Chemical Engineering Journal 165 (2010) 851–858

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Surface water treatment with tannin-based coagulants from *Quebracho* (*Schinopsis balansae*)

J. Sánchez-Martín [a,*], M. González-Velasco [b], J. Beltrán-Heredia [a,1]

[a] *Department of Chemical Engineering and Physical Chemistry, University of Extremadura. Avda. de Elvas, s/n, 06071 Badajoz, Spain*
[b] *Department of Mathematics, University of Extremadura, Avda. de Elvas, s/n, 06071 Badajoz, Spain*

ARTICLE INFO

Article history:
Received 1 September 2010
Received in revised form 11 October 2010
Accepted 12 October 2010

Keywords:
Tannins
Surface water
Turbidity removal
Coagulation–flocculation
Natural coagulation agent

ABSTRACT

Tannin-based coagulant agent called *Silvafloc* was tested on surface river water clarification. This novel coagulant can be used in drinking water treatment, and consist of a chemically modified tannin extract from *Schinopsis balansae*, commonly known as *Quebracho colorado*. Low coagulant doses reached high turbidity removal percentage and operational conditions of neutral pH and room temperature allow up to 90% turbidity removal with 20 mg L^{-1} of coagulant. Rapid and slow mixing periods in Jar test as well as stirring intensity were evaluated and they were found to be less influent than coagulant dosage. *Silvafloc* drives to a significative disinfection (around 99.9% for *fecal streptococcus* and *fecal coliforms* and up to 70% for *total coliforms*). Treated water also presented very low content in polyphenols (about 0.4 mg L^{-1}) and organic matter content was not increased, but removed about 30%. If compared with other natural or inorganic coagulants, *Silvafloc* is more efficient than aluminium sulphate, a classical metal salt for water clarification.

1. Introduction

This paper aims to study water treatment agents that may differ from industrial and commercial ones which are widely characterized. Given the need to implement water treatment technologies that are appropriate for drinking water clarification, and adapted to the constraints of developing countries, the potential of natural coagulants as sustainable and readily available options is increasingly being recognized and studied at laboratory level. The most advantage these agents seems to present is the fact that they are typically easy for unskilled personnel to handle and maintain. Some examples are *Moringa oleifera* [1] or *Opuntia ficus* [2].

Silvafloc is a trademark that belongs to Silvateam (Italy). It is a tannin-based product, which is modified by a physico-chemical process and presents interesting coagulant activity. It is obtained from *Schinopsis balansae* bark, a very common tree in tropical and ecuatorial areas. Production process is under intelectual patent law, but similar procedures are widely reported as Mannich base reaction [3]. Specific industrial process for other similar products is referred by US patent number 6,478,986 B1 [4] and it involves tannin polymerization through the addition of formaldehyde (37%), ammonium chloride and commercial hydrochloric acid. The resulting product is obtained under thermal control and it has a viscous appearance with ca. 36% active material.

Schinopsis balansae, commonly known as *Quebracho*, is a tree from South America. It was considered the first source of tannins until *Acacia mearnsii* de Wild replaced it because of its high percentage tannin content and its relatively easy reproduction procedure. However, *Quebracho* is still now an important feedstock for tannin production [5] and its content in condensed tannins has been thoroughly determined in specific studies [6,7].

The term *tannins* covers many families of chemical compounds. Traditionally, they have been used for tanning animal skins, hence their name, but one also finds several of them used as coagulants. Their natural origin is as secondary metabolites of plants [8], occurring in the bark, fruit, leaves, etc. While *Acacia* and *Schinopsis* bark constitute the principal source of tannins for the leather industry, the bark of other non-tropical trees such as *Quercus*, *Castanea* or *Pinus* can also be tannin rich.

About *Quebracho* tannin extract composition it is known to be mainly composed of combinations of resorcinol, catechol and pyrogallol building blocks [9]. That complex chemical structure can be used in order to include several active groups that may enhance the coagulant activity of the agent [10].

There are not many scientific references about tannins water treatment capacity. Özacar and Sengil [11] characterized tannins obtained from *valonia*, an autoctonous tree from Turkey, and used them for wastewater coagulation treatment. According to authors, tannin extract can be combined with $Al_2(SO_4)_3$ in order to improve sludge removal.

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[*] Corresponding author.
E-mail addresses: jsanmar@unex.es (J. Sánchez-Martín), mvelasco@unex.es (M. González-Velasco), jbelther@unex.es (J. Beltrán-Heredia).
[1] Tel.: +34 924289300x9033; fax: +34 924289385.

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doi:10.1016/j.cej.2010.10.030

Zhan and Zhao [12] tried to remove lead from water by using an adsorbent, tannin-based gel. Heavy metal ions were adsorbed onto formaldehyde-immobilized tannin gels. This usage of tannins has been reported elsewhere [13,14].

Özacar and Sengil [15] kept on researching and gave special data about trihalomethanes formation and other undesirable compounds. They worked always with tannin–$Al_2(SO_4)_3$ combination.

Palma et al. [16] used tannins extracted *in situ* from *Pinus radiata* bark in order to polymerize a solid which was used in heavy metals removal. Bark itself was combined with a tannin solid into adsorption columns.

There are some examples of using forest and vegetal wastes in order to remediate specific situations of pollution, such is the case of Seki et al. [17] or Aoyama et al. [18].

Regarding the main scope of water treatment according to these prescriptions they are found several previous papers that pointed out the use of tannins as a coagulant aid [19,20] or other cationic compounds [21].

The chemical modification made on *Schinopsis balansae* tannin is not quite difficult and different variations have been reported under several patents [22–25]. Namely, tannins undergo Mannich aminomethylation by reaction with an aldehyde and an amine [26]. The resulting *tannin Mannich* polymer possesses a higher molecular weight due to formaldehyde and Mannich base crosslinking, and also possesses ampholytic character due to the presence of both cationic amines and anionic phenols on the polymer. Universal water supply is one of the most important challenges scientific community faces to in the present days. It is an important task to research on because, water treatment for human consumption is a technically overcome issue in developed countries, but it is still a lethal difficulty in less developed regions [27]. That is how we think current technologies must be re-arranged in order to facilitate their usage according to availability, non-dependency and affordability principles [28].

Our previous works presented the same scope regarding either the elimination of special pollutants from wastewater [29–31] or enhancing possible surface water treatment [32,33]. The current investigation keeps on researching on this direction: treating surface water (river or lake water) in order to improve its quality and make it more adequate to human consumption. The objective of the present work was to characterize the coagulant activity of *Silvafloc* as surface water treatment agent.

2. Materials and methods

2.1. Raw water

Surface water was collected from Guadiana river in Badajoz (South West Spain, Extremadura Community). This choice of studying an actual surface water avoided the need to simulate turbidity with different physicochemical procedures, such as kaolin addition [34]. This water was treated on the same day of its collection. Its average characteristics are given in Table 1.

2.2. Coagulant agents

For preliminary screening on surface water clarification, some coagulant agents were used:

- *Moringa oleifera* is a polyelectrolyte coagulant which presents a very interesting coagulant activity. It was extracted at lab-scale and used as it is previously reported [32].
- *Tanfloc* is a tannin-based coagulant supplied by TANAC (Brazil) which was previously characterized in similar studies [19].

Table 1
Raw water characterization data.

Parameter	Value	Units
Conductivity	400 ± 10	$\mu S\,cm^{-1}$
Suspended solids	15 ± 1	$mg\,L^{-1}$
Total solids	452 ± 13	$mg\,L^{-1}$
Turbidity	80 ± 5	NTU
Calcium	37.7 ± 0.4	$Ca^{2+}\,mg\,L^{-1}$
Hardness	152 ± 7	$CaCO_3\,mg\,L^{-1}$
Ammonium	1.81 ± 0.04	$N\,mg\,L^{-1}$
Nitrate	5.3 ± 0.2	$NO_3^-\,mg\,L^{-1}$
Nitrite	0.03 ± 0.01	$N\,mg\,L^{-1}$
Chloride	40.4 ± 0.3	$Cl^-\,mg\,L^{-1}$
$KMnO_4$ oxidability	14.7 ± 0.4	$O_2\,mg\,L^{-1}$
Phosphate	0.04 ± 0.01	$P\,mg\,L^{-1}$
Total phosphorus	0.06 ± 0.01	$P\,mg\,L^{-1}$
Total coliforms	623 ± 10	Colonies per 100 mL
Fecal coliforms	400 ± 10	Colonies per 100 mL
Fecal streptococcus	140 ± 10	Colonies per 100 mL

- Aluminium sulphate $Al_2(SO_4)_3\cdot 18H_2O$ was supplied by SIGMA (USA).

2.3. Coagulant characterization

Silvafloc coagulant is the product of a Mannich reaction that involves *Schinopsis balansae* tannin. This chemical modification is usually known as cationization of tannins. By means of this reaction a quaternary ammonium is introduced in the general structure of the tannin in order to give cationic character to tannin flocculant. This way is fully described previously in Pulkkinen and Mikkonen [35] and more extensively in Tramontini and Angiolini [3].

Briefly, *Silvafloc* may be the reaction product of three reagents: monoethanolamine (MEA), formaldehyde and the tannin extract mixture. Firstly, MEA and formaldehyde may react in the way described in (1):

$$H_2N{-}(CH_2{-}CH_2OH){+}HCHO \rightarrow CH_2{=}N{-}CH_2{-}CH_2OH{+}H_2O \tag{1}$$

what yields the reactive specie called *imine*. This may react with aqueous tannin extract mixture to form *Silvafloc* whose chemical formula may respond to (2):

$$\text{tannin}(CH_2 - NH - CH_2 - CH_2OH)_n \tag{2}$$

The expanded structure is shown in Fig. 1 according to Pizzi [5]. FTIR, ^1H and ^{13}C NMR of *Silvafloc* confirmed this hypothesis.

2.4. Experimental procedures

2.4.1. Standard Jar-test trial and turbidity measurements

Experimental procedure was the following: 1 L of surface turbidity-known water was put into a beaker. The corresponding amount of coagulant was added, and beaker was put into a Jar-test apparatus (VELP-Scientifica JLT4). It was stirred for 2 min time at 100 rpm. Then, a slow agitation was programmed: 30 rpm for 20 min time. After 1 h, turbidity was measured with a HI93703 turbidimeter (Hanna Instruments). Primary standard solutions of 0

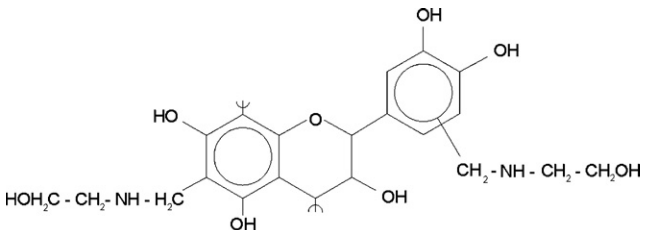

Fig. 1. Possible structure of *Silvafloc* according to chemical reaction mechanism and FTIR and NMR analyses.

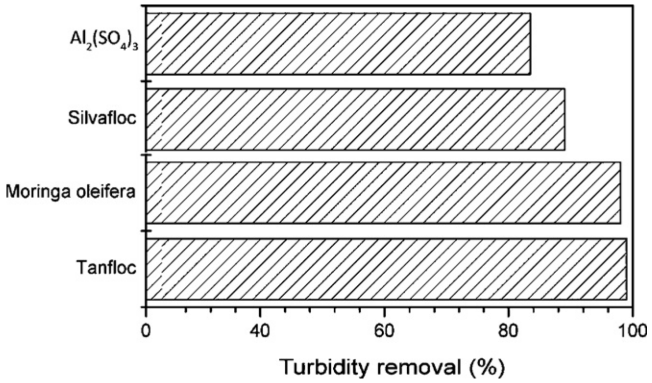

Fig. 2. Preliminary screening in surface water clarification. Coagulant dosage: 15 mg L^{-1}, 20 °C, natural pH.

and 10 NTU (supplied by Hanna Instruments) were used for calibration. Turbidity sample was taken from the center of the beaker, 3 cm from surface. Reported turbidity value was the average of three measures.

2.4.2. *Microbiological analyses*

Microorganisms were analyzed for *fecal* and *total coliforms* bacteria using selective media, m-FC with rosolic acid for *fecal* and m-Endo for *total coliforms*, respectively (*Millipore*). KF-Broth was used for analyzing *fecal streptococcus* (*Whatman*). Membrane filtration technique was used as well [36].

2.4.3. *Tannin concentration*

Tannin concentration was determined by *Folin–Ciocalteau* test [37,38]. Results are expressed in tannic acid equivalent mg L^{-1}.

2.4.4. *$KMnO_4$ oxidability*

Organic oxidable matter in treated water was evaluated according to $KMnO_4$ test as it is referred in Almeida et al. (2000) [39].

2.4.5. *Statistical analyses*

For each experiment, the influence of coagulation and flocculation stages was studied by means of a factorial design with only a single replicate. Once the absence of interaction between factors was checked (using a graphical method based on the interaction lot) the corresponding analysis of variances was developed. Subsequently, in order to find differences between levels of each factor, Tukey's test for multiple comparisons was applied.

Data was represented using a multiple Box-plot. The influence of the agitation speed, agitation time and flocculant dosage on turbidity removal was studied using a three-factorial design.

Statistical significance was set at p-value ≤ 0.05. All data analysis was performed using the language and environment for statistical computering R ("GNU") version 2.7.0 [40] and SPSS version 15.0 statistical package (SPSS Inc., Chicago, IL).

3. Results and discussion

3.1. *Preliminar screening of surface water*

Several experiments of surface water clarification were carried out with four coagulant agents: three natural ones (*Moringa oleifera*, *Silvafloc* and *Tanfloc*) and a traditional inorganic salt which is commonly used in coagulation procedure in drinking water treatment plant: aluminium sulphate.

As Fig. 2 shows, the level of turbidity removal is quite similar in the four cases. The graphic presents the turbidity reduction in river raw water after a standard Jar-test procedure (2 min rapid mixing plus 20 min slow mixing and 1 h of sedimentation). Doses of 15 mg L^{-1} were added of each coagulant agent.

Natural coagulants presented higher performance in turbidity removal, as is evident from Fig. 2. *Moringa oleifera* coagulant ability is known for a long time, and it is suggested as a natural effective coagulant agent for turbid water clarification [41]. Regarding *Tanfloc* it is also a very effective tannin-based coagulant as it is referred in our previous work [33]. The fact these natural coagulants were more efficient than aluminium sulphate is due to their net-forming ability: while alum seems to act just as a coagulant, the long molecules of natural coagulants (either polyelectrolyte, in the case of *Moringa*, or tannin Mannich base, in the case of *Tanfloc* and *Silvafloc*) are able to destabilize colloidal material in the raw water [43] and re-arrange a flocculant action [20,42].

3.2. *Optimum coagulant dosage*

Optimum dosage was established according to the performance in turbidity removal. Coagulant dosages were varied between 1 and 30 mg L^{-1} in a standard Jar-test procedure. Results are shown in Fig. 3.

As Fig. 3 depicts, it is possible to achieve a relevant turbidity removal with low levels of coagulant. This fact has to do with the high efficiency that this coagulant presents in the destabilization of colloids. The final concentration of suspended solids, which are the main compounds of turbidity, presented very low levels with coagulant dosages of 5 mg L^{-1}. Percentage removal was progressively raised from 0 to 80% with low coagulant doses, such as 10, 15 or 20 mg L^{-1}. This range was selected for analysing the rest of influencing parameters.

Other researchers have worked on real water with coagulation and flocculation process [44]. Aluminium has been reported as a coagulant–flocculant agent in higher dosages (around 20–30 mg L^{-1}) for similar river surface water. In addition, it has been found to be a risk factor in Alzheimer's and other diseases [45].

3.3. *pH*

Trials with different coagulant concentrations were carried out, varying pH conditions between 4 and 9. Results of this series are shown in Fig. 4. Standard Jar-test procedure was carried out in order to test the affection of this parameter. Coagulation and flocculation process is more effective with slightly acid pH (near to 4) even with the control series, as it is common in these kinds of processes [46]. This may be explained by the appearence of positive-charged or non-soluble species in the water that should act as natural coagulants. However, the effectiveness of the *Silvafloc* is quite constant

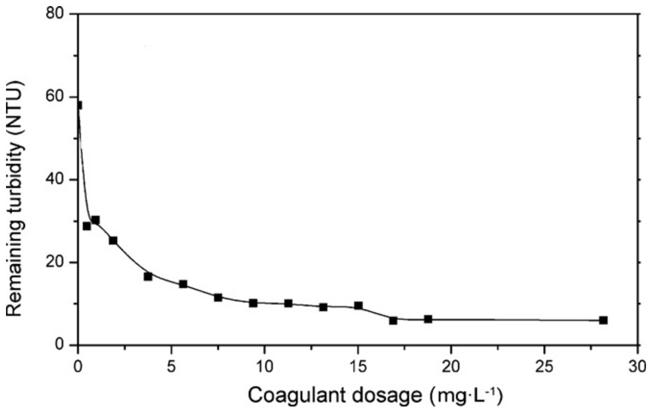

Fig. 3. Turbidity removal evolution with coagulant dosage. 20 °C, natural pH.

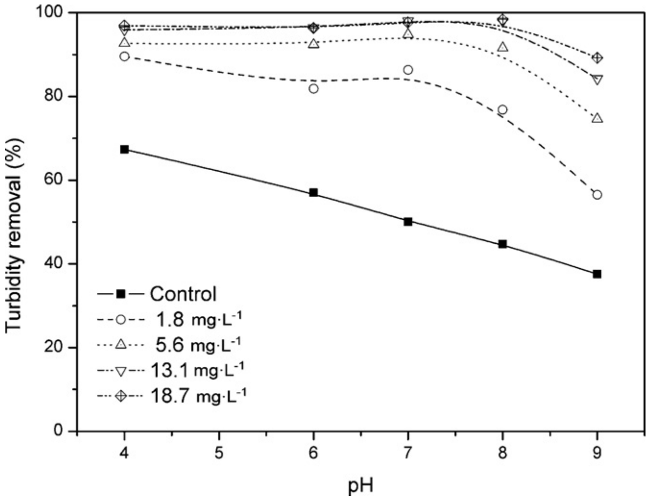

Fig. 4. pH influence on turbidity removal. 20 °C.

and stable all along the pH range where it was tested, so this fact is an advantage since no pH dependence is shown in this case. The natural origin of this coagulant makes its effectiveness fluctuations are not so acute. Usually, coagulants charged positively tend to undergo a decrease in the their cationic form at basic pH levels and then, electrostatic attraction between the cationic chains and the negatively charged active centers in turbidity materials become weak. *Silvafloc* seems to have a more amphoteric nature so this effect is slightly presented at the most low dosage (1.8 mg L^{-1}).

3.4. Temperature

Trials with different coagulation temperature were carried out. Temperature was varied between 10 and 40 °C, as is presented in Fig. 5. This range is selected because surface water may have different origins and they can affect temperature levels. Seasonal fluctuation may decrease temperature down to 10 °C, while in lakes or little not-running water ponds, it can reach 40 °C. As temperature increases effectiveness of the process tends to be lower, but the general performance level is not under 80%. This behavior is commonly recognize and attributed to thermal breaking of flocs.

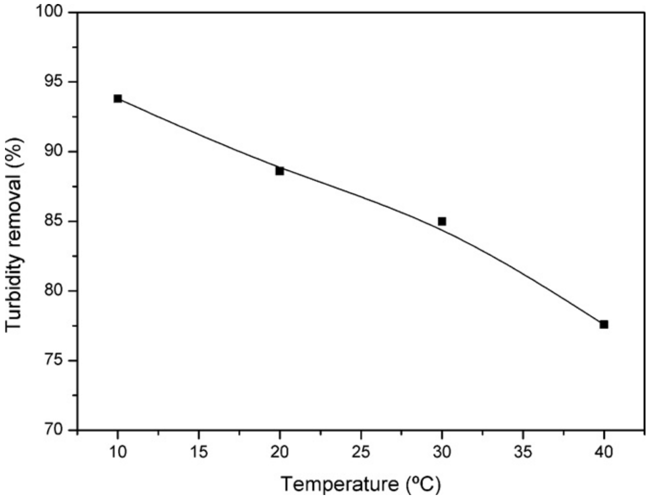

Fig. 5. Temperature influence on turbidity removal. Coagulant dosage: 10 mg L^{-1}, natural pH.

3.5. Raw water initial turbidity

In order to test the ability in surface water clarification with different initial turbidity levels, trials varying the initial turbidity of raw water were carried out. Turbidity levels varied between 32 and 110 NTU. As can be appreciated in Fig. 6, process effectiveness does not experiment any significative variation if coagulant dose is higher than 1.8 mg L^{-1} because the turbidity removal is reaching its maximum. Every dose achieves a rather high turbidity removal and normal fluctuation is attributed to experimental process. Low dosages involve more fluctuations, no effect is appreciated at higher dosis. It is highly recommended to carry out a preliminary study as it is made in Section 3.2 for each kind of water in order to adjust coagulant dosage.

3.6. Variables in flocculation procedure

Two aspects of coagulation process have been studied: the importance of each agitation stage in Jar-test procedure regarding to their duration and the importance of agitation speed in a time-variable one-stage Jar-test procedure. Both variables have been studied from a statistical point of view.

3.6.1. Rapid and slow mixing stages in Jar test

In order to characterize the importance of rapid mixing (also called *coagulation*, 100 rpm) and slow mixing stage (also called *flocculation*, 30 rpm) one referred to the other and both referred to coagulant dosage, different trials have been carried out. Rapid mixing time was varied between 0 and 10 min, slow mixing time was varied between 10 and 60 min. Finally, dosage range was placed between 1.8 and 18.7 mg L^{-1}. The applied model includes one replication for each combination.

For each coagulant dosage, a separate evaluation has been carried out. Statistic study has been performed on the basis of a factorial design with two factors (*coagulation* and *flocculation*) and one cell observation. Fig. 7 points out the fact that there is no interaction between factors (parallel line for each data series). The corresponding ANOVA study allows us to evaluate the influence of both factors in final turbidity. The model results significative (p-value ≤ 0.05) just in cases of coagulation with the two first doses (0.024 for 1.8 mg L^{-1} and 0.044 for 5.6 mg L^{-1}). This means that just for these two cases, coagulation time is important enough to be considered as a significative factor.

As long as doses are increased, these p-values go far from the significance. This fact reinforces the idea that dosage is much more

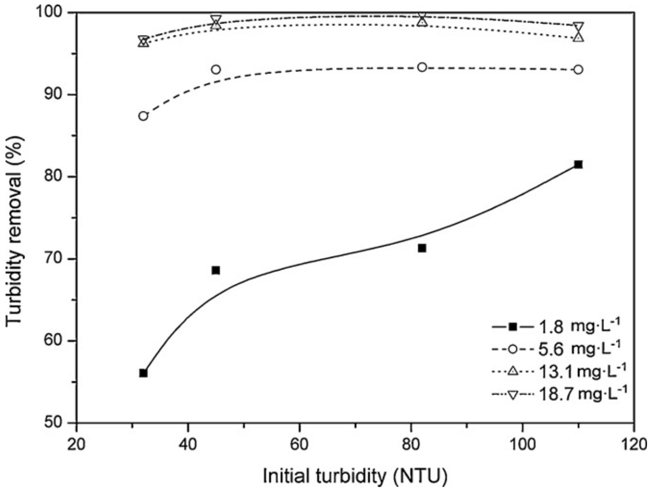

Fig. 6. Raw water turbidity charge influence on turbidity removal. 20 °C, natural pH.

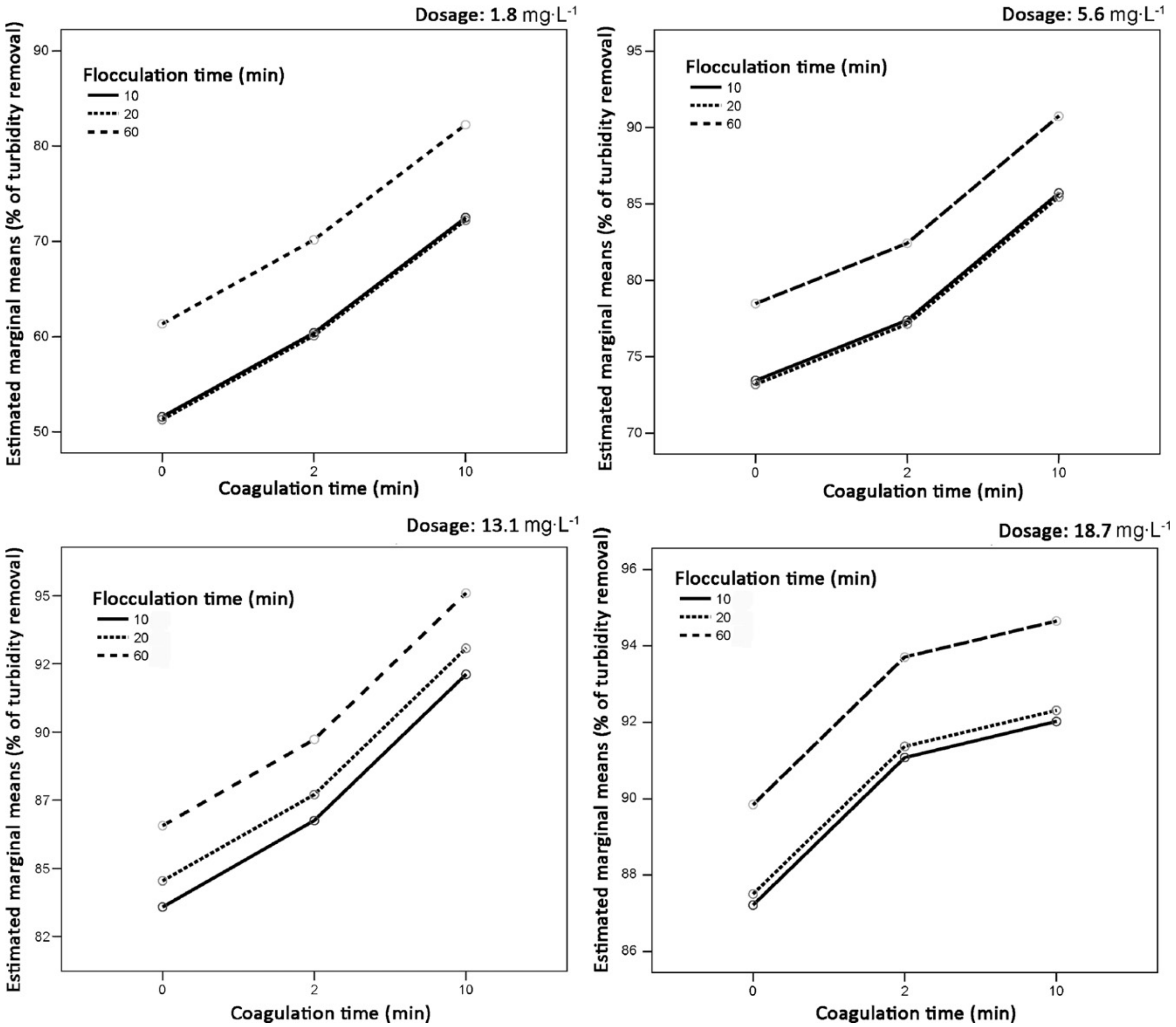

Fig. 7. Interaction graphics of the different factors and levels. 20 °C, natural pH.

important on final turbidity than the other two factors, so the affection of each agitation stage can be studied just in case dosage does not exhaust the process effectiveness. In Fig. 7 it is also possible to observe that the slopes reflect this fact: increasing doses means raising the turbidity removal. The lines become next one to each other and the absolute removal percentage is higher.

Tukey's multiple comparison method gives significance data about the difference between means. Significative *p*-values are obtained in the cases of varying rapid mixing time from 0 to 10 min in doses of 1.8 and 5.6 mg L^{-1} of *Silvafloc*. In the case of 13.1 mg L^{-1}, the same modification in coagulation time gives a near-to-significance value (0.054).

It is particularly interesting the case of 1.8 mg L^{-1} dose. Table 2 shows the different *p*-values and upper and lower limits in 95% confidence interval for means differences. It is possible to obtain significative differences between 0 and 10 min for this dosage. In this case, the mean of turbidity removal would decrease between 37.02 and 4.79 units (*p*-value equal to 0.021). In the case of 5.6 mg L^{-1}, this variation would be between 23.74 and 0.78 units (*p*-value equal to 0.041).

Analogous behavior can be observed with the following dosages. Absolute turbidity removal values are considerably higher as dosage is incremented. The number of significative mean differences in the multiple comparison procedure is decreased as well. No more statistical significance of the observed differences were found.

3.7. Agitation speed

In order to evaluate the importance of agitation speed and process period in a one-stage procedure, several trials were carried out. Working parameters were the following ones: agitation speed (10–100 rpm); agitation time (10–60 min) and coagulant dosage (1.8–18.7 mg L^{-1}).

A statistical study similar to previous case was carried out, but a strong interaction was found between the three factors. Due to

Table 2
Significative *p*-values and 95% confidence intervals for mean differences in coagulation stages.

Dosage	Coagulation first value	Coagulation second value	*p*-Value	Confidence interval (95%)	
				Upper limit	Lower limit
1.8 mg L^{-1}	10 min	0 min	0.021	37.02	4.79
5.6 mg L^{-1}	10 min	0 min	0.041	23.74	0.78

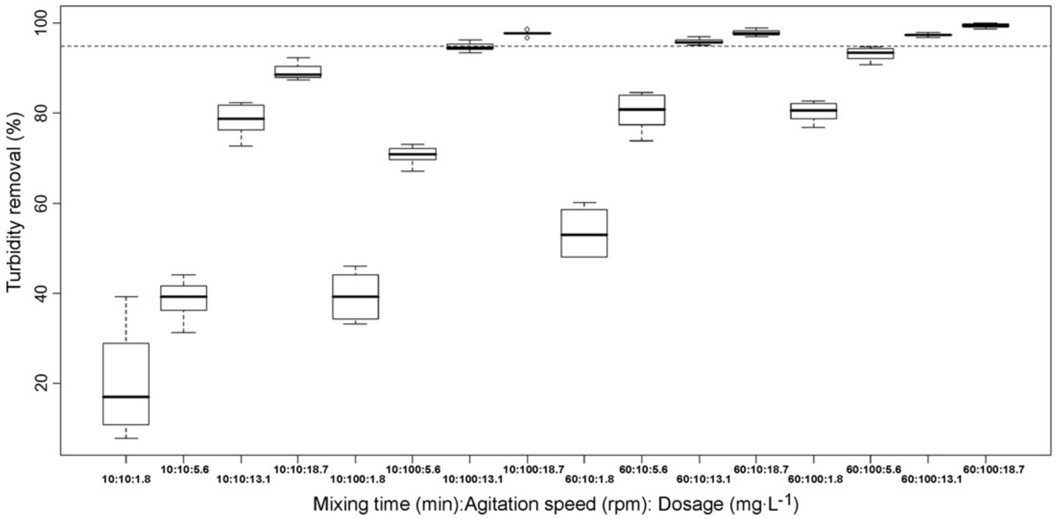

Fig. 8. Box-plot graphic of the several factor combinations. 20 °C, natural pH.

this fact, a new model should be carried out, in which 8 replications were done for each combination. This new factorial design took into account as many categories as possible combination of the three parameters were done. Fig. 8 represents a Box-plot where every combination is showed according to stage duration, dosage and agitation speed. Percentual turbidity removal is referred.

As a first consideration, several combinations may be taken into account. A turbidity removal of 95% is achieved in 6 cases with different values of agitation speed, stage duration and dosage. Dispersion is less in these experiments than in the others, with lower turbidity removal percentage. Pointed rule separates these 6 cases.

In order to know if there is any significative difference between them, Kruskal–Wallis test has been applied. With a p-value < 0.0001, this non-parametric statistic guarantees us no distinguishable difference appears among their effectiveness. Multiple comparisons by Tukey's method also confirm this fact (p-value > 0.05). An economical study of stirring costs may be done in order to select the best combination.

The main question that has to be answered is whether a long, slow stage is preferable to a fast, short process in economical terms, bearing in mind a similar turbidity removal. Stirring considerations may be carried out.

For the particular case of a blade stirrer, the power required by it depends on the speed of rotation (n, s^{-1}), the stirrer diameter (d, m), the density (ρ, $\mathrm{kg\,m}^{-3}$) and the kinematic viscosity of the medium (ν, $\mathrm{m}^2\,\mathrm{s}^{-1}$). Newton or power number (N_e) is specific for each stirrer and vessel. A characteristic curve [47] puts in relation N_e and Reynolds number (given by Eq. (3)):

$$Re = \frac{nd^2}{\nu} \tag{3}$$

For the present case Re is equal to 6.70×10^4 for 100 rpm and to 2.01×10^4 for 30 rpm. Ullmann's Encyclopedia [47] sets N_e values in 0.5 and in 0.9, respectively, for each case. Eq. (4) shows the relationship between power and N_e:

$$P = N_e n^3 d^5 \rho \tag{4}$$

where P is the required power (W).

As it is known, required work (W h) is given by Eq. (5):

$$W = Pt \tag{5}$$

where t is the working time (min).

According to this, power requirements relationship between fast and slow agitation, referring to process duration, is given by expression (6):

$$\frac{W_{100}}{W_{30}} = \frac{N_{e100} n_{100}^3 d^5 \rho t_{100}}{N_{e30} n_{30}^3 d^5 \rho t_{30}} \tag{6}$$

which shows a relationship between W_{100} and W_{30} equal to 3.43. It reveals a higher energy efficiency of the long, slow stage instead of the short, fast one. As dosage is not too high in any case, combinations with a slow agitation and long duration would be preferable. Optimum then is set in 60:10:18.7 (Fig. 8).

3.8. Treated water quality

In order to verify the improvement in water quality, several parameters were evaluated on treated water, once the treatment is finished.

3.8.1. $KMnO_4$ oxidability

Results are shown in Fig. 9. As can be appreciated, after flocculant addition total organic matter increases linearly, but no further increasing is observed after the flocculation process, so all organic matter added by coagulant is removed. A slight decreasing in organic matter is achieved (around 30%) if compared to initial organic matter content. No higher percentage is observed due

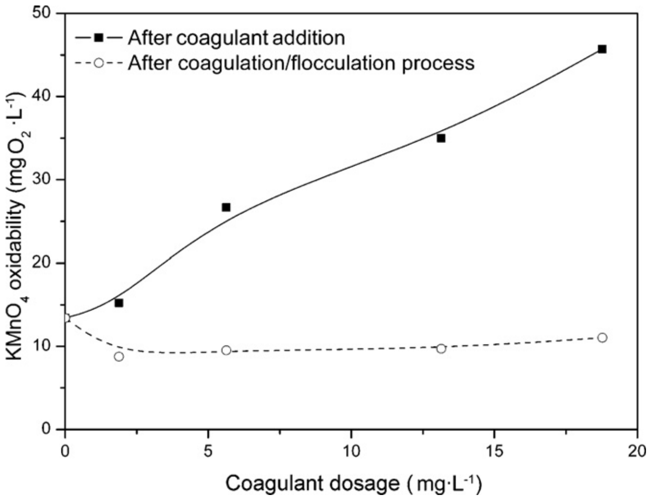

Fig. 9. $KMnO_4$ oxidability in treated water. 20 °C, natural pH.

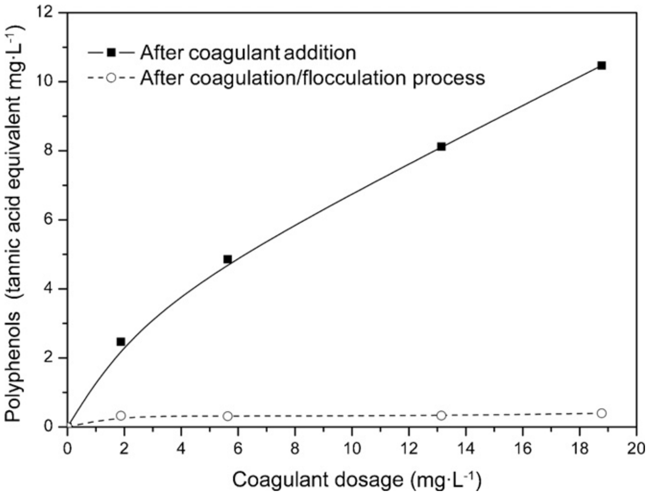

Fig. 10. Polyphenols concentration in treated water. 20 °C, natural pH.

surely to the low initial content, which is around 13.5 mg O_2 L^{-1}. Seasonal fluctuations may be taken into account for further studies [48].

3.8.2. Residual polyphenols

As *Silvafloc* is a modified tannin extract, polyphenols content in treated water must be determined in order to discard high tannin residual level. Two variables are defined then: the tannin concentration immediately after the Jar-test and what is presented after sedimentation time. Fig. 10 shows how first variable increases with coagulant dose, while second one keeps stable, although coagulant dose increases. Residual polyphenols level in water is around 0.4 mg L^{-1} (as tannic acid mg L^{-1} equivalent), much lower than other values, e.g. in tea beverage [49].

3.8.3. Microorganisms

Since disinfection aspects have been thoroughly considered in other works [50], finally, microorganisms removal was determined in treated water. Fig. 11 indicates how the three studied species are removed by the action of *Silvafloc*. As it is depicted, microorganism populations are observed before and after coagulation and flocculation treatment. This removal is increased as doses increases and it is clear that by removing turbidity (that is, organic suspended matter) microorganisms undergo a loss of their natural supporting structure, so high removal is achieved. Above all, in cases of *streptococcus* and *fecal coliforms* an almost total removal is achieved.

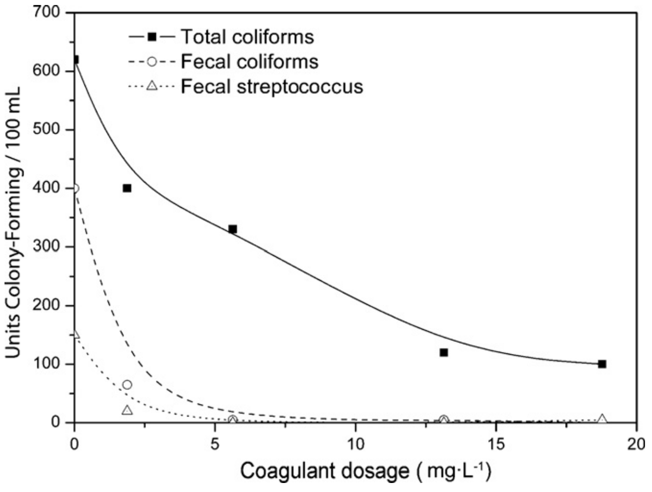

Fig. 11. Microorganisms reduction in treated water. 20 °C, natural pH.

4. Conclusions

Schinopsis balansae derived tannin is presented as a highly effective treatment agent for surface water clarification. Turbidity reduction achieves up to 80% with relatively low dosages and the process is not affected by temperature or pH. The two stages of classical Jar-test were influent in the final result of turbidity removal. The study of several combination of time and speed agitation conducted to an optimum one step treatment, according to economic principles. This combination is stated at 10 rpm, 60 min and 18.7 mg L^{-1}. Treated water presented less organic matter (permanganate oxygen demand), very low tannin concentration and high microorganism decreasing.

Acknowledgments

Authors want to thank COMISIÓN INTERMINISTERIAL DE CIENCIA Y TECNOLOGÍA (CICYT CTQ 2010-14823/PPQ project) as well as to JUNTA DE EXTREMADURA (PRI-07A031 project).

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