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Characterizing the performance of coagulation-flocculation using natural coagulants as pretreatment of tannery wastewater

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Abstract

Coagulation/flocculation followed by clarification is the most widely used process for treating wastewater from tannery industry. The coagulation step usually consists of the rapid dispersal of a coagulant into the wastewater followed by an intense agitation commonly defined as rapid mixing. The most widely used coagulants are aluminum (III) and iron (III) salts. However, there are two major drawbacks inherently associated with these such as the addition of chemicals and the increased ionic conductivity of the treated wastewater. In order to avoid such problems, the performance of different biopolymers (chitosan, alginate and starch) in the coagulation process for the pretreatment of two different tannery wastewater samples (liming and quenching washing water) was characterized. The various operating parameters optimized in this study were the duration and the stirring speed, the type and added coagulant dosage. The optimal stirring time and speed were 5 min and 200 r/min respectively and the optimal coagulant dosage was varied between 100 and 200 mg/L. The maximum removal efficiencies for turbidity and ionic conductivity observed were 87% and 55% respectively, in the case of treating wash water from liming process.

1. Introduction

Environmental pollution is a global problem that affects the entire population. Therefore, the environmental protection has recently given rise to a continuous increase in the number of environmental laws and regulations, making it increasingly difficult assimilation for small and medium companies, including those in the chain of tanning who encounter serious difficulties and problems to comply with the environmental protection in the legislation in force [1-4].

In fact, the leather tanning is the transformation of a putrescible material, the skin that is a by-product of the meat industry, to a rot proof and resistant material that is leather, ready to be used for the production shoes, leather goods, clothing... This leather-making process uses a large quantity of water and chemicals such as surfactants, acids, dyes, sulphated oils, salts, and especially hardeners such as chromium [5,6]. However, this transformation generates big amounts of polluted water containing solid waste, organic skin, salts and chemicals that is discharged either in the sewer system, or in public pipes or in nature.

Despite the installation of wastewater treatment plants in most tanneries, the usual techniques of wastewater treatment have variable yields and therefore, tanners still confronted with environmental problems. The coagulation/flocculation process using inorganic coagulants is the most common pre-treatment in the removal of organic matter [7-11]. However, there are two major drawbacks inherently associated with these such as the addition of chemicals and the increased ionic conductivity of the treated wastewater [12-15].

To overcome these problems involved in chemical coagulants, the studies on natural coagulants produced or extracted from plants gain momentum [16]. Hence, it becomes essential to search for a novel natural coagulant, which can be used in small quantity and produce less amount of non-hazardous sludge.Generally, biopolymers are introduced into solution as bioflocculants to improve the performance of chemical coagulants but not as biocoagulants [17].

Natural coagulants have been tried in the treatment of lignin from wastewater such as Ipomoea dasysperma on the decolourization of textile dye [18] and cactus as coagulant in turbid water treatment [19]. Few natural coagulants have been used in treating the highly turbid wastewater.

Chitosan, a polycationic polymer and waste product from the sea food processing industry, is an abundant natural resource that has, as yet, not been fully utilized. Advantages of this polymer include availability, low cost, high biocompatibility, biodegradability and ease of chemical modification. Chitosan exhibits a variety of physical-chemical and biological properties resulting in numerous applications in fields such as cosmetics, biomedical engineering, pharmaceuticals, ophthalmology, biotechnology, agriculture, textiles, oenology, food processing and nutrition. This amino-biopolymer has also received a great deal of attention in the last decades in water treatment processes for the removal of particulate and dissolved contaminants. In particular, the development of chitosan-based materials as useful coagulants and flocculants is an expanding field in the area of water and wastewater treatment. Their coagulation and flocculation properties can be used to remove particulate inorganic or organic suspensions, and also dissolved organic substances [20].
Similar to chitosan, alginate is also a natural polymer with abundant natural resources. As a polymeric acid, alginate can form salt with metal ions. Whilst chitosan can bind metal ions via chelation with the amine groups, most divalent metal ions can form water insoluble salt with alginate [21]. This polymeric matrix, offering advantages such as biodegradability, hydrophilic properties, natural origin, and abundance combined with its ability to form stable hydrogels due to the presence of specially coordinated carboxylic binding sites [22]. The polymeric matrix also determines the mechanical strength and chemical resistance of the final particle, which would be utilized for successive adsorption–desorption process [23]. These polymeric materials have several advantages included easier handling, requiring less complex separation systems and provide a greater opportunity for reuse and recovery [24].

In the same context, starch, a natural polysaccharide that consists of large number of glucose units, joined by glycosidic bonds, has been reported to improve performance efficiency in water and wastewater treatment operations [25].
An attempt has therefore been made in this article to characterize the performance of different biopolymers (chitosan, alginate and corn starch) in the coagulation process for the pretreatment of two different tannery wastewater samples before membrane separation process in order to recycle the treated water in different stages of the tannery process. The various operating parameters optimized in this study were the duration and the stirring speed, the type and added coagulant dosage.

2. Material and Methods

2.1. Chemicals

Three natural coagulants (bio-polymers) were selected for this work : corn-starch, sodium-alginate and chitosan. Chitosan and sodium alginate used were analytical grade and purchased from Sigma Aldrich. The corn-starch used is bought from the grocer (the one used for cooking). No dissolution of these polymers has been done. The addition of these coagulants in the sample was in powder form (without adjustment of pH).Table 1 presents some chemical characteristics of used coagulants.

Table1 : Natural coagulants characteristics

Coagulant	***Sodium alginate***	***Chitosan***	***Starch***
Chemical formula	$[Na\ C_6\ H_7\ O_6]_n$	$[C_6\ H_{11}\ N\ O_4]_n$	$[C_6\ H_{10}\ O_5]_n$
Solubility	soluble	insoluble	50 g/L in water at 90°C
Isoelectric Point (IEP)	5.4	6.8	7.5

The experiments were conducted with various dosages of the coagulant (100, 200 and 500 mg/L). The two important parameters optimized were the mixing speed and coagulation time.
The coagulants were introduced in wastewater samples in separate experimental batches without any adjustment of pH. Once the coagulant was added, small and fluffy flocs started to form in the wastewater solution. These flocs became bigger when we approach the optimum dosage.
In order to determine the optimum conditions for a benefic outcome of coagulation process, the turbidity and conductivity removals were measured after the slow stirring process (flocculation) and settling. The removal efficiencies of conductivity and turbidity after the steady states were reached.

2.2. Analytical measurements

- <u>*Ionic conductivity :*</u>

It was measured using a conductivity/TDS/°C Meter Kit (model SenseLine F430T) and turbidity was measured using WTW 555IR turbid-meter.

- *Jar test coagulation :*

Coagulation-flocculation treatment was carried out in a conventional jar test apparatus (model JLT4 Floc tester QA1014X). The experimental procedure is as follow:

- rapid stirring after the addition of coagulant (200 or 300 rpm for 5 or 15 min),
- mild stirring without addition of any flocculent (30 rpm for 30 min),
- and settling for 30 min.

The efficiency of the treatment was estimated by the reduction of conductivity and turbidity using the following equation:

$$R\ (\%) = \frac{x_i - x_f}{x_i} \text{ x } 100$$

where R denotes the reduction rate, x is the value of the conductivity or turbidity, i indicates the initial value (before coagulation-flocculation process) and f indicates the final value (after coagulation-flocculation process). The experiments were conducted using 500 mL of wastewater sample in each beaker of the Jar test apparatus.

2.3. Wastewater samples

Two wastewater samples were collected at the outlet of the quenching wash process and the liming wah process in a Tunisian tannery.The aim of the quenching operation is to offer to the skin its natural swelling state, at the same time to remove dirt and filth (droppings, blood, mud, etc), soluble protein substances and preservatives. This process increases the flexibility of the treated skin by restoring its lost water. Several additives such as caustic, wetting agents and lactic acid could be used.During liming process, hair, wool and epidermis are removed from the skin using various chemical products such as lime and sodium sulfate.

3. Results and discussion

Table 2 summarizes the physical-chemical characteristics of the two supplied samples.This table shows that quenching and liming wash water samples present high conductivity, salinity, turbidity and COD.

Table 2 : Physical-chemical characteristics of the tannery wastewater samples

Parameter	sampling 1 07 January 2015		sampling 2 31 March 2015	
	Quenching effluent	Liming effluent	Quenching effluent	Liming effluent
Temperature (°C)	19.0	18.7	20.1	21.0
pH	6.53	12.70	6.58	11.27
Conductivity (mS/cm)	55.10	24.60	41.81	22.00
Turbidity (NTU)	1030	680	984	108
Salinity (g/L)	33.7	14.9	30.6	14.6
TDS (g/L)	22.0	11.7	21.2	11.0
COD (mg/L)	32000	18000	29800	23000
Na (mg/L)	15763.19	4209.56	12363.21	3909.11
K (mg/L)	139.93	27.01	160.13	24.61
Ca (mg/L)	16.84	27.12	13.43	27.67
Mg (mg/L)	197.84	14.64	107.83	4.65
Cl (mg/L)	16569.11	5976.58	13517.18	5638.76
SO_4 (mg/L)	1007.09	1213.50	1161.21	1203.19

3.1. Performance of liming wash water samples

The effect of coagulant dosage of three different bio-polymers on the percentage removal of turbidity of liming wash water under various operating conditions is presented in figure 1(a-d). It can be seen from the figure that the percentage removal of turbidity varied between 87 and 96.2% for all tested coagulants. However, no

significant increase was observed when coagulant dosage was varied. In fact, 100 mg/L of coagulant was sufficient to remove more than 87% of turbidity.
Figure 1 (a, b c and d) shows also that chitosan as coagulant presented a very encouraging result: the rates varied between 94 and 96.4% and the best performance was obtained for an optimal dosage of chitosan equal to 200 mg/L under the operating conditions: t = 5 min and speed = 200 rpm.
In the case of alginate and starch as coagulants, the percentage removal varied between 91-95% and 87-94% respectively, which are considered as very interesting results.
Knowing that liming effluents pH is about 12 and that isoelectric point of studied coagulants are less than 12 (IEP <pH : negatively charged coagulants), we obtained similar results for all tested bio-polymers.
The effect of coagulant dosage of three different bio-polymers on the percentage removal of ionic conductivities of liming wash water under various operating conditions is presented in figure 2(a-d).

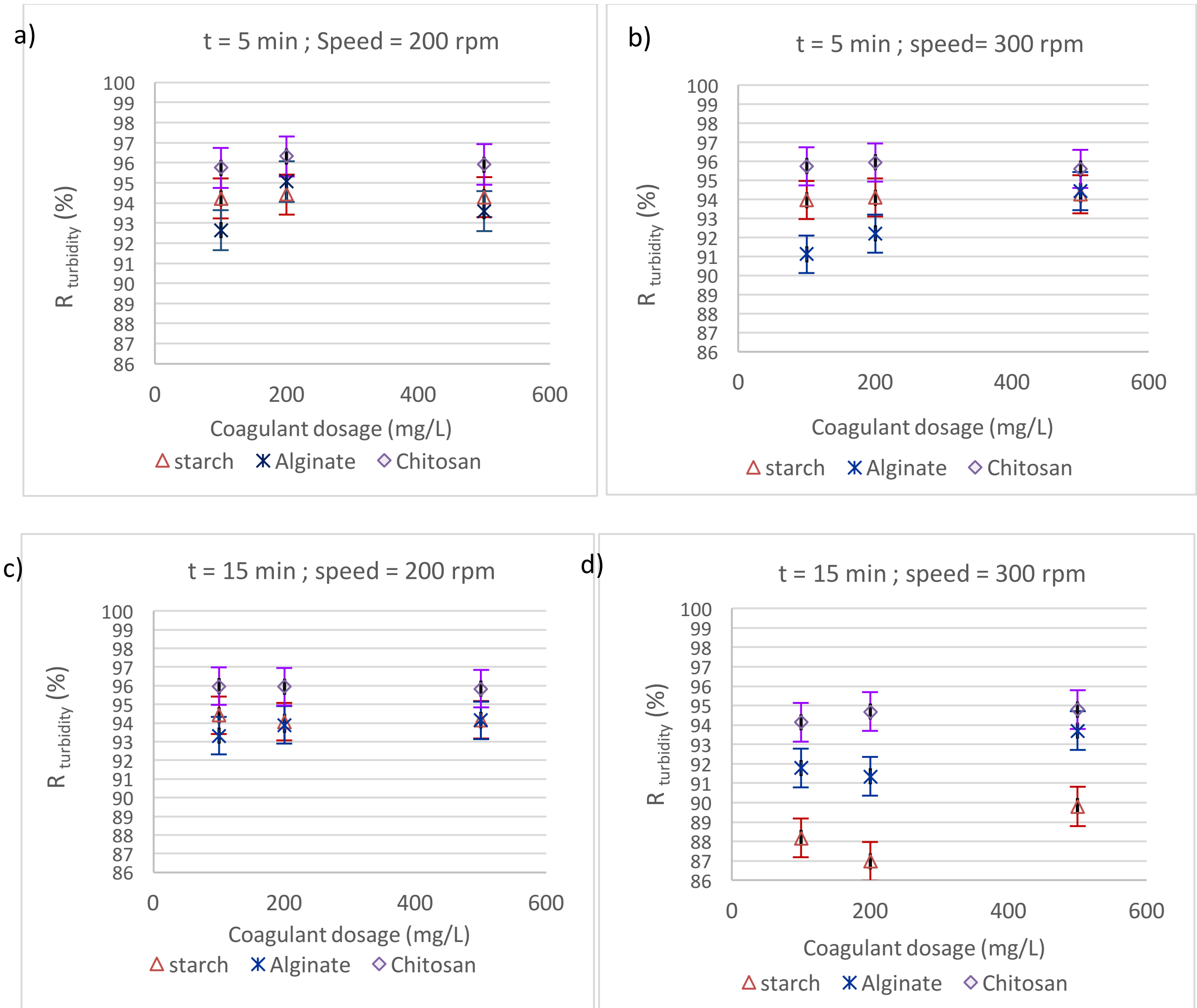

Figure1 : Variation of turbidity reduction of liming effluent versus coagulant dosage
a) t = 5 min ; Speed = 200 rpm   b) t = 5 min ; Speed = 300 rpm
c)t = 15 min ; Speed = 200 rpm d)t = 15 min ; Speed = 300 rpm

Figure 2(a-d) demonstrate that tested bio-polymers have the capacity to adsorb the ionic entities and consequently to reduce the ionic conductivity of the solution. Indeed, the removal of ionic conductivity varied between 55.5 and 62%, what favors the use of polymers with regard to salts that systematically increase the ionic conductivity since they are soluble in aqueous solutions.
In fact, a preliminary study made in laboratory has shown that aluminum and iron salts may coagulate the polluting particles from the tannery waste at fairly high doses (greater than 2 g/L). Additionally, these chemical coagulants, in no case, were unable to lower down the ionic conductivity of the treated water, but rather their

use resulted in a net increase in the conductivity and salinity. These findings show the advantage of using biopolymers for the clarification of water.

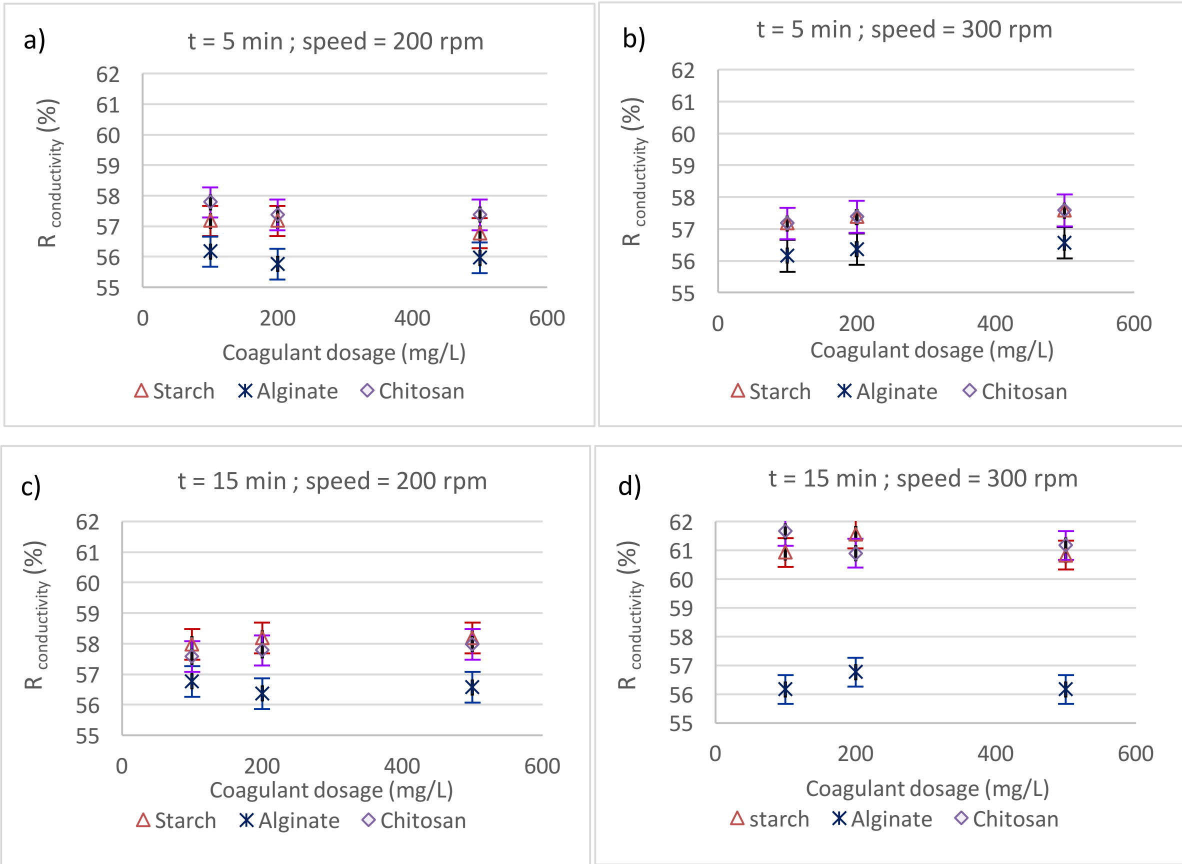

Figure2 : Variation of ionic conductivity reduction of liming effluent versus coagulant dosage
a) t = 5 min ; Speed = 200 rpm   b) t = 5 min ; Speed = 300 rpm
c)t = 15 min ; Speed = 200 rpm d)t = 15 min ; Speed = 300 rpm

As shown in figure 2, alginate presents the lowest removal efficiency of ionic conductivity. This result is expected since alginate as coagulant presents a very high solubility in aqueous solution compared to chitosan and starch as coagulants. The obtained removal efficiencies did not exceed 57% in the case of alginate within the framework of current experimentation within the domain of studied coagulant dosage.
In the case of chitosan, the maximum removal efficiency of ionic conductivity observed was 61.5% [figure 2(d): t = 15 min and speed = 300 rpm] for a dosage of chitosan equal to 100 mg/L.
On the other hand, in the case of starch, the performance was comparable to those of chitosan although it was not the case during the study of the turbidity reduction (figure 1). Indeed, the coagulation by means of starch presented the maximum removal efficiency equal to that of chitosan under identical operating conditions (t = 15 min and speed = 300 rpm) but for an optimal dosage of starch at 200 mg/L.

3.2. Performance of quenching wash water samples

Figure 3 illustrates the removal efficiency of turbidity of quenching wash water samples under various operating conditions and for the same studied bio-polymers: chitosan, corn-starch and alginate.Figure 3 shows that the efficiency of the treatment by coagulation-flocculation depends strongly on the type of coagulant. In contrast to the case of liming wash waters, the removal efficiency of turbidity for quenching wash waters varied between 5% and 90%. In fact, figure 3(a-b) relative to a stirring time of 5 min, the order of the removal efficiency of turbidity is as follow: R(Chitosan) < R(Starch) < R(Alginate). The decrease in the efficiency of coagulation using chitosan could be linked to the pH of quenching wash water, which was about 6.5. In fact, at this pH, chitosan presents neutral charge (IEP ≈ pH) but alginate and starch are positively and negatively charged respectively which increase their efficiency as coagulants.

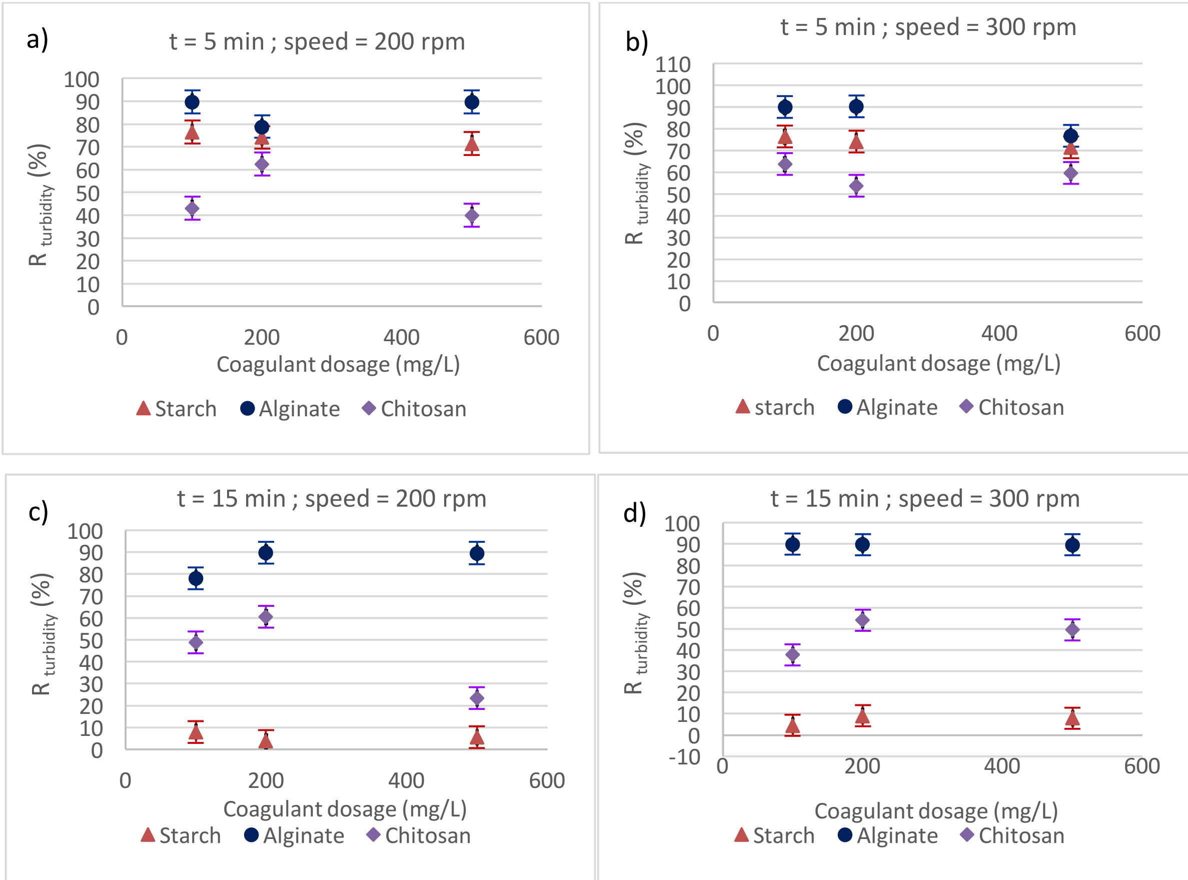

Figure3 : Variation of turbidity reduction of quenching effluent versus coagulant dosage
a) t = 5 min ; Speed = 200 rpm b) t = 5 min ; Speed = 300 rpm
c)t = 15 min ; Speed = 200 rpm d)t = 15 min ; Speed = 300 rpm

However, in the case of stirring time equal to 15 min (figure 3(c-d)), the corn-starch as coagulant considerably loses effectiveness as the observed removal efficiencies were less than 10%. This result could be attributed to the destruction of the flocs formed as a result of exceeding the optimum stirring time.

In the case of chitosan and alginate, similar results were obtained when stirring time was increased from 5 to 15 min for both 200 and 300 rpm stirring speed.

The maximum removal efficiencies observed for alginate, corn-starch and chitosan were 90%, 75% and 60% respectively at coagulant dosage of 100 mg/L; stirring time of 5 min and stirring speed of 300 rpm.

Zemmouri et al. [26] have used chitosan as coagulant in water treatment supplied from a dam and they showed that chitosan was not too efficient as alum, if it is used as primary coagulant for treating a dam raw water. However, when chitosan was applied as coagulation aid agent with aluminum sulfate, highest turbidity removal (97 %) was carried out with 0.2 mg/L of chitosan after 45 minutes of settling time. These results could confirm that the chitosan efficiency is highly dependent on the initial turbidity, on chitosan dosage and on water characteristics.

Figure 4(a-d) illustrates the removal efficiency of the ionic conductivity of quenching wash water samples versus coagulant dosage for tested bio-polymers under various operating conditions.

The results of this study show that coagulants are less effective in reducing the initial ionic conductivity, which represents more than double of initial ionic conductivity of liming effluents (55 and 24 mS/cm respectively). Indeed, the removal efficiency observed for the various studied polymers did not exceed 26%. However, we can consider that it is a rather interesting result as far as the portion eliminated from ionic entities is so important and that we do not assist to an increase of the initial ionic conductivity comparing to conventional coagulants.

The maximum removal efficiencies of the ionic conductivity were observed in the case of the starch (pH<IEP). On the other hand, the lowest removal efficiencies were registered in the case of the chitosan (IEP ≈ pH).

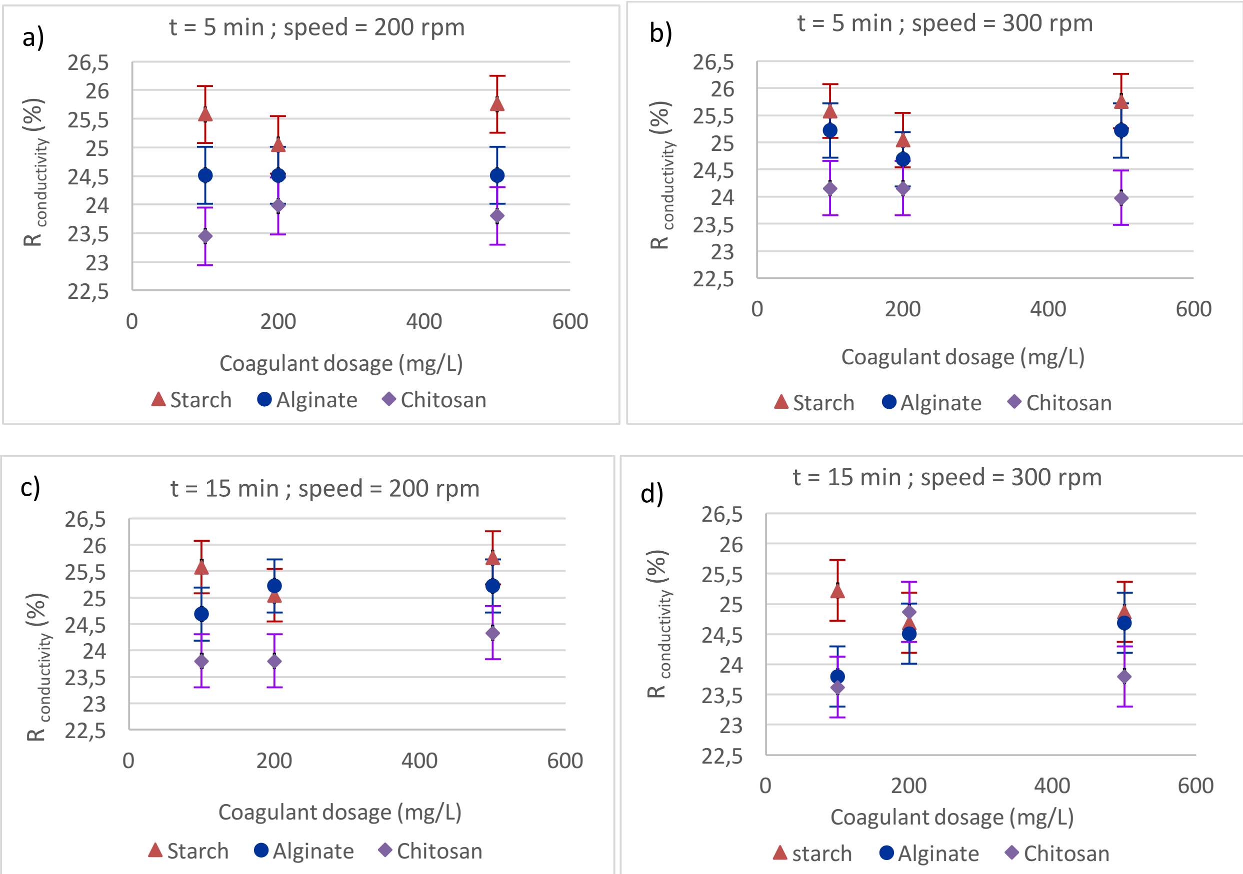

Figure4 : Variation of ionic conductivity reduction of quenching effluent versus coagulant dosage
a) t = 5 min ; Speed = 200 rpm b) t = 5 min ; Speed = 300 rpm
c)t = 15 min ; Speed = 200 rpm d)t = 15 min ; Speed = 300 rpm

Conclusion

In conclusion, the results obtained in this study show that coagulation/flocculation process using natural polymers seems to be a very good alternative as pre-treatment before membrane separation to attain considerable turbidity and ionic conductivity reduction of tannery wastewater. The optimization of several parameters shows that bio-polymers could be more effective than conventional coagulants and the results showed that initial ionic conductivity of wastewater could be reduced considerably, which was not the case of conventional coagulants. Liming wash water study proves that chitosan, sodium alginate or starch presented removal efficiencies exceeding 87 and 55 % for turbidity and conductivity respectively. The best removal efficiency was obtained using 200 mg/L chitosan dosage under optimum conditions.

For quenching wash water treatment, owing to its higher initial ionic conductivity and pH, the coagulation efficiency decreased (90% and 26% for turbidity and ionic conductivity) but obtained results still interesting comparing to conventional coagulants.

5. Acknowledgments

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