Chemical Engineering Journal 162 (2010) 1019–1025

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

New coagulant agents from tannin extracts: Preliminary optimisation studies

J. Beltrán-Heredia, J. Sánchez-Martín*, M.C. Gómez-Muñoz

Universidad de Extremadura, Department of Chemical Engineering and Physical Chemistry, Avda. de Elvas, s/n, 06071 Badajoz, Spain

ARTICLE INFO

Article history:
Received 30 April 2010
Received in revised form 1 July 2010
Accepted 2 July 2010

Keywords:
Tannins
Acacia mearnsii de Wild
Schinopsis balansae
Cationization
Natural coagulant agents
Coagulation

ABSTRACT

Among the multiple uses of tannins, the production of coagulant agents is considered one of the most interesting one. The synthesis of tannin-derived coagulants is studied through a factorial design in order to evaluate the possible combinations between two types of tannin extracts (*Acacia mearnsii* de Wild and *Schinopsis balansae*) under three commercially-available products (*Clarotan*, *Weibull Black* and *Quebracho colorado*) and three types of amine compounds (*ammonium chloride*, *glycidyltrimethylammonium chloride* and *diethanolamine*). After several reproducibility verifications, the optimum product was found to be the one from *Clarotan* and *diethanolamine*, which was very effective if tested with surface river water, dye or surfactant-polluted wastewater. Real surface water was clarified with low coagulant dosages (ca. 10 mg L^{-1}), while dye concentration was reduced from 100 to 8 mg L^{-1} and surfactant concentration decreased from 50 to 7.5 mg L^{-1} with coagulant dosage of ca. 150 mg L^{-1}.

1. Introduction

Taking care of water resources is an important task to work on which is becoming more and more relevant in the last years. United Nations and World Health Organization have alert the international community about the growing menace of water scarcity or the uncontrolled disposal of pollutants in aqueous effluents. If considered as an affecting parameter to human lifes, water question is surely one of the main factors that are involved in the human development. Moreover, water is a transversal dimension in the challenge of Millenium Development Goals as it is widely known.

Concerns about water availability and reuse are not new. For many years human community is worried about hydric stress that is becoming one of the main problems in many areas [1]. Water is a central point in a wide cycle that links human beings, poverty, health and education and its implications towards the human development are crucial. Global present world has a double challenge regarding water management: on one hand water resources may be optimised in order to guarantee an adecuate availability for the large majority of the people. Nowadays, more than one in six do not have acces to safe fresh water [2]. This fact is even more acute if we take into account the shortage of safe water has a concomitant effect with living without basic sanitation, which is the case of 2.5 billion people [3].

Undoubtaly, this water shortage hits in an unequal way depending on the developing situation of countries. Israel can produce shrimp inside the desert by using advanced techniques of extracting water from beneath it [4] while almost 40% of total nicaraguan population has no home acces to tap water [5]. That fact reveals water subject is not linked to global technological advances, but to particular adequate systems of solving specific situations [6].

Technology is one of the mechanisms human beings can apply for fighting against poverty [7], but as it is a cultural construct is not free from social implications [8]. The concept of *appropriate technology* arose in mid-1970s and included some aspects that may be especially cared of in order to guarantee the social and environmental feasibility of a technical proposal. The target is to develop a new technological paradigm suitable mostly in developing countries (but not only) that lays on the following principles [9]:

- Environmental friendly (sustainability), that is, it does not endanger next generationss resources.
- Cultural suitability, that is, the solutions to given problems does not interfere with social manners or modals.
- Technological transfer, not external dependency of mechanisms, apparatus or equipments.

These premisses are summarized in one: technology must match both the user and the need in complexity and scale [8]. Relatively new research concerns are recently open in order to adequate first-line knowledges in this sense [10] for applying new discovers to so-called Third World.

* Corresponding author. Tel.: +34 924289300x9033; fax: +34 924289385.
E-mail addresses: jbelther@unex.es (J. Beltrán-Heredia), jsanmar@unex.es (J. Sánchez-Martín), cargomu@gmail.es (M.C. Gómez-Muñoz).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.07.011

Bearing in mind all above, it is important to keep on researching on new agents for water treatment according to appropriate technology principles.

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 flocculants. Their natural origin is as secondary metabolites of plants [11], 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 ilex*, *suber*, and *robur*, *Castanea*, and *Pinus* can also be tannin-rich.

New coagulants may be investigated in order to facilitate water treatment needs in a more environmental-friendly manner and even more easy handling way. Lowering the price of reagents is also a very important task. In this context, cationic tannins may be the source of new coagulating agents. Lab scale experiments have demonstrated it is possible to synthesize tannin-derived coagulant from several tannin feedstocks: *Acacia mearnsii* de Wild, *Schinopsis balansae*, *Pinus pinaster*. through a very simple procedure that involves Mannich base reaction. These water treatment coagulants are successfully tested on surfactant removal, dye elimination, municipal wastewater remediation or surface water clarification. Some commercial initiatives have arisen with these technological basis.

Tannins are mostly water-soluble polyphenolic compounds of molecular weight ranged between 500 and some thousands Daltons. There are three kinds: hydrolysable, condensed and complex tannin [12]. The chemical complexity of tannins and the fact that they are usually taken from natural matrix without a very thorough purification make knowing their structure a very difficult task. A full study about tannins, chemical structure and properties can be found in previous scientific literature [13].

Cationization of tannins is known as a chemical procedure that confers cationic character to the organic tannin matrix, so the main characteristics (such as solubility, stability at different pH levels or heavy metals quelating activity) are kept while other ones are added. These new abilities that appear have to do with the coagulating potential, since positive charged agents may destabilized anionic colloids once mixed in aqueous solution. Destabilization and subsequent settlement provoke the removal of a wide variety of anionic substances such as dyes, surfactants or organic matter.

The chemical procedure for making tannins become cationic is known to follow a *Mannich* reaction path and different variations have been reported under several patents [14–17]. Namely, tannins undergo *Mannich* aminomethylation by reaction with an aldehyde and an amine [18]. 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. The scientific literature refers a reaction mechanism that involves a tannin mixture, mainly polyphenol tannins whose structure may be similar to flavonoid structures such as resorcinol A and pyrogallol B rings. Briefly, *Mannich* reaction is described as the introduction of a quaternary nitrogen into the tannin complex structure [19].

Two main ways of obtaining *Mannich* bases are reported in scientific literature: one involving the NH_4Cl and another one involving other types of nitrogen compounds, such as mono or diethanolamine. The reaction is completed in both cases by the controlled addition of formaldehyde in a lower proportion than in gelification. Higher doses of formaldehyde would drive to tanning gelification and therefore it makes the product insoluble [20].

Although these kind of coagulants are quite well known, very few examples of investigations have been found about them. Regarding the main scope of water treatment treatment according these prescriptions they are found several previous papers that pointed out the use of tannins as a coagulant aid [21] or other cationic compounds [22]. Specifically, the use of tannin-based coagulants, in the sense we are pointing out, has been researched by [23], as well as in our own previous papers [24,25].

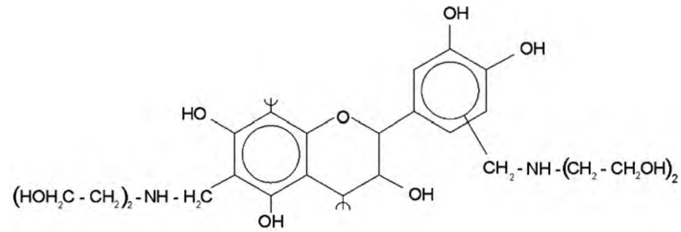

Fig. 1. Probable chemical structure of tannin-derived coagulant.

The production processes of these coagulants are not completely known, but by following the rules of *Mannich* reactions one can surely make an approach of their synthesis. E.g. in the case of diethanolamine (DEA), formaldehyde and the tannin extract mixture. Firstly, DEA and formaldehyde may react in the way described in Eq. (1):

$$HN\text{–}(CH2\text{–}CH_2OH)_2 + HCHO \rightarrow CH_2{=}N^+\text{–}(CH_2\text{–}CH_2OH)_2 + H_2O \quad (1)$$

what yields the reactive specie called *imine*. This may react with aqueous tannin extract mixture to form the coagulant whose chemical formula may respond to Eq. (2) and the expanded structure is shown in Fig. 1:

$$\text{tannin–}[CH_2\text{–}NH\text{–}(CH_2\text{–}CH_2OH)_2]_n \quad (2)$$

Environmental aspects are considered a primary target to work on, but usually economical and availability criteria are not taken into account when a technical solution is proposed for water remediation or clarification. This investigation focus its interest in advanced water treatment by means of a new coagulation process that is (a) cheaper than others, (b) based on a natural product, so its biodegradability is higher than other coagulants, and (c) using a coagulant agent that has no need of pH adjustment, so its usage is easier than others. If these and other economical considerations are not taken into account, the possibility of becoming clean is not a universal chance [26].

In this sense, we have developped a statistically significant study on the production of these kind of coagulants. Three types of amine (*glycidyltrimethylammonium*, *diethanolamine* and *ammonium chloride*) were tested with three types of tannin extracts (*Weibull black*, *Quebracho colorado* and *Clarotan*). A factorial design of experiments was carried out in order to evaluate the most interesting combination for surface water clarification, surfactant removal or dye elimination.

2. Materials and methods

2.1. Coagulant syntheses

The reagents involved in the cationization process are:

(1) Tannin extracts from *Schinopsis balansae* and from *Acacia mearnsii* de Wild. Commercial trademarks are *Quebracho ATO* (Q) for the first one and *Clarotan* (C) and *Weibull black* (W) for the second one. The three tannin extracts were supplied by TANAC Inc. (Brazil).
(2) Reagents involved in the coagulant synthesis are *ammonium chloride* (Cl), *diethanolamine* (D), *glycidyltrimethylammonium chloride* (G) and *formaldehyde* (F). The four products were supplied by SIGMA in commercial purity grade.

Table 1
Production processes of different tannin coagulants.

Amine	Tannin (g)	Amine (g)	Formaldehyde (g)	Reference
Ammonium chloride (Cl)	2.5	2.5	1.5	[40]
Diethanolamine (D)	2.5	10.8	1.5	[41]
Glycidyltrimethylammonium chloride (G)	2.5	2.5	0.06	[42]

According to previous data (Table 1), the cationization processes were conducted as follows:

- Certain fixed amount of tannin extract was diluted in distilled water at room temperature. Then the sample is thermostated at the reaction temperature (30 °C).
- Certain amount of amine is added to the mix: diethanolamine, ammonium chloride or glycidyltrimethylammonium chloride.
- Always under thermal control, formaldehyde is added to the reaction mixture. A peristaltic pump (MASTERFLEX, ColeParmer) must be used in this step, so it lasts 90 min at least.
- The product so obtained must be kept under agitation and at the same temperature for 24 h.

The final product is put in a 50 mL-flask and filled up to the mark with distilled water.

2.2. Real water samples

Surface water was selected to work on. It was taken from Guadiana river, at Badajoz (Southwest of Spain). It is pretended with this decision to study the problem from a real point of view, avoiding turbid water simulation with different chemical-physical proccedings. River water was treated the same day it was collected. The characteristics of this water are showed in Table 2.

2.3. Buffered solution

The trials with added dye (textile wastewater simulation) and surfactant (laundry water simulation) were performed with pH-stable media. To this end, a pH-7 buffer solution was prepared of 24 g of NaH_2PO_4 and 17.60 g of Na_2HPO_4 in 20 L of water. The pH was then adjusted to 7 with HCl 1 M or NaOH 1 M. All reagents were analytical grade from PANREAC.

2.4. Model compounds

Palatine Fast Black WAN, an azoic dye ($C_{60}H_{36}N_9Na_3O_{21}S_3{\cdot}Cr_2$) with molecular weight equal to 1488 g mol^{-1}, was selected as a model compound. It was provided by Aldrich. Sodium dodecyl benzene sulfonate ($C_{18}H_{29}SO_3Na$) has a molecular weight equal to 348.48 g mol^{-1} and it was supplied in analytical grade as powder by Fluka.

Chemical structures of both compounds are shown in Supplementary Data.

Table 2
Raw water characterization data.

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

2.5. General water clarification trial

1 L of surface turbidity-known water was put into a beaker. Certain dose of coagulant was added, and 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 min and another one at 30 rpm for 20 min. 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.

2.6. General dye removal trial

1000 mg L^{-1} dye solution was prepared. Different volumes of this initial solution were put into 100 mL-flask, and certain amount of coagulant were added. Final volume was reached with buffered solution. 30 rpm stirring was applied for 1 h, until equilibrium was achieved. Then, a sample was taken and was centrifuged. Photometric analysis was carried out in a 1-cm glass cell. The maximum absorbance wavelength was 565 nm and a linear relationship of absorbance versus dye concentration was checked at this wavelength in the concentration range of this experimental work. An HELλIOS UV/VIS spectrophotometer was used for photometric measures.

2.7. Surfactant removal trials

500 mg L^{-1} surfactant stock solution was prepared. Different volumes of this stock solution were put into recipients, and controlled quantity of coagulant was added. Final volume was reached with pH 7 buffered solution. A slow blade-stirring agitation (30 rpm) was applied for 1 h, until equilibrium was achieved. Kinetic studies of our specific research and previous studies [27] reported this period was enough for guarantee equilibrium. Then, a sample was collected and it was centrifuged. Surfactant removal was determined by visible spectrophotometry according to previous literature [28].

2.8. Mathematical and statistical procedures

Design of experiments was carried out by using *SPSS 14.0 for Windows* [29]. Two replicates of each combination were synthesized, and each one was tested three times with every target water (surface river water, surfactant and dye). A total of 162 tests were carried out, according to this experimental procedure.

The basis of the statistical method are found in the interaction of variables. Briefly, it can be summarized as follows:

(1) Up to nine different products were obtained from the possible combinations between tannin extract and amine compound. Two replications of each product were synthesized.

Table 3
Experimental conditions for testing the coagulants.

Water sample	Initial pollutant concentration	Coagulant dosage (mL L^{-1})
River	123 NTU	0.25
Dye	250 mg L^{-1}	10
Surfactant	50 mg L^{-1}	10

(2) A factorial design including two variables (*Tannin* and *Amine*) and three qualitative levels (*Q*, *W* and *C* for *Tannin*; *G*, *D* and *Cl* for *Amine*) was attempted and studied by ANOVA report. That gives us the significancy of the system.
(3) If ANOVA test shows there is interaction between variables, then the three experiments for each replication were put into consideration and significant differences between each one of the six corresponding values are searched for. If a new ANOVA test on this evaluation states no difference can be established inside each group of six observations, then the test repetitions are considered indistinguishable and no replications of the syntheses are taken into account.
(4) Without syntheses replications, the six experiments for each coagulant product can be studied as partial observations of the same phenomenon, so a full study where nine categories are considered (one for each product) can be carried out. ANOVA report on this new design (multicategorical analysis) should drive us to an optimum coagulant product.

More explanations on the statistical procedure and a graphical representation of this method can be found in Supplementary Data.

3. Results and discussion

Every test was carried out with the initial conditions expressed in Table 3. As can be observed, the coagulant dosages were varied in order to avoid the complete removal of every pollutant, so differences can be appreciated and significative variations can be established.

3.1. Interaction of variables

Fig. 2 shows the interaction graphics of the involved variables according to the factorial model design. The trials with each nitrogenant agents are represented by the different lines, tannin extracts are placed along the *X*-axis. *Palatine Fast Blak WAN* was the model compound for simulating textile wastewater. Tests were carried out with an initial dye concentration of 100 mg L^{-1} or SDBS initial concentration of 50 mg L^{-1}. Turbidity removal is considered in the case of surface river water treatment. Coagulant dosage was 500 mg L^{-1} in the case of textile and laundry simulated wastewater and 12.5 in the case of surface river water.

As can be seen there are two different behaviors. Regarding the surface river water, there is no interaction between variables, as no cross is found on the lines within the working range. This should be caused by the nature of the suspended organic matter that is presented in the river water. Their lightness and the low electrical charge [30] can make easier for the coagulant to reach the suspended colloidal molecules, so the difference between the three procedures is more evident. Therefore, it is clear that DEA must be used in the coagulant synthesis if the target is to clarify surface river water.

On the contrary, for wastewater samples, the interaction is clear too, not only from the graphical analyses, but also because of the ANOVA report which gives a *p*-value for interaction lower than 0.05 in each case. The complexity of the different pollutants should interfere in the destabilization of each one [31] and the model is not so simple in this case. If the scope is treating laundry or textile simulated wastewater, we must go on with the following step in the statistical procedure.

3.2. Indistinguishable observations

In order to guarantee the reproducibility of the syntheses, the two different replicates of each combination were tested and compared, and ANOVA statistical test for the indistinguishability was applied. As Fig. 3 depicts, this assumption is feasible according to the proximity of both lines in each case and taking into account the *p*-value ANOVA test gives, which is above 0.05, so no difference can be established among the two synthesized products. The replicability of the experiment is therefore achieved.

3.3. Optimum determination

As no differences can be observed among the two replicates of each product, the three trials that were done in order to test the coagulant ability of the coagulants can be included as part of a series of six tests of only one coagulant product. Because of that, the nine products can be compared with every objective variable: surface water clarification, dye removal and surfactant elimination. A box-and-whisker plot, which shows the results of the six tests, is presented in Fig. 4. This is a multicategorical analysis, in which each product is tested and compared to the rest of them.

Regarding surface water treatment, a clear positive tendency on DEA-produced coagulants is appreciated, no matter what kind of tannin extract was used. This behavior was previously determined according to the no interaction among variables that was expressed in Section 3.1.

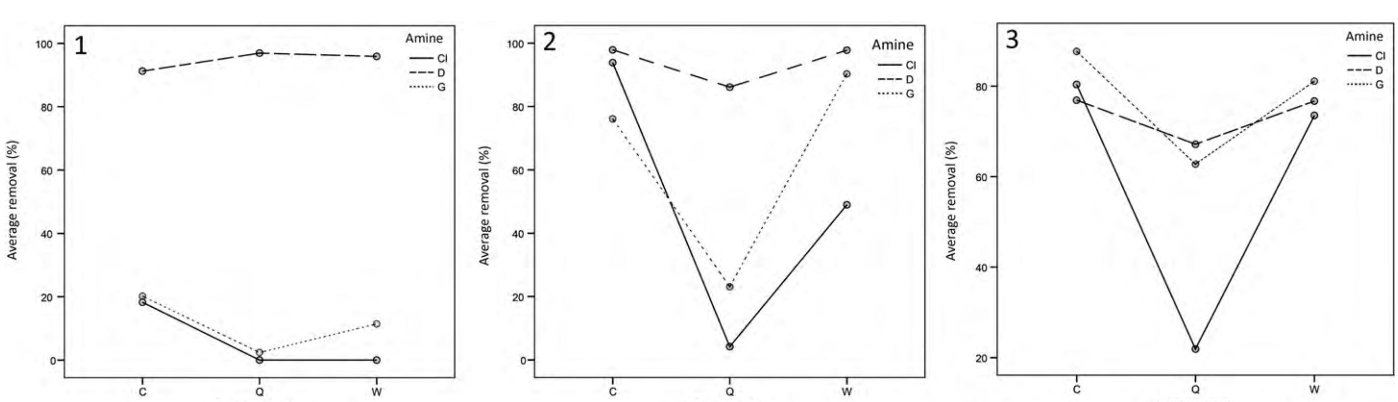

Fig. 2. Interaction graphics in qualitative optimizing. (1) Surface river water, (2) simulated textile wastewater and (3) simulated laundry wastewater.

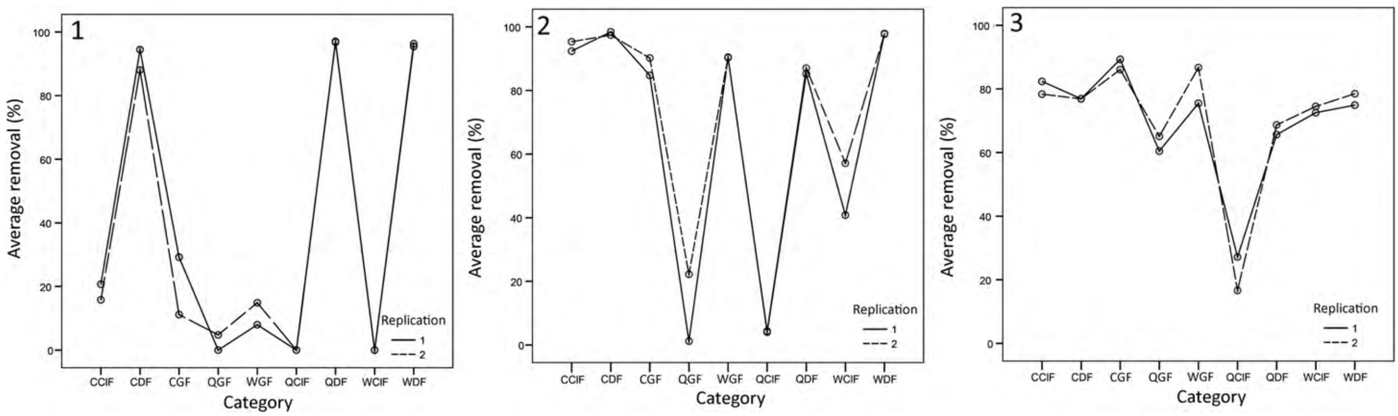

Fig. 3. Comparison of the two replicates of each combination tannin-amine. (1) Surface river water, (2) simulated textile wastewater, and (3) simulated laundry wastewater.

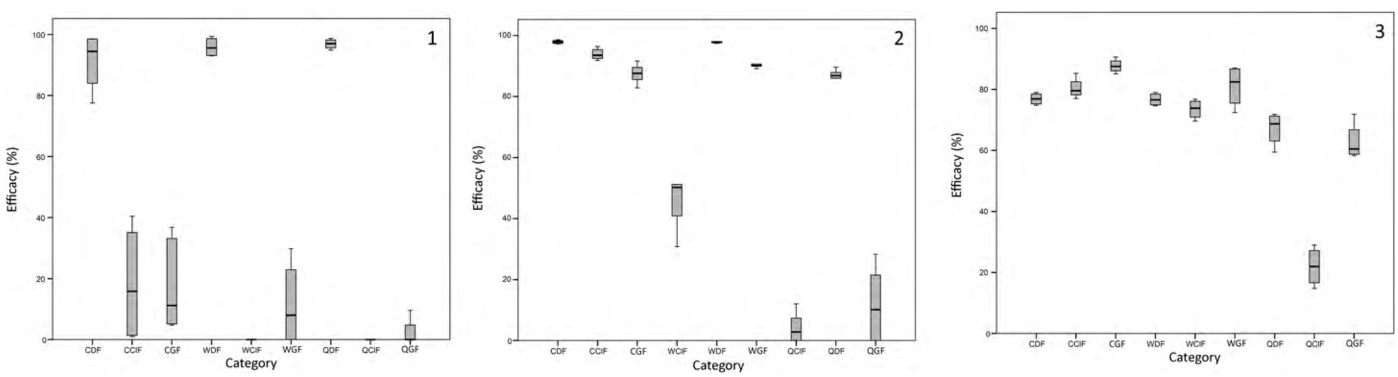

Fig. 4. Box plot for the nine products in coagulation of three types of water. (1) Surface river water, (2) simulated textile wastewater and (3) simulated laundry wastewater.

For evaluating the system coagulant-SDBS or coagulant-Palatine Fast Black WAN, we have to study ANOVA test which gives us significativity data about these results. In a first approach, we can see there is a set of coagulants that work significantly better than the rest of them: they are those derived from *Acacia mearnsii* de Wild: *Clarotan* and *Weibull black*. Combinations with DEA are especially effective, either in terms of pollutant removal or low dispersion. This tendency is presented more clearly in the removal of Palatine Fast Black WAN, while a wider dispersion of results is presented in the case of SDBS.

The reaction mechanism that probably acts here is presented in Fig. 5, which may explain the more reactive character of DEA derived coagulant in front of the one which is derived from the ammonium chloride or even from the *glycidyltrimethyl ammonium chloride*.

Tukey's test for multiple comparison did not give significative differences above 75% in both dye or surfactant removal. These data are shown in Supplementary Data, where the homogeneous subsets (DHS) are presented. 3 subsets are arranged in the case of dye removal, while up to 5 were established regarding SDBS removal. This has to do with the increasing dispersion the last data presented, so more groups can be identified. It is also important to point out

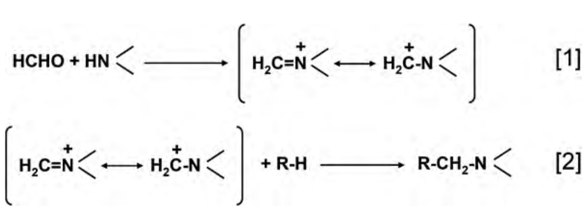

Fig. 5. Reaction mechanism of aminomethylation. [1] Formation of imine and [2] Formation of Mannich base.

the fact that no overlapping is observed among the subsets that are related to dye removal, so clear differences can be appreciated in this case. This again may be explained by the more affinity the dye presents towards the coagulant.

On the contrary, the 5 subsets that are obtained for SDBS elimination presented several cases that are not distinguishable and could be inserted in various groups.

Quebracho derived coagulants seem to be less effective, according not only to the graphical representation, but also to Tukey multiple comparison (data not shown). Probably the differences between coagulants must be found in the fact that tannin extracts are not exactly equal in their chemical composition, so the cationization and polymerization is affected not only by the chemical nitrogenant agent but also by the specific tannin structure [32,33].

3.4. Functional characterization of the optimum

In view of these results, an intermediate solution was selected. *Clarotan* was chosen as tannin source for a standard cationization. So-called CDF (*Clarotan* with DEA and formaldehyde) coagulant was used in water clarification, dye removal and surfactant elimination.

The way this new coagulant forms coagules and flocs suggests it follows a *bridging procedure*. This is caused by a flocculent clarification of the surface water and it is characteristically slow, without the typical sedimentation zones [34,35,31].

Fig. 6 presents the removal of turbidity as coagulant dosage is increased in the clarification of surface river water by *CDF*. As can be seen, low dosages of the coagulant easily remove almost the whole turbidity. Several previous works with similar products (commercial tannin-derived from *Acacia mearnsii* de Wild, *Tanfloc* [36]) showed comparable efficiencies. A rapid decrease of turbidity levels is achieved once doses of 3 mg L^{-1} are applied.

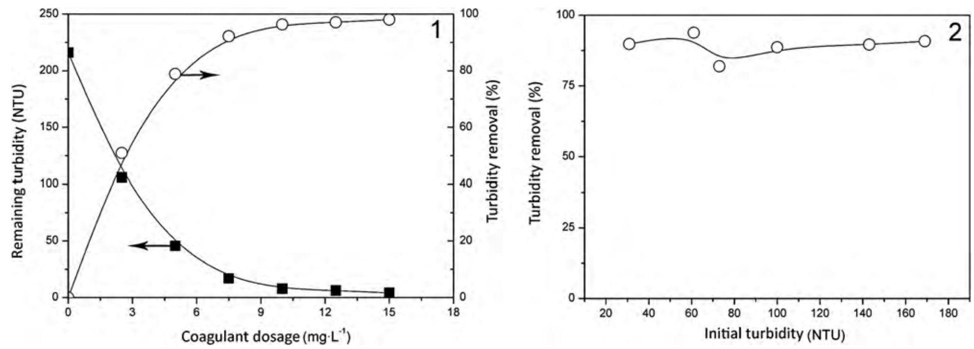

Fig. 6. Turbidity clarification in river water treatment. (1) Increasing coagulant dosage and (2) increasing initial turbidity level.

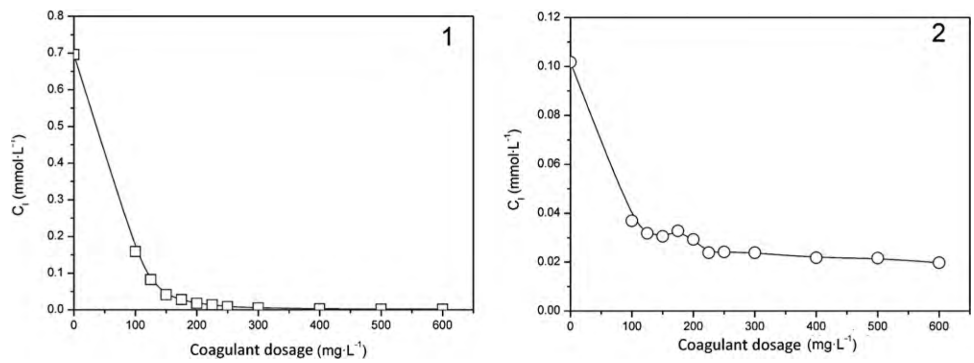

Fig. 7. Wastewater treatment. (1) Simulated textile wastewater and (2) simulated laundry wastewater.

On the other hand, the coagulation process is rather stable regarding the initial turbidity charge of the surface water. As can be appreciated from the same Fig. 7, turbidity levels between 40 and 180 NTU are treated with 5 mg L^{-1} and the removal is kept above 80%.

Regarding the coagulant dosage on dye removal (Fig. 7), it is showed that dye concentration undergoes a rapid and dramatic decrease from the first coagulant dosage. The efficacy of the coagulant is very high therefore, 100 mg L^{-1} can reduce up to 80% the initial dye concentration. However, a flocculent sedimentation is presented regarding the value of sludge production (ca. 200 mL L^{-1} in Imhoff's cone test). This yields to a Sludge Volume Index (SVI) equal to 317 mL g^{-1}. This relatively high value recommends the usage of a flocculant agent, beyond the coagulant effect of the tannin-derived product [37,38].

Other experimental series were done in order to determine the influence of variables on the removal of SDBS. A fixed dose of 0.10 mmol L^{-1} of surfactant was evaluated to be removed with different doses of coagulant. As can be showed in the same Fig. 7, final surfactant concentration tends to decrease as *CDF* dose increases. However, it is observed that the efficiency of the process arrives to a maximum, and higher doses of coagulant does not achieve lower surfactant concentrations. There is a residual surfactant concentration that is no possible to remove through this flocculation process, and seems to be about 0.02 mmol L^{-1}. This can be due to the existence of an 'equilibrium surfactant concentration' which is highly difficult to remove, as reported previously [39].

4. Conclusions

Tannin-derived coagulants can be easily produced by means of the *Mannich* reaction procedure. Among the different nitrogenant compounds that can introduce the cationic character to the tannin structure, *diethanolamine* seems to be the best one in order to produce coagulants for surface water clarification. Regarding the treatment of industrial wastewater effluents, tannins from *Acacia mearnsii* de Wild combined with either *diethanolamine*, *glycidyltrimethylammonium chloride* or even *ammonium chloride* lead to efficient coagulant products. If studied in a multicategorical analysis, *Clarotan* with *diethanolamine* and *formaldehyde* is the intermediate optimum product which can be applied for dye and surfactant removal and surface water clarification. Average dosages of 100 mg L^{-1} of coagulant can remove high percentages of Palatine Fast Black WAN or *sodium dodecylbenzene sulfonate*. Further studies should be carried out in order to characterize even more the behavior of this new coagulant with these and other wastewater samples.

Acknowledgments

This investigation has been supported by the COMISIÓN INTERMINISTERIAL DE CIENCIA Y TECNOLOGÍA (CICYT) CTQ 2007-60255/PPQ project as well by JUNTA DE EXTREMADURA under PRI-07A031 project.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.07.011.

References

[1] UNESCO, World Water Assessment Programme. The United Nations World Water Development Report 3: Water in a Changing World, Earthscan, London, UK, 2009.

[2] WHO, UNICEF, Joint Programme on Water Supply and Sanitation, WHO Library Cataloguing-in-Publication Data, Geneva, Switzerland, 2009.

[3] WHO, United Nation-Global Annual Assessment of Sanitation and Drinking Water, World Health Organization, Geneva, 2008.

[4] S. Appelbaum, J. Garada, J.K. Mishra, Growth and survival of the white leg shrimp (*Litopenaeus vannamei*) reared intensively in the brackish water of the

israeli Negev desert, Israeli Journal of Aquaculture-Bamidgeh 54 (1) (2002) 41–48.
[5] WHO, UNICEF, Meeting the MDG Drinking Water and Sanitation Target: The Urban and Rural Challenge of the Decade, WHO Library Cataloguing-in-Publication Data, Geneva, Switzerland, 2007.
[6] P.A. Wilderer, Applying sustainable water management concepts in rural and urban areas: some thoughts about reasons, means and needs, Water Science and Technology 49 (7) (2004) 8–16.
[7] WHO, Appropriate Technology for the Treatment of Wastewaters for Small Rural Communities, World Health Organization, Geneva, 1985.
[8] R.C. Dorf, Sustainable and Appropriate Technologies. Technology, Humans and Society, Academic Press, San Diego, 2001.
[9] B. Bowonder, Appropriate technology for developing countries: some issues, Technological Forecasting and Social Change 15 (1979) 55–67.
[10] S.M. Miller, E.J. Fugate, V.O. Craver, J.A. Smith, J.B. Zimmerman, Towards understanding the efficacy and mechanism of Opuntia spp. as a natural coagulant for potential application in water treatment, Environmental Science Technology 42 (12) (2008) 4274–4279.
[11] P. Schofield, D.M. Mbugua, A.N. Pell, Analysis of condensed tannins: a review, Animal Feed Science and Technology 91 (1) (2001) 21–40.
[12] E. Haslam, Plant Polyphenols—Vegetables and Tannins Revisited, Cambridge University Press, Cambridge, 1989.
[13] A. Pizzi, Tannins: major sources, properties and applications, Monomers, Polymers and Composites from Renewable Sources, Elsevier, Amsterdam, 2008.
[14] J.E. Quamme, A.H. Kemp, Stable tannin based polymer compound, US patent 4,558,080 (1985).
[15] S.R. Vasconcellos, P.D. Boyce, L.P. Smith, Methods for the flocculation of coal fines and insoluble metals in coal mine waters, US patent 4,183,575 (1993).
[16] P.E. Reed, M.R. Finck, Modified tannin mannich polymers, US patent 5,659,002 (1997).
[17] D.B. Mitchel, R.L. Minnis, T.P. Curran, S.M. Deboo, J.A. Kelly, R. Patwardhan, W.-T. Tai, Treatment of aqueous systems using a chemically modified tannin, US patent 5,843,337 (1998).
[18] D.G. Roux, D. Ferreira, H.L. Hundt, E. Malan, Structure, stereochemistry, and reactivity of natural condensed tannins as basis for their extended industrial application, Applied Polymer Symposium 1 (28) (1975) 335–353.
[19] M. Tramontini, L. Angiolini, Mannich Bases. Chemistry and Uses, CRC Press, Boca Raton, 1994.
[20] A. Pizzi, Advanced Wood Adhesives Technology, Marcel Dekker, New York, 1994.
[21] J. Roussy, P. Philippe Chastellan, M. Van Vooren, E. Guibal, Treatment of ink-containing wastewater by coagulation/flocculation using biopolymers, Water SA 31 (3) (2005) 369–376.
[22] P. Polasek, S. Mutl, Cationic polymers in water treatment. Part 1: treatability of water with cationic polymers, Water SA 28 (1) (2002) 69–82.
[23] N. Graham, F. Gang, G. Fowler, M. Watts, Characterisation and coagulation performance of a tannin-based cationic polymer: a preliminary assessment, Colloids and Surfaces A: Physicochemical and Engineering Aspects 327 (1–3) (2008) 9–16.
[24] J. Beltrán-Heredia, J. Sánchez-Martín, C. Solera-Hernández, Removal of sodium dodecyl benzene sulfonate from water by means of a new tannin-based coagulant: optimisation studies through design of experiments, Chemical Engineering Journal 153 (1–3) (2009) 56–61.
[25] J. Beltrán-Heredia, J. Sánchez-Martn, Removing heavy metals from polluted surface water with a tannin-based flocculant agent, Journal of Hazardous Materials 165 (1–3) (2008) 1215–1218.
[26] S. Bhatia, Z. Othman, A.L. Ahmand, Coagulation-flocculation process for POME treatment using *moringa oleifera* seed extract: optimization studies, Chemical Engineering Journal 133 (1) (2007) 205–212.
[27] Y. Chen, S. Liu, G. Wang, A kinetic investigation of cationic starch adsorption and flocculation in kaolin suspension, Chemical Engineering Journal 133 (1–3) (2007) 325–333s.
[28] K. Tôei, H. Fujii, Spectrophotometric determination of traces of anionic surfactants with methylene blue derivatives, Analytica Chimica Acta 90 (1977) 319–322.
[29] SPSS Inc., SPSS 14.0 Developer's guide, SPSS Inc., Chicago, IL, 2005.
[30] N. Graham, F. Gang, G. Fowler, M. Watts, R. Camm, Evaluation of a tannin-based cationic polymer as a coagulant for coloured humic water, Journal of Water Supply: Research and Technology AQUA 58 (2) (2008) 75–84.
[31] Y.H. Kim, Coagulants and Flocculants. Theory and Practice, Tall Oak Publishing, Littleton, 1995.
[32] W. Streit, D. Fengel, Purified tannins from quebracho colorado, Phytochemistry 36 (2) (1994) 481–484.
[33] N. Vivas, M.F. Nonier, N. Vivas de Gaulejac, C. Absalon, A. Bertrand, M. Mirabel, Differentiation of proanthocyanidin tannins from seeds, skins and stem of grapes (*vitis vinifera*) and heartwood of quebracho (*schinopsis balansae*) by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry and thiacidolysis/liquid chromatography/electrospray ionization mass spectrometry, Analytica Chimica Acta 513 (1) (2004) 247–256.
[34] W.W. Nazaroff, L. Álvarez-Cohen, Environmental Engineering Science, John Wiley and sons, New York, 2001.
[35] Z. Dymaczewski, E.S. Kempa, M.M. Sozanski, Coagulation as a structure forming separation process in water and wastewater treatment, Water Science and Technology 36 (4) (1997) 25–32.
[36] J. Sánchez-Martín, M. González-Velasco, J. Beltrán-Heredia, Acacia mearnsii de wild tannin-based flocculant in surface water treatment, Journal of Wood Chemistry and Technology 29 (2) (2009) 119–135.
[37] M. Özacar, A. Sengil, Effectiveness of tannins obtained from *Valonia* as a coagulant aid for dewatering of sludge, Water Research 34 (4) (2000) 1407–1412.
[38] M. Özacar, A. Sengil, Evaluation of tannin biopolymer as a coagulant aid for coagulation of colloidal particles, Colloids and Surfaces A: Physicochemical and Engineering Aspects 229 (1) (2003) 85–96.
[39] E. Ayranci, O. Duman, Removal of anionic surfactants from aqueous solutions by adsorption onto high area activated carbon cloth studied by in situ UV spectroscopy, Journal of Hazardous Materials 148 (1–2) (2007) 75–82.
[40] L.H. Lamb, O.G. Decusati, Manufacturing process for quaternary ammonium tannate, a vegetable coagulating and flocculating agent, US patent 6,478,986 B1 (2002).
[41] A.T. Lindert, S.M. Wolpert, Tannin mannich adducts for improving corrosion resistance of metals, US patent 4,944,812 (1990).
[42] R.W. Hemingway, P.E. Laks (Eds.), Preparation and Performance of Tannin based Flocculants Second North American Tannin Conference on Plant Polyphenols. Biogenesis, Chemical Properties and Significance, Plenum Press, New York, 1992.