RESEARCHS / INVESTIGACIÓN

Effectiveness of chitosan as natural coagulant in treating turbid waters

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Abstract: Aluminum, Lime and iron coagulants are commonly used in most industries for many decades to coagulate particles in surface water also removing turbidity from the water prior to flocculation, sedimentation or filtration. Although effective, inorganic coagulants have several disadvantages, there has been a concern about the relation between aluminum residuals in treated water and Alzheimer disease and toxic effects of metallic coagulants on the aquatic environment. Hence nowadays, there has been great attention in the improvement of natural coagulants in treated water such as chitosan; chitosan is a natural linear cellulose-like copolymer of glucosamine and N-acetyl-glucosamine widely distributed in nature. The present study was aimed to investigate the effects of chitosan on the removal of suspended solids (bentonite clay) from water. A series of batch flocculation tests with chitosan under different conditions was conducted. The results indicate that chitosan is a potent coagulant for bentonite suspension. Coagulation of chitosan showed efficiency of 96.9%. The coagulant performed well at concentration of 1g chitosan/100 ml water at PH=6.

Key words: Chitosan, coagulation, flocculation, bentonite, turbidity, water

Introduction

Water is a key substance in all natural and human activities, the production of potable water from rawest water sources usually use coagulation-flocculation techniques for removing turbidity in the form of suspended and colloidal materials.[1]. Coagulants are used that added to the water to withdraw the forces that stabilize the colloidal particles and causing the particles to suspend in the water [2]. Once the coagulant is introduced in the water the individual colloids must aggregate and grow bigger so that the impurities can be settled down at the bottom of the beaker and separated from the water suspension (as shown in table 1).

Some inorganic coagulants like Aluminum and iron are used in most industries, when aluminum is used as coagulant in water treatment, it can have caused several bad effect on human health such as intestinal constipation, loss of memory, convulsions, abdominal colic's, loss of energy and learning difficulties. In recent years, chitosan and moringa oleifera have been applied as coagulant in water treatment [4]. Chitosan is a derivative of chitin which naturally occurs in shells of crustaceans, fungi and insects. Chitosan is obtained from partial deacetylation of chitin which is removal of acetyl groups (-CH3CO) on N-acetyl glucosamine (GlcNAc) units of chitin polymer to reveal amino groups (-NH2) (as shown in Figure 1).

Coagulant Applications	Effective Characteristics	Natural Water Properties
Coagulants Extraction	Settling time	Alkalinity
Coagulants Solubility	Turbulence	Availability of Bacterias
Coagulants Dosage	Rapid Mixing	Presence of Elements (Cl, Na, Mn, Si, Fl, NH3, Fe)
Charge on Particles	Slow Mixing	Total dissolved solids
Basicity of a coagulant	Coagulant adds quantity	Suspended Solids
	Particles type	Temperature Turbidity Dissolved Oxygen

Table 1. Factors Affecting Coagulation

Various types of coagulants show potential application in treating water and wastewater. It ranges from chemical to non-chemical coagulant. The coagulant also could be synthetic material or natural coagulant with the properties of coagulant having +ve charge, these positive charge proteins would bind to the -ve charged particles in the solution that cause turbidity [3]. Coagulants normally in form of natural (as shown is Table 2) & inorganic (as in Table 3). Both coagulants aim to remove pollutant in form of physical (solids & turbidity) or chemical (BOD & COD).

Natural Coagulants	Turbidity
Cicer Aretinum	81.20%
Moringa Oleifera	82.02%
Cactus	78.54%

Table 2. Natural coagulants Efficiency

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Name	Advantages	Disadvantages
Aluminiumsulphate (Alum) Al2 (SO4)3. 18H2O	Easy to handle and apply; most commonly used; produces less sludge than lime; most effective between pH 6.5 and 7.5	Adds dissolved solids (salts) to waster; effective over a limited PH range.
Sodium Aluminate Na2Al2O4	Effective in hard waters; small dosage usually needed	Often used with alum; high cost; ineffective in soft waters
Polyaluminium Chloride (PAC) Al13(OH)20(SO)4.Cl15	In some applications, Floc, formed is more dense and faster settling than alum	Not commonly used; little full scale data compared to other aluminum derivatives
Ferric Sulfate Fe2(SO4)	Effective between pH 4-6 and 8.8-9.2	Ads dissolved solids(salts) to water; usually need to add alkalinity
Ferric Chloride FeCl3.6H2O	Effective between pH 4 and 11	Adds dissolved solids (salts) to water; consumes twice as much alkalinity as alum
Ferrous Sulfate (Copperas) FeSO4 .7H2O	Not as pH sensitive as lime	Ads dissolved solids(salts) to water; usually need to add alkalinity
Lime Ca(OH)2	Commonly used; very effective; may not add salts to effluent	pH dependent; produces large quantities of sludge; overdose can result in poor effluent quality

Table 3. Inorganic Coagulants: Advantages and Disadvantages

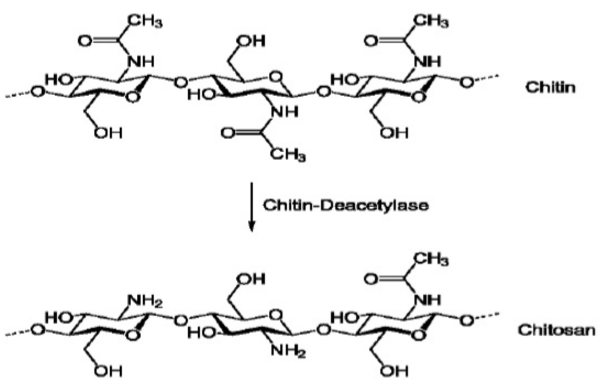

Figure 1: De-acetylation of chitin to obtain chitosan, acetyl group (-CH3CO) on acetyl glucosamine monomer on chitin chain is removed to reveal amino group (-NH2) becoming glucosamine monomer making chitosan.

It is a long chain carbohydrate that is non-soluble in water but dissolves in most acids, and contains positively charged moieties. Possessing properties such as non-toxicity, biocompatibility, and biodegradability, chitosan has been studied for its application in many sectors such as industrial wastewater treatment, pharmaceuticals, cosmetics, agriculture, and biomedical use. 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-NH3. Chitosan is inexpensive, and nontoxic for mammals [5]. 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 [5], in addition chitosan has been studied for use as a coagulant or flocculants in river water and in wastewater. In laboratory studies chitosan has been reported to perform well as a coagulant for removing Chlorella sp. In algal turbid water [6], removing turbidity from sea water [7], and for microalgae harvesting [8]. It has several industrial and commercial uses, can be recycled, and is an excellent chelating agent for many metals such as arsenic, molybdenum, cadmium, chromium, lead, and cobalt [9]. The effective coagulation for turbidity removal was achieved in tap water when using lower doses of chitosan required for complete charge neutralization of the bentonite [10].

The infrared (IR) absorption spectra of chitosan and chitin are presented in (figure 2). It can be observed that three types of absorption bands exist: the amide (I) bands of chitosan characterized by absorption at approximately 1655-1630 cm^{-1}, the amide (II) bands of chitin at approximately 1560 cm-1 and the absorption bands for -OH groups at 3450 cm^{-1} [11] and the presence of very reactive amino (-NH_2) and hydroxyl (-OH) groups in its backbone, which makes chitosan to be used as an effective adsorbent material for the removal of water pollutants. Anionic particles of bentonite are electrostatically attracted by the protonated amino groups of chitosan [12]. This reaction facilitates the neutralization of the anionic charges which can bind together and settle rapidly by the effect of gravity. The practical application of chitosan in terms of chitosan dose, PH, stirring and time effect. As water treatment coagulant is examined in the study presented here.

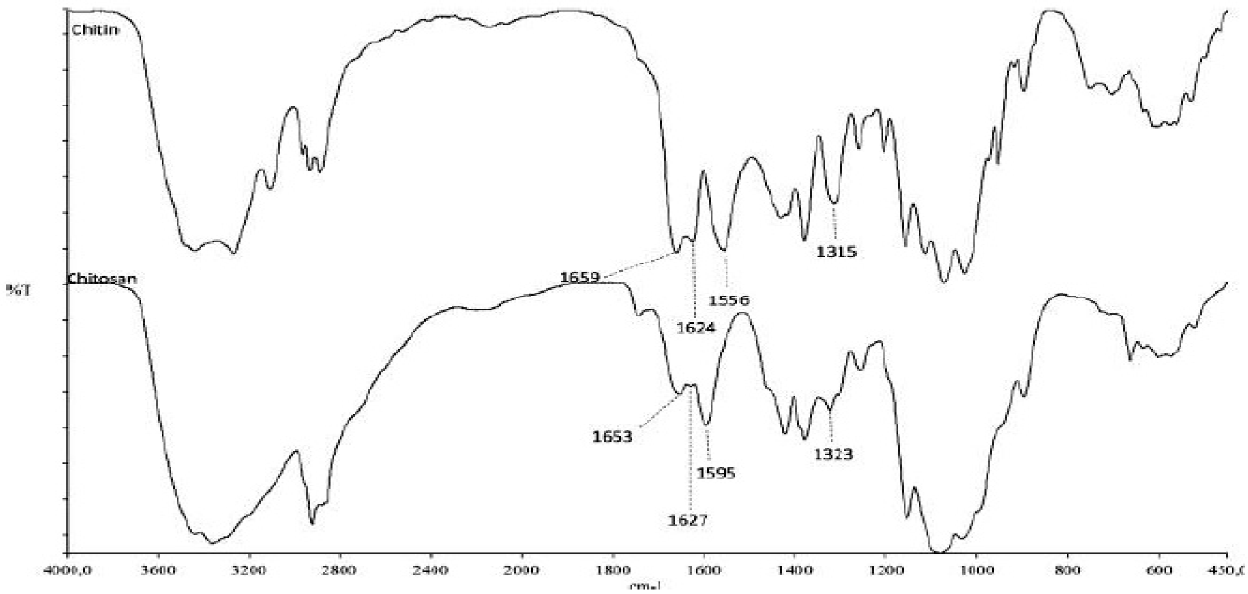

Figure 2: Infrared spectra of chitin (A) and chitosan (B) (12)

Materials and methods

Preparation of synthetic water

10 gm. of kaolinite was added to 1L of tap water. The suspension was stirred slowly at 20 rpm for 1hr for uniform dispersion of kaolinite particle. The suspension was then stand for 24hr. this suspension was used as the stock solution for the preparation of turbid water samples of varying turbidities. Original PH=7 and Temperature 30^{0}C. The PH was controlled by adding either strong acid (H_2SO_4) or strong base (NaOH). Turbidity of raw water was 1 NTU.

Preparation of chitosan solution

Chitosan (Deactylated chitin: poly-[1-4]-B-glucosamine). (C6H-11NO4) n with minimum 85% deactyl prepared from crab shells was obtained from ACROS ORGANICS Company. It was in the form of a pale brown powder soluble in dilute acetic acid hydrochloric acids. With molecular weight 100.000-300.000. Chitosan powder (5 mg) was weighed into a glass beaker, mixed with10mL of 0.1 M HCl solution, and kept for about one hour to dissolve. It was then diluted to 500 ml distilled water solution stirred at 100 rpm with a magnetic stirrer until the solution was completely dissolved. It was observed that chitosan solution in acid undergo some changes in properties over period; the solutions were prepared freshly before each set of experiments [13], Stock solution was stored at room temperature (25°C).

Test water

In this study, the test water (six beakers) was filled with 500ml synthetic water. Then kaolinite and chitosan were added (Coagulant was added with rapid mixing for 2 minutes at 100 rpm, slow mixing for 30 minutes at 30 rpm. The mixer is turned off and flocs are allowed to settle for 30 minute [14]. The samples were taken from the top 4 in of the suspension. Turbidity was measured on the settled water filtered through Whatman 40 (8um) filter paper of each beaker and then measured by Nephelometer, Turbidity becomes 5 NTU, and Hardness measurements were conducted by EDTA titrimetric Method. Six chemical water quality parameters were tested: PH, turbidity, Temperature, time, stirring, chemical dosage of chitosan. Water at PH 6 and PH 9 was compared with the standard test water control at neutral PH of 7.0. The PH was adjusted using 1M hydrochloric acid (HCl) and 1M sodium hydroxide (NaOH). For effects of turbidity level on chitosan coagulation, turbidity was set at 5 and 10,15,20,25 NTU compared to control water turbidity of 1 NTU and kaolinite was used as the turbidity source. Doses of chitosan were: 1,3,10 and 30 mg/L,

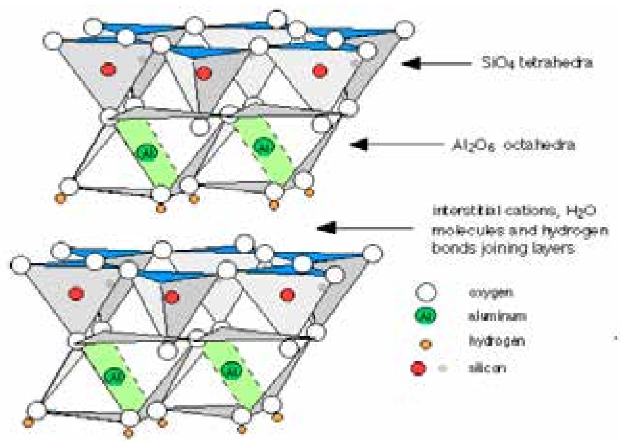

Figure 3: Kaolinite structure

Results and discussion

Optimal dosage of chitosan

We all agree about that The lowest turbidity in the suspension is the optimal dosage condition so at chitosan dose 1,3mg/L, kaolinite removals were high 96%, at chitosan dose above than 3mg/L, there was decrease (or) no removal of kaolinite turbidity by chitosan. Overall, kaolinite reductions were significantly lower as chitosan dose become higher.

Chitosan dose	Turbidity reduction %
1	96.9
3	96
10	60
30	43

Table 4. Relation between chitosan dose and turbidity reduction%

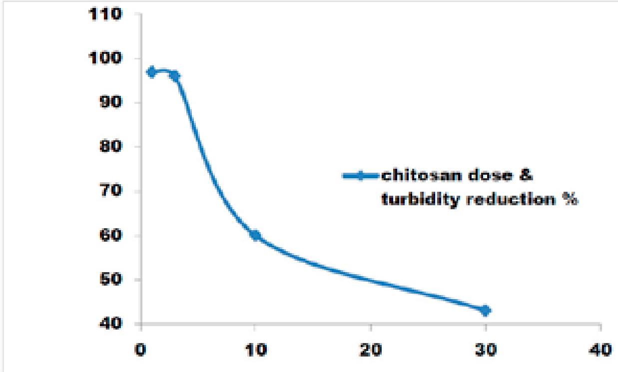

Figure 4. Relation between chitosan dose and turbidity reduction%

Effects of water PH on turbidity removal.

Effects of water PH on removal of kaolinite turbidity.

Kaolinite turbidity was (5, 5 NTU), temperature of the turbid water was (35° C), chitosan dosage (1g/L), stirring (300 rpm). As the PH was increased, chitosan was less effective as a coagulant on settled water turbidity [15]. The PH selected for optimum selected water turbidity removal was 5, 6,7,8,9. In the PH range of 5 to 7, the residual turbidities of supernatant can be reduced to less than 1 NTU. But at PH 6 lowest turbidity achieved 0.65 NTU. These results also indicate that the residual turbidities are increased at PH 8, 9.

Residual turbidity(NTU)	PH VALUE
0.95	5
0.65	6
0.85	7
1.5	8
4	9

Table 5. Relation between Turbidity and PH value

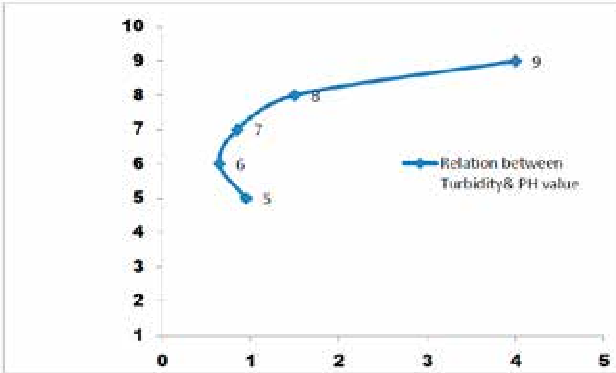

Figure 5. Relation between Turbidity and PH value

Effect of contact tine on turbidity removal.

Kaolinite turbidity was (5, 5 NTU), chitosan dosage (1g/L), stirring (300 rpm), PH= (6). Temperature (25°C). Time was the only factor that decreases turbidity gradually.

Turbidity removal (NTU)	Contact time(min)
7	5
2.5	10
2	15
1.8	20
1.3	25
1.3	30

Table 6. Relation between turbidity Removal and contact time (min)

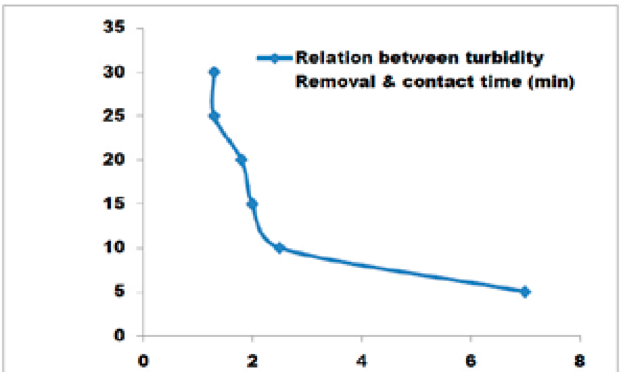

Figure 6. Relation between turbidity removal and contact time (min)

Effect of Temperature on turbidity removal.

Kaolinite turbidity was (5, 5 NTU), different temperature of the turbid water from (25 to 43° C) chitosan dosage (1g/L), stirring (300 rpm), PH= (6), time of the turbid water was (30 min). the influence of temperature on the rate of turbidity was rising at increasing temperature.

Turbidity removal %	Temperature(°C)
96.9	25
96.3	30
95.8	35
95.4	40

Table 7. Relation between turbidity removal (%) and Temperature (°C)

Conclusion

Overall, the results of this study provide evidence that Chitosan had significant effects on the efficiency of kaolinite turbidity reduction from test water; chitosan dose had significant effects on kaolinite turbidity reduction from test water. Only lower doses were needed for effective removal of kaolinite turbidity from water, with chitosan doses for 96.9% turbidity removal is 1gm/L. Higher chitosan dose was less effective and provided poor kaolinite turbidity removal than did lower doses which overdosing of chitosan can result in destabilization of a dispersion. The optimal conditions were determined on the basis of turbidity removal. In addition, the principal factors affecting coagulation were determined throughout the study, including optimal coagulant dosage, Time, PH and Temperature. The optimum PH found for coagulation to remove settled water turbidity was 6.0, sedimentation and paper filtration lowered treated water turbidity 96.9% for chitosan.

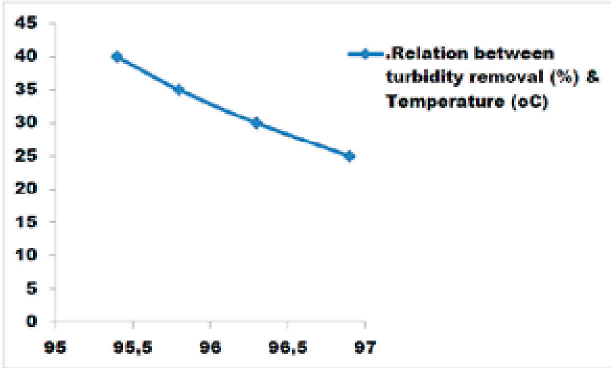

Figure 7. Relation between turbidity removal (%) and Temperature (°C)

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