Use of chitosan in coagulation flocculation of raw water of Keddara and Beni Amrane dams

Hassiba Zemmouri, Slimane Kadouche, Hakim Lounici, Madjid Hadioui and Nabil Mameri

ABSTRACT

The effectiveness of chitosan as a coagulant flocculant in surface water treatment has been studied. Tests were carried out in laboratory on treated and raw water. The treated water was mixed with high and low concentrations of bentonite to simulate turbid water. This treated water provides from water treatment plant of Algiers (Boudouaou site) which is supplied by both dams of Keddara and Beni Amrane. The raw water comes directly from these two dams. Chitosan with 85% degree of deacetylation and derived from crab chitin has been used. The performance of coagulation flocculation process has been assessed by measuring the supernatant turbidity for different doses of chitosan, initial turbidity, water quality and pH. The obtained results show that chitosan can be used in a large pH range. Chitosan is effective for coagulation of bentonite suspension and for raw water with high initial turbidity. Otherwise, chitosan is inefficient for raw water with very low initial turbidity. In this case, the use of chitosan as aid coagulant with aluminium sulfate (main coagulant) allows more effectiveness in removing turbidity.

Key words | Bentonite, chitosan, coagulation flocculation, raw water, turbidity

INTRODUCTION

Surface waters contain impurities which affect their appearance and may have harmful effects for consumers. These impurities may be present either in dissolved or in colloidal suspension forms. Turbidity is caused by colloidal particles, characterized by a very small diameter and electronegatively charged generating inter-colloidal repulsion forces. These two properties give to colloids a lower sedimentation speed (Amirtharajah & O’Melia 1990).

Coagulation flocculation process is commonly used in water treatment in order to remove turbidity and natural organic matter. This process occurs in two stages to accelerate the colloids sedimentation by the injection and the scattering of chemical coagulants (Amirtharajah & O’Melia 1990). These coagulants aggregate the colloidal particles and dissolved organic matter and easily eliminate them by sedimentation, flotation or filtration. Coagulation is generally induced by metals salts. The most widely and commonly used are aluminium and iron salts. The addition of these chemicals engenders colloidal destabilization by electronegative charge neutralization of colloids leading to the formation of micro-flocs (Roussy et al. 2005). Flocculation permits, by the addition of synthetic polymers such as polyacrylamide, to bind the micro-flocs together through slow mixing. Then, a simple separation step eliminates the flocs. However, the use of these chemicals, particularly aluminium, may have several environmental consequences: (a) human health implications such as Alzheimer’s and other diseases with carcinogenic properties (McLachlan...
For several decades, the polymeric flocculants are also applied in coagulation flocculation process. They have been used in water and wastewater treatment (Zahrim et al. 2011). These flocculants are classified into three types: anionic, non-ionic and cationic polymers (Seki et al. 2010). Compared with metals salts, synthetic polymers are used in very low quantities to produce large flakes more stable (Renault et al. 2009). However, the sludge formed has a limited potential for recycling due to their non-biodegradability (Zahrim et al. 2011). Generally, anionic and non-ionic flocculants are of low toxicity, but cationic types such as polyacrylamides are more toxic. Their toxicity is a real problem. It is due to unreacted monomers such as acrylamide and reaction by products of the polymers in water. Acrylamide has been shown to be carcinogenic, to cause severe neurotoxic effects (Tardiff et al. 2010).

Consequently, different environmentally friendly coagulants are proposed. If they are locally available, biopolymers can be suggested as an interesting alternative for water treatment. Recently, an increasing interest has been heading for developing biomaterials. These later include modified starches, celluloses, chitosans, and microbial materials produced by micro-organisms as well as bacteria, fungi and yeast. Because they are natural materials, locally available, they may have a very low cost. Technically, these bioproducts are easy to use, don't endanger the handler and they have a wider effective dosage range for flocculation of colloidal suspensions (Renault et al. 2009). Moreover, sludge treated with bioflocculants can be reused on agricultural land (Seki et al. 2010). Since in raw water most natural colloids are negatively charged, cationic polyelectrolytes have a particular potential flocculants. Chitosan is the most promising cationic biopolymer for intense applications (Renault et al. 2009).

As shown in Figure 1, chitosan is a β-(1 → 4) linked polysaccharide made up of D-glucosamine residue [poly- β-(1-4)-D-glucosamine]. It is an N-deacetylated derivative of chitin. This latter is the second most abundant natural biopolymer next to cellulose. It is the main component of crustaceans’ shells and marine arthropods (Nomanbhay & Palanisamy 2005). Chitosan differs from chitin by the amine groups (–NH₂). These groups give to chitosan an interesting cationic character in acidic medium (Chen et al. 2003). They are responsible for its flocculent activity. Depending on its preparation conditions, chitosan is characterized by its molecular weight and deacetylation degree (DD): the molar fraction of deacetylated units (Roussy et al. 2005).

Due to its biodegradability, no toxicity, polyelectrolytic nature, ability to form intermolecular hydrogen bonds, efficient against bacteria, viruses, fungi and tendency to flocculation, chitosan is able to overcome the nuisances of traditional coagulants (McLachlan 1995). According to its excellent properties, the chitosan, considered as renewable resources, is recommended as a suitable flocculant for many applications in colloidal particles (Pan et al. 1999; Huang et al. 2000), river silts (Divakaran & Pillai 2002), organic matters (Cheng et al. 2005), micro-organisms (Strand et al. 2003), treatment of dyes in effluents (Guibal & Roussy 2007), etc.

The aim of this research work is to evaluate the efficiency of chitosan as a biomaterial for surface natural water treatment by coagulation flocculation process. For this propose, coagulation flocculation sedimentation tests were conducted in laboratory using a conventional Jar Test. In this study, two kinds of water were tested. The first one was treated water mixed with a bentonite suspension representing turbid surface water. This treated water comes from drinking water treatment plant of Boudouaou (situatued at about 30 km east of Algiers) supplied by both Keddara and Beni Amrane dams. The second was raw water from both dams mentioned above. The performance of the coagulation flocculation was assessed by measuring the supernatant residual turbidity of the aqueous solution for various parameters, namely settling time, initial turbidity, chitosan dose and pH.

![Figure 1](https://iwaponline.com/ws/article-pdf/11/2/202/416460/202.pdf)

Figure 1 | Schematic representation of structural similarity between: (a) completely acetylated chitin; (b) cellulose; (c) chitosan.
MATERIALS AND METHODS

Preparation of chitosan solution

Chitosan C3646 was purchased from Sigma®. It came from crab shell chitin and was characterized by a DD of 85%. 100 mg of chitosan were dissolved in 1 mL of acetic acid (85% w/w) under agitation after hydrated overnight in 99 mL of demineralized water. The final polymer solution was maintained at pH 4. All reagents used in the experiment were of laboratory grade.

Preparation of synthetic water with bentonite suspension

Bentonite has been chosen for this study for its abundance and availability. The simulation of the suspended solution was realized on the same batch of bentonite, from the Roussel deposit of Maghnia (West Algeria). The main characteristics of the bentonite are given in Table 1. Samples of tap water were mixed with bentonite. This latter was ground and sieved before being used and the sieve fraction below 200 μm was maintained for all tests. The initial suspensions were mixed at 500 rpm for 5 min. Thereafter, the suspensions were allowed to settle for 20 min. This operation was followed by filtration of the supernatant to remove the large particles that were not suspended.

Table 1 | Chemical analysis of the bentonite (Bouras 2003)

<table>
<thead>
<tr>
<th>Elements</th>
<th>% On weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>69.4</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>14.7</td>
</tr>
<tr>
<td>FeO₃</td>
<td>1.2</td>
</tr>
<tr>
<td>MgO</td>
<td>1.1</td>
</tr>
<tr>
<td>CaO</td>
<td>0.3</td>
</tr>
<tr>
<td>NaO</td>
<td>0.5</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.8</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.2</td>
</tr>
<tr>
<td>As</td>
<td>0.02</td>
</tr>
<tr>
<td>PAF</td>
<td>11</td>
</tr>
</tbody>
</table>

PAF: Fire loss to 900 °C.

Raw water sample

The properties of raw water from Algiers dams are given in Table 2. The water was analyzed, according to the Standard Methods, with minimal delay just after collection.

Coagulation flocculation experiments (Jar test)

The simulation of coagulation flocculation process was carried out through a conventional Jar Test (Brand: Janke and Hunkeler®) having five agitators with variable speed and five trains each one equipped with a 1 L beaker. As soon as chitosan solution was added to the bentonite colloidal suspension, the mixture was strongly stirred at 200 rpm for 3 min. This step was followed by a slow mixing (40 rpm) for 20 min. Thereafter, the solution was allowed to settle for 10, 15, 30, 60 and 120 min. To analytically assess the coagulation flocculation effectiveness, the supernatant was removed from the top of the solution by siphoning through measurement of the turbidity using a turbidimeter (Hanna Instruments®: LP2000). This setup was developed to comply with the International Standard ISO 7027. The turbidity is expressed in nephelometric turbidity units (NTU). The pH of the solution was adjusted by the addition of 0.1N HCl solution.

RESULTS AND DISCUSSION

Chitosan solubilization

The solubility of chitosan is a very difficult parameter to control (Rinaudo et al. 1999). Hence, it is one of the important parameters that must be taken into account to study the
chitosan efficiency. Chitosan is a hydrophilic copolymer; it can be dissolved in dilute organic or inorganic acid solutions.

In this study, acetic acid (AcOH), a common solvent, was chosen for this bioflocculant. After dissolution, the obtained solution was very clear, proving that chitosan was completely soluble. The acid medium is used to solubilize and enhance the ionization of amine groups in C2 of D-glucosamine residues (Rinaudo et al. 1999). Their pKa is about 6.3 (Rinaudo et al. 1999). At pH below 4, chitosan acquired a high charge density (Chen et al. 2005). Note that chitosan solubilization depends on the DD. It is estimated that 85% of deacetylation allows a complete dissolution (No & Hur 1998).

**Bentonite suspension**

The mixture of fine particles of bentonite in tap water induces a detachment of these particles due to their strong hydration. The dispersion of bentonite releases very fine colloidal particles. They remain in a suspension state which is difficult to be removed from the dispersion by sedimentation or ultracentrifugation. The two mechanisms (strong hydration and dispersion) are believed to play an important role in the detachment of bentonite colloidal particles, and increase the solubility and stabilization of the colloids (Missana et al. 2003).

**Flocculation test**

In order to study the feasibility of using chitosan as bioflocculant in the process of coagulation flocculation, numerous tests were conducted. Several doses of chitosan (0.05, 0.1, 0.15, 0.25, 0.5, 1, 1.5 and 2 mg L⁻¹) were applied to destabilize the bentonite suspension with high (~250 NTU) and low (~9 NTU) initial turbidities, for different settling times (10, 15, 30, 60 and 120 min).

Figure 2 represents the characteristics giving the turbidity variation as a function of the chitosan dose for high and low initial turbidities, under actual pH (7.8–8.1) conditions of the solution and for different settling times. For all initial turbidities that have been chosen, it is shown that the turbidity drops sharply to its cancellation (almost total reduction) with increasing chitosan dose between the values of 0.05–0.2 mg L⁻¹. In this chitosan concentration range, complete destabilization of the bentonite solution was obtained. However, the re-stabilization of the solution (increase of turbidity) was observed with 0.5 mg L⁻¹ of high initial turbidity and with 1 mg L⁻¹ of low one. Indeed, the optimal dose of chitosan corresponding to the low residual turbidity is between 0.05 and 0.2 mg L⁻¹.

Figure 2 | Effect of chitosan dose for two initial turbidities: (a) ~9 NTU and (b) ~250 NTU and different settling times.
similar to the cobwebs. They appear in the early seconds of slow agitation of the flocculation process. They settle quickly, even before the period of slow agitation is over. According to experiments, it is found that the increase of settling time improves the turbidity removal. Pan et al. (1999) and Huang et al. (2000) have also observed larger flocs of better quality and faster settling velocity when using modified chitosan for coagulation of colloidal particles.

**Effect of pH**

As pH affects the ionization degree of chitosan and the reaction medium, determination of its optimal value is more than required. Therefore, to study the pH effect on turbidity removal by chitosan, a pH range from 4 to 9 was considered. In this part, two chitosan doses (0.25 and 1.5 mg L\(^{-1}\)) and different settling times (10, 15, 30, 60 and 120 min) have been chosen. The results in Figure 2 show that chitosan is able to initiate the flocculation of the phytoplankton suspension from aquaculture tanks either in slightly acidic, neutral or alkaline conditions.

Figure 3 indicates that chitosan is able to initiate the flocculation of bentonite suspension from either in slightly acidic, neutral or alkaline conditions. It is shown that 0.25 mg L\(^{-1}\) chitosan generates an almost complete removal of turbidity at pH ranging from 4 to 8. This interval defines the range of pH where low chitosan concentration is more effective. Above this value (pH 8), the residual turbidity increases and the bentonite suspension tends towards stability. At chitosan concentration of 2 mg L\(^{-1}\), the solution re-stability widens for all pH values except pH 9, where a decrease in turbidity is recorded. This decrease corresponds to the bentonite solution destabilization.

In general, the results of such figure show that pH 6 is an interesting limit. Beyond this value, the pH effect on the effectiveness of turbidity removal is not important. On the other hand, the removal of turbidity increases with decreasing pH value below pH 6. According to Nomanbhay & Palanisamy (2005), the pK\(_a\) of amine groups is between 6.2 and 6.4 for a complete dissociation of chitosan (about 90% of DD). The pK\(_a\) may reach 6.5 according to Rinaudo et al. (1999). At lower pH, amine groups of chitosan are protonated leading to the formation of \(-\text{NH}_3^+\) functional groups. The acidic medium allow all the free \(\text{NH}_2\) ions to be neutralized by H\(^+\) ions and transformed into \(-\text{NH}_3^+\) ions. Nomanbhay & Palanisamy (2005) have found an extent of chitosan protonation from 9, 50, 91 and 99% at pH 7.3, 6.3, 5.3 and 4.3, respectively. This means that at pH 4 or below, more than 90% of the amine groups are protonated. An interaction between \(\text{NH}_3^+\) functional groups and anionic mineral particles are induced to do so. Although, it is reported by Sorlier et al. (2001) that pH effect can change based on the degree of deacetylation and ionic strength, and could also be related to change in clay chemistry (Roussy et al. 2005). Above the pK\(_a\) value, chitosan begins to precipitate. Under these conditions, the adsorbent functional groups, initially positively charged, will be negatively charged, thereby giving the anionic chitosan coating. This creates an electrostatic repulsion and therefore a re-stabilization of the solution. The destabilization of alkaline solution requires the addition of high

![Figure 3](https://iwaponline.com/ws/article-pdf/11/2/202/416460/202.pdf)
doses of chitosan. Cheng et al. (2005) reported that positive charges on the chitosan surface will significantly decrease when solution pH increases. Indeed, the contribution by the charge neutralization of the chitosan to destabilize the particles becomes less important as pH increases. Thus, the bridging was the major mechanism for chitosan to destabilize the colloidal particles in the high pH range. The dosage of coagulant needs to be increased when pH increases, and the charge reversal is not clear in the low pH range (Cheng et al. 2005).

**Coagulation flocculation mechanism induced by chitosan**

Chitosan is a positively charged polyelectrolyte in an acid medium. This property provides the ability to easily coagulate the suspended particles negatively charged. Protonated amine groups of chitosan attract bentonite anionic particles (associations, inter- and intra-channel). This reaction neutralizes all anionic charges and destabilizes colloidal system (Cheng et al. 2005). The small bentonite particles bind together forming large flocs (bridging mechanism). These flocs settle rapidly by gravity effect. On the other hand, dissolved organic substances can also be adsorbed by chitosan (adsorption mechanism) into aggregates which can then easily settle (Pan et al. 1999).

If the amount of chitosan added to the solution is in excess, the protonated amine groups (cationic charges) cause a further stabilization of the suspension and reduce efficiency of the process. Roussy et al. (2005) attribute the chitosan neutralizing charge ability to molecular weight, while the rate of destabilization is related to the DD. The same findings were made by Divakaran & Pillai (2001). Many authors have studied the coagulation flocculation mechanism induced by chitosan. They have shown that the coagulation flocculation process involves numerous mechanisms such as: electrostatic patch and aggregation phenomenon (Pan et al. 1999), trapping coagulation (Huang et al. 2000), charge neutralization (Chen et al. 2005) and bridging (Roussy et al. 2005). The best known is that chitosan is involved in the process of coagulation flocculation by dual mechanism: charge neutralization and bridging (Roussy et al. 2005). Both mechanisms dominate the process of coagulation flocculation in a wide range of pH from 4 to 8 which makes the process easier to control in a large scale. Beyond this pH range, Strand et al. (2005) reported that coagulation flocculation is induced by two mechanisms: charge neutralization and sweep-up. These mechanisms are induced by the effect of the precipitation of chitosan in an alkaline environment.

**Raw water flocculation**

Jar tests were conducted also to test the flocculation ability of chitosan for two kinds of raw water of Beni Amrane dam having high initial turbidity 155 NTU and, Keddara dam having a low initial turbidity 5 NTU.

In order to determine the most appropriate coagulant dose, the residual turbidity of the supernatant of Beni Amrane and Keddara raw water is plotted in Figure 4 as function of chitosan dosage, at actual pH and settling time of 30 min. A large difference between residual turbidity of Beni Amrane and Keddara raw water has been observed. It is recorded a significant removal of turbidity of approximately 87% (20 NTU) in the raw water from Beni Amrane at 0.15 mg L⁻¹ of chitosan. Beyond this dosage, turbidity increases. It is probably due to the re-stabilization of the unstable solution.

Beni Amrane raw water contains both mineral suspension and organic matter. Chitosan is effective in reducing the turbidity of mineral suspensions and most of colloidal form organic matter. However, it has only little effect on
the removal of dissolving organic matter (Chen et al. 2003). Consequently, the turbidity of this water does not be removed completely.

Concerning Keddara raw water, the characteristic given the variation of residual turbidity as function of chitosan dose did not display any change in shape. A lowest turbidity reduction, with 5% (4 NTU) after 45 min of settling for all chitosan doses applied (0.05–40 mg L⁻¹), was recorded.

In summary, chitosan is effective for the turbidity reduction of raw water of Beni Amran dam with a high initial turbidity (155 NTU) and inefficient for turbidity removal in the case of Keddara raw water with low initial turbidity (5 NTU).

During the second phase (slow agitation) of coagulation flocculation process of Beni Amran raw water it was observed that flocs appear rapidly with large size. They were fibrous forming cobwebs. Concerning Keddara water, no formation of any flocs for all chitosan doses has been observed. This could be attributed to low turbidity and colloids presence in these waters. Indeed, the concentration effect of colloidal particles in water is important because they serve as cores to the coagulation (Gidas 1998). If the concentration of colloids in the water is low, there are too few particles to ensure good flocculation, even though, they are neutralized. Another inconvenience of waters that contain few colloids comes because it is easy to add coagulant and to reverse the load of the particles instead of neutralizing it. The obtained results indicate that chitosan effectiveness in removing turbidity of raw water is highly dependent on initial turbidity and on flocculant dose.

Relying on previous results showing the chitosan inefficiency as a primary coagulant for the treatment of raw water having low turbidity, a set of experiments of coagulation flocculation were conducted to test chitosan as an auxiliary polyelectrolyte coagulant. Alum sulfate (50 mg L⁻¹) was used as coagulant for this experiment. The previously mentioned analytical parameters were considered to evaluate treated water.

Figure 5 indicates that the major turbidity decrease is carried out with 0.2 mg L⁻¹ of chitosan. The highest removal percentage is equal to 97% after 30 min of settling. It is noted that beyond the optimal point, the value of residual turbidity increases; this means that suspension tends towards the re-stabilization. No change in pH was observed. According to the coagulation flocculation sedimentation process, we have observed the formation of flocs at the time of the addition of the chitosan. They are bigger than those obtained when using chitosan as primary coagulant. They were of rounded shapes, glued one to the other, forming in the middle of the backer a big ball. They settled well in less than 10 min. The final solution became very clear and very limpid. According to Roussy et al. (2005), the ionic sulfate compounds have a significant effect on the chitosan’s sorption. Although, it is reported that chitosan has a higher molecular weight in the presence of sulfates. Van Duin & Hermans (1999) justified their hypothesis by the fact that chitosan formed the large aggregates and could precipitate in the presence of sulfate. Bina et al. (2009) reported that the use of chitosan as aid coagulant in coagulation flocculation process decreases the residual Al³⁺ in treated water. They also reported that taking into account the low dosage of chitosan in these experiments (less than 1 mg L⁻¹), the amount of introduced organic carbon remained was low enough (less than 0.8 mg L⁻¹) to make its contribution negligible for the coagulation flocculation performance. Thus, chitosan could be used as natural aid coagulant for drinking water treatment with the lowest risks of organic release.

By comparing raw water results to bentonite suspension ones, we deduce that the quality of water influences strongly the chitosan effectiveness as coagulant flocculant. Thus, it is very important to have information on the water to determine whether treatment using chitosan will be efficient for all or specific water.
CONCLUSION

Experiments were conducted to determine the chitosan ability as natural floculant for surface water treatment. Two kinds of water were tested. The first one was bentonite suspension mixed with tap water and the second was raw water from Keddara and Beni Amrane dams, collected from Bou douaou water treatment plant.

Through these experiments, it is found that chitosan was very effective for the coagulation of bentonite suspensions with high and low concentrations. The pH effect study shows that chitosan may be effective in a wide range of pH. A low dose of chitosan is enough to reduce significantly the turbidity in an acid solution. However, it is necessary to increase the dose in alkaline solutions. The increasing amounts of chitosan acid solution lead to change the pH of the solution. Chitosan is no effective for Keddara raw water having a very low initial turbidity. Otherwise, aluminium sulfate as main coagulant and chitosan as an auxiliary polyelectrolyte coagulant is most effective in turbidity removal (97%). On the other hand, chitosan has more effectiveness in removing turbidity of Beni Amrane raw water having a high initial turbidity. Therefore, chitosan efficiency is highly dependent on both initial turbidity and chitosan dosage.

The organic carbon contribution on the coagulation flocculation performance is negligible because chitosan is used in small doses. Hence, chitosan could be used as natural aid coagulant for drinking water treatment with the lowest risks of organic release.

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