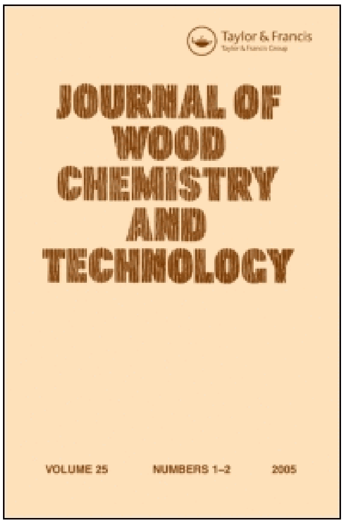

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J. Sánchez-Martín[a]; M. González-Velasco[b]; J. Beltrán-Heredia[a]
[a] Department of Chemical Engineering and Physical Chemistry, University of Extremadura, Badajoz, Spain [b] Department of Mathematics, University of Extremadura, Badajoz, Spain

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Acacia mearnsii de Wild Tannin-Based Flocculant in Surface Water Treatment

J. Sánchez-Martín,[1] M. González-Velasco,[2] and J. Beltrán-Heredia[1]
[1]Department of Chemical Engineering and Physical Chemistry, University of Extremadura, Badajoz, Spain
[2]Department of Mathematics, University of Extremadura, Badajoz, Spain

Abstract: Drinking water and wastewater treatment usually requires a coagulation/flocculation stage. Some disadvantages are presented by usual agents, above all linked to environmental, economical, and health aspects. Effectiveness of a new wood-derived flocculant agent has been studied, it consists of *Acacia mearnsii* modified tannin extract. Results have been very satisfactory; low flocculant dosage (up to 10 mg·L^{-1}) may remove almost all suspended matter in surface water. Flocculant works better in acid pH (4–5), but an accurate dose minimizes the influence of this factor. Temperature does not affect effectiveness, but high initial turbidity may raise process efficiency. Duration of coagulation and flocculation stages seems to affect both positively to turbidity removal and in a non-interaction way. Dosage is much more important than both coagulation or flocculation stages. Treated water does not present either organic matter significantly increasing or a high residual tannin concentration. Microorganisms as *total coliforms, fecal coliforms*, and *fecal streptococcus* have been reduced up to 80%, 90%, and 99%, respectively.

Keywords: Coagulation–flocculation, natural flocculants, surface water, tannins, turbidity removal

INTRODUCTION

This article aims to study water treatment agents that may differ from industrial and commercial ones. Implementation of an adequate technology for

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Address correspondence to J. Sánchez-Martín, Department of Chemical Engineering and Physical Chemistry, University of Extremadura, Avda. de Elvas, s/n, 06071, Badajoz, Spain. E-mail: jsanmar@unex.es

water treatment, above all in developing countries, is the scope of this and other works. Sustainable and available technologies that fit to poverty situation may be characterized and researched at laboratory scale. In this sense, natural coagulants/flocculants are wide-spread, easy-handling resources that are not difficult to maintain by non-qualified personal. There are some examples of these agents, as *Moringa oleifera* [1]or *Opuntia ficus*.[2]

Vegetal products have been studied by several researchers for a long time as a source of water treatment agents. Particularly, wood-derived matters are considered as high effective adsorbents.[3,4] Usually, the common way of modifying original natural matters involves thermical process and a pore characterization. Chemical modifications are not completely known[5] due to the complex nature of wood materials.

Tanfloc is a trademark that belongs to TANAC (Brasil). It is a tannin-based product, which is modified by a physico-chemical process, and has a high flocculant power. It is obtained from *Acacia mearnsii de Wild* bark. This tree is very common in Brasil and it has a high concentration of tannins. Production process is under intelectual patent law, but similar procedures are widely reported as Mannich base reaction.[6,7] Specific industrial process for *Tanfloc* is referred by U.S. patent number 6,478,986 B1.[8] It involves tannin polymerization by addition of formaldehyde (37%), ammonium chloride, and commercial hydrochloric acid. The product so obtained under certain temperature conditions has a viscous appearance with 36% of active material.

Under *tannins* denomination there are lots of chemical families. Tannins have been used traditionally for tanning animal skins, but it is possible to find several products that are distributed as flocculants. Tannins come from vegetal secondary metabolytes[9]: bark, fruits, leaves, and so on. Bark from *Acacia* and *Schinopsis* are main tannin feedstock. However, it is not needed to search for tropical species: *Quercus ilex, suber*, or *robur* as well as *Castanea* or *Pinus* also have tannin-rich bark.

Few authors have investigated about tannins water treatment capacity, although their ability in removing heavy metals is well demonstrated.[10] Özacar and Sengil[11] characterized tannins obtained from *valonia*, an autoctonous tree from Turkey, and used them for coagulation-flocculation process of wastewater. Authors demostrated that tannin has a very good effect, combined with $Al_2(SO_4)_3$ in order to enhance further stages of sludge removal.

Zhan and Zhaob[12] tried to remove lead from water by using an adsorbent, tannin-based gel. Process of metal removal is improved by tannin gelification. In the same sense, there are other references ([13, 14], and recently[15]).

Özacar and Sengil[16] enhanced the previous article and gave special data about trihalomethanes formation and other undesirable compounds, as well as treated water safety. They worked always with a tannin–$Al_2(SO_4)_3$ combination.

Palma et al.[17] used tannins extracted *in situ* from *Pinus radiata* bark in order to polymerize a solid which is used in heavy metals removal. Bark itself was combined with a tannin solid into adsorption columns.

Previous studies have been found about *Tanfloc* coagulant activity.[18,19] The main aim of the present investigation is to characterize the coagulant and flocculant activity of this new tannin-based product as a surface water treatment. The chemical modification made on *Acacia mearnsii* tannin is not quite difficult and different variations have been reported under several patents.[20–23] Namely, tannins undergo Mannich aminomethylation by reaction with an aldehyde and an amine. 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. This is the reason it can work as a natural flocculant.

Therefore, this investigation should be considered as an initial approach to these kind of coagulant and flocculant agents.

MATERIALS AND METHODS

Tanfloc is the commercial coagulant agent that was used in this investigation. According to TANAC specification, *Tanfloc* is a vegetal water-extract tannin, mainly constituted of flavonoid structures with an average molecular weight of 1.7 kDa. It is presented as powder. More groups as hydrocolloids gums and other soluble salts are included in Tanfloc structure. Chemical modification includes a quaternary nitrogen that gives *Tanfloc* cationic character.

The industrial production of *Tanfloc* involves the reaction between formalin, ammonium chloride, and commercial hydrochloric acid. The mixture is stirred and heated and tannin extract is added. The reaction keeps on during several hours more and then a viscous mixture with 40% of solids content is achieved. Allowing it to evaporate, *Tanfloc* in its powder form is produced.[8]

Toxicological information referring to *Tanfloc* is given by TANAC. There are not indicated health risks at the working dosages, as semilethal dosage in mice was determined to be in 9,241 $mg \cdot kg^{-1}$. In the case of alum, for example, another supplier (commercial GODÓ, Spain) gives a semilethal dosage of 1,735 $mg \cdot kg^{-1}$.

In order to compare *Tanfloc* ability in removing suspended matter with other traditional coagulant agents, aluminium sulfate $Al_2(SO_4)_3 \cdot 18H_2O$ (PANREAC) was tested.

Raw surface water was obtained from Guadiana river at Badajoz (southwest of Spain). The experimental procedure was the following: 1 L of surface turbidity-known water was put into a beaker. Certain dose of flocculant was added, and the beaker was put into a Jar-test apparatus (VELP-Scientifica JLT4). Standard Jar-test procedure consisted of two stirring periods: one at 100 rpm for 2 minutes and other one at 30 rpm for 20 minutes. In order to study the influence of these two periods, their duration and agitation intensity were varied. Turbidity was measured with a HI93703 turbidimeter (Hanna Instruments)

1 h after Jart-test was finished. Turbidity sample was obtained from the center of the beaker, 3 cm from surface.

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 described in APHA[24] was used as well.

Disinfectant effectiveness was determined by adding 10 mg of flocculant to 1 L of raw surface water, and it was kept stirring for 3 h. Different samples were collected, and microorganism concentrations were measured.

Tannin concentration was determined by the *Folin-Ciocalteau* test.[25,26] Results are expressed in tannic acid equivalent mg·L^{-1}.

RESULTS AND DISCUSSION

Raw Water Characterization

Surface water was selected to work on. It was taken from Guadiana river, at Badajoz. It is intended with this decision to study the problem from a real point of view, avoiding turbid water simulation with a different chemical-physical procedure as kaolin addition.[27] River water was treated the same day it was collected, and its average characteristics are shown in Table 1.

Optimum Flocculant Dosage

Different assays were done in order to determine the optimum dosage of flocculant, as well as to observe turbidity removal evolution with flocculant dosage. Flocculant dosage was varied between 1 and 8 mg·L^{-1} and standard Jar-test procedure was used. Results are shown in Figure 1.

As it is appreciated, dosage between 1 and 6 mg·L^{-1} carry out significative turbidity removal. This range was selected for analyzing all other parameters that influence turbidity removal.

A very high efficiency in turbidity removal is considered with reduced flocculant concentrations. Equal doses of alum have achieved a reduction of 82%, compared to 97% of turbidity removal that is achieved with the same dose of *Tanfloc*.

Other researchers have worked on real water with coagulation and flocculation process.[28] Aluminium has been reported as a coagulant-flocculant agent in higher dosage (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.[29]

Table 1. Raw water characterization data

Parameter	Units	Value
Conductivity	$\mu S \cdot cm^{-1}$	400
pH		7.5
Suspended solids	$mg \cdot L^{-1}$	15
Total solids	$mg \cdot L^{-1}$	452
Turbidity	NTU	123.3
Calcium	Ca^{2+} $mg \cdot L^{-1}$	37.7
Hardness	$CaCO_3$ $mg \cdot L^{-1}$	152
Ammonium	N $mg \cdot L^{-1}$	1.81
Nitrate	NO_3 $mg \cdot L^{-1}$	5.3
Nitrite	N $mg \cdot L^{-1}$	0.033
Chloride	Cl^- $mg \cdot L^{-1}$	40.4
$KMnO_4$ oxidability	O_2 $mg \cdot L^{-1}$	19.3
Phosphate	P $mg \cdot L^{-1}$	0.044
Total phosphorus	P $mg \cdot L^{-1}$	0.064
Total coliforms	Colonies/100 mL	800
Fecal coliforms	Colonies/100 mL	400
Fecal streptococcus	Colonies/100 mL	140

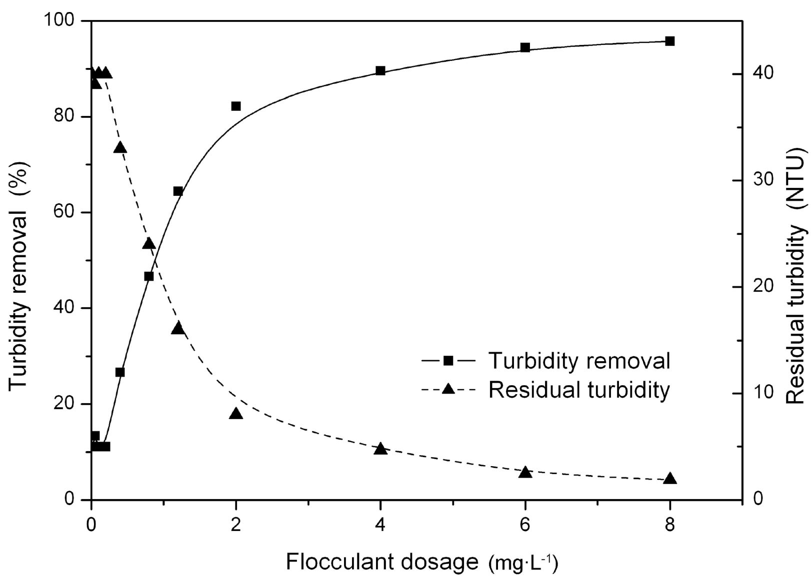

Figure 1. Turbidity removal evolution with flocculant dosage.

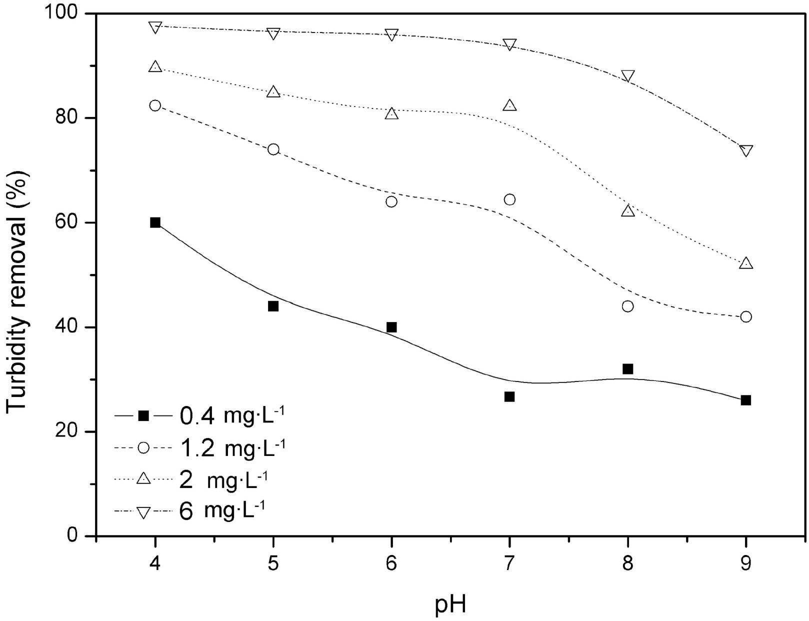

Figure 2. pH influence on turbidity removal.

pH

Assays with different flocculant concentrations were carried out, varying pH conditions between 4 and 9. Results of this series are shown in Figure 2. Standard Jar-test assay was carried out. Coagulation-flocculation process is more effective with slightly acid pH (near to 4). However, with a neutral pH value, flocculant effectiveness is high enough. In scaled-up installation no pH modification will be needed.

This behavior may be due to the structural nature of tannin-based flocculant, which is known to be denaturized at alkaline pH.

Similar results affecting other flocculant agents have been reported,[30] where different coagulants including alum were tested in order to evaluate their efficiency for suspended matter removing. However, a big pH dependency was found by varying pH values between 6 and 8.5, which is not shown in the present results.

Temperature

Assays with different flocculation temperature were carried out. Temperature was varied between 10 and 40°C. No significative effectiveness variations were observed, above all in assays with high concentration of flocculant (data not

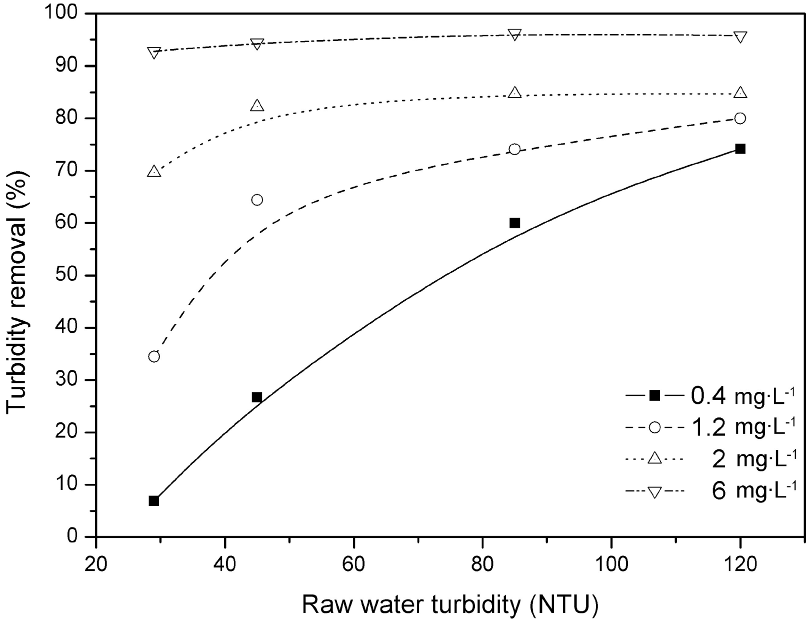

Figure 3. Raw water turbidity charge influence on turbidity removal.

shown). In the same sense, differences between coagulation and flocculation at 19 and 28°C were found as well.[30] The results obtained there agree with ours.

Raw Water Initial Turbidity

Assays varying raw water initial turbidity were carried out. Turbidity varied between 20 and 120 NTU. As can be appreciated in Figure 3, process effectiveness improves gradually by increasing initial turbidity. This difference is significative above all with low flocculant dosage (0.4, 1.2 mg·L^{-1}). In higher doses, no improvement is appreciated.

The reason that explains this behavior may be found in the fact that flocs become more compacted and more stable as suspended matter is increased. *Tanfloc* acts as flocculant too, not only as coagulant agent. Nature of flocs that are formed from surface water is not very heavy, so with the same dose of *Tanfloc*, these flocs tend to be bigger.

Variables in Flocculation Assay

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

Statistical Analyses

For each assay, the influence of coagulation and flocculation stages was studied by way 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 were 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 $\leq .05$. All data analysis was performed using the language and environment for statistical computering R ("GNU") version 2.7.0[31] and SPSS version 15.0 statistical package (SPSS Inc., Chicago, Illinois).

Duration of Each Agitation Stage

In order to characterize the importance of rapid stage (coagulation, 100 rpm) and slow stage (flocculation, 30 rpm), one referred to the other and both referred to coagulant dosage, different assays were carried out. Coagulation time has been varied between 1 and 30 minutes, flocculation time between 10 and 60 minutes, and dosage between 0.4 and 6 mg·L^{-1}. The applied model includes one replication for each combination.

As Figure 4 shows, for each dosage, no interaction is found between coagulation and flocculation time as long as no cross takes place and all the lines are parallel. By carrying out the corresponding analysis of variance for coagulation and flocculation stages for each coagulant dosage, it was found that significant differences in means appear just in the case of 0.4 mg·L^{-1} for both coagulant and flocculant stage and in the case of flocculant stage for 2 mg·L^{-1} (p-values are .005, .029, and .049, respectively). In the rest of the cases, near to significant p-values are obtained just in the case of flocculation, while they become progressively higher in the case of coagulation. This fact may reflect the growing importance of dosage in front of flocculant and coagulant stages duration. Coagulation and flocculation processes may be improved in a high level just by increasing dosage, so the importance of the duration of coagulation and flocculation stages may decrease.

The importance of these two agitation stages are particularly interesting in the case of 0.4 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 significant differences between 30 minutes, and any other

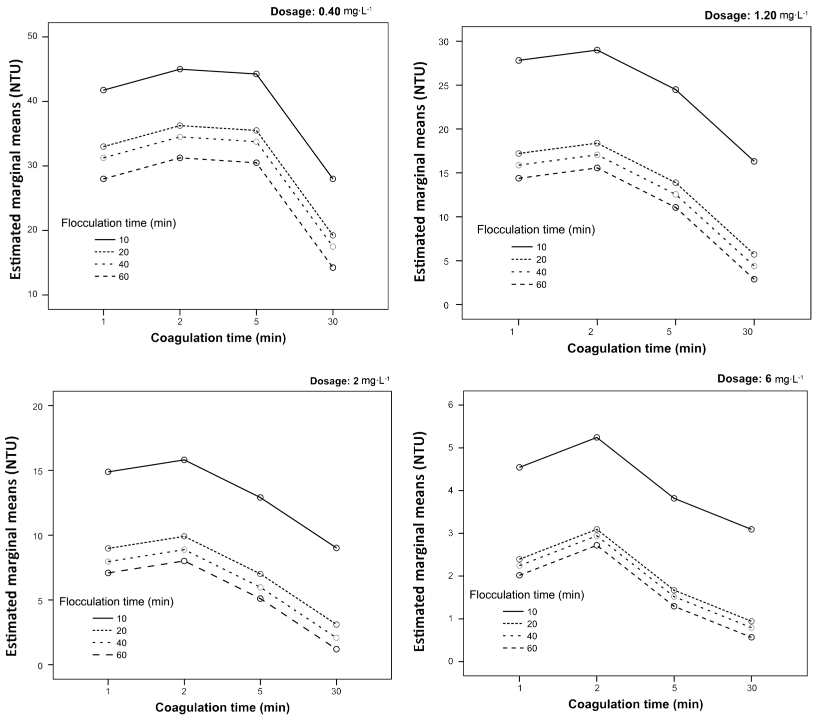

Figure 4. Interaction graphics of the different factors and levels.

value in coagulation (p-values equal to .023, .07, and .09 referring to 1, 2, and 5 minutes) and between 10 and 60 minutes in flocculation (p-value equal to 0.023).

Analogous behavior can be observed with the following dosages (1.2, 2, and 6 mg·L^{-1}). Absolute NTU values are considerably lower as dosage

Table 2. Significative p-values and 95% confidence intervals for mean differences in both coagulation and flocculation stages for 0.4 mg·L^{-1}

Coagulation first value	Coagulation second value	Confidence interval (95%)		
		p-value	Upper limit	Lower limit
30 min	1 min	0.023	−25.57	−1.93
	2 min	0.007	−28.82	−5.18
	5 min	0.009	−28.07	−4.43
Flocculation first value	Flocculation second value			
10 min	60 min	0.023	1.93	25.57

is incremented. The number of significative mean differences in the multiple comparation procedure is decreased as well. It is possible to find statistical differences in the means just between 10 and 60 minutes for coagulation stage in the case of 2 mg·L^{-1} dosage (p-value equal to .049). No more statistical significativity of the observed differences were found.

Time-Variable One-Stage Jar-Test Procedure

In order to evaluate the importance of agitation speed and process period in a one-stage procedure, several assays were carried out. Varying parameters were the following ones: agitation speed (10 to 200 rpm); agitation time (10 to 60 min), and flocculant dosage (0.4 to 10 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 this fact, a new model should be carried out, in which four 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. Figure 5 represents a boxplot where every combination is shown according to stage duration, dosage, and agitation speed. In this case, percentual turbidity removal is reported.

As a first consideration, several combinations may be taken into account. A turbidity removal of 95% is achieved in 7 cases with different values of agitation speed, stage duration, and dosage. 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, kg·m^{-3}), and the kinematic viscosity of the medium (ν, m$^2 \cdot$ s^{-1}). Newton or power number (N_e) is specific for each stirrer and vessel. Table 3 reports the used nomenclature. A characteristic curve[32] puts in relation N_e and Reynolds number (given by Eq. [1]).

$$Re = \frac{n \cdot d^2}{v} \tag{1}$$

For the present case Re is equal to $6.70 \cdot 10^4$ for 100 rpm and to $2.01 \cdot 10^4$ for 30 rpm. *Ullmann's Encyclopedia*[32] sets N_e values in 0.5 and in 0.9, respectively, for each case. Eq. (2) shows the relationship between power and Ne.

$$P = N_e \cdot n^2 \cdot d^5 \cdot \rho \tag{2}$$

where P is the required power (W).

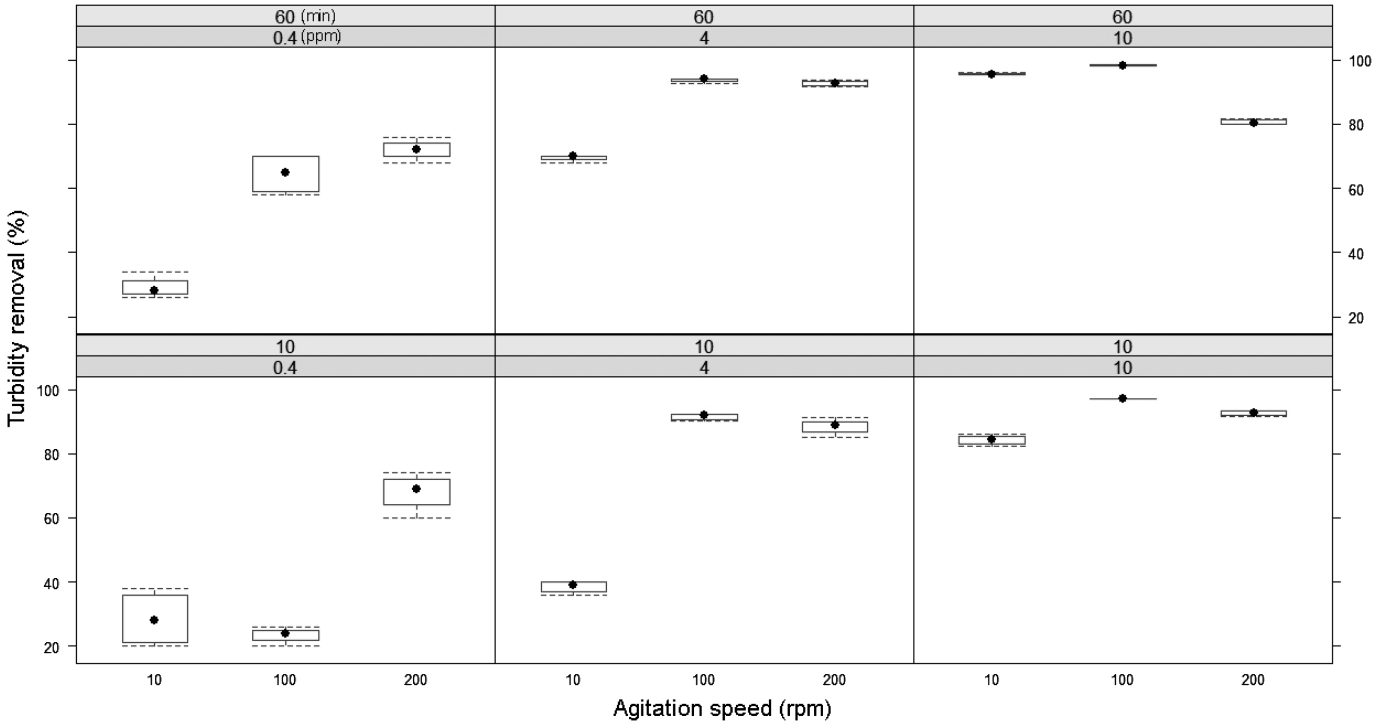

Figure 5. Box-plot graphic of the several factor combinations.

Table 3. Nomenclature

Variable	Symbol	Units
Reynolds number	Re	dimensionless
Rotation speed	n	s^{-1}
Stirrer diameter	d	m
Density	ρ	$kg \cdot m^{-3}$
Kinematic viscosity	ν	$m^2 \cdot s^{-1}$
Newton or Power Number	Ne	dimensionless
Power	P	W

According to this, power requirements relationship between fast and slow agitation, referring to process duration, is given by Eq. (3).

$$\frac{W_{100}}{W_{30}} = \frac{N_{e100} \cdot n_{100}^3 \cdot d^5 \cdot \rho \cdot T_{100}}{N_{e30} \cdot n_{30}^2 \cdot d^5 \cdot \rho \cdot T_{30}} \tag{3}$$

which shows a relationship between W_{100} and W_{30} equal to 3.43. It reveals a higher energy effciency 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 60:10:10 (upper right quadrant in Figure 5). The fact that the product we are working with presents a rather affordable price leads to this solution as the cheapest way of obtaining a more than acceptable turbidity removal. Increasing agitation speed is more expensive than prolonging the treatment period.

Treated Water Quality

$KMnO_4$ Oxidability

Organic oxidable matter in treated water was evaluated according to $KMnO_4$ test. Results are shown in Table 4. As can be appreciated, a gradual loss of

Table 4. Reduction in $KMnO_4$ oxidability with application of *Tanfloc*

Flocculant dosage ($mg \cdot L^{-1}$)	$KMnO_4$ oxidability (O_2 $mg \cdot L^{-1}$)
0	34.61
2	27.69
5	6.92
7	9.23
10	20.76

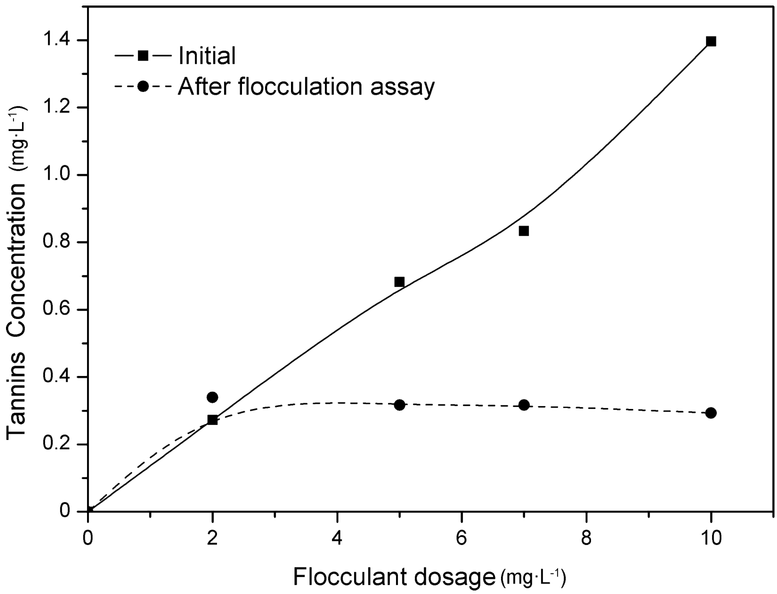

Figure 6. Tannins concentration in treated water.

organic matter is observed, until a minimum (around 6 mg·L^{-1} of flocculant), then organic matter begins to raise. This may be due to the fact that sedimentation is not completely effective until this minimum point (95% turbidity removal). Higher doses lead to a flocculant concentration that remains in water, without flocculate; lower doses do not remove all turbidity. Seasonal fluctuations may be taken into account for further studies.[33]

Residual Tannins

As *Tanfloc* is a modified tannin extract, it has been determined tannin content before flocculation assay (just after flocculant addition), and those that remain in equilibrium after assay. Figure 6 shows how the first variable increases with flocculant dose, while the second one keeps stable, although flocculant dose increases. Residual tannins level in water is around 0.3 mg·L^{-1} (measured as tannic acid mg·L^{-1} equivalent), much lower than other values, for example in tea drink.[34]

Microorganisms

As disinfection aspects have been thoroughly considered in other works,[35] finally, microorganisms removal was determined in treated water. Figure 7 indicates results for the three studied species. In it, microorganism populations

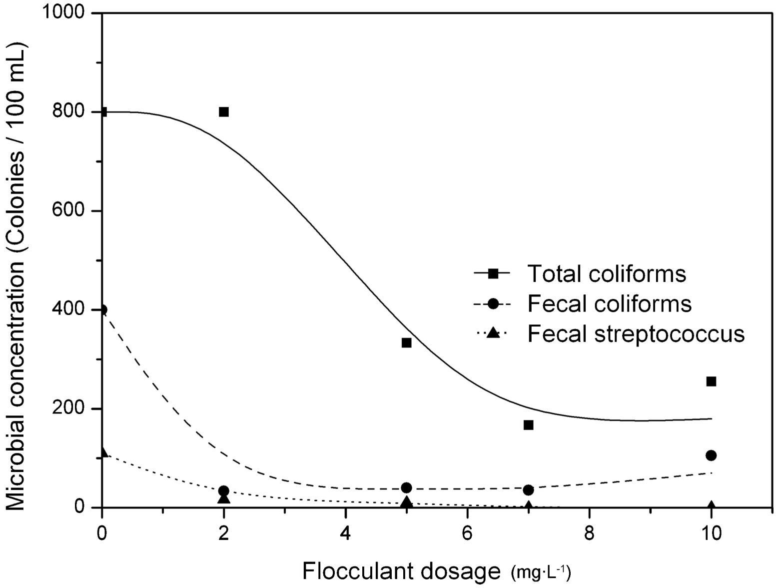

Figure 7. Microorganism reduction in treated water.

are observed before and after flocculant treatment. This microorganisms removal is increased as dose increases. It is clear that by removing turbidity (that is, organic suspended matter) microorganisms may lose their natural supporting structure, so a high removal is achieved. Table 5 shows the results of another assay: *Tanfloc* 10 mg·L^{-1} dosage was added to a continuously stirred vessel, and different samples were taken out. As can be appreciated, the process has a partial disinfection effciency. It reached a high removal of the three species.

Table 5. Disinfectant effectiveness

	Microorganisms survival (%)		
Time (min)	Total coliforms	Fecal coliforms	Fecal streptococcus
0	100	100	100
10	60.2	100	100
30	46.7	59.4	27.3
90	32.3	43.3	30.3
210	28.3	40.5	18.2

CONCLUSIONS

This investigation has revealed the following conclusions:

- *Acacia mearnsii*–derived tannin flocculant is a highly effective treatment agent for surface water. Turbidity reduction achieves 99% at relatively low dosage (around 10 $mg{\cdot}L^{-1}$).
- Temperature does not affect tannin effectiveness so much, although low pH seems to enhance turbidity removal activity.
- The higher initial turbidity is, the higher percentual turbidity removal is achieved with the same low dosage of *Tanfloc*.
- Referring to flocculation assay, both coagulation and flocculation stages are important. They are factors with no cross interaction, so by increasing them separately turbidity removal is increased. The importance of dosage is much more significant than coagulation and flocculation stage duration.
- Several combinations of time and speed agitation may be done for determining the optimum in a one-stage treatment. According to economic principles, the best combination should be 10 rpm for 60 minutes with a 10 $mg{\cdot}L^{-1}$ dosage.
- Treated water presents less COD (measured as $KMnO_4$ oxidability), a very low remaining tannins concentration (0.3 $mg{\cdot}L^{-1}$), and a high microorganism decrease, so water quality is highly improved by this treatment.

REFERENCES

1. Fuglie, L.J. *The Miracle Tree. The Multiple Atributes of Moringa*. Technical Centre for Agricultural and Rural Cooperation, 2001.
2. Young, K.; Anzalone, A.; Alcantar, N.A. Using the Mexican cactus as a natural-based process for removing contaminants in drinking water. Polym. Mat. Sci. & Eng. **2005**, *93*, 965–966.
3. Pulido, L.L.; Hata, T.; Imamura, Y.; Ishihara, S.; Kajimoto, T. Removal of mercury and other metals by carbonized wood powder from aqueous solutions of their salts. J. Wood Sci. **1998**, *4*(3), 237–243.
4. Geay, M.; Marchetti, V.; Clément, A.; Loubinoux, B.; Gérardin, P. Decontamination of synthetic solutions containing heavy metals using chemically modified sawdusts bearing polyacrylic acid chains. J. Wood Sci. **2000**, *46*(4), 331–333.
5. Kawamoto, H.; Nakatsubo, F.; Murakami, K. Relationship between the B-ring hydroxylation pattern of condensed tannins and their protein-precipitating capacity. J. Wood Chem. Technol. **1990**, *10* (3), 401–409.
6. Roux, D.G.; Ferreira, D.; Hundt, H.L.; Malan, E. Structure, stereochemistry, and reactivity of natural condensed tannins as basis for their extended industrial application. Appl. Polym. Symposium. **1975**, *1*(28), 335–353.
7. Tramontini, M.; Angiolini, L. *Mannich Bases. Chemistry and Uses*; CRC Press: Boca Raton, FL, 1994.

8. Lamb, L.H.; Decusati, O.G. Manufacturing process for quaternary ammonium tannate, a vegetable coagulating and flocculating agent. US patent 6,478,986 B1, 2002.
9. Schofield, P.; Mbugua, D.M.; Pell, A.N. Analysis of condensed tannins: A review. Animal Feed Sci. Technol. **2001**, *91*(1), 21–40.
10. Satoshi, Y.; Fumiaki, N. Effects of the hydroxylation patterns and degrees of polymerization of condensed tannins on their metal-chelating capacity. J. Wood Chem. Technol. **2008**, *18*(2), 193–205.
11. Ozacar, M.; Sengil, A. Effectiveness of tannins obtained from *Valonia* as a coagulant aid for dewatering of sludge. Water Res. **2000**, *34*(4), 1407–1412.
12. Zhan, X.-M.; Zhaob, X. Mechanism of lead adsorption from aqueous solutions using an adsorbent synthesized from natural condensed tannin. Water Res. **2003**, *37*(16), 3905–3912.
13. Nakano, Y.; Takeshita, K.; Tsutsumi, T. Adsorption mechanism of hexavalent chromium by redox within condensed-tannin gel. Water Res. **2001**, *35*(2), 496–500.
14. Kim, Y.-H.; Nakano, Y. Adsorption mechanism of palladium by redox within condensed-tannin gel. Water Res. **2005**, *39*(7), 1324–1330.
15. Tondi, G.; Oo, C.W.; Pizzi, A.; Thevenon, M.F. Metal absorption of tannin-based rigid foams. *Industrial Crops and Products*, **2009**, *29*(2–3), 335–340.
16. Özacar, M.; Sengil, A. Evaluation of tannin biopolymer as a coagulant aid for coagulation of colloidal particles. Colloids and Surfaces A: Physicochem. Eng. Aspects **2003**, *229*(1), 85–96.
17. Palma, G.; Freer, J.; Baeza, J. Removal of metal ions by modified *Pinus radiata* bark and tannins from water solutions. Water Res. **2003**, *37*(20), 4974–4980.
18. Graham, N.; Gang, F.; Fowler, G.; Watts, M. Characterisation and coagulation performance of a tannin-based cationic polymer: A preliminary assessment. *Colloids and Surfaces A*: Physicochem. Eng. Aspects **2008**, *327*(1–3), 9–16.
19. Beltrán-Heredia, J.; Sánchez-Martín, J. Removing heavy metals from polluted surface water with a tannin-based flocculant agent. J. Hazardous Mat. In Press 2008 .
20. Quamme, J.E.; Kemp, A.H. Stable tannin based polymer compound. US patent 4,558,080, 1985.
21. Vasconcellos, S.R.; Boyce, P.D.; Smith, L.P. Methods for the flocculation of coal fines and insoluble metals in coal mine waters. US patent 4,183,575, 1993.
22. Reed, P.E.; Finck, M.R. Modified tannin mannich polymers US patent 5,659,002, 1997.
23. Mitchel, D.B.; Minnis, R.L.; Curran, T.P.; Deboo, S.M.; Kelly, J.A.; Patwardhan, R.; Tai, W.-T. Treatment of aqueous systems using a chemically modified tannin US patent 5,843,337, 1998.
24. APHA. *Standard Methods for the Examination of Water and Wastewater, 20th ed.* American Public Health Association and American Water Works Association and Water Environment Association, 1998.
25. Bianco, M.A.; Savolainen, H. Phenolic acids as indicators of wood tannins. Sci. Total Environ. **1997**, *203*(1), 79–82.
26. Box, J.D. Investigation of the Folin-Ciocalteau phenol reagent for the determination of polyphenolic substances in natural waters. Water Res. **1983**, *17*(5), 511–525.

27. Ghebremichael, K.A. *Moringa Seed and Pumice as Alternative Natural Materials for Drinking Water Treatment*. Ph.D. thesis, KTH Land and Water Resources Engineering, 2004.
28. Franceschi, M.; Giroua, A.; Carro-Diaz, A.M.; Maurette, M.T.; Puech-Costes, E. Optimisation of the coagulation–flocculation process of raw water by optimal design method. Water Res. **2002**, *36*(14), 3561–3572.
29. Flaten, P. Aluminium as a risk factor in Alzheimer's disease, with emphasis in drinking water. Brain Res. Bulletin **2001**, *55*(2), 187–196.
30. Zouboulis, A.I.; Traskas, G. Comparable evaluation of various commercially available aluminium-based coagulants for the treatment of surface water and for the post-treatment of urban wastewater. J. Chem. Technol. Biotechnol. **2002**, *80*(10), 1136–1147.
31. R Development Core Team. R: *A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna, Austria, 2008.
32. Zlokarnik, M. *Ullmann's Encyclopedia of Industrial Chemistry*. 6th edition, 2002.
33. Sharp, E.L.; Parsons, S.A.; Jefferson, B. Seasonal variations in natural organic matter and its impact on coagulation in water treatment. Sci. Total Environ. **2006**, *363*(1–3), 183–194.
34. Hung, Y.-T.; Chen, P.-C.; Chen, R.L.-C.; Cheng, T.-J. Determining the levels of tannin in tea by amperometry of ferricyanide pre-reaction with a sample in a flow-injection system. *Sensors and Actuators B*: Chem. **2007**, *130*(1), 135–140.
35. Sadiq, R.; Rodriguez, M.J. Disinfection by-products (dbps) in drinking water and predictive models for their occurrence: A review. Sci. Total Environ. **2004**, *32*1(1–3) 21–46.