Removal of dissolved and colloidal matter from surface waters by composite flocculant aluminum salt-sodium alginate

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**Abstract**

Colloidal matter present in the surface water is an undesirable element that must be treated appropriately to make the water drinkable. The most commonly used process is coagulation–flocculation, followed by sand filtration to obtain excellent water quality with a turbidity limit value not exceeding 0.5 NTU. Despite the effectiveness obtained by this process, the reagents used poses problems in terms of their residual concentrations after treatment. This study focused on the removal of dissolved and colloidal matter from surface waters, used as a source for drinking water, by using a composite flocculant consisting of aluminum salt and sodium alginate. The tests were carried out on the waters taken from the Sidi Saïd Maâchou dam located on the Oum Er-Rbia River in Morocco, whose turbidity was adjusted to 100 NTU and permanganate index of 7.16 mg O\textsubscript{2} L\textsuperscript{-1} that involved the organic matter. For the composite flocculant, tests showed 98% elimination of turbidity and 36% of organic substances for a dose of 4 mg L\textsuperscript{-1} of aluminum and 1.6 mg L\textsuperscript{-1} of sodium alginate. In contrast to the conventional method, it expends the aluminum six times more to achieve a reduction rate of 90% of turbidity and 28% of organic substances with a slight increase in conductivity. Several operating parameters were optimized to reduce the treatment cost.

**Keywords:** Coagulation; Flocculation; Composite flocculant; Dam water; Water treatment

1. Introduction

With socio-economic and demographic development, the need for drinking water is increasing. The available water resources are subject to various sources of pollution; thus affecting their quality and requiring appropriate treatment. The most commonly used process to remove colloidal contamination is coagulation–flocculation because of its simplicity and effectiveness in removing turbidity, color and some contaminants [1,2]. In recent years, this process has improved in terms of the reagents nature, including inorganic flocculants, organic flocculants and composite flocculants. However, composite flocculants are increasingly used in water treatment because of their superior efficiency over traditional inorganic flocculants and their low cost compared to organic flocculants [3].

Conventional coagulation–flocculation is carried out in two steps. The first one is called coagulation. It consists of

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destabilizing the suspended particles using commonly aluminum- or Iron-based metal coagulants [4,5]. The second one is called flocculation. It consists of aggregating the particles formed during the destabilization of the suspended matter into large agglomerates that can easily be separated by settling. The flocculants or flocculation adjuvants are in their majority, polymers of very high molecular weight. They can be mineral, natural organic or synthetic organic in nature. Synthetic chemical flocculants remain the most widely used due to their cost-effectiveness and high efficiency. However, in line with health and environmental concerns, their use has become limited. In that regard, biofloculants present great importance for health and ease of biodegradation, as well as their environmentally-friendly behavior [6]. Biofloculants are natural organic substances having a macromolecular size. They are able to flocculate colloidal matter and suspended solids [7]. These macromolecules commonly contain backbones of polysaccharides, proteins and nucleic acids [8]. The main sources of these macromolecular substances are algae, fungi, bacteria and actinobacteria [9]. The limitation of the direct application of these biofloculants is related to low yield of production and high-cost [10]. Alternatively, composite flocculants containing a mixture of inorganic flocculant and biofloculant can overcome individual flocculant defects by increasing treatment efficiency and dewaterability of the sludge [11–13]. Among these biofloculants, alginate is a linear polysaccharide block copolymer extracted from the cell walls of brown algae, which includes the 1,4-bonded β-D-mannuronic acid and α-L-guluronic acid residues [14]. This anionic biopolymer is widely used in pharmaceutical and food industry. Also, the alginate is used in water treatment as a flocculant to accelerate the rate of aggregate formation [15,16].

This study aims to compare the removal efficiency of colloidal suspension by aluminum salts and sodium alginate using conventional coagulation–flocculation and composite flocculant. The different operating parameters were optimized to improve the coagulation process with the composite flocculant. The process performance was monitored by using turbidity, conductivity, hardness, pH, permanganate index and Fourier-transform infrared (FTIR) spectroscopy.

2. Materials and methods

2.1. Preparation of reconstituted solutions

The tests were carried out on reconstituted solutions prepared in the laboratory by water taken from the Sidi Said Maâchou dam (Fig. 1), located at the mouth of the Oum Er-Rbia River (Morocco) and soil from the same location. The soil–water mixture was left to settle for 2 h to remove coarse matter. Then the supernatant had undergone several adjustments to obtain a reconstituted solution with the desired turbidity.

2.2. Preparation of composite flocculant

A stock solution of composite flocculant was prepared by dissolving a 5/2 ratio of Al(OH) in 250 mL of distilled water. The solution contains 11.18 g of aluminum chloride hexahydrate (AlCl₃·6H₂O) and 0.5 g mass of sodium alginate was stirred at low speed for 24 h before treatment to ensure better homogenization.

2.3. Coagulation–flocculation tests

The coagulation–flocculation tests were carried out on the solutions reconstituted in a jar-test model JF/6 Isco Milan Italy at six posts. Three series of experiments were conducted. In the first series, conventional coagulation–flocculation was performed on 500 mL volume solutions at a speed of 250 rpm for 3 min (coagulation), and at a speed of 25 rpm for 20 min (flocculation). After a 30 min settling time, the supernatant is recovered for analysis.

In the second series, the composite flocculant was added to reconstituted solutions. The tests were carried out under the same conditions as the first series.

The third series was established to optimize the treatment parameters. These parameters are alternated varied one by one while maintaining the other constants. These parameters are coagulant rate, flocculant rate, rapid agitation time, rapid agitation rate, slow agitation time, agitation rate, and settling time.

2.4. pH adjustment

The aluminum ion (Al³⁺) in aqueous solution hydrolyzes to form many entities such as hydrolyzed monomer and polymer complexes: Al(OH)₂⁺, Al(OH)₃⁺, Al₂(OH)₄⁺, Al₃(OH)₅⁺, Al₄(OH)₆⁺, Al₅(OH)₇⁺, etc. and release protons according to the following reaction:

$$\text{Al}_{\text{aq}}^{3+} + x \cdot \text{H}_2\text{O} \rightarrow \text{Al(OH)}_{x}^{(3-x)} + x \cdot \text{H}^+$$

These entities promote electrostatic coagulation due to their positive charges. When pH ≥ 4, the hydrolyzed complex of the polynuclear structure $\text{Al}_{\text{aq}}^{3+}(\text{OH})_n$ gives Al(OH)$_3$ by precipitation and polymers [17,18]. These can contribute to the removal by adsorption of soluble organic compounds and suspended matter.

Fig. 1. Geographical location satellite image of the Sidi Said Maâchou dam (Google Earth).
To avoid excessive acidification and to further promote coagulation by adsorption, pH adjustment was performed by adding caustic soda (NaOH) at a concentration of 0.1 M. The following formula calculates the quantities of NaOH added:

$$\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3$$

where $[\text{OH}^-]$ is the hydroxide mass concentration; $M(\text{OH})$ is the hydroxide molar mass; $[\text{Al}^3+]$ is the aluminum mass concentration; $M(\text{Al})$ is the aluminum molar mass.

2.5. Parameters and measurement methods

During our tests, turbidity, conductivity, hardness, pH, and permanganate index parameters were monitored. The sample turbidity was measured in a nephelometric turbidity unit (NTU) using a Palintest 7000 photometer (Palintest Limited, Tyne & Wear, UK). The pH and the temperature were measured using a multi-parameter digital device Hach HQ40d (Hach Company, Loveland, Colorado, USA). pH was monitored before and after treatment, while the solution temperature fluctuated around 20°C–23°C throughout the entire operational period. The sample conductivity was measured by an Orion conductivity meter, model 125. The water hardness was measured using the ethylenediaminetetraacetic acid volumetric titration method (NF T 90-003/1984). The concentration of organic matter in solutions was determined by the permanganate index (PI) according to standard method NF T 90-050. The flocculants were characterized using a Fourier-transform infrared FTIR spectrophotometer (JASCO FT/IR-4600, Japan) in the wavelengths range of 1,850 to 1,350 cm$^{-1}$.

3. Results and discussions

3.1. Conventional coagulation–flocculation test

A series of conventional coagulation–flocculation tests were carried out by adding coagulant (AlCl$_3$·6H$_2$O) followed by the flocculant (sodium alginate).

The turbidity was decreased with a fixed alginate concentration of 1.6 mg L$^{-1}$ and an increased dose of Al$^{3+}$, as shown in Fig. 2a. For an optimal dose of 25 mg L$^{-1}$ of aluminum, the turbidity reduction reached 90% accompanied by the removal of 28% of the organic matter (Table 1). This reduction in the colloidal suspension is due to the mechanism involved between the particle and the coagulant Al$^{3+}$: complexing between the soluble hydrolyzed forms of aluminum and the colloidal matter, and/or adsorption on the solid aluminum hydroxide flocs Al(OH)$_3$. Nevertheless, pH around neutrality presents the optimal range for the removal of mineral and organic matter. The coagulation, in this optimal range, is done preferably by adsorption on aluminum hydroxide flocs Al(OH)$_3$ with an acidic Lewis character; thus allowing it to fix the negatively charged suspended matter, and also the dissolved matter [19–21]. Indeed, the long-chain structure and high molecular weight of alginate promote the adsorption and bridging of colloids or Al-colloid. Their numerous –COO$^-$ and –OH sites increase coagulation efficiency and accelerate the sedimentation rate [22]. The improvement of colloid removal by charge neutralization effect is a suggestion that has been abandoned due to the negative charge of alginate [23]. In this process, firstly, the negatively charged colloidal suspension was destabilized by the action of positively charged aluminum monomers and/or polymers, forming small Al-colloid flocs. Secondly, the alginate was added to convert the small flocs formed in the previous step into larger flocs by adsorption and bridging.

However, during the process, pH decreases until it stabilizes around 7 (Fig. 2b), due to the release of Al$^{3+}$ in solution. The conductivity, meanwhile, increases with the dose of the coagulant (Table 1), but this increase remains in small proportions. The presence of AlCl$_3$ (123.5 mg L$^{-1}$) and NaOH (47 mg L$^{-1}$) was expected to result in a substantial increase in the conductivity via their ions, but this is not the case as shown in Fig. 3. This could be explained by the formation in addition to Al(OH)$_3$ other solid compounds including sodium and chlorides in their structures, and/or the absorption of part of the chlorides on the Al(OH)$_3$ flocs directly or
in combination with the clay sheets through metal bridges [24–26].

The total hardness decreases (Table 1) due to the contribution of calcium and magnesium in the formation of insoluble compounds with the suspended matter by two mechanisms. The first one is the formation of direct insoluble form between cations and suspended matter that can result in sedimentation. The second one is the incorporation of cations in the binding between suspended solids and aluminum hydroxide. It results in the formation of a bridge between these two species [27].

3.2. Coagulation–flocculation test using a composite flocculant

The tests on the composite flocculant (aluminum-alginate complex) were conducted to be compared with the conventional method. These tests showed higher turbidity removal, which reaches a level of 98% (Fig. 4) by using doses of 4 mg L\(^{-1}\) and 1.6 mg L\(^{-1}\) for coagulant and flocculant, respectively. Contrary to the composite flocculant, the conventional method gives a 90% reduction rate with coagulant quantities six-time more (Fig. 2a). Concerning dissolved organic matter, there is a 36% reduction for composite flocculant (Table 2) compared to 28% for conventional coagulation–flocculation (Table 1). For the conductivity, it increases but remains low compared to coagulation–flocculation tests. Despite the addition of NaOH for pH adjustment, the conductivity increases by 1.3% compared to 6.8% for conventional coagulation–flocculation. This is due to the minimum amount of reagents consumed for the abatement of the colloidal suspension. In addition, the decrease in total hardness reveals the contribution of the constituent elements of this parameter (calcium, magnesium) to the destabilization of colloidal particles [28]. A similar evolution was documented by Xia et al. [29] during a comparison between poly-aluminum ferric chloride (PAFC) and the inorganic-organic-type composite flocculant. The composite flocculant was composed of anionic microbial bioflocculant, Klebsiella Variicola B16 and PAFC. They observed that the incorporation of PAFC into the anionic bioflocculant

<table>
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<tr>
<th>Parameters</th>
<th>Solution before treatment</th>
<th>Solution after treatment</th>
</tr>
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<tr>
<td>pH</td>
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<td>6.97</td>
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<td>Total hardness (°F)</td>
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</table>

Fig. 3. Conductivity evolution for solutions without and with pH adjustment.

Fig. 4. Evolution of turbidity for composite flocculant.

<table>
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<tr>
<th>Parameters</th>
<th>Solution before treatment</th>
<th>Solution after treatment</th>
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</tr>
<tr>
<td>pH</td>
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<td>7.16</td>
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<td>Conductivity (mS cm(^{-1}))</td>
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<td>2.96</td>
</tr>
<tr>
<td>Permanganate index (mgO(_2) L(^{-1}))</td>
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<td>4.56</td>
</tr>
<tr>
<td>Total hardness (°F)</td>
<td>35</td>
<td>32.6</td>
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(consisting mainly of the polysaccharide), had reduced the concentration of PAFC by 58% compared to the use of PAFC alone for an initial turbidity 100 NTU. Indeed, the addition of a composite flocculant containing a mass of 10.5 mg L\(^{-1}\) of PAFC and 4.5 mg L\(^{-1}\) of Klebsiella Varicola B16 allowed 95% of turbidity reduction efficiency.

The improvement in the efficiency of coagulation with composite flocculant can be explained by the combination of AlCl\(_3\) and polymer Alginate, providing a high molecular weight material on which the coagulant is anchored, synergizing coagulation and flocculation. This system allows the removal of colloidal suspensions by absorption on colloid-Al-alginate or colloid-Al-alginate-Al-colloid chains. In this order, the analysis of composite flocculant by FTIR spectroscopy has shown the displacement of the carboxylic group, which presents the key to the sorption of the metal by the alginate acid (Fig. 5). The characteristic bands obtained by FTIR are a strong asymmetrical stretching and a slightly weaker symmetrical stretching vibration COO\(^{-}\) [30,31]. However, the variation between these two peaks (\(\Delta v = CO_{asym} - CO_{sym}\)) reflects the carboxylate structure with metal by comparison with the variation of sodium alginate peaks [31]. In fact, the \(\Delta v\) (COO\(^{-}\)) value of Al\(^{3+}\) is lower than that of Na\(^{+}\), which shows that the coordination between aluminum and alginate sodium takes place via bidentate chelation.

These results are similar to those found in the literature [32,33]; they have shown that the new generation of coagulants (composite flocculant) is significantly more effective than the conventional one. Thus, reducing the effect of pH and improving the removal of suspended solids with a minimum concentration of aluminum.

3.3. Optimization of operating parameters for composite flocculant

The optimization results of the operating parameters are represented in Table 3:

These tests made the optimization of the operating settings possible with the composite flocculant in the coagulation–flocculation process. The results are due to the enhanced coagulation. It improves coagulation and aggregation, resulting in a compact and less voluminous sludge compared to the conventional method which accelerates sedimentation [34,35].

3.4. Cost treatment study

An economic study was established based on the results obtained after optimization of the operating parameters. This study includes all the changes implemented.

3.4.1. Expression of cost

The operating cost per meter cube (m\(^3\)) of treatment with the composite flocculant is the sum of the electrical energy value consumed and the reagents used during treatment.

\[
\text{Treatment cost (USD} \cdot \text{m}^3) = \sum \text{Unit Price} (\text{USD} \cdot \text{m}^3) \times \sum \text{Consumption in m}^3 \cdot \text{Sale Price} (3)
\]

The power is calculated by the relation, which is valid in the case where the agitation is mechanical [36].

\[
P = \frac{1}{2} \times C_d \times A \times \rho \times V_r^3 (4)
\]

where \(P\) is the power dissipated in the liquid (W); \(C_d\) is the drag coefficient (it is equal to 1.8 for flat blades); \(A\) is the blade surface (m\(^2\)); \(\rho\) is the liquid density (kg m\(^{-3}\)); \(V_r\) is the blade relative speed in respect to the liquid speed surrounding it, approximately \(0.75 \times \) peripheral blade speed (\(V_p\)):

\[
V_r = 2 \times \pi \times d \times N / 60 (5)
\]

where \(d\) represents the distance from the blade tip to the axis of rotation (m) and \(N\) is the number of agitation (min).

The processing cost was calculated (Table 4) by using all the charges involved in Eqs. (3)–(5). The electric energy price corresponds to the last tranche (consumption \(> 500\) kWh). This tranche has a higher price. It’s delivered by Lyonnaise des Eaux de Casablanca (LYDEC) to the industrial sector located in the Greater Casablanca Region, Morocco. For reagents, the price used is that of the international element costs per ton.

<table>
<thead>
<tr>
<th>Test</th>
<th>Parameter</th>
<th>Value</th>
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<td>1</td>
<td>Aluminum mass (mg L(^{-1}))</td>
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</tr>
<tr>
<td>2</td>
<td>Sodium alginate mass (mg L(^{-1}))</td>
<td>1.2</td>
</tr>
<tr>
<td>3</td>
<td>Fast stirring time (min)</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>Fast stirring speed (tours min(^{-1}))</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>Slow stirring time (min)</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>Slow stirring speed (tours min(^{-1}))</td>
<td>25</td>
</tr>
<tr>
<td>7</td>
<td>Settling time (min)</td>
<td>20</td>
</tr>
</tbody>
</table>

Fig. 5. FTIR spectra of the sodium alginate and aluminum-alginate complexes in the region of 1,350–1,850 cm\(^{-1}\).
The use of composite flocculant for surface water treatment seems effective. It minimizes the concentration of reagents and the energy dissipated during the agitation by increasing the aggregation capacity. The aggregation capacity accelerates sedimentation leading to an operating cost of increasing due to the fact that the price of this bioflocculant is increasing by the second. This competitiveness is increasing due to the fact that the price of this bioflocculant is steadily declining thanks to the high demand for this type of polymer to industrialize.

4. Conclusions

Our study explored a new generation of coagulation reagents made by a composite flocculant, resulting from the incorporation of inorganic materials (\(\text{AlCl}_3, 6\text{H}_2\text{O}\)) in a natural organic polymer (sodium alginate). The results obtained indicate that the coupling of coagulant-flocculant is more effective than their use separately in terms of the colloidal suspension removal and the reagents consumed. For initial turbidity of 100 NTU and 7.16 mgO\(\text{L}^{-3}\), the dissolved organic matter. The rapid agitation rate (coagulation) was 100 rpm for 1 min, and the slow agitation rate (flocculation) was 25 rpm for 10 min. The settling time was 20 min. All these optimized parameters had the effect of reducing the treatment cost.

**References**


