Performance of chitosan as a primary coagulant for the wastewater treatment

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Abstract

Chitosan (1,4,2-amino-2-deoxy- β-D-glucan), a component of the shell of marine crustaceans, is one of the most abundant organic polymers present in nature. Because of its positive charge and molecular structure, chitosan possesses valuable properties as a metal-recovering and water-purifying agent. Given the increasing use of chemical coagulants to improve the water treatment process, studying chitosan has become very important. The goal of this study was the performance of chitosan as a primary coagulant for the removal of copper (Cu^{2+}) and turbidity from wastewater. The removal of zinc by chitosan was also investigated. Coagulation-flocculation-sedimentation experiments were performed by jar tests (Phipps and Bird, USA) on drinking water mixed with sanitary sewage, with industrial wastewater and with a bentonite suspension. The results showed that chitosan is superior to alum when used as a primary coagulant in a mixture of drinking water with industrial wastewater. 40 mg/L of chitosan permitted 100% elimination of copper from drinking water mixed with industrial wastewater at proportions of 35 and 47%. The use of chitosan as a primary coagulant is more effective than the other classical coagulant in term of toxicity and waste disposal. Chitosan is superior to alum especially when the turbidity and alkalinity of water is high. In our study, the main factors affecting the coagulation-flocculation by chitosan were the physico-chemical characteristics of raw water and the type and concentration of different chemical compounds present in the water.

1 Introduction

Metals discharged or transported into the environment, may undergo transformations and can have a large environmental, public health, and economic impact. Recently, growing concern on the part of governments, organisations and the public has been observed at the international level regarding the increase in aquatic pollution by toxic metals coming from human activities. Wastewater containing heavy metals comes from many sources. The metal-plating industry is the one that releases the highest amount of heavy metals in solution. This particular industry generates the largest wastewater volumes that contain concentrations of chromium, nickel, copper, zinc, iron, and cadmium superior to 1 mg/L (Pepper et al., 1996). Among all the industrial metal discharges, copper, zinc, lead, manganese, and arsenic represent the most important metals in terms of quantity encountered in water in Canada. Due to stricter environmental control of wastewater discharge containing heavy metallic ions, practical solutions have become obligatory. In order to resolve these problems, researchers have focused their efforts on developing treatment methods (physico-chemical and biological processes) and disposal methods for toxic waste. The treatment methods, such as chemical precipitation, electrodeposition, ion exchange, membrane separation, inverse osmosis, oxidation-reduction, evaporation, and extraction by solvents have already been applied. Adsorption technologies, specifically those using chelating resin, have been widely demonstrated and promoted as being feasible technology (Yang et al., 1984). The use of micro-organisms for the elimination of metallic ions in solution has been also studied for 30 years. Depending on the aqueous effluent composition, effluent flow rate, and the metallic ion concentrations, the industrial application of these processes is limited, either because of the high operation costs or because of the failure of the treatment method to obtain a degree of purification that satisfies the regulatory standards for water quality (Brower et al., 1997).

An efficient technology used at this present time is the coagulation-flocculation process with a metallic trivalent salt: alum. Alum's performance has already been demonstrated several times, and it has other advantages such as its cost-effectiveness, the ease with which it can be handled, and its availability. However, the use of alum produces considerable quantities of sludge of which the dehydration and evacuation are difficult, alum floc is generally much weaker in cold-water flocculation, its effectiveness is strongly pH dependent, and finished water may have high residual aluminium concentrations. In spite of its wide use, alum is a secondary pollution source and a source of worry because of its toxicity. To reduce these undesirable effects, synthetic organic polymers are sometimes used alone or combined with alum. The use of organic polymers may increase the rate of settling, reduce costs, and improve sludge quality. Unfortunately, they may react with other chemicals added in wastewater treatment and form undesirable products. They exhibit a degree of selectivity with respect to certain types of colloids. They increase the organic load and they can be carcinogens in certain conditions (Kawamura, 1991 and Mallevialle, 1984).

The emergence of new technologies named clean technologies is helping to solve a large part of all the wastewater treatment problems involving heavy metals. Natural polymers like chitin and chitosan can be used as coagulant and flocculent aids. Chitosan is proposed here as a remedy for all the problems encountered with metallic trivalent salts and synthetic polyelectrolytes. Because these compounds are biodegradable, they promote sludge digestion by micro-organisms. Compared to alum, natural organic polymers reduce the volume of sludge produced. Chitosan has received growing interest in the water treatment field for other reasons too: it is an abundant and renewable resource, it is non-petroleum based and non-toxic, it has been shown to stimulate plant growth, it can be regenerated by desorption, and it is effective in cold water.

Chitosan possesses general coagulant-flocculent characteristics with respect to bio-molecules and surfaces. The chitosan $(C_6H_{11}NO_4)_n$ is a modified form of chitin, the second most abundant natural polymer after cellulose. It is derived from the chitin found in the organic exoskeleton of crustacean such as crabs, shrimps, prawns and lobsters. Chitosan is a positively charged polysaccharide, highly cationic, composed of poly-acetyl-glucoamine units, linked by beta 1-4 bonds into a linear polymer. The chemical structure of chitosan and that of cellulose are similar except that chitosan possesses a primary amino group, is positively charged, and can be easily modified. Chitosan is obtained from natural chitin after N-deacetylation and alkaline treatments. These are some of the general physico-chemical properties of chitosan: high molecular weight, solubility in most dilute acidic solutions, insolubility at pH's above 6,5, high charge density (positive), compatibility with strong cationics, ability to form clear aqueous solutions with excellent heat and shear stability, excellent flocculent characteristics, availability in low to extra-high viscosity grades (Vanson CIE).

The promising perspectives of chitosan use have led an engineering team of MIT (Murcott and Harleman, 1992) to realise extensive work on this subject. Their recent experimental results have shown that chitosan performs well both as a primary coagulant and a coagulant aid/flocculent aid in metal removal. Chitosan (4 to 6 mg/L) as primary coagulant successfully removed greater than 88% of the zinc, copper, aluminium, chromium, and iron in sanitary wastewater. Chitosan and bentonite perform very well in terms of turbidity and colour removal under cold and hot conditions, and do not decrease pH. Besides this study done by Murcott and Harleman, no research has been conducted on the potential use of chitosan as a primary coagulant or flocculent aid in eliminating metals from wastewater, particularly copper, by the coagulation-flocculation process. Murcott and Harlemann (1992) found that chitosan acts very effectively within a limited pH range, like other cationic polymers. An excess chitosan dose will have a negative effect on coagulation. When a metal salt is used as a primary coagulant, its effectiveness increases constantly until it reaches a steady state. In general, the optimal concentration is the lowest one necessary to reach the desired goal. So there is a small range where using a cationic polymer as a primary coagulant is very effective.

The main objective of the present experimental research was to verify if chitosan acts as a primary coagulant in water treatment and to demonstrate the potential and viability of chitosan in the elimination of copper (Cu^{2+}) and turbidity from wastewater produced by various industrial and urban activities. The experimental results were used to explain the reactivity of chitosan with metals (copper and zinc) and its important effect on the quality of treated water. In common with other chemical coagulants, the performance of chitosan was evaluated through jar tests, an effective tool for comparing alternate chemical types, dosages, and mixing regimes. The effectiveness of chitosan as a main coagulant for the removal of copper and turbidity was tested on various drinking water/ industrial wastewater mixtures, on drinking water/ sanitary sewage mixtures, and on drinking water mixed with clay (a bentonite suspension at different concentrations). In addition, the effect of the turbidity , the bentonite concentration, the pH, the copper concentration, the ionic force created by the addition of an electrolyte ($CaCl_2$), the anionic polymer (Pam 703 or Percol 727), and the type of chitosan were studied. A comparison with alum was made. The industrial wastewater and the sanitary sewage were respectively from the siderurgical industry and a municipal wastewater treatment plant.

2. Experimental Section

2.1 Material and Analytical Methods

Coagulation-flocculation-sedimentation experiments were conducted in the laboratory in 2-L beakers with a conic bottom using a conventional jar test apparatus (Phipps & Bird). An atomic absorption spectrophotometer (Varian, AA-975 model) equipped with an acetylene-air burner for the copper and the zinc was used throughout the measurements of the residual concentrations of metals in the test batch. After coagulation-flocculation-sedimentation, the samples were acidified immediately with nitric acid (100%) at a pH < 2 and kept in the refrigerator. Then, they were digested for two hours on a heating plate at a temperature of approximately 100°C before being analysed by atomic absorption. A pH-meter (Accumet 915 model), a turbidimeter (John Meunier, 2100P Hach model) were used to measure the initial and final pH and turbidity of the wastewater batch solution. All the analytical methods employed for the measured parameters were realised in accordance with the 19th edition of Standard Methods for the Examination of Water and Wastewater (APHA et al., 1995).

2.2 Coagulants, Flocculent Polymers, and Other Products

The chitosan extracted from carapace crab shells was commercially available in the form of yellowish flakes from Amersham Life Science Inc. and in the form of fine powder from Vanson Chemical. The alum used as the other coagulant, the bentonite used as the coagulant aid, and the copper and zinc standards were

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commercially available from Anachemia. The flocculent polymers Percol 727 and Pam 703 came from Allied Colloid. The other products from Anachemia used in the experiments were the linoleic acid, crystal phenol and calcium chloride. A solution of 150 mg/L of kerosene was also used for a batch flocculation experiment.

2.3 Operating Procedures

A series of 2L beakers was agitated identically. The reagents were first mixed rapidly at 200 rpm for 4 to 5 minutes; then the flocculation regime was realised at a slower speed at 40 rpm for 10 minutes. Finally, the mixing solution was left to rest in order to enhance the sedimentation; then the floating was collected after six minutes and visually appreciated. A constant floating volume of 400-500 mL was taken immediately after the coagulation-flocculation-sedimentation regime experiments from each 2L-beaker. The prises were purged in order to get rid of any kind of impurities before proceeding to sample clear water. Turbidity, total alkalinity, pH, and copper concentration were measured on all the samples before and after the coagulation-flocculation-sedimentation regime. For each coagulation-flocculation experiment, a blank experiment was realised under the same experimental conditions. When the agitation stopped, the propellers were removed rapidly in order not to obstruct the sedimentation of the aggregates. The mixing regime and the temperature (20-25°C) were kept constant for all the experiments. The alum and the Pam 703 concentrations added in all the experiments were fixed at 7 and 0.4 mg/L respectively.

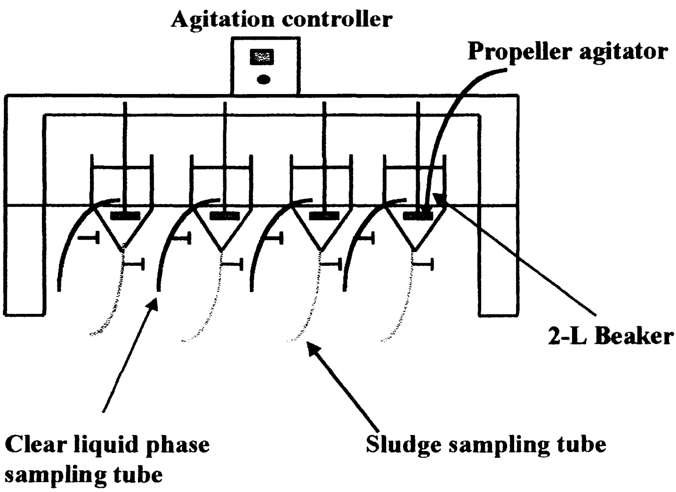

Figure 1: Experimental set-up

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3. Results and Discussion

Figure 2 shows the degree of copper removal by chitosan achieved in drinking water mixed with sanitary sewage and in drinking water mixed with industrial wastewater at a proportion of 25 %. The results show that chitosan is superior to alum (94% Vs 58.8%) when used as a primary coagulant in a mixture of drinking water with industrial wastewater at a proportion of 25%. However, alum eliminates copper more effectively from drinking water mixed with sanitary sewage. With regard to eliminating copper, no significant effects were observed when bentonite was added to drinking water mixed with industrial wastewater. Also, the injection of Pam 703 into the mixtures did not enhance the elimination of copper and turbidity because of the degree of turbidity of the water. According to these observations, chitosan has a greater affinity than alum for the type of particles found in industrial wastewater.

In this case, the COD of the industrial wastewater was the same as the COD of the sanitary sewage, but the suspended matters in the industrial wastewater were inferior to those in the sanitary sewage. The major difference between the percentage of copper elimination achieved in the drinking water/industrial wastewater mixture and that achieved in the drinking water/sanitary sewage mixture is explained by the type of organic particulate present in the industrial wastewater and the high degree of neutralisation in industrial wastewater. The turbidity in the drinking water mixed with industrial wastewater also plays an important role in the interaction between copper and chitosan, which is not the case for the drinking water mixed with sanitary sewage. Water treatment is more difficult when water has few colloids and low alkalinity.

Figure 3 shows the degree of copper and turbidity removal for drinking water/industrial wastewater and drinking water/bentonite mixtures at different proportions as a function of the initial turbidity. The initial turbidities of these two kinds of mixtures were equivalent. 40 mg/L of chitosan eliminated turbidity and particularly copper very effectively from drinking water that was mixed with industrial wastewater at proportions of 25, 35, and 47% (47, 65, and 99 Utn). The degree of copper elimination was 94, 100, and 100%, which is exceptional, and the degree of turbidity removal was also excellent: 91, 97, and 99% respectively. On the other hand, for similar turbidities with a drinking water/bentonite mixture at concentrations of 160, 200, and 260 mg/L (53, 71, and 92 Utn), the degree of copper removal was only 49, 58, and 70%. These results confirm the importance of the particle type in the industrial wastewater. For an initial turbidity mixture of 50 Utn, the chitosan eliminated much more copper and turbidity from the drinking water/industrial wastewater compared with the drinking water/bentonite mixture. However, for turbidities inferior to 50 Utn, the degree of removal of turbidity achieved by chitosan was superior in the drinking water/bentonite mixture. The aggregates formed during the flocculation regime with the drinking water/industrial wastewater mixture were the most remarkable. The sludge obtained after sedimentation was composed of bunk layers with distinct colours.

Figure 4 shows the degree of copper and turbidity removal achieved by chitosan as a function of the bentonite concentration (20 to 1000 mg/L) in drinking water with a pH from 6,67 to 6,95. Copper removal efficiency increases with the initial bentonite concentration in drinking water. The removal of copper becomes significant with a bentonite concentration of 160 mg/L (53 Utn), which corresponds to 49% and more. For a bentonite concentration of 1000 mg/L (538 Utn), the elimination of turbidity is complete. The same figure shows a continuous increase in the degree of turbidity removal achieved by chitosan as a function of the bentonite concentration. With a bentonite concentration of 200 mg/L (71 Utn), the turbitidy removal was the same (94%).

Figure 5 shows the removal of copper and turbidity as a function of the chitosan concentration for two drinking water/bentonite mixtures with 30 and 260 mg/L bentonite concentrations and with a copper concentration of 4 mg/L. Within a small concentration range, chitosan was found to eliminate turbidity and especially copper from drinking water containing 30 and 260 mg/L of bentonite and 4 mg/L of copper. The optimum copper and turbidity concentration was the concentration at the peak of the performance curve. 1.5 and 5 mg/L of chitosan for a drinking water/bentonite (30 mg/L) mixture; 40 and 2.5 mg/L of chitosan for a drinking water/bentonite (260 mg/L) mixture. This tendency was completely different in the experiments with 30 mg/L of copper; in the latter case, the elimination of copper and turbidity decreased as the chitosan concentration increased. Chitosan proved to be ineffective for a treating water with 30 mg/L of copper added as a salt, $CuSO_4 \bullet 5H20$, especially in the case of drinking water containing only 30 mg/L of bentonite; this result can be explained by the high ionic charge in the drinking water compared to the much smaller charge of the bentonite solution. This high ionic charge destroyed the electrostatic equilibrium of the solution and resulted in an abrupt change of zeta potential.

Bentonite is an ideal colloidal particle for increasing the efficiency of chitosan in removing copper and turbidity from drinking water. The elimination of copper is higher for water with high pHs and for water containing a great deal of suspended matter. In spite of their different viscosity in solution, the two types of chitosan used eliminated copper and turbidity with the same efficiency. The addition of an adequate concentration of electrolyte ($CaCl_2$) enhanced the elimination of copper in comparison with the experiment without the electrolyte. The degree of removal of zinc achieved by chitosan and by alum was inferior to the degree of removal of copper under the same conditions for drinking water mixed with 260 mg/L of bentonite; this result was probably obtained because the zinc (Zn^{2+}) added was in a metallic ion form. Because of their chemical structure, the phenol and the linoleic acid in the water interacted positively with the chitosan by forming solid hydrogen bonds, thus eliminating the copper. Chitosan used as a primary coagulant effectively eliminated 97 % of the COD from drinking water containing 2.5% of rinse water from the plastic and adhesive industry. Chitosan proved to have an important chemical affinity with a kerosene suspension, eliminating 65% of its turbidity. However, chitosan showed an efficiency comparable to that of alum at a smaller concentration for the experiment performed on drinking water containing 5% of industrial wastewater.

The large difference between the copper elimination achieved in drinking water/industrial wastewater, drinking water/sanitary sewage, and drinking water/bentonite mixtures is explained by the high COD and the high degree of neutralisation in industrial wastewater, as well as by the presence of fatty acids, resinic acids, and phenolic compounds not present in the other mixtures.

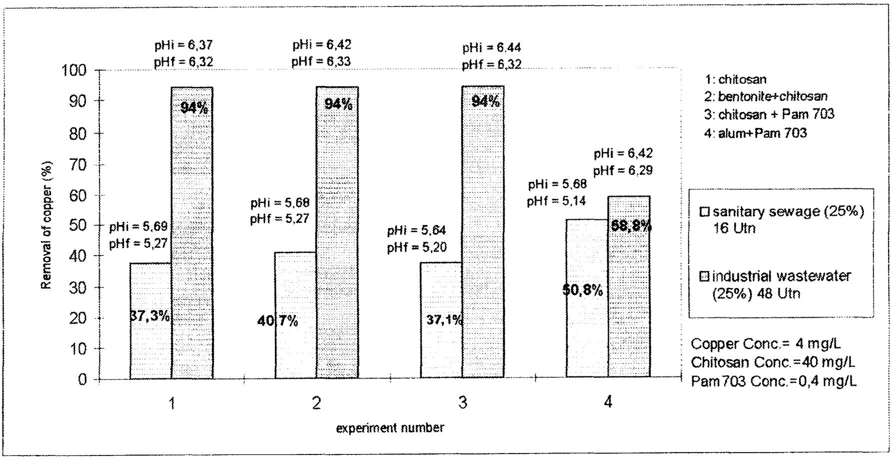

Figure 2: Degree of copper removal achieved by chitosan in drinking water/sanitary sewage and drinking water/industrial wastewater mixtures.

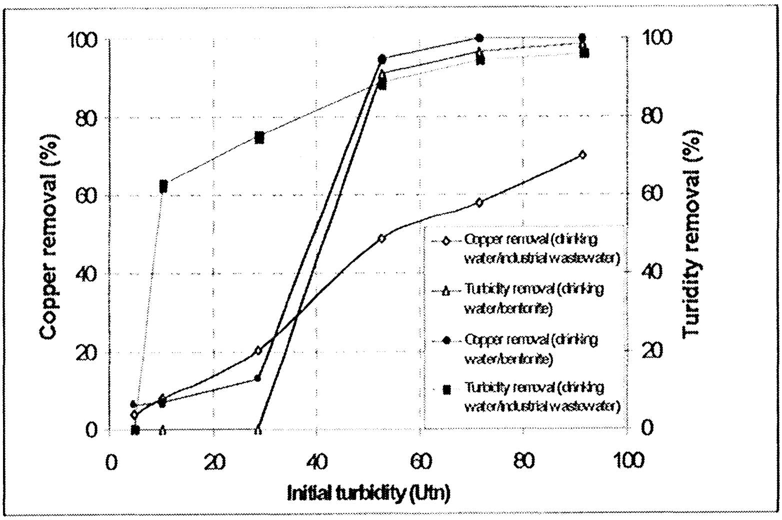

Figure 3: Effect of initial turbidity on copper and turbidity removal for two different drinking water mixtures.

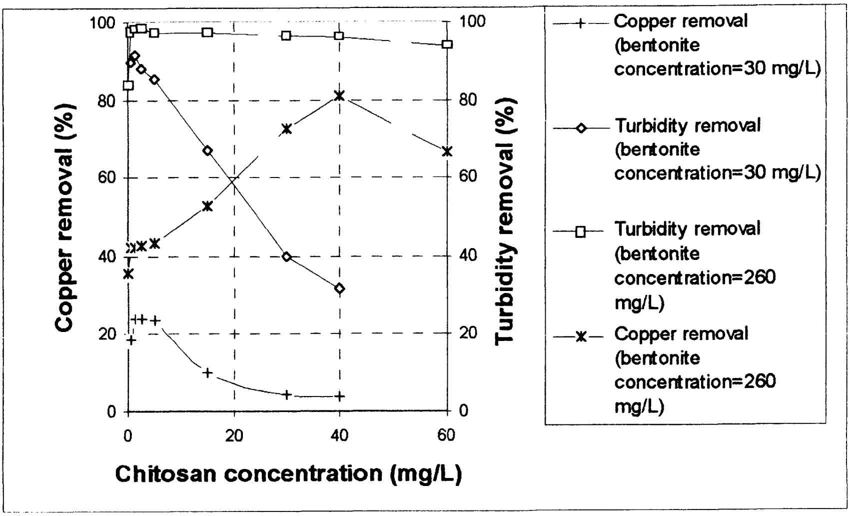

Figure 4: Influence of the degree of bentonite concentration and the initial turbidity on the degree of copper and turbidity removal achieved by chitosan in drinking water.

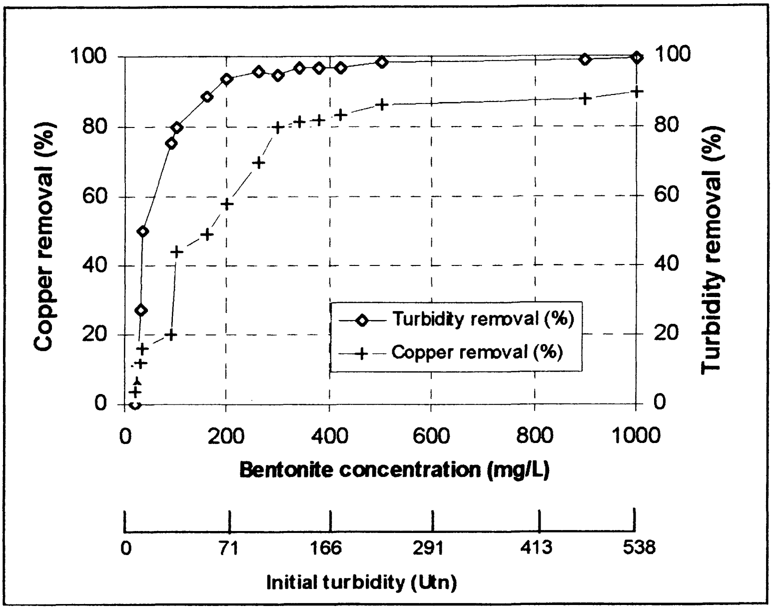

Figure 5: Influence of the chitosan concentration on the degree of copper and turbidity removal for two drinking water/bentonite mixtures.

4 Conclusion

Chitosan is competitive compared with alum: it is not toxic, it is biodegradable, it consumes less alkalinity, it produces less sludge, and it can be regenerated. Given its effectiveness in cold water, chitosan may be used in nordic regions like Canada. Chitosan could also be used to recuperate precious metals in the electroplating industry and for primary and tertiary treatments of wastewaters. The research carried out in the laboratory demonstrates that coagulation-flocculation with chitosan as a primary coagulant is an effective way to eliminate copper and turbidity. In this process, the type of particles, the particle concentration (SS), the turbidity, the pH, the alkalinity, the concentration of chitosan, the addition of an electrolyte, and the nature of the organic matter in the water are all determinant. Testing the process on a pilot scale would lead to a definitive conclusion regarding the efficacy and profitability of chitosan as a primary coagulant for treating water in the batch treatment process.

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