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Evaluation of a modified chitosan biopolymer for coagulation of colloidal particles

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Abstract

Chitosan, a deacetylated derivative of chitin, is a biodegradable cationic polymer. Chitosan can be a potential substitute for aluminum salts and synthetic polyelectrolytes in water treatment because it can: (1) avoid the health effects from residual aluminum (III) and synthetic polymers; (2) produce biodegradable sludge; and (3) reuse the crab shell. Chitosan can be modified with various pretreatments including dissolution in acid solution and various deacetylation conditions to improve its coagulation efficiency. In this study, coagulations of synthetic and real water with the modified chitosan, mixed coagulant of chitosan and PACl at various ratios, and PACl were compared. The efficiency was evaluated by the factors of settling rate, floc diameter, and residual turbidity. Coagulation with chitosan alone required least dosage. Chitosan coagulants also produced larger floc with higher settling velocity. Satisfactory results were obtained from the mixed coagulant of chitosan/PACl = 4:1. Although low pH decreased the optimal dosage, the flocs produced were smaller with slower settling rate. Increasing the rapid mixing strength improved the coagulation only when the applied dosage was less than the optimum dosage. Studies using other particles such as kaolinite and clay indicate that the properties of particles have a significant effect on the chitosan coagulation efficiency.

Keywords: Bentonite; Biopolymer; Chitosan; Coagulation; Kaolinite

1. Introduction

Colloid particles are removed from water with the coagulation/flocculation process. Of all the available coagulants, aluminum sulfate and polyaluminum chloride (PACl) are the most widely used, because they are cheap, effective and easy to handle. Most important of all, aluminum can be overdosed to ensure coagulation efficiency. However, over-use of aluminum salt coagulants elevates the aluminum concentration and turbidity in the treated water, which in turn devaluates the treatment process. McLachlan also reported that intake of a large quantity of aluminum salt may cause Alzheimer's disease [1]. The search for a better alternative to meet the increasing demand for water quality has become an important area of study. Polymers combined with alum or polymers alone have been applied in the coagulation,

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and gradually gained popularity in water treatments. Synthetic polyelectrolytes produce sludge of better dewatering characteristics. The sludge is smaller in volume than those from conventional alum flocculation, and facilitates filtration. However, their long-term effects on human health are not well understood.

Chitin is a cellulose-like biopolymer widely distributed in nature, especially in marine invertebrates, insects, fungi, and yeasts. Its deacetylated product, chitosan, is readily soluble in acidic solutions, which makes it more available for applications. Chitosan is a biodegradable, non-toxic, linear cationic polymer of high molecular weight. Knorr [2] discovered that chitosan was an effective agent for coagulation of suspended solids from various food processing wastes. Since chitin is the second most abundant biopolymer, the application in coagulation not only avoids the health threat from alum treatment, but also allows recycling of a large amount of crab shell. The feasibility of applying chitosan in the coagulation of colloidal particles was assessed in our laboratory [3]. We found that chitosan can be a potent coagulant for surface water treatment, especially for source waters of medium and low turbidity. From various treatments of chitosan, we further recommended that the optimal pretreatment condition to prepare modified chitosan coagulant is deacetylation by 45% alkali pretreatment for 60 min and dissolution in 0.1% hydrochloric acid. In this study, extensive research was conducted to evaluate the coagulation performance of the coagulant mixtures prepared from various combinations of this modified chitosan with PACl to find the optimal treatment conditions.

2. Materials and method

2.1. Preparation of chitosan

Chitin, isolated from crab shell, was ground to powder form. This powdered chitin was then deacetylated with NaOH (45% w/w) in a 100°C water bath for 60 min and the reaction was terminated by an ice bath. Following that, the product was cleaned several times with deionized water until the pH of the suspension reached 7. The suspended particles were collected with a membrane filter and dried at 80°C for 48 h. The chitosan powder was modified with a novel method, different from the previous one, to achieve better performance.

2.2. Preparation of chitosan solution and coagulant mixture

The modified chitosan was added to 1% hydrochloric acid and mixed at 100 rpm for 60 min or until dissolved to make 1% stock solution. Prior to each experiment, stock solution was added to the deionized water and mildly mixed with magnetic stirring to prepare the coagulant solution of desired concentration. The coagulant mixtures were prepared by mixing the chitosan and PACl in 1:4, 1:1, and 4:1 mass ratios.

2.3. Turbid water

Model waters with desired turbidity were prepared by mixing given amounts of bentonite (Hayashi Co., Japan), kaolinite powders (Nakaray Co., Japan) and clay with deionized water, and $NaClO_4$ was added to maintain the ionic strength at 10^{-2} N. Raw surface water was collected from the Hsinchu water treatment plant, Taiwan.

2.4. Coagulation tests

A conventional jar test apparatus was used for flocculation experiments. For all trials, the pH of the suspension was adjusted by adding a strong base (0.1 M NaOH) or a strong acid (0.1 M $HClO_4$). The reactor was set at 100 rpm paddle speed, containing model or natural water. As soon as the chitosan reagent was added, the water was fast mixed for 3 min followed by 20 min of slow mixing (at 30 rpm). After standing for 10 min, the supernatant from the top 1 in of the suspension was withdrawn for turbidity measurement (HACH Ratio, USA). The settling velocity and diameter of flocs were measured by recording the settling travel of individual floc aggregate in a

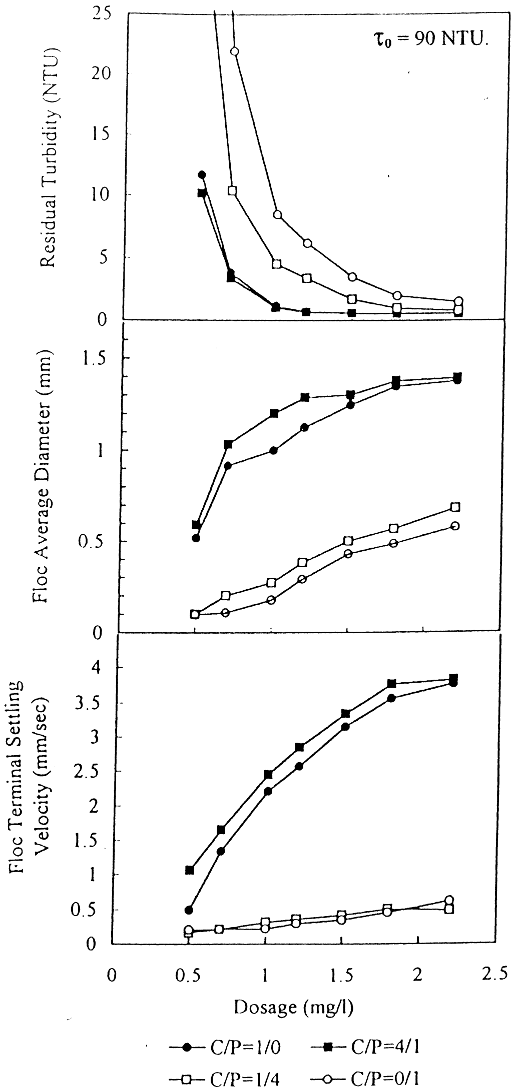

Fig. 1. Coagulation profiles of the bentonite water by modified chitosan and the mixed coagulants of chitosan and PACl in C/P ratios of 1:0, 1:4, 4:1, and 0:1. $\tau_0 = 90$ NTU.

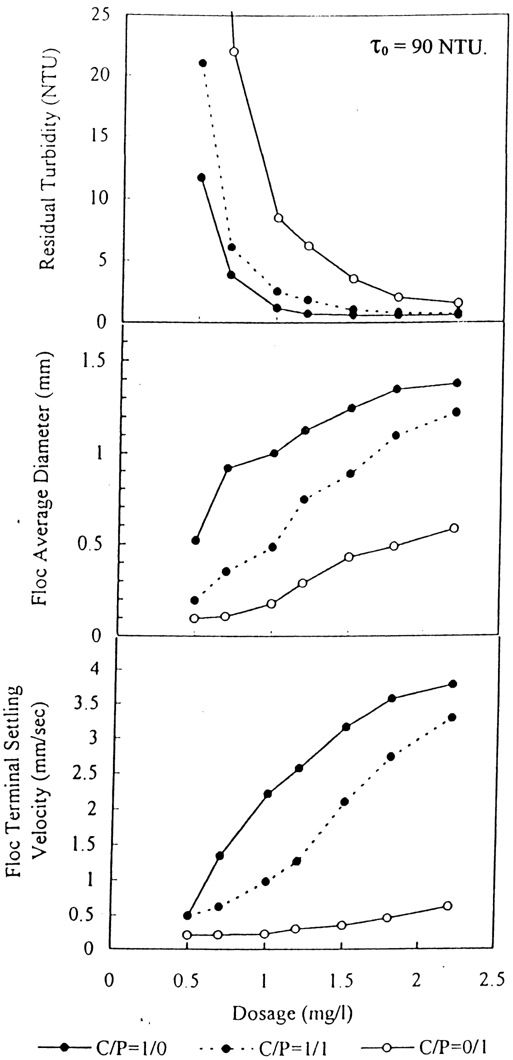

Fig. 2. Coagulation profiles of the bentonite water by modified chitosan and the mixed coagulants of chitosan and PACl in C/P ratios of 1:0, 1:1, and 0:1. $\tau_0 = 90$ NTU.

quiescent column through a video camera equipped with close-up lens [4].

3. Results and discussion

3.1. Effectiveness of mixed coagulant

In this study, the modified chitosan was mixed with PACl in various mass ratios to prepare the mixed coagulants, and the effectiveness of coagulation on model water or natural water was evaluated. The results are presented in Figs. 1 and 2, which clearly show that adding chitosan in the mixed coagulant significantly improves the coagulation. To reach the same level of turbidity removal, the required amount of chitosan is only half that of PACl. Chitosan coagulation also produced flocs of better quality, namely larger flocs and faster settling velocity. When chitosan and PACl were mixed in 1:4 ratio, the required amount of mixed coagulant was less than that of PACl alone. However, there is no significant change in floc size and settling rate. When chitosan and PACl were mixed in 4:1 (C/P), the performance was close to that of chitosan alone. The coagulation effectiveness of 1:1 mixture lies between those of pure chitosan and PACl coagulants (Fig. 2). The optimum dosage at C/P = 1:1 is apparently much less than that needed by pure PACl coagulant. Considering the cost of chitosan, a 1:1 mass ratio of chitosan and PACl mixed coagulant may be a good choice for substituting pure PACl in the plant operation.

3.2. pH effect on coagulation efficiency

A series of jar tests was conducted to study the coagulation effectiveness of the modified chitosan under various pH conditions (i.e. 3, 4, 5, 6, and 7) while other parameters were kept constant. Relationships between chitosan dosage and residual turbidity, floc size as well as settling rate were obtained. For the benefit of discussion, the optimum dosage is defined as the point at which the greatest tangent to the coagulation profile occurs. The relationship between the optimum dosage and pH value is illustrated in Fig. 3, which shows that the optimum chitosan dosage is smaller in

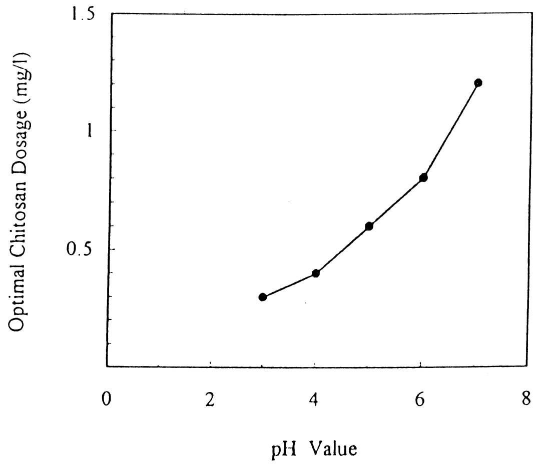

Fig. 3. Effect of pH on optimal flocculation dosage of pure chitosan.

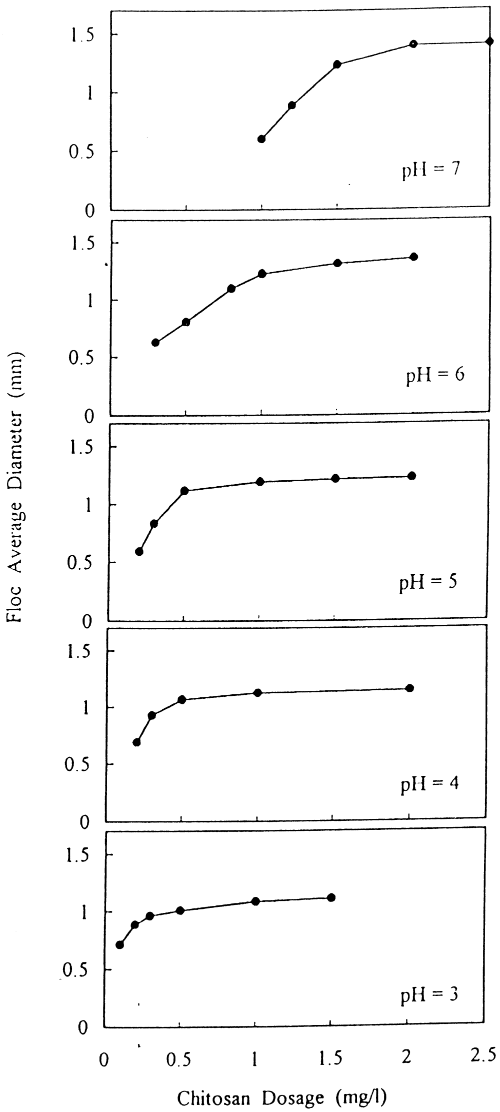

Fig. 4. The relationship between the dosage of pure chitosan and floc average diameter in coagulation of bentonite water at various pH values.

acidic solutions. This phenomenon can be attributed to the increase in number of protonated amine groups on chitosan at lower pH. Destabilization of particles was enhanced by the increase in charged groups followed by charge neutralization, resulting in a decrease in optimum dosage.

The diameter and floc settling velocity of the flocs at various pH values are shown in Figs. 4 and 5. The results indicate that, although better

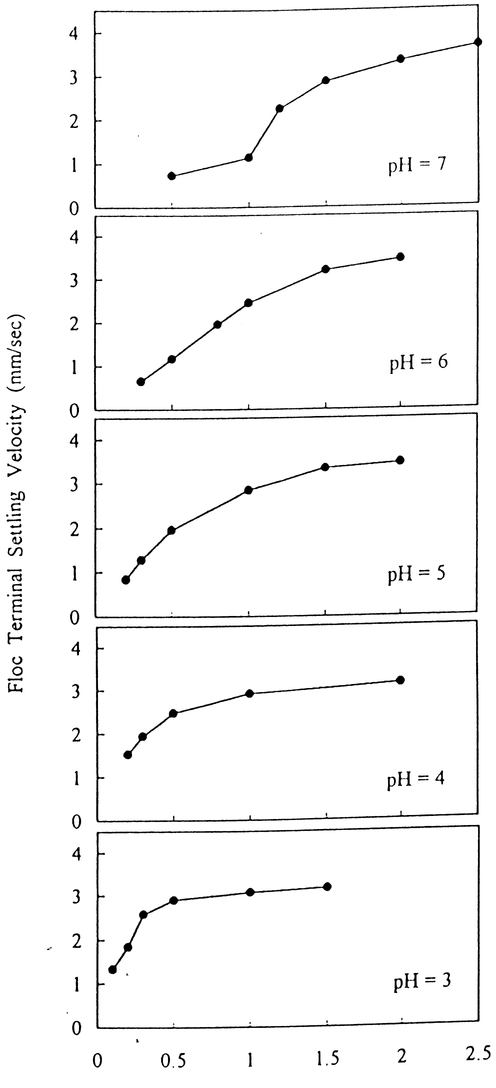

Fig. 5. The relationship between the dosage of pure chitosan and floc terminal settling velocity in coagulation of bentonite water at various pH values.

turbidity removal is observed at lower pH, the resulting floc diameter is smaller, accompanied by a slower settling velocity. This may be explained by the variation in the configuration of chitosan. In neutral solutions, because of the more coiled structure, the chitosan polymer is able to produce larger and denser flocs. In acidic solutions, it becomes a more extended chain (more charged), and therefore produces smaller and looser flocs.

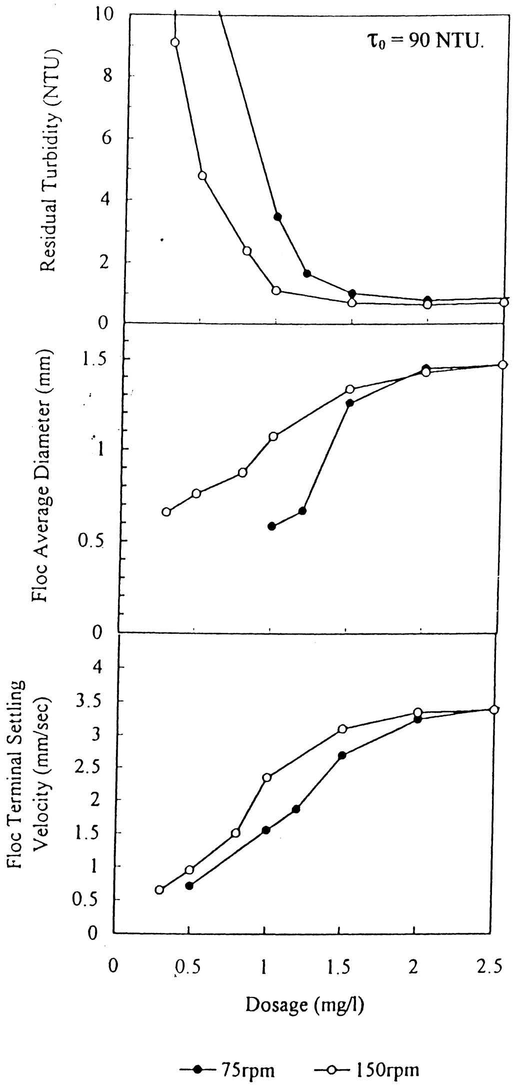

Fig. 6. The effect of mixing speed (75 rpm and 150 rpm) on coagulation of bentonite water by pure chitosan. $\tau_0 = 90$ NTU.

Similar experiments were performed on synthetic kaolinite and clay waters. Although it is possible to remove the particles of kaolinite and clay, the efficiency is quite poor, and the optimal dosage is hard to control (not shown). It indicates that the property of the colloid particle is important in chitosan coagulation.

3.3. Effect of mixing speed on coagulation

Chitosan in 90 NTU synthetic bentonite water

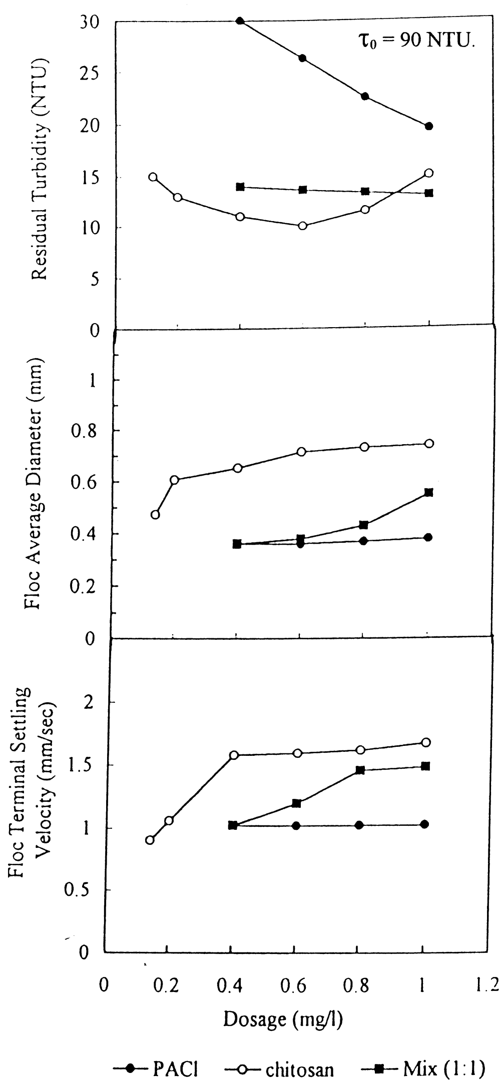

Fig. 7. Coagulation profiles of chitosan, PACl and mixed coagulant on natural water.

of pH 7 was mixed at either 75 rpm or 150 rpm for 20 min, followed by 30 rpm for 20 min. Fig. 6 shows the effect of the mixing speed on the coagulation, in which a faster speed requires less optimal dosage. After reaching optimal dosage, no significant difference in the size of the flocs and the settling velocity was observed. Therefore, it is suggested that the speed of mixing may affect the coagulation only before reaching the optimal dosage.

3.4. Raw water application

A series of trials on the raw water was conducted at pH 7 to compare the performance of the modified chitosan, PACl, and 1:1 mixed coagulants. Fig. 7 shows that chitosan and the mixed coagulant have a similar degree of turbidity removal, which is far better than PACl alone. Water treated with chitosan produces the largest flocs and the settling velocity is about 1.5 times faster than that of PACl. The size of the mixed coagulant flocs is somewhat in between. Considering the cost of chitosan, the 1:1 mixed modified coagulants can be a practical choice for application.

4. Conclusions

Coagulation of chitosan and PACl on synthetic turbid waters showed that the optimal dosage of chitosan was less, and the size of the flocs was larger, with a faster settling rate. When chitosan and PACl are mixed in a mass ratio of 4:1, the settling rate of the resulting floc is the highest when compared to pure chitosan and PACl. At C/P = 1:1, the coagulation effectiveness is between those of chitosan and PACl. Less coagulant was required for more acidic water, although smaller flocs were produced. Increasing the speed during rapid mixing can reduce the amount of optimum dosage. The coagulation of bentonite, kaolinite and clay shows that the property of the colloid particle is important in chitosan coagulation. Results of coagulation on natural water suggest that partially replacing PACl with chitosan in the water treatment process can be cost effective.

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