bentonite was around 88.5% and 87.8% for 0.05 mM $NaHSO_4$-conditioned chitosan and 78.8% and 75.2% for unconditioned chitosan. The coagulating efficiency of 0.05 mM $NaHSO_4$ conditioned chitosan was much higher than unconditioned chitosan at pH 5 and 6 due to significant protonation of the amine group of chitosan by $NaHSO_4$ during conditioning. Therefore, during conditioning, $NaHSO_4$ contributed significantly to the coagulation of bentonite suspension through charge neutralization.

Approximately 83.9% and 72.8% removal of bentonite was found at pH 7 with 0.05 mM $NaHSO_4$-conditioned and unconditioned chitosan, respectively. Approximately 10–25% of amine groups of chitosan should be cationic at pH 7, although this has been reported to be a function of the degree of deacetylation of chitosan and ionic strength [24]. The higher coagulating efficiency of 0.05 mM $NaHSO_4$-conditioned chitosan than unconditioned chitosan was due to the protonation of amine groups of chitosan by $NaHSO_4$ during conditioning. The coagulating capacity of both unconditioned and 0.05 mM $NaHSO_4$-conditioned chitosan was low at pH 8. Conditioning of chitosan could not produce any significant change because most of the amine groups of chitosan were unprotonated at pH 8. Removal percentage at pH 8 was slightly higher with $NaHSO_4$ conditioned chitosan (60.4 %) than with unconditioned chitosan (58.6 %). The effect of pH change on bentonite removal by chitosan was also carried out after adjusting pH with H_2SO_4 and the results are similar to the results obtained with HCl (data not shown). The coagulation of bentonite using both unconditioned and $NaHSO_4$-conditioned chitosan is not dependent on the type of acid (HCl or H_2SO_4) used for pH adjustment in bentonite suspension. However, H_2SO_4 conditioned chitosan showed better coagulating efficiency than unconditioned chitosan due to protonation of chitosan during conditioning with H_2SO_4.

The effects of pH variation on removal percentage of bentonite using different dosages of unconditioned chitosan and $NaHSO_4$ 0.05 mM-conditioned chitosan are shown in Fig. 7A for some selected pHs. The maximum bentonite removal was observed at multiple chitosan concentrations and within this concentration range no change in the removal percentage was found. Therefore, the optimal dosage of chitosan was determined to be the lowest concentration of chitosan when the multiple chitosan concentrations were found for the highest removal percentage of bentonite. For example, the maximum bentonite removal at pH 3 was found at a concentration of 2 mg/l for both unconditioned and 0.05 mM $NaHSO_4$ conditioned chitosan and no further increase in bentonite removal was found with increase in chitosan concentration up to 8 mg/l. Overall, maximum bentonite removal at all pH tested in this study occurred at chitosan concentration of 5–8 mg/l. The optimum dosage was found to vary with pH of the suspension. The relationship between the optimal chitosan concentration and pH value is illustrated in Fig. 7B, and shows that optimum chitosan dosage was smaller in acidic pH. This suggests that the increase in number of protonated amine groups on chitosan at lower pH resulted in a decrease in optimum dosage. The optimum dosage of conditioned chitosan was lower than unconditioned chitosan at pH 7 and 8. This phenomenon can be attributed to the higher number of protonated amine groups of conditioned chitosan.

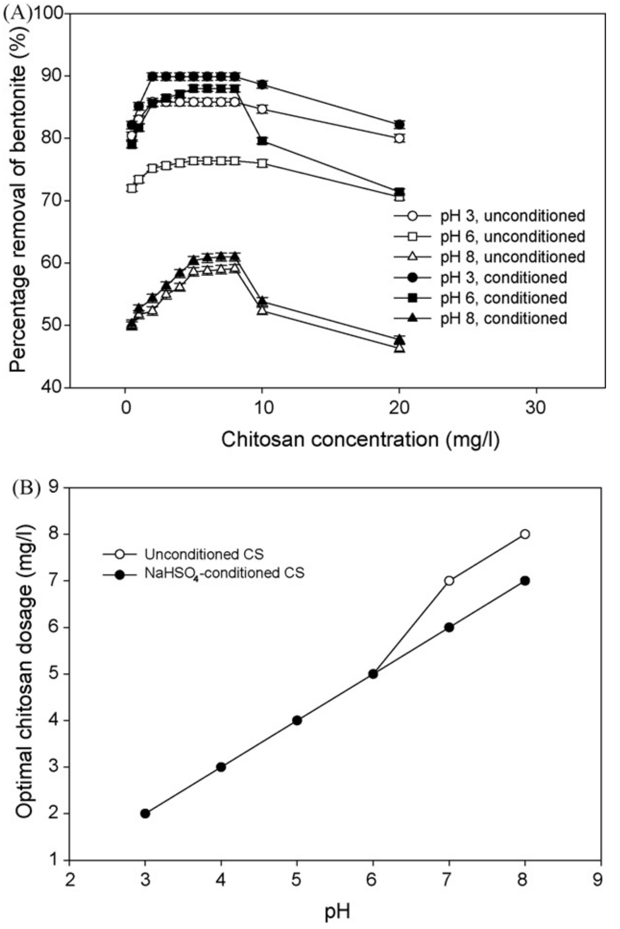

Fig. 7. Effects of pH variation on the removal of bentonite using different dosages of unconditioned chitosan and $NaHSO_4$ 0.05 mM-conditioned chitosan (A), and optimal chitosan concentration at the various pH conditions (B).

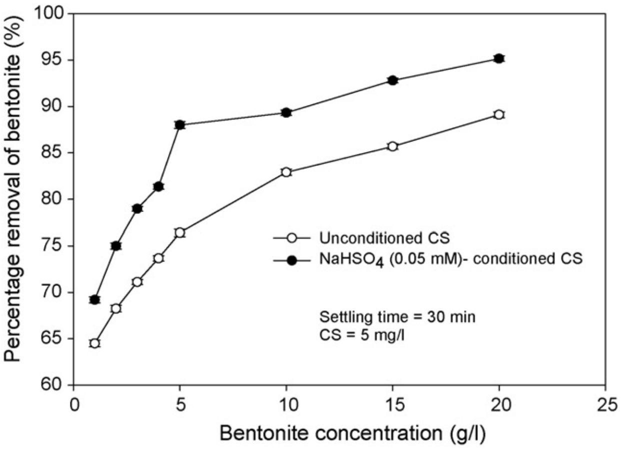

Fig. 8. Effects of bentonite concentration on the removal of bentonite (%) at pH 6 using unconditioned, and $NaHSO_4$ conditioned, chitosan at 5 mg/l.

3.6. *Effect of bentonite dosage*

Fig. 8 shows that the percentage removal of bentonite was increased with an increase in bentonite concentration, using 5 mg/l unconditioned and $NaHSO_4$ 0.05 mM-conditioned chitosan. It was noted that bentonite concentration beyond 5 g/l produced a sharp increase in percentage removal. In other words, in some samples, clearer solution was obtained after 30 min settling with more bentonite dosage. The remaining suspended solids were 0.31, 0.97 and 1.1 g/l for 1, 10 and 20 g/l of the initial bentonite dosage using $NaHSO_4$-conditioned chitosan, respectively. Therefore, increase in bentonite dosage may produce some acceleration in self-coagulation and this would result in a higher percentage of bentonite removal [25].

3.7. *Coagulation performance evaluation*

Different research groups reported coagulation of particles and colloids using chitosan over the years. Divakaran and Pillai [8] reported flocculation of silt in river water using chitosan in the pH range 4–9. The silt flocculation was maximum at pH 7.5 and the maximum 90% removal of turbidity was achieved at this pH using chitosan at a concentration of 1 mg/l and with initial turbidity value at 40 NTU. Roussy et al. [19] showed that more than 95% of residual turbidity was removed from 5 g/l bentonite suspension using less than 0.1 mg/l chitosan in either tap water (TW) or demineralized water (DW) at pH 5 or in TW at pH 7. Coagulation was better in TW than DW and lower dosages of chitosan were required at pH 5 than pH 7. The improved performance of chitosan in TW was due to presence of sulfate and other counter-ions in TW. Chen et al. [26] observed better flocculation of bentonite with higher molecular weight (MW) chitosan and the required dosage also decreased with increasing degree of deacetylation (DD). In recent years, several modification methods of chitosan as a coagulant were proposed to improve coagulation of colloidal particles [10,16]. Huang et al. [10] have studied the effect of the type of acid to prepare chitosan solution and observed more efficient coagulation of clay particles with acetic acid. Pan et al. [16] examined the mixture of chitosan and PACl at various ratios, but did not observe any enhancement of coagulating efficiency. This is the first approach to use $NaHSO_4$ as a conditioning agent for chitosan to increase its bentonite coagulation efficiency. In this study, chitosan conditioned with only a small amount (0.05 mM) of $NaHSO_4$ produced better bentonite coagulation than unconditioned chitosan at all pH. For example, using 5 mg/l of $NaHSO_4$ (0.05 mM) conditioned chitosan at pH 6, the concentration of suspended solid was decreased approximately 2 times, from 1.23 g/l (76% removal) to 0.62 g/l (88% removal), compared to unconditioned chitosan.

4. Conclusion

Chitosan was effectively used for the coagulation of a bentonite suspension. Maximum coagulation of bentonite was achieved at 5 mg/l chitosan concentration and the removal percentage was around 76% at pH 6 after 30 min. Among the five additives used for conditioning, at all concentrations $NaHSO_4$ was found to be the most effective for enhancing the coagulating efficiency of chitosan. Percentage removal of bentonite increased from 76% to 88% after conditioning chitosan with 0.05 mM $NaHSO_4$. Coagulation of bentonite by chitosan was very sensitive to pH and less chitosan dosage was required in acidic pH. The increase in percentage removal of bentonite with decrease in pH explains the strong contribution of the charge neutralization effects because of electrostatic interactions at an acidic pH. $NaHSO_4$-conditioned chitosan showed better coagulating efficiency than unconditioned chitosan at all pH values tested in this study. $NaHSO_4$-conditioning of chitosan is a simple and cost-effective method and can be easily applied to wastewater treatment facilities.

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