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Optimization of the synthesis of a new coagulant from a tannin extract

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ABSTRACT

The current article studies the optimization of a new coagulant agent for water purification and wastewater remediation. Design of experiments is used for optimizing the production of this new tannin-based coagulant by using *Acacia mearnsii* de Wild tannin extract, NH_4Cl and formaldehyde. The effectiveness of this product was confirmed on dye-polluted wastewater and surfactant wastewater. This cationic coagulant seems to be sensitive to temperature and tannin–NH_4Cl ratio (g of ammonium chloride per g of tannin extract). NH_4Cl ratio was found to be more influent than temperature and no interaction is presented between these two parameters. For each system, an optimum combination NH_4Cl ratio and temperature was found: 24.9 °C and 2 g g^{-1} for dye removal and 36.4 °C and 1.87 g g^{-1} for surfactant elimination. The optimal conditions were merged to produce a combined coagulant that was tested on dye, surfactant, surface river water and municipal wastewater. Predicted levels of remediation were experimentally confirmed.

1. Introduction

Effluents from textile, chemical or mining industries represent harmful and noxious menaces nowadays and they should be treated before dumping into the environment. Life equilibrium is so fragile that minimum concentrations of contaminants such as surfactants, dyes or heavy metals can cause great damages in fauna and flora [1].

Therefore, water treatment has become a very important researching task nowadays. For many years scientific community has been working on new methods for water treatment. Some posibilities are rather well known, such as filtration, disinfection or coagulation, but new cheaper and affordable water treatment processes are still needed [2].

Coagulation is a very well known process of destabilizing colloids and other substances that usually appear dispersed in water. It is considered a chemical treatment as it implies the addition of a coagulant. Stable colloids in water normally present negative charges all around their surface. Coagulant is able to cause the neutralization of these charges, so colloidal particles become unstable and tend to settle because of gravity [3]. Typical coagulant agents are inorganic salts such as $Al_2(SO_4)_3$ or $FeCl_3$, as well as synthetic polyacrylamides.

Once pollutants are electrically neutralized, particles should tend to grow and form flocs. The operation of growing, enlarging and subsequently settling is known as *flocculation*. Depending on the nature of the coagulant agent, flocculation will take place directly or the addition of another chemical is required. The whole process (coagulation and flocculation) is needed for the removal of pullutants.

Tannins are mostly vegetal water-soluble polyphenolic compounds. Their molecular weight is ranged between 500 and some thousands Daltons. Trees such as *Schinopsis balansae* (Quebracho), *Castanea sativa* (Chestnut) or *Acacia mearnsii* de Wild (Black wattle) are traditional tannin sources. From a chemical point of view, there are three kinds of tannins: hydrolysable, condensed and combined ones [4]. These products are rather chemically complex and they are usually taken from a natural matrix, without a very exhaustive purification. Because of that, it is rather difficult to know their structure exactly. A full study about tannins, chemical structure and properties can be found in previous scientific literature [5].

Regarding water treatment, tannins can be used in two main ways: gelified and cationized. Tannin gelification is a chemical procedure that immobilizes tannins inside an insoluble matrix [6] so their properties, e.g. metal chelation, are kept available. A rather efficient adsorbent agent is produced then. This procedure was widely reported either in scientific literature or in patents. Experimental conditions of gelification involve the use of formaldehyde (or other aldehyde) in a basic or acid aqueous solution. Examples of basic gelification are shown in previous scientific papers [7–9] and in patents such as US patent 5,158,711 [10]. Acid gelification is also presented by other researchers [11,12].

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Cationization of tannins consists in a chemical reaction that confers cationic character to the organic tannin matrix, so the main characteristics (such as solubility, stability at different pH levels or heavy metals chelating activity) are kept while other ones are added. The new abilities are related with the coagulating activity because products with positive charge may destabilize anionic colloids once they are mixed in aqueous solution. A wide variety of anionic substances can be destabilized and subsequently removed with these kinds of coagulants.

The chemical procedure of cationization is thought to follow a *Mannich* reaction path and different variations were reported under several patents [13–16]. Briefly, *Mannich* reaction is described as the introduction of a quaternary nitrogen inside the tannin complex structure [17]. Tannins undergo *Mannich* aminomethylation by reaction with an aldehyde and an amine [18]. The resulting *tannin Mannich* polymer possesses higher molecular weight due to formaldehyde and *Mannich base* crosslinking. Ampholytic character is also obtained 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 whose structure may be similar to flavonoid structures such as resorcinol A and pyrogallol B rings. Therefore, by following the rules of *Mannich* reactions we can surely make an approach of their syntheses [19]. In the particular case of producing coagulants from NH_4Cl and tannin extract, the reaction mechanism may be as it is reported in Eq. (1):

$$\text{Tannin–H} + CH_2O + NH_4Cl \rightarrow \text{Tannin–}CH_2NH_3^+Cl^- + H_2O \quad (1)$$

Not many investigations are found about these kinds of coagulants. Some of them pointed out the use of tannins as a coagulant aid [20] or other cationic compounds [21]. Specifically, the use of tannin-based coagulants was researched only by Graham et al. [22], as well as by us [23–25].

This investigation is focused in advanced water treatment through a new coagulation process that is (a) cheaper than others; (b) based on a natural product; (c) easy to handle and maintain for unskilled personnel. Taking care of environmental subjects may include these and others considerations that make the possibility of becoming clean a universal chance.

We have performed a statistically significant study on the production of these kinds of coagulants. Design of experiments was carried out in order to evaluate the influence of parameters such as the ratio of amine compound and tannin mixture or the reaction temperature. Coagulant products obtained by this procedure were tested on surfactant removal, dye elimination, municipal wastewater remediation and surface water clarification.

2. Materials and methods

2.1. Coagulant syntheses

The reagents involved in the cationization process were:

(1) Tannin extract from *Acacia mearnsii* de Wild was supplied by TANAC Inc. (Brazil). Commercial denomination was *Weibull Black* and it presents a tannin content of 72% minimum.
(2) *Ammonium chloride* and *formaldehyde* were commercial grade from SIGMA.

The cationization process was conducted as follows:

- 2.5 g of tannin extract were diluted in distilled water at room temperature. Then the sample was thermostated at the reaction temperature.
- Certain amount of ammonium chloride was added to the mix.
- Always under thermal control, 5 mL of formaldehyde was added to the reaction mixture. A peristaltic pump (MASTERFLEX, ColeParmer) must be used in this step, so it last 90 min at least. This addition is quite different from the amount of formaldehyde other authors have reported [27,28].
- This product must be kept under stirring and at the same temperature for 24 h.

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

2.2. Buffered solution

The trials with added dye (textile wastewater simulation) and surfactant (laundry wastewater simulation) were performed with pH-stable media according to preliminary data [29]. To this end, a pH-7 buffer solution was prepared by mixing 1.2 g of NaH_2PO_4 and 0.885 g of Na_2HPO_4 in 1-L flask and filled to the mark with distilled water. The pH was then adjusted to 7 with HCl 0.5 M and NaOH 0.5 M. All reagents were analytical grade from PANREAC.

2.3. Model compounds

Alizarin Violet 3R, an anthraquinonic dye ($C_{28}H_{20}N_2Na_2O_2S_2$) with molecular weight equal to 622.6 g mol^{-1}, was selected as a model compound for textile wastewater simulation. 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 by Fluka in analytical grade.

For general screening of pollutant removal, other dyes and detergents were used. Their specifications and chemical structures are presented in Supplementary Material, while the structure of Alizarin Violet 3R and sodium dodecyl benzene sulfonate are presented in Fig. 1.

2.4. Other natural and inorganic coagulants

Apart from cationic *Weibull black* optimum coagulant, other six natural coagulant products were tested in a comparative screening. Three of them were tannin-derived coagulants, currently available in the market, such as *Acquapol C-1*, *Acquapol S5T*, *Tanfloc* or *Silvafloc*. The last one is supplied by SILVATEAM, S.A. (Italy) and is based on tannins from *Schinopsis balansae* or red quebracho. The rest of them are derived from *Acacia mearnsii* de Wild or black wattle and were supplied by ACQUACHIMICA (*Acquapol*) or TANAC, S.A. Both companies are from Brazil. Differences between *Silvafloc*, *Acquapol C-1* and *S5T* and *Tanfloc* lay on tannin nature and on chemical modification, which is under copyright law. *Tanfloc* and *Acquapol C-1* are presented as powder, while *Silvafloc* and *Acquapol S5T* are presented as a dense, sticky solution.

Moringa oleifera was obtained from SETROPA (The Netherlands) and the extraction of the active agent was carried out as described elsewhere [24]. The result is a white homogeneous milky liquid. *Moringa* stock solution was used the same day it was prepared in order to avoid ageing, although there are references that point the stability of the extract [30].

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

2.5. Municipal wastewater and surface river water samples

Surface water was collected from the Guadiana River, in Badajoz (south-west Spain, Extremadura Community). Since we are working on real water there was no need of kaolin addition [31]. This water was treated on the day of its collection.

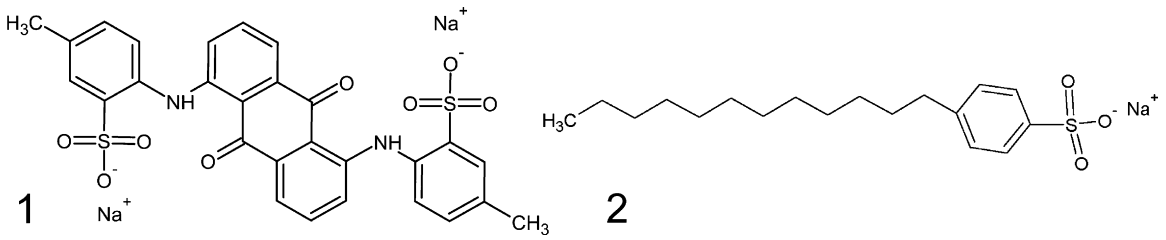

Fig. 1. Chemical structures of pollutants: (1) Alizarin Violet 3R; (2) sodium dodecylbenzene sulfonate.

Real municipal wastewater was collected from a sewage treatment plant and treated the same day of its collection. This effluent is considered to be a hazardous product [32] since it normally contains contaminants from industrial and residential zones. It is mandatory to treat it in order to avoid environmental [33] and health problems [34,35]. Our samples were taken from the sewage treatment plant of La Albuera, a small town near the city of Badajoz. This treatment plant was constructed about 5 years ago. It receives municipal wastewater from approximately 4 000 people. The sources of contamination are household effluent and some agricultural waste and slurry. The effluent has a moderately low COD and the average incoming flow rate is 41 $m^3\,h^{-1}$, with the maximum permissible being 125 $m^3\,h^{-1}$. The water sample was collected after the removal of large solids, but before the separation of oil and sand. Its main physicochemical properties are given in Table 1, and are within the range reported by the plant's management [36]. Compared with the literature data for other sewage wastewaters [37,38], this water has a lower pollutant load. This is probably due to the nature of the waste, especially its domestic origin.

2.6. General dye removal trials

A dye solution of 1 000 mg L^{-1} was prepared. This was used as stock solution. Aliquots of 100 mL of this simulated textile wastewater were mixed with the equivalent dose of coagulant for each case. Stirring at 30 rpm for 1 h was applied, until equilibrium was achieved. Then, a sample was taken and it 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 deduced at this wavelength inside the concentration range of this experimental work.

Table 1
Surface water and municipal wastewater characterization data.

Parameter	Municipal wastewater	Surface water	Units
pH	8.2	7.5	
Conductivity	1,006	400	$\mu S\,cm^{-1}$
Suspended solids	100	15	mg L^{-1}
Total solids	650	452	mg L^{-1}
Turbidity	82.5	123.3	NTU
Chloride	21.3	40.4	Cl^- mg L^{-1}
Calcium	94.6	37.7	Ca^{2+} mg L^{-1}
Hardness	444	152	$CaCO_3$ mg L^{-1}
Ammonium	2.1	1.81	N mg L^{-1}
Nitrate	22.5	5.3	NO_3 mg L^{-1}
Nitrite	0.04	0.033	N mg L^{-1}
Phosphate	7.3	0.044	P mg L^{-1}
Total phosphorus	11.9	0.064	P mg L^{-1}
Chemical oxygen demand	320	N/A[a]	O_2 mg L^{-1}
Biological oxygen demand	262	N/A[a]	O_2 mg L^{-1}
$KMnO_4$ oxidability	65.6	19.3	O_2 mg L^{-1}
Polyphenols	6.4	N/A[a]	Tannic acid equivalent mg L^{-1}
Anionic surfactants	19.6	N/A[a]	mg L^{-1}
Total coliforms	N/A[a]	800	Colonies/100 mL
Faecal coliforms	N/A[a]	400	Colonies/100 mL
Faecal streptococcus	N/A[a]	140	Colonies/100 mL

[a] Not appropriate.

2.7. General surfactant removal trials

A surfactant solution of 500 mg L^{-1} was prepared. Different volumes of this stock solution were put into 100 mL-flask, and certain amount of coagulant was added. Final volume was reached with pH-7 buffer solution. A slow blade-stirring agitation (30 rpm) was applied for 1 h then, until equilibrium was achieved. Kinetics and previous studies carried out [39] reported that this period was enough to guarantee equilibrium. Then, a sample was collected and centrifuged. Surfactant removal was determined by visible spectrophotometry according to a method based on its association with methylene blue [40]. The spectrophotometer used was a HEλIOS UV/VIS.

2.8. General water and wastewater clarification trials

1 L of surface water or municipal wastewater was put into a beaker. Certain dose of coagulant 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 min and other one at 30 rpm for 20 min. Turbidity was measured with a HI93703 turbidimeter (Hanna Instruments) 1 h after Jar-test was finished. Turbidity sample was obtained from the center of the beaker, 3 cm from surface.

2.9. Mathematical and statistical procedures

A factorial central composite design (CCD) orthogonal and rotatable design was used for the optimization of the quantitative variables such as temperature and ammonium chloride ratio. Each experiment of the planned series was made three times, so the average value was kept for the CCD analysis under response surface methodology. Design of experiments section was statistically analyzed by using *StatGraphics Plus for Windows 5.1* [41].

3. Results and discussion

The statistical study of the cationization process drives to an optimum coagulant. This section presents: (a) the statistical evidences of this optimal combination of the working variables; (b) the functional characterization of this optimum in four fields: dye removal, surfactant elimination and real water and wastewater treatment; (c) then, the effectiveness of this coagulant was compared with other coagulant agents, either natural or synthetic ones. The way this new coagulant forms coagules and flocs suggests it follows a *bridging mechanism*. This is caused by a flocculent clarification of the colloids and other anionic suspended materials and it is characteristically slow, without the typical sedimentation zones [3,42,43].

3.1. Design of experiments

It is not possible to predict the influence of different variables on the final response unless experimentation is carried out. Although some theoretical approaches can be done (e.g. the reaction mechanism of the cationization), the empirical evidence of the real influence of the operative conditions can be established just through the experimentation. Design of experiments is a statistical procedure that can reduce significantly the number of experiments, keeping, however, the reliability of the conclusions at a high standard.

The traditional experimental method, one factor at a time approach, can hardly be used to stablish relationships among all the experimental input factors and the output responses. Even through the traditional approach can be useful in finding predominant factors in this situation, it is difficult to observe an optimum value of the working parameters as no interaction among them is considered. To solve this problem and to obtain a probable optimum, design of experiment (DOE) offers a better alternative to study the effect of variables and their response with minimum number of experiments [44].

Using design of experiments based on response surface methodology (RSM), the aggregate mix proportions can be arrived with minimum number of experiments without the need for studying all possible combination experiments. *StatGraphichs* software provides a useful and powerful mathematical and statistical tool in order to develop the experimental planning (in a random order for avoiding hidden effects) and to analyse the results, searching for conclusions.

The data collected must be analyzed in a statistically manner using regression. In developing the regression equation, the test factors were coded according to Eq. (2):

$$\chi_i = \frac{X_i - X_i^x}{\Delta X_i} \quad (2)$$

where χ_i is the coded value of the ith independent variable, X_i the natural value of the ith independent variable, X_i^x the natural value of the ith independent variable at the center point and ΔX_i is the value of the step change.

Each response (Y) can be represented by a mathematical equation that correlates the response surface (Eq. (3)):

$$Y = b_0 + \sum_{j=1}^{k} b_j \chi_j + \sum_{i \neq j; i=1}^{k} b_{ij} \chi_i \chi_j + \sum_{j=1}^{k} b_{jj} \chi_j^2 \quad (3)$$

where Y is the predicted response, b_0 the offset term, b_j the linear effect, b_{ij} the first-order interaction effect, b_{jj} the squared effect and k is the number of independent variables.

We have selected a central composite design (CCD) which is one of the most popular class of second-order design. It involves the use of a two-level factorial design with 2^k points combined with $2k$ axial points and n center runs, k being the number of factors. The total number of experiments, N, with k factors is

$$N = 2^k + 2 \cdot k + n \quad (4)$$

n is considered to be 8 and the axial distance is $\sqrt{2}$ in order to guarantee an orthogonal and rotatable design.

One of the most important tasks in designing a plan of experiments inside a CCD is determining the variables to be studied and the region in which those variables are expected to present an optimum. The usual way of evaluating these two researching aspects is by carrying out a previous analysis of the effect of several variables in order to select two or more of them. In the case of cationization from *Acacia mearnsii* tannin extract, this stage was developed (data not shown) and the most interesting factors to work on were the ammonium chloride–tannin ratio and the temperature. Consequently, the particular DOE we are arranging has the experiments that are expressed in Table 2.

Table 2
Experimental planning in DOE.

Number of run	Coded NH_4Cl ratio	Coded temperature	Real NH_4Cl ratio[a]	Real temperature[b]
1	0	0	1.28	40
2	0	0	1.28	40
3	−1.41	0	0.37	40
4	0	0	1.28	40
5	1	−1	1.92	20
6	0	0	1.28	40
7	0	1.41	1.28	68
8	0	0	1.28	40
9	−1	1	0.64	60
10	0	0	1.28	40
11	0	0	1.28	40
12	−1	−1	0.64	20
13	1	1	1.92	60
14	1.41	0	2.19	40
15	0	0	1.28	40
16	0	−1.41	1.28	12

[a] g of NH_4Cl per g of tannin extract.
[b] °C.

3.1.1. ANOVA report

Pollutant percentage removal (%) was the target variable in the optimization stages. In a first approach, one must refer the ANOVA analysis because it shows the significance of the different parameters. According to the RSM, five factors are considered in this particular case. Either in the case of dye removal or surfactant elimination, three of them have a p-value below 0.05 (significativity limit), so they are statistically significative. Non-linear polynomic regression is carried out by taking into account Eq. (3). For dye removal, this regression is given by Eq. (5):

$$\% = 70.82 - 1.97 \cdot T + 6.97 \cdot C - 1.58 \cdot T^2 - 3.17 \cdot C^2 - 0.36 \cdot T \cdot C \quad (5)$$

and Eq. (6) is the expression for surfactant removal:

$$\% = 66.49 + 0.07 \cdot T + 6.69 \cdot C - 3.05 \cdot T^2 - 3.74 \cdot C^2 - 1.29 \cdot T \cdot C \quad (6)$$

where T are the values of temperature and C are the values of NH_4Cl ratio. Significative confidence intervals are based on α level of 0.05 and they are showed in Table 3. The adjusted correlation factors r^2 are above 0.80 in both cases, and an optimum is also presented. This tendency is showed by Fig. 2.

The fact that ANOVA report gives high r^2 correlation factors allows us to present the CCD model and the DOE procedure as a consistent statistical method for analysing the system. This aspect is very important in order to scale up the results of the current investigation: the model that was applied to this phenomenon explains properly the behavior of the system.

Table 3
Confidence intervals in polynomial regression.

Coefficient	Lower level	Upper level
SDBS removal		
Constant	65.50	67.48
C	4.49	8.85
T^2	−5.24	−0.86
C^2	−5.93	−1.55
Alizarin Violet 3R removal		
Constant	68.87	72.77
T	−3.91	−0.01
C	5.02	8.92
C^2	−5.12	−1.22

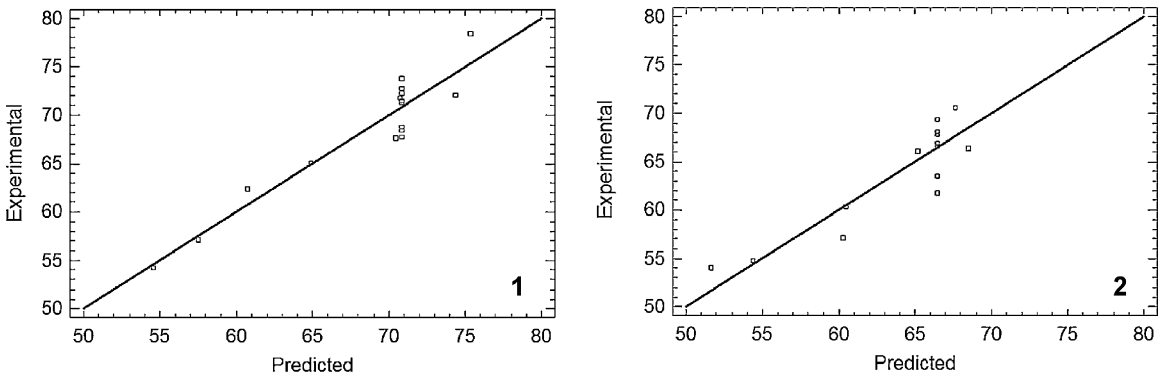

Fig. 2. Correlation of CCD model. Predicted versus experimental percentual removal: (1) Alizarin Violet 3R; (2) sodium dodecylbenzene sulfonate.

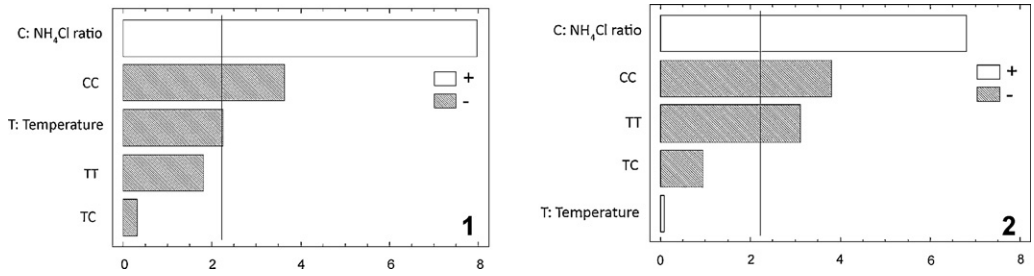

Fig. 3. *Pareto* graphics for temperature and NH_4Cl–tannin ratio: (1) removal of Alizarin Violet 3R; (2) removal of sodium dodecylbenzene sulfonate.

3.1.2. Significant graphics

Modelization is made on the basis of five factors which correspond to Eq. (3). A graphical expression of the ANOVA test may be the *Pareto* graphic (Fig. 3). Bars represent the standarized effects of each involved factor, considering them as temperature, NH_4Cl ratio and the combinations of both. Nonfilled bars are a graphical representation of positive-affecting factors, such as NH_4Cl ratio. This means that this factor appears in expression (3) behind a positive sign. On the other hand, filled bars represent negative-affecting factors. The vertical rule stands near to 2 and has to do with the signification level of ANOVA test, which is equal to 95% of confidence. Bars trespassing the vertical rule are inside the signification region, while bars behind it are not statistically significative.

Pareto graphic also gives us an idea of how factors affect on the final response of percentage removal. Positive bars indicate that by varying the variable the response increases. Negative bars indicate the contrary. As can be shown, as NH_4Cl ratio increases the response is increased as well. Temperature seems not to be so important in the final response, but the amine ratio (*C*) presents a positive influence. This may have to do with the polymerization process, where the coagulant final content is directly related with the amine amount. On the other hand, the process is not so sensitive to thermal variations, although out of the working region differences can appear.

3.1.3. Main effects

The evaluation of the CCD model also drives to the study of the main effects of the involved variables. This can be appreciated in Fig. 4. Two curves are drawn representing the effect of varying each variable while the other one keeps constant. The effect of NH_4Cl ratio is much more influent than temperature in both cases: dye or surfactant removal. An optimum combination appears in the two curves of the studied systems. This is again an effect on the cationization reaction: although a small variation is presented when temperature changes from −1 (lower) to +1 (upper) value, the influence of NH_4Cl ratio on the final response is obviously higher. One must attend to the amount of amine in the reaction mix rather than to the temperature.

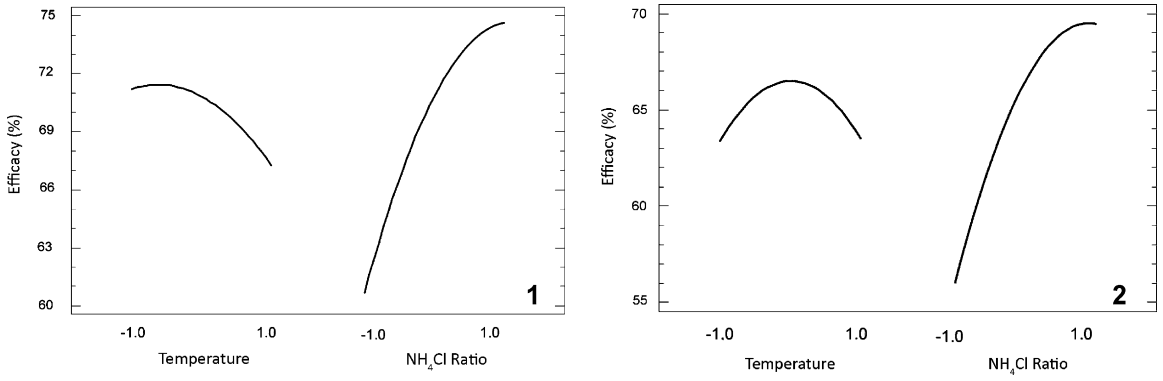

Fig. 4. Main effects for temperature and NH_4Cl–tannin ratio: (1) removal of Alizarin Violet 3R; (2) removal of sodium dodecylbenzene sulfonate. Coded levels.

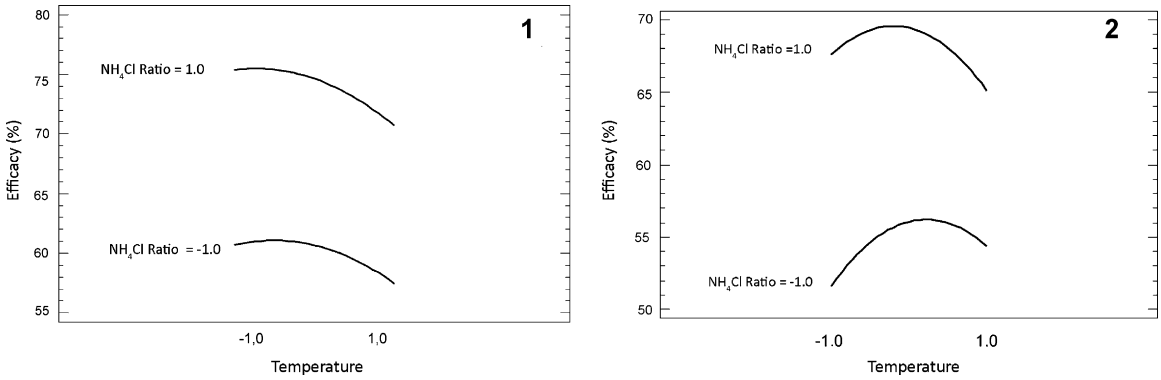

Fig. 5. Interaction graphics for temperature and NH_4Cl–tannin ratio: (1) removal of Alizarin Violet 3R; (2) removal of sodium dodecylbenzene sulfonate. Coded levels.

3.1.4. Interaction between variables

The fact that interaction does not appear between the two studied variables is evident from Fig. 5. The two curves represent the evolution of the response by varying temperature in the extremes of the CCD model, that is, with coded NH_4Cl ratio equal to 1 and equal to −1. Since the curves present an almost parallel behavior, it may be assumed that there is no interaction and the modification of one of them does not affect the other one. This result is valid only inside the working region, out of it the influence of temperature may be increased and interaction may appear therefore.

3.1.5. Response surface and contour plot

The most important graphical representation in the RSM is the surface graphic (Fig. 6). It plots Eq. (3) and allows to evaluate from a qualitative point of view how the behavior of the whole studied system is. As can be appreciated, the response is a quite convex surface inside the studied region, but the ruling variable is the NH_4Cl ratio. Contour plots are drawn as well for a better comprehension of the surface. The maximum appears, as said before, at 24.9 °C and 2 g g^{-1} for dye removal and at 36.4 °C and 1.87 g g^{-1} for surfactant elimination. Predicted percentage removal of each pollutant were 75.5% in Alizarin Violet 3R and 69.5% in sodium dodecylbenzene sulfonate (SDBS). Deviations of less than 5% were found between experimental and predicted values.

According to these results, a combined optimum with average ammonium chloride ratio and reaction temperature was synthesized in order to test its ability either with dyes, surfactants, surface river water and municipal wastewater. Experimental conditions for this coagulant were 2 g of NH_4Cl per g of tannin and 30 °C.

3.2. Characterization of coagulant ability of the optimum

Optimum coagulant was obtained with the specific combination mentioned above and it was characterized in the two water treatment fields: textile and laundry wastewater. The characterization of the optimum product was made on the basis of the efficiency. To this end, one must define an objective measure of the efficiency of the removal of the specific contaminant in relationship with the amount of coagulant. The parameter extensively used in adsorption processes is the adsorption capacity, q. Our working hypothesis was that contaminant removal by coagulation and flocculation occurs in two stages. Firstly, there is destabilization of colloids which may be governed by chemical interactions between molecules of the coagulant (cationic, positively charged) and of the contaminant (anionic, negatively charged). Then, once the coagulant-contaminant complex is formed, flocs begin to grow by sorption mechanisms. This should be the controlling stage, so that the entire process can be simulated as an adsorption phenomenon. Previous studies have found the coagulation capacity q to be a suitable evaluation parameter [45].

Adsorption capacity (q) was determined according to the following equation (7):

$$q = \frac{(C_0 - C_l) \cdot V}{W} \tag{7}$$

where C_0 is the initial contaminant concentration (mmol L^{-1}), C_l equilibrium contaminant concentration in bulk solution (mmol L^{-1}), V the volume of solution (L) and W is the coagulant mass (g).

A full characterization, including the physical and chemical quality of the effluents, should be carried out in further studies. According to previous works [26] the efficacy of such new coagulants may be high also for the specific removal of nitrogen, phosphate or other undesirable compounds.

3.2.1. Dye removal

Fig. 7 presents two screenings on dye removal. The first subfigure (1) represents the ability of the optimum coagulant (WClF) in

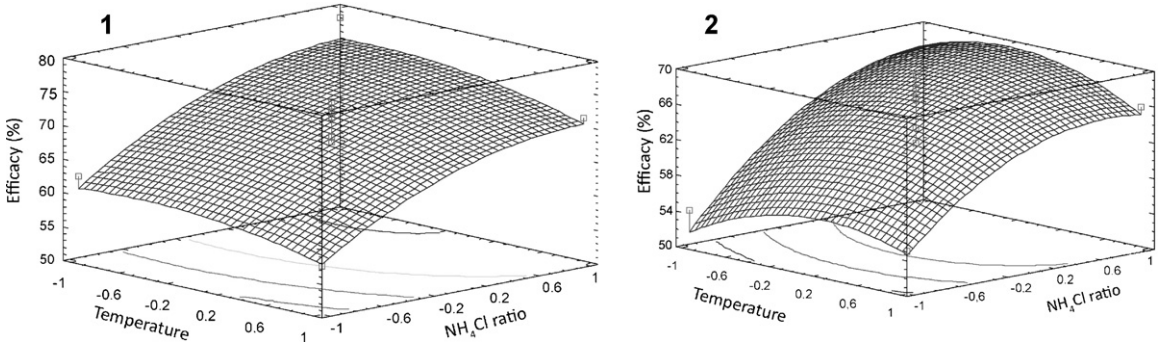

Fig. 6. Surface plot for temperature and NH_4Cl-tannin ratio: (1) removal of Alizarin Violet 3R; (2) removal of sodium dodecylbenzene sulfonate. Coded levels.

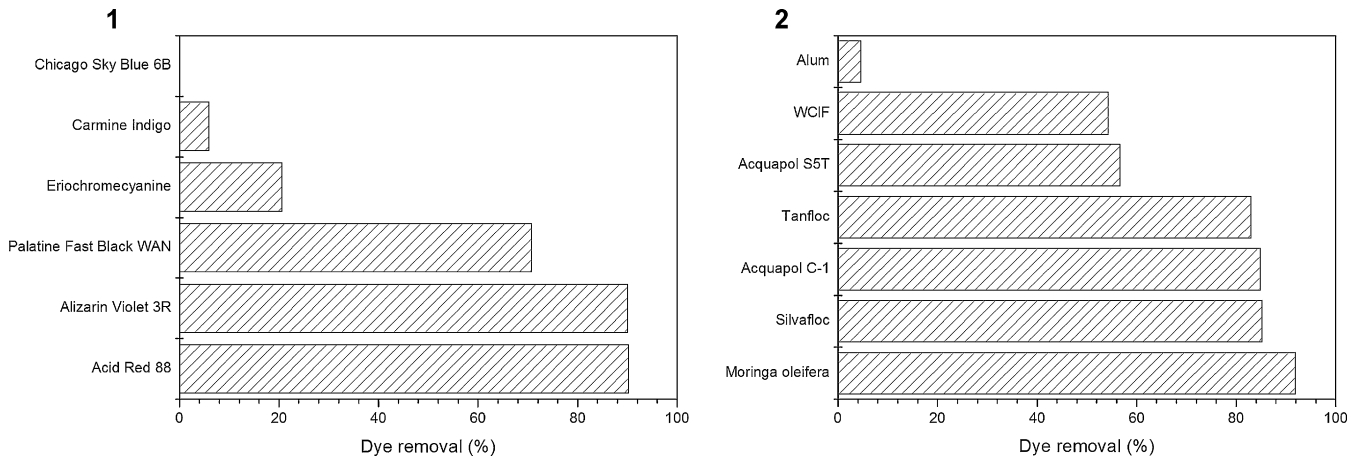

Fig. 7. Efficiency of the optimum coagulant in removing dyes: (1) interaction with other dyes; (2) comparison with other coagulants.

removing four types of dyes: azoic (Chicago Sky Blue 6B, Palatine Fast Black WAN and Acid Red 88); indigoid (Carmine Indigo), triphenylmethane (Eriochromecyanine) and anthraquinonic (Alizarin Violet 3R). The trials were made with an initial dye concentration of 100 mg L^{-1} and a coagulant dosage of 100 mg L^{-1} too. As can be appreciated, differences in the removal efficiency are evident. Although it is very difficult to establish a clear reason for this variability, based on previous studies one can assume that azoic dyes are, generally, easier to remove than the rest of the types, except Chicago Sky Blue 6B, which presents almost null affinity to the coagulant. This fact can be explained by the absence of metal ions (such as those Cr^{6+} in Palatine Fast Black WAN) combined with a bigger size in a less polar molecule. Both Acid Red 88 and Palatine Fast Black WAN presents a very high affinity to the coagulant. Carmine Indigo and Eriochromecyanine presents a relatively low response to the coagulant action of WClF; this was previously reported with similar coagulant agents [29], and Alizarin Violet 3R is therefore a good candidate for further studies since it presents a high affinity.

The second subfigure (2) is the comparison with other coagulants. Experimental conditions were the same as before: 100 mg L^{-1} of coagulant and 100 mg L^{-1} of dye. The most relevant aspect here is the fact that the removal of Alizarin Violet 3R by means of our new tannin-derived coagulant is even higher than with alum, the usual inorganic salt used in traditional drinking and wastewater treatment. Obviously, since the coagulant is not purified, its efficiency is lower than what presented *Silvafloc* or *Tanfloc*.

The ability of WClF in removing Alizarin Violet 3R from aqueous solutions can be appreciated from Fig. 8. As it is evident from this graphical representation, increasing dosages of coagulant drove to a rapid dye elimination. *q* values are comparable to those obtained with other natural coagulants, such as *Tanfloc* [46], *Acquapol* [29] or *Moringa oleifera* seed extract [47].

3.2.2. Surfactant removal

Solutions of 50 mg L^{-1} of surfactant were treated with 100 mg L^{-1} of coagulant in order to evaluate the abilty of this coagulant in removing several types of tensioactives. It is shown in Fig. 9, subfigure (1). As can be appreciated, the efficiency of this coagulant is quite different depending on the kind of detergent. The most persistant one is the sodium laurylsulfate (SLS), probably due to its low molecular weight. Then, a wide variaty of removal levels is presented from SNS-POE (ca. 22%) to SLES-POE (ca. 55%) and the reasons can be found on the different molecular structure and surface charged centers. The biggest molecule is the SDDED and it corresponds to the highest removal in the screening therefore.

On the other hand, subfigure (2) presents the comparison with other coagulants. Although this time WClF is the less efficient coagulant, the relevant aspect is that more than 50% of SDBS is removed with a relatively low coagulant dosage. The difference with the most efficient coagulant (*Moringa oleifera*) is equal to 35%, so purification studies on WClF should be developed.

Once the preliminar screenings were performed, SDBS was selected as compound model for anionic tensioactives. Although the pollutant content undergoes a rapid decrease (Fig. 10), surfactant remnant appears, a residual amount of detergent which is not removable by coagulation action. This effect can be due to the existence of an 'equilibrium surfactant concentration' which is highly difficult to remove, as reported previously [48]. The main reduction of surfactant concentration appears with low coagulant dosages (ca. 200–300 mg L^{-1}). *q* level is also comparable again to those obtained in previous investigations [45,49].

3.2.3. Municipal wastewater clarification

Although the complex matrix of a real municipal wastewater usually does not allow an exact evaluation of the complete action of a coagulant on it, we have tested WClF with this kind of effluent and we have evaluated two main target variables: turbidity removal and the elimination of surfactants. This is shown in Fig. 11. As can be clearly appreciated, the turbidity removal is very acute, with a pronounced decrease from 80 to almost 0 NTU. Regarding surfac-

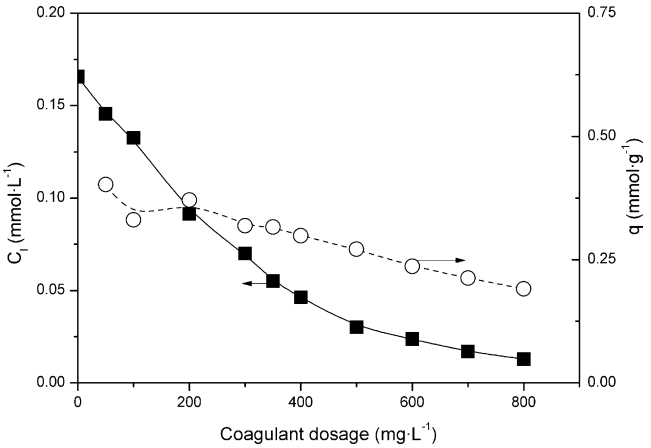

Fig. 8. Coagulant dosage in removing Alizarin Violet 3R.

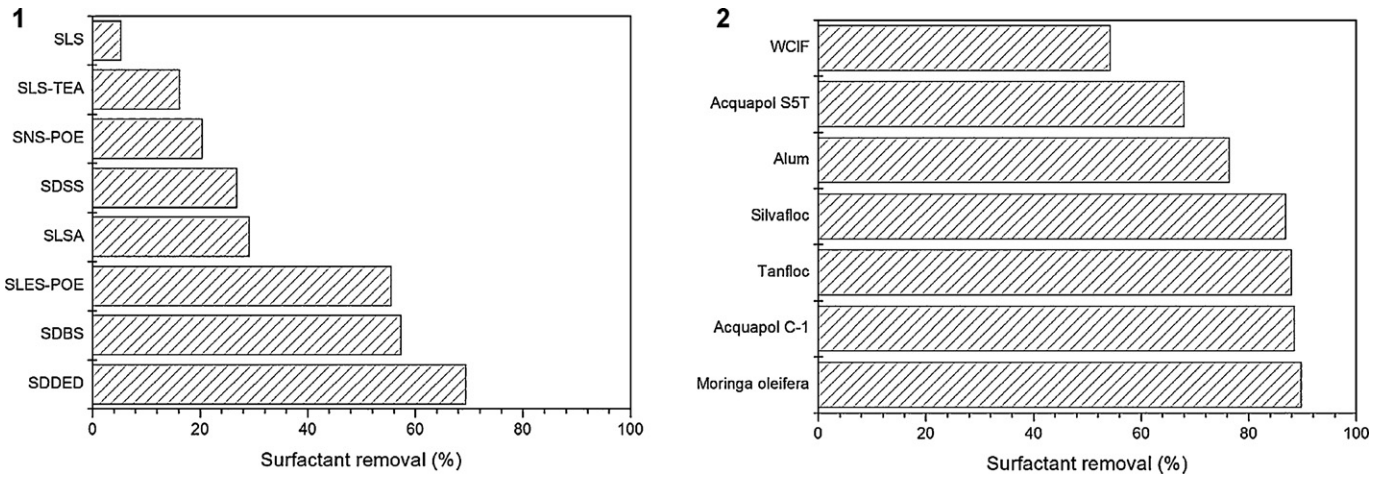

Fig. 9. Efficiency of the optimum coagulant in removing surfactants: (1) interaction with other surfactants; (2) comparison with other coagulants.

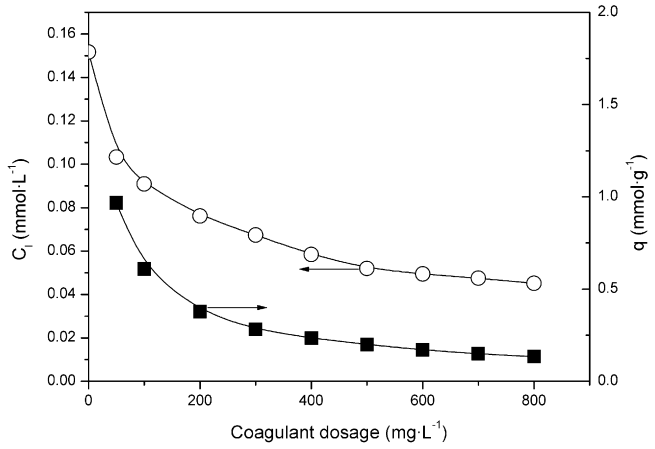

Fig. 10. Coagulant dosage in removing sodium dodecylbenzene sulfonate.

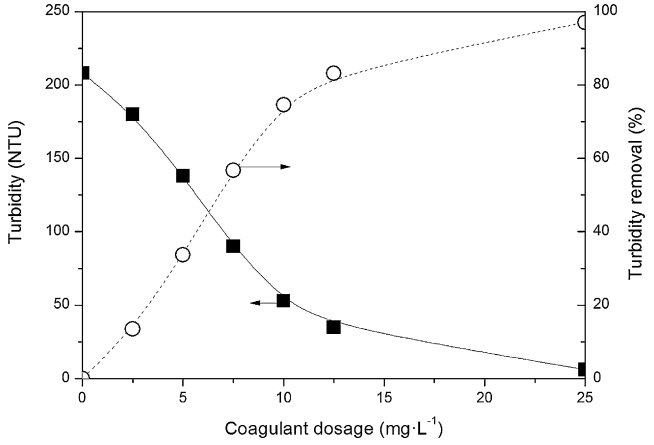

Fig. 12. Surface river water clarification.

tant elimination, the final concentration is around 30% of the initial one, a removal efficiency that is comparable to the levels reported previously in similar studies [50].

3.2.4. Surface river water clarification

The efficiency of this optimum coagulant on the clarification of surface river water, such as the one from Guadiana river, is well demonstrated if one observes the results that are shown in Fig. 12. Low levels of coagulant are able to remove almost the large majority of natural turbidity presented in the samples. The total removal of these suspended colloidal material is achieved with 12.5–25 mg L^{-1}. No microbiological tests were performed after the clarification trial, but presumably the quality of the surface treated water is enhanced also in this aspect, according to the elimination of suspended matter that are usually a physical support for microbial life and pathogen life. Although these doses are quite higher if compared with other similar studies, purification of the product must be proposed in order to improve the performance of this kind of coagulant. If compared with other coagulants and in the same conditions, the lab-synthesized coagulant is similar to *Tanfloc* [22,23], *Silvafloc* [51] or even *Moringa oleifera* [52].

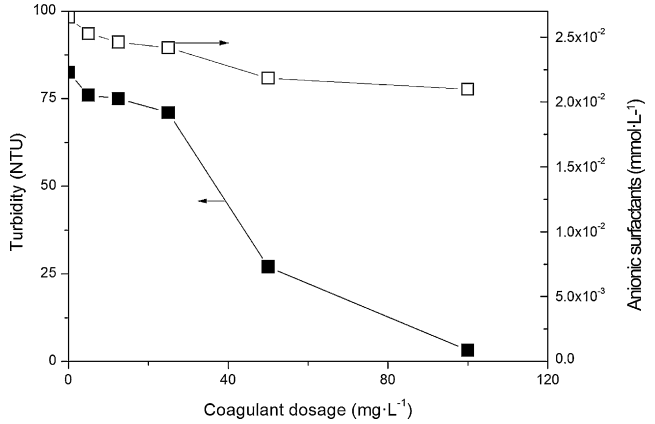

Fig. 11. Municipal wastewater treatment.

4. Conclusions

The synthesis of new tannin-based coagulants from *Acacia mearnsii* de Wild tannin extract (*Weibull black*) has been optimized through design of experiments and response surface methodology. Reaction temperature and NH_4Cl–tannin extract ratio were the considered variables, and coagulant products were tested on simulated textile and laundry wastewater. The amount of amine was significantly more influent than temperature, although both variables were statistically significant. Optimum temperatures were around 30 °C in both cases and optimum amine–tannin ratios were around 2 g g^{-1} as well. The two optimal coagulants easily reached q values up to 0.25 mmol g^{-1} in both cases, what is a very satisfactory level. A combined optimum coagulant resulted efficient in the

treatment of sewage wastewater and in the clarification of surface river water.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.12.075.

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