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EFFECTIVENESS OF CHITOSAN AS NATURAL COAGULANT AID IN TREATING TURBID WATERS

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ABSTRACT

During the last decade, there has been a concern about the relation between aluminum residuals in treated water and Alzheimer disease, and more interest has been considered on the development of natural coagulants such as chitosan. Chitosan, a natural linear biopolyaminosaccharide, is obtained by alkaline deacetylation of chitin. The present study was aimed to investigate the effects of alum as coagulant in conjunction with chitosan as coagulant aid on the removal of turbidity, hardness and *Escherichia coli* from water. A conventional jar test apparatus was employed for the tests. The optimum pH was observed between 7 to 7.5 for all turbidities. The optimum doses of alum and chitosan when used in conjunction, were 10mg/L and 1mg/L, 5mg/L and 0.5mg/L, and 5mg/L and 0.5mg/L in low, medium and high turbidities, respectively. Turbidity removal efficiency was resulted between %74.3 to %98.2 by alum in conjunction with chitosan. Residual Al^{+3} in treated water was less than 0.2 mg/L, meeting the international guidelines. The results showed that turbidity decrease provided also a primary *Escherichia coli* reduction of 2-4 log units within the first 1 to 2 hr of treatment. Hardness removal efficiency decreased when the total hardness increased from 102 to 476mg/L as $CaCO_3$. At low initial turbidity, chitosan showed marginally better performance on hardness, especially at the ranges of 100 to 210 mg/L as $CaCO_3$. In conclusion, coagulant aid showed a useful method for coagulation process. By using natural coagulants, considerable savings in chemicals and sludge handling cost may be achieved.

Key words: Chitosan, Coagulant aid, Hardness removal, Escherichia .coli removal, Water treatment

INTRODUCTION

The production of potable water from most raw water sources usually entails the use of a coagulation/flocculation stage to remove turbidity in the form of suspended and colloidal material. This process plays a major role in surface water treatment by reducing turbidity, bacteria, algae, color, organic compounds and clay particles. The presence of suspended particles would clog filters or impair disinfection process, thereby dramatically minimizing the risk of waterborne diseases (Mackenzie and Cornwell, 1991; Fatoki and Ogunfowokan, 2002).

With aluminum salts, there is a concern about residuals in the treated water and Alzheimer disease and, whilst iron salts are cheaper options, the cost of any imported chemicals can be a serious problem for developing countries. Thus, in recent years, there has been considerable interest in the development of natural coagulants such as chitosan. By using natural coagulants, considerable savings in chemicals and sludge handling cost may be achieved (Diaz *et al*., 1999).

In recent years, chitosan and Moringa Oleifera have been applied as coagulant in water treatment (Folkard *et al*., 2000). Chitosan, a natural linear biopolyaminosaccharide, is obtained by alkaline deacetylation of chitin, which is the principal component of protective cuticles of crustaceans such as crabs, shrimps, prawns, lobsters, and cell

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walls of some fungi such as aspergillus and mucor. Chitosan is a weak base and is insoluble in water and in organic solvent. However, it is soluble in dilute aqueous acidic solutions (pH<6.5), which can convert glucosamine units into soluble form $R–NH^{+}_{3}$.Chitosan is inexpensive, biodegradable and nontoxic for mammals(Qin *et al*.,2006).

Chitosan molecule has the ability to interact with bacterial surface and is adsorbed on the surface of the cells and stack on the microbial cell surface and forming impervious layer around the cell, leading to the block of the channels (Qin *et al*.,2006).

There are many studies on the removal of turbidity, bacteria, parasite eggs such as Ascaris and Fasciola hepatica eggs from drinking water by using roughing filters and sand filtration (Tabatabaei *et al*., 2007; Nouri *et al*., 2008). In addition, chitosan has been studied for use as a coagulant or flocculant for a wide variety of suspensions including silt in river water to microorganisms. The effective coagulation for turbidity removal was achieved in tap water when using much lower doses of chitosan than would be required for complete charge neutralization of the bentonite (Roussy *et al*., 2005). The documents and practical experiences with the effects of alum in conjunction with chitosan on turbidity, bacteria and hardness in water treatment have not been reported. Thus, the objective of this experimental study was to evaluate turbidity, hardness and Escherichia.coli removal by alum in conjunction with chitosan in turbid waters.

MATERIALS AND METHODS

Preparation of synthetic water

10 g of kaolin was added to 1 L of distilled water. The suspension was stirred slowly at 20 rpm for 1 hr for uniform dispersion of kaolin particle. The suspension was then permitted to stand for 24 hr to allow for complete hydration of the kaolin. This suspension was used as the stock solution for the preparation of water samples of varying turbidities for the coagulation tests. Three groups of turbidities were considered, namely; low turbidity (10–20 NTU), medium turbidity (100–120 NTU) and high turbidity (200-220 NTU). According to Table 1, alkalinity and hardness [$MgSO_4.7H_2O$ (magnesium hardness) and $CaCl_2.5H_2O$(calcium hardness)] were added to water samples to produce water similar to natural water(Katayon *et al*., 2006).

Preparation of alum solution

Alum solution was prepared by dissolving 10g Alum ($Al_2(SO4)_3.18H_2O$) in distilled water and the solution volume was increased to 1 L. Each 1 mL of this stock solution was equal 10 mg/L when added to 1 L of water to be tested.

Preparation of chitosan solution

Chitosan (Deactylated chitin; poly- [1- 4] - β- glucosamine) with minimum %85 deactyl prepared from crab shells was obtained from GMA Chemical Company. It was in the form of a pale brown powder soluble in dilute acetic and hydrochloric acids. Chitosan powder(100 mg) was accurately weighed into a glass beaker, mixed with 10 mL of 0.1M HCl solution, and kept aside for about one hour to dissolve. It was then diluted to 100 mL with distilled water to obtain a solution containing 1.0 mg chitosan per mL of solution. As it was observed that chitosan solutions in acid undergo some change in properties over a period, the solutions were prepared freshly before each set of experiments (Divakaran and Pillai, 2002). HCl was considered to be a better choice for chitosan preparation from the viewpoint of organic input(Vaidya and Bulusu,1984).

Enumeration of Escherichia coli (E.coli)

Escherichia coli (ATCC1339) was provided from A.T.T.C (American Type Culture Collection). It was used as the test bacteria in all artificial contamination experiments. It was grown using nutrient agar culture into incubator at 37°C for 24 hr and kept at 4°C. Confirmation of *E.coli* was performed by subculturing into EMB agar as selective culture by streak plate method. Enumeration of *E.coli* was carried out with most probable number (MPN index) technique (APHA, 2005).

Experimental procedure

A conventional jar test apparatus, the Phipps & Bird Six-Paddle Stirrer, was employed for the tests, with six 2-L square plexiglas jars, called as Gator Jars (ASTM, 1995; Kawamura, 2000).

All tests were carried out with 1L samples in 2L beakers. After determining of optimum mixing intensity and duration, the experiments were run by using synthetic water having low, medium and high turbidities. pH was adjusted with 0.1 M H_2SO_4 and 0.1M NaOH. Alum suspensions were added to the samples at a flash mixing speed of 100 rpm. After one minute, the desired dose of chitosan as natural coagulant aid was added. The stirring speed was then lowered to 40 rpm for 7.5 min and 20 rpm for 7.5 min in slow mixing. At the end of the stirring period, the beakers were removed slowly and the flocs were allowed to settle for 20 min. The samples were taken from the top 4 in of the suspension. Turbidity and hardness measurements were conducted using turbidimeter (HACH, 2100P) and EDTA titrimetric Method (2340C), respectively. Residual Al^{+3} was measured by Eriochrome Cyanine R Method (APHA, AWWA, WPCF, 2005).

RESULTS

Jar tests were conducted to determine optimum pH values and dosage of alum. The results are presented in Fig. 1. Based on this figure, it was seen that alum produces appreciable reduction of turbidity only between pH 7-7.5 and the residual turbidity decreased to < 5 NTU. In order to determine optimum dosage of alum, experiments were conducted by changing the dosage of alum between 5 to 50 mg/L on synthetic water having initial turbidities ranging from 10 to 220 NTU. The results of this part are shown in Fig. 2. As shown in Fig. 2, optimum doses of alum for three different initial turbidities were 20, 40, and 20 mg/L, respectively.

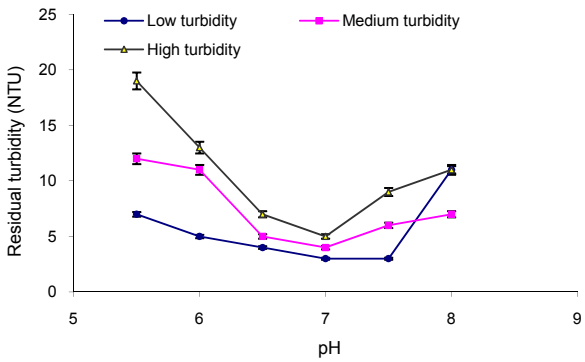


Fig1: Determination of optimum pH for alum

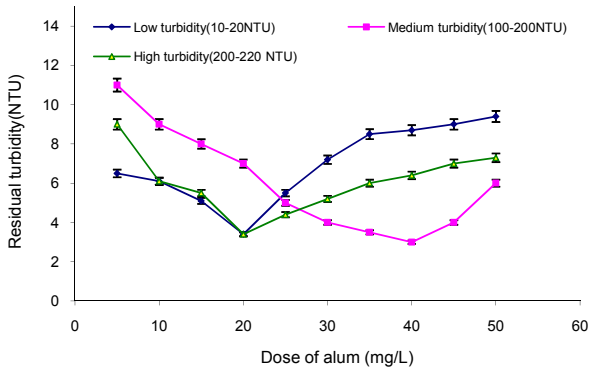
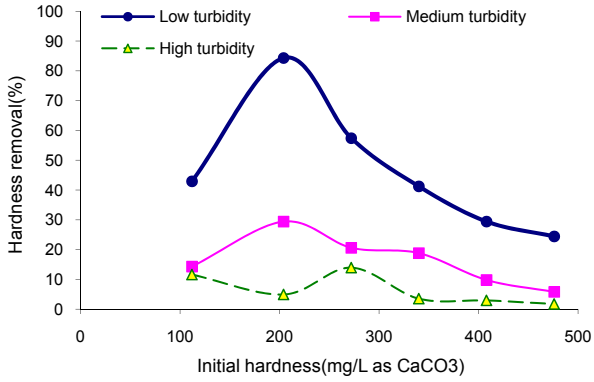


Fig2 : Determination of optimum dose of alum in different turbidities

After the jar tests, studies were carried out to estimate residual Al^{+3} levels in treated water for different turbidities by standard method. Results indicated that in optimum conditions, residual Al^{+3} for low, medium, and high turbidities were 1.3, 1.6, and 1 mg/L, respectively after jar tests. The performances of chitosan in different turbidities are shown in Tables 2 to 4. According to the Tables, the optimum dose of alum and chitosan when used in conjunction, were 10mg/L and 1mg/L, 5mg/L and 0.5mg/L in low and medium turbidities and for high turbidity, it was 5mg/L and 0.5mg/L , respectively. The turbidity removal efficiency in low, medium and high turbidities were obtained about % 74.3, %96 and %98.2, respectively. In blank samples, the percentage of turbidity removal was %5.8 , %48.6 and %18 in low, medium and high turbid water, respectively. Addition of chitosan contributed to TOC increase in the turbid water samples from zero(blank) to 1.2 mg/L , 0.8mg/L and 0.8mg/L in low , medium and high turbidities, respectively. Coagulation processes decreased the amount of total organic carbon in water samples as 0.7mg/L, 0.5mg/L and 0.7mg/L in low, medium and high turbidities, respectively.

The effects of coagulation process on hardness are presented in Fig. 3. It is observed that for varying levels of initial hardness as 100 to 500 mg/L as $CaCO_3$, increasing turbidity from 10 NTU to 220 NTU resulted in significant decrease of hardness removal which reached to %1.7. The maximum of hardness removal was obtained as %84.3 by chitosan in low turbid water with initial hardness about 204 mg/L as $CaCO_3$. Several experiments

were carried out to determine the comparative performance of chitosan on *E.coli* in different turbidities according to Table 5. The number of *E.coli* decreased during 24 hr in all of turbidities. The removal efficiency of *E.coli* were %99.8 , %99.9 and %99 in low, medium and high turbid water after 1 hr(the end of jar test), respectively. The conclusive evidence was found for the influence of chitosan in increasing the number of *E.coli*. The regrowth of *E.coli* was not observed in experiments after 24 hr (Table 5).



DISCUSSION

The effectiveness of alum, commonly used as a coagulant, is severely affected by low or high pH. In optimum conditions, the white flocs were large and rigid, and settled well in less than 10 min. This finding is in agreement with other studies at optimum pH (Lin *et al.*, 1971; Ebeling *et al.*, 2003). The optimum pH was between 7-7.5 and was similar to the obtained results by Divakaran (Divakaran and Pillai, 2002).

For clays with a low exchange capacity like kaolinites, the flocculation mechanism by sweeping dominates when the pH is in the range of 7 to 8.5 (Franceschi *et al*., 2002). According to Fig. 2, alum resulted in producing treated water with turbidities less than 5 NTU in all ranges of turbidity. At high turbidity, a significant improvement in residual water turbidity was observed with increased settling times. The supernatant was clear after about 20 min settling. Flocs were larger and settling time was lower. The results showed that above optimum dosage, the suspensions showed a tendency to restabilize.

WHO recommends that if turbidity is more than 5 NTU, some treatment is necessary to remove the turbidity before the water can be effectively disinfected with chlorine (WHO, 1996). The use of alum as a coagulant for water treatment often leads to higher concentrations of aluminum in the treated water than in the raw water itself. There is now abundant evidence that aluminum may cause adverse effects on the nervous system (Health Protection Branch of Health, Canada, 2008). In a US.EPA survey of 186 water utilities, it was found that after coagulation with Al^{+3} salts, the Al^{+3} concentration in the treated water varied from 0.01 to 2.37 mg/L(Srinivasan,1999). US.EPA promulgated a secondary maximum contaminant level range of 0.05 to 0.2 mg/L for residual Al^{+3} (US Environmental Protection Agency, 2003). Our results did not meet the USEPA standards and residual$Al^{+3}$was higher than 0.2 mg/L. In order to decrease the residual Al^{+3}concentration in treated water, and possible adverse effects of aluminum in drinking water on human health, chitosan as coagulant aid in conjunction with alum may be used.

The results of this study indicated that coagulation aid should be added one minute after addition of alum. Poor performance was obtained when coagulant aid and alum were added simultaneously. This was in agreement with studies done on other natural polyelectrolytes as coagulant aid (Bina, 1995). The use of chitosan as coagulant aid in flocculation process decreased alum dose and the residual turbidity dropped to 3.9 NTU without filtration, irrespective of initial turbidity (Tables 2, 3 and 4). These results agree well with Iran drinking water standards (Iranian Institute of Standard and Industrial Researches, 1993). There was an improvement in the floc size when chitosan was used as a coagulant aid in conjunction with alum as compared to either chitosan or alum alone. The results clearly showed that the dosage of coagulant and coagulant aid decreased with increasing turbidity. In addition, chitosan significantly reduced the required dosage of alum between 50 to 87.5%, thereby reducing costs of treatment.

The results showed that the performance of chitosan in different turbidities were significant difference in turbidity removal ($p<0.01$) and the values of the residual Al^{+3} in low, medium, and

high turbidities were not more than 0.2 mg/L and meets present standards(USEPA). Chitosan did not change pH in water treatment process.

It was also found that chitosan did not affect the alkalinity. The high content of amine groups in chitosan provides cationic charge at acidic pH and can destabilize colloidal suspension to promote the growth of large, rapid-settling floc that can then flocculate (Roussy *et al*., 2005). Because it is a long –chain polymer with positive charges at natural water pH, it can effectively coagulate natural particulate and colloidal materials,which are negatively charged, through adsorption, charge neutralization, inter-particle bridging as well as hydrophobic flocculation (Li and Kegley, 2005).

The addition of chitosan contributes toTOC increase in the solution that could affect the coagulation mechanism.Chitosan reduced TOC values to < 00.8 mg/L, which was lower than controllevel.The amount of TOC from chitosan as coagulant was less than 4 mg/L after coagulation (Haung *et al*, 2000). Taking into account the low dosage of chitosan in these experiments (systematically less than 1 mg/L), the amount of organic carbon introduced remained was low enough (less than 0.8 mg/L) to make its contribution negligible on the coagulation-flocculation performance. However, no clear correlation was found between the TOC level of the water samples and their flocculation behavior. The results showed that chitosan could be used as natural coagulant aid for drinking water treatment with the lowest risks of organic release.

Based on the results shown in Fig. 3, chitosan has not considerable potential to be used in the treatment of hard waters, especially in medium and high turbidities. Statistical analysis showed significant differences between hardness removal in low turbidity by chitosan with medium and high turbidities ($p<0.01$). At low initial turbidity coagulation, performance of alum in conjunction with chitosan was much more significant than higher initial turbidity, especially at ranges of hardness between 100 to 210 mg/L as $CaCO_3$. It can be seen that the removal of hardness decreased with increasing hardness values. The presence of bivalent cations such as Ca^{+2} and Mg^{+2} increased the ion strength of solution and the destabilization of colloidal particles (Okuda *et al*., 2001).

E.coli is the best coliform indicator of fecal contamination from human and animal wastes. *E.coli* presence is more representative of fecal pollution because it is present in higher numbers in fecal material and generally not elsewhere in the environment (Tyagi *et al*., 2006). Results showed that the reduction in the number of *E.coli* increases with increasing time. Rapid reduction of *E.coli* was observed in first 1 hour of the experiment. A greater percentage of *E.coli* was eliminated in higher turbidities (in higher turbidities, removal efficiency reached to %99.99, Table 5).The aggregation and, thus, removal of *E.coli* was directly proportional to the concentration of particles in the suspension. Chitosan as natural coagulant aid showed antibacterial effects of 2 to 4 log reductions. Antimicrobial effects of water-insoluble chitosan were attributed to both its flocculation and bactericidal activities. A bridging mechanism has been reported for bacterial coagulation by chitosan (Roussy, 2005).

Chitosan molecules can stack on the microbial cell surface, thereby forming an impervious layer around the cell that blocks the channels, which are crucial for living cells (Qin, 2006). On the other hand, cell reduction in microorganisms, such as *E.coli*, occurred without noticeable cell aggregation by chitosan. This indicates that flocculation was not the only mechanism by which microbial reduction occurred. It was found when samples were stored during 24 hours; regrowth of *E.coli* was not observed in all turbidities. It should be noted that the test water contained no nutrient to support regrowth of *E.coli* and chitosan is not a nutrient source for it. Another experiment was designed to check the effect of alum alone. Regrowth of *E.coli* was not observed for unaided alum after 24 hours. The number of *E.coli* after resuspension of sediment reached to the initial numbers after 24 hours, and showed that it can not be inactivated by alum. Such findings has been previously reported by Bina (Bina, 1995).

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