Communication

Removal of Anionic Surfactants in Aqueous Solutions with *Moringa Oleifera* Seed Extract Coagulant

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Abstract: *Moringa oleifera* seed extract was confirmed as a feasible coagulant in removing surfactants from aqueous effluents. Amongst them, long-chain anionic detergents such as *Polyoxyethylene (3.5) sodium lauryl ether sulfate* (SLES) was selected as a model compound for evaluating the coagulation response. The system coagulant-detergent was stable with different temperatures and pH, and the efficiency was very promising. *Moringa oleifera* was an effective coagulant since it was capable to reach up to 0.245 mg·mg^{-1} coagulation capacity according to Gu-Zhu model. Design of experiments presented an optimum combination of coagulant dosage and initial surfactant concentration of 234 mg·L^{-1} and 76 mg·L^{-1} respectively.

Keywords: surfactants; *Moringa oleifera*; coagulation; wastewater treatment; natural coagulants

1. Introduction

Emerging pollutants are a rising problem nowadays, especially regarding water resources and their fragility, which is more than evident. United Nations and World Health Organiza-

tion have alert the international community about the growing menace of water scarcity or the uncontrolled disposal of pollutants in aqueous effluents [1]. 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. Water is a central point in a wide cycle that links human beings, poverty, health and education and obviously its implications towards the human development are crucial. Global present world has a double challenge regarding water management: on the one hand water resources may be optimised in order to guarantee an adecuate availability for the large majority of the people; on the other hand, water remediation must be a constant task to work on all along the world.

When talking about emerging pollutants one may refer a wide group of chemical families. The term *surfactants* involves perhaps one of the main dangerous and noxious contaminants. Due to their multiple applications, surfactants are nowadays omnipresent compounds in modern life and they can be found in a large variety of everyday products: soaps, detergents, pharmaceuticals, personal care products, etc., but are also employed in other industrial fields that surely make their disposal into the environment a major task to take care of: high-technology devices, paints, and leather production [2]. These are the reasons last data reported that more than 12 M tonnes are used annually and consequently the magnitude of such contamination, especially to aqueous environment, is very relevant [3].

Surfactants may cause dangerous destabilization on aqueous flora and fauna. According to previous literature, detergents and other tensioactive may modify environmental equilibrium by contaminating lakes and groundwater [4]. Moreover, they usually present a sinergistic binding effect on pharmaceuticals, hence the impact of such chemicals and their toxicity for both humans and animals is consideraby increased [5].

Obviously, there already exist several methods for removing surfactants from aqueous effluents. The principal ones may involve chemical association [7], electrochemical removal [8] or adsorption on activated carbon [6]. But there is still a challenge on developing new removal methods that may be even cheaper and easy to apply. The great impact of surfactants nowadays is claiming for more research efforts.

Removing surfactants from water flows has become a priority of many research groups. As is known, there are several types of surfactant depending on their ionic character: anionic, cationic, amphoteric, non-ionic, etc. Amongst them, the most ubiquitous tensioactives are anionic ones, and particularly those with long carbon chain [9]. In them, the risk of bioaccumulation of sulfonated surfactants, such as polyoxyethylene (3.5) sodium lauryl ether sulfate (SLES), has been fully characterized [10].

We have been researching on *Moringa oleifera* as a water treatment agent for several years. As a tropical multi-purpose tree, *Moringa oleifera* presents very interesting properties from the point of view of developing cooperation, as it is a widespread, easy-available water treatment method. It is known that the use of *Moringa oleifera* as water treatment can imply two different

ways: a) One as a primary source of activated carbon [11,12] and b) Another one through seed extraction, by which a coagulant product is obtained [13–15]. This last method is rather more effective and accurate, as we have previously pointed out [16–18]. The main strenght of this treatment process lays on the fact that it is not technologically difficult to operate by non-qualified personnel, it is easy to work with and it is free from external dependency of reagents, as it would happen with other products ($Al_2(SO_4)_3$, $FeCl_3$). Because of those reasons, Food and Agricultural Organization (FAO) recommended it as proper and advisable way for treating water [19].

In the current global world, environmental aspects do not belong to particular geographical areas, but they are international concerns. Therefore, economical and availability criteria must be taken into account if we want to present a universal possibility of becoming clean [20]. In this sense, *Moringa oleifera* seed coagulant may be an advanced water treatment which is cheaper and biodegradable, easy to handle by non qualified personnel and, consequently, adequate for situations of low technological development.

The current work presents a study on the removal of the specific contaminant SLES from aqueous effluents. Polluted waters (such as those linked to laundry industry) have been subjected to coagulant action of *Moringa oleifera* seed extract. After two preliminary screening of coagulant action of the seed extract in comparison with other coagulants and with other surfactants, the process has been studied under three complementary points of view: firstly a traditional study of the influence of several working variables was performed (coagulant dosage, initial surfactant concentration, pH and temperature). Then, the surfactant-coagulant system was studied according to a statistical design of experiments for identifying interactions between variables. Theoretical models were finally applied as a mandatory stage prior to pilot plant implementation.

2. Results and Discussion

As said before, this investigation presents four parts: 1) the preliminary evaluation of the coagulant activity of *Moringa oleifera* seed extract with several surfactants and in comparison with other products, 2) the evaluation of some relevant variables in these coagulant-surfactant systems, such as pH, temperature or coagulant dosage, 3) the study of the interaction between variables according to the Response Surface Methodology in a design of experiments, 4) finally, a theoretical model is proposed for explaining the coagulant phenomenon.

2.1. Preliminary screenings

Two different screenings were carried out: one for comparing the ability of *Moringa oleifera* in the removal of different surfactants and another one regarding the comparison between the extract and other coagulants. This last study was subjected to ANOVA tests for confirming replicability of the coagulation process.

Removal of different surfactants

A fixed dose of ca. 160 mg·L^{-1} of coagulant was applied to different solutions of detergents with a surfactant concentration of ca. 50 mg·L^{-1}. The percentage removal of each effluent is represented in figure 1. As can be clearly appreciated, the large majority of surfactants are easily removable through coagulation. SDDED presented a more refractory nature, maybe due to the presence of two sulfonate groups in both extremes of the carbon chain, that might difficult the electrostatic neutralization with the cationic proteins of the coagulant [27]. Moreover, the weight and lenght of each surfactant can affect to the affinity coagulant-detergent, since the performance of the removal of SNS was significantly lower than the rest. This was also observed in similar trials and previous studies [28]. The rest of the surfactants presented a more similar performance from 60-75%, an interesting and promising removal rate that surely must be studied in further works.

**Figure 1.** Preliminary screening for surfactant removal with *Moringa oleifera* seed extract.
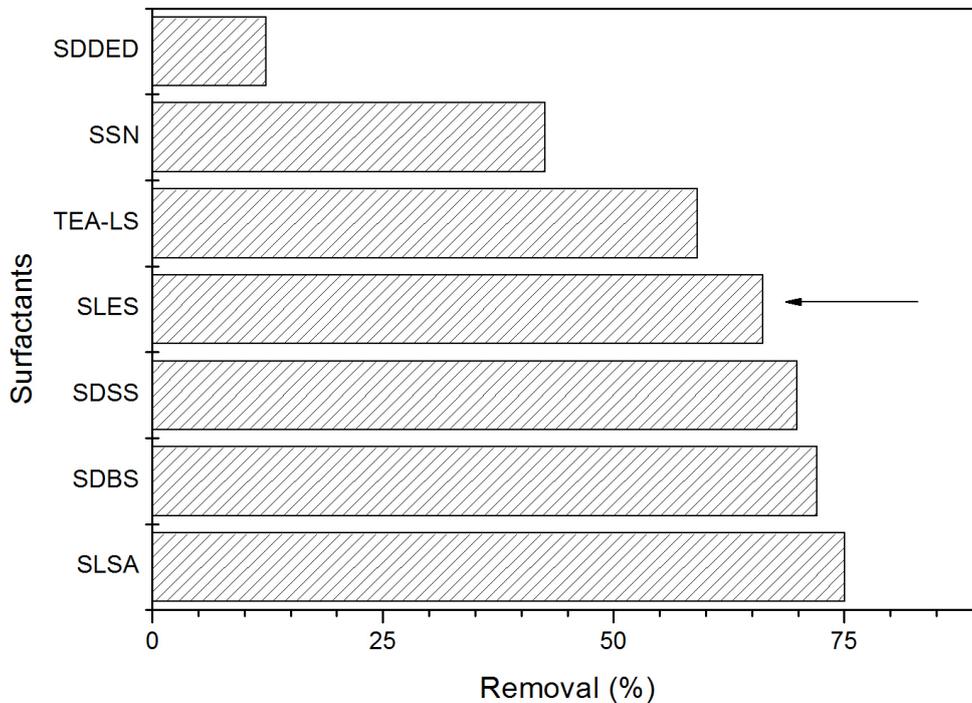
Comparison with other coagulants

In order to confirm the feasibility of *Moringa oleifera* coagulant for water and wastewater treatment, it is needed to compare the effectiveness of such product with other similar and

traditional coagulants. That is the case of natural coagulants based on tannin extracts (Silvafloc, Tanfloc, Acquapol C1 and S5T) and the classical aluminium metal salt (namely *alum*). To this end, equal doses of coagulant (160 mg·L^{-1}) were applied to solutions of ca. 50 mg·L^{-1} of detergent. Each trial was performed twice in order to confirm the reproducibility of this study. Figure 2 shows the results whereas the replicability of the trial is presented in figure 3.

Figure 2. Comparison with other coagulants.
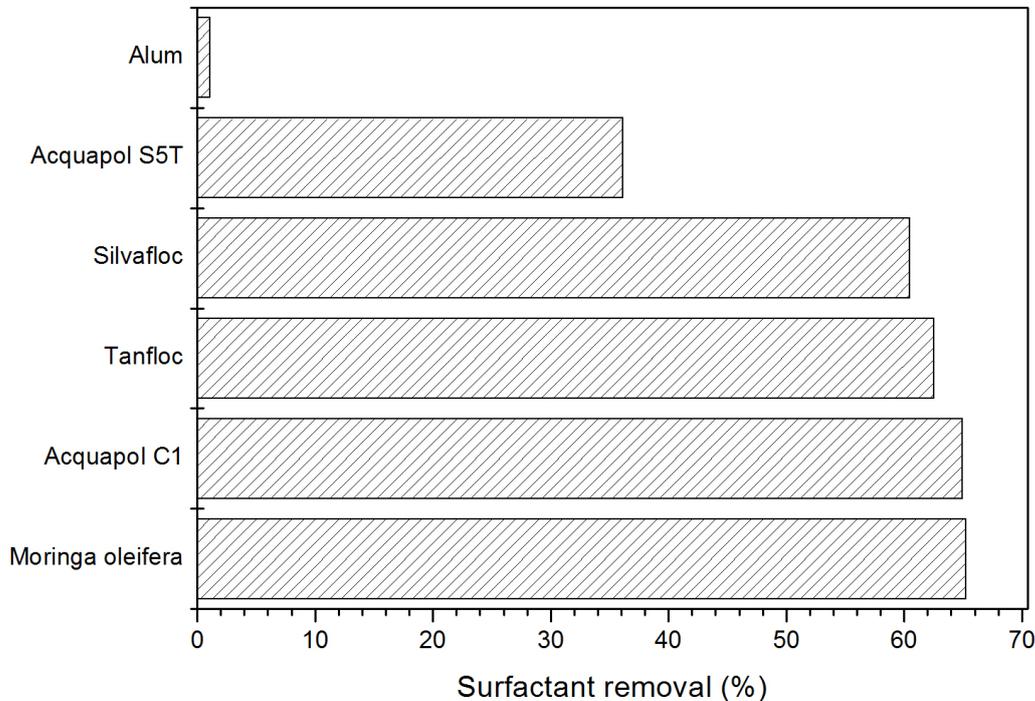
As both figures depict, the efficiency of *Moringa oleifera* seed extract is place in the first level of performace, it reaches 65% of SLES removal. On the contrary, alum is the least effective coagulant, which presents almost null removal. The rest of coagulants are rather effective with significative differences between Acquapol S5T and the rest of them. These differences may be attribuited to the specific production process of each coagulant (in the case of Acquapol S5T it is presumably the aminomethylation of *Acacia mearnsii*) and to the purification level of the main material (tannin extract).

On the other hand, the reproducibility of the trial is well guaranteed since ANOVA test for indistinguishability presented a p-value of 0.90 related to the variable *replicate*. That means this variable does not explain the model (since it is above 0.05, which is the significance level), consequently there is no difference between replicates and the experiment is fully reproducible (figure 3).

Figure 3. Replicability test.
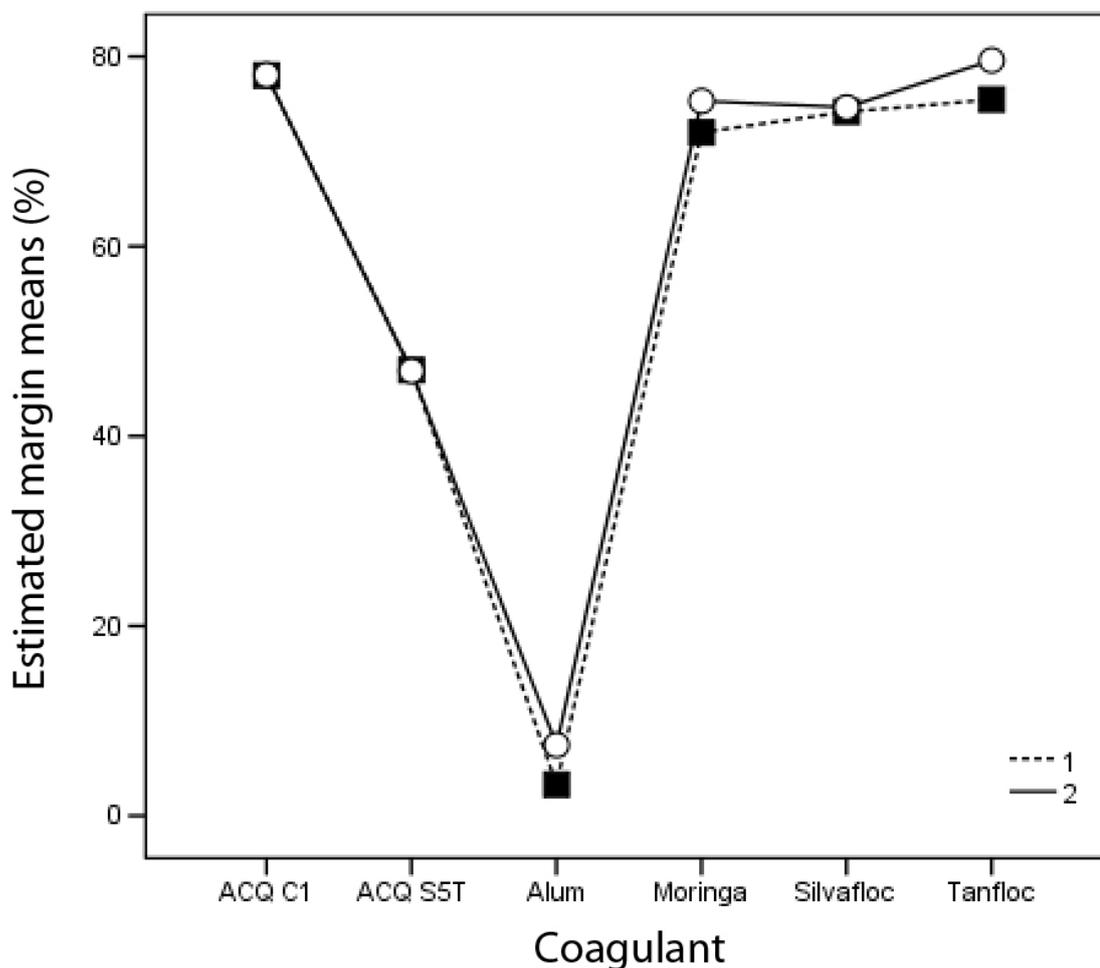
2.2. *Influence of variables*

A classical evaluation of the influence of different variables was carried out regarding coagulant dosage, initial surfactant concentration, pH and temperature in the general Jar test. These series are presented in figure 4.

We have worked on the hypothesis that surfactant removal by coagulation process may involve two stages. This conjecture is adopted in previous similar works [28]. This process may involve a first destabilization of colloids, probably ruled by chemical interactions between coagulant molecules (cationic, positive charged) and contaminant molecules (anionic, negative charged); and a second stage when the complex coagulant-surfactant is formed. Then, flocks begin to grow by sorption mechanisms and when certain flock size is reached, they begin to settle by gravity. The adsorption phase should be the controlling stage, so the whole process can be simulated as an adsorption phenomenon. Other similar hypothesis are made and applied

previously [29]. So that, adsorption capacity q is included as a measure of the efficiency of the process. q is defined as:

$$q = \frac{(C_0 - C_l) \cdot V}{W} \tag{1}$$

where C_0 is initial surfactant concentration, (mg·L^{-1}),

C_l is equilibrium pollutant concentration in bulk solution, (mg·L^{-1}),

V is the volume of solution, (L),

and W is coagulant mass (mg).

Figure 4. Influence of variables. 1) Coagulant dosage, 2) Initial Surfactant Concentration, 3) pH, 4) Temperature.
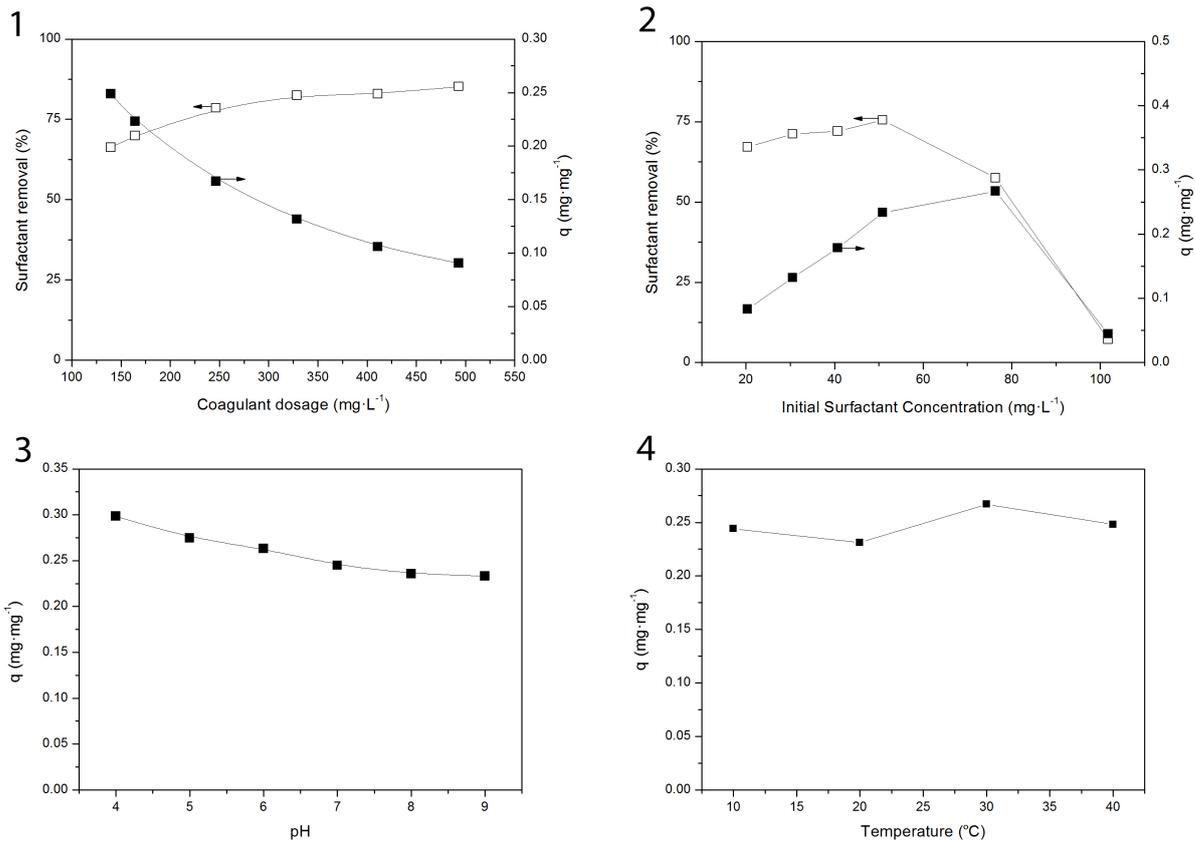
The first subfigure (1) presents the increase of SLES removal percentage as the coagulant dosage raises up. A fixed initial pollutant concentration (ca. 50 mg·L^{-1}) underwent a progressive decrease when increasing doses of coagulant were applied. Surfactant seems to present a residual concentration of ca. 7 mg·L^{-1} not removable by coagulation. This was also observed by other researchers [30] and this phenomenon is discussed in our previous works [18]. A high

efficiency of the coagulant is easily reached and this is reflected on the high q levels, which are naturally higher at low coagulant dosages.

If initial pollutant concentration (also called *charge*) is varied, the efficiency of the coagulation systems tends to differ from standard conditions. Not only percentage removal but also q capacity should be observed in this evaluation. To this end, a fixed amount of coagulant (ca. 160 mg·L^{-1}) was applied to different initial concentrations of surfactant. As subfigure (2) depicts, increasing initial pollutant concentrations leads to a loss of percentage removal. However, q capacity, which is indicative of the efficiency of the product, tends to grow subsequently up to a maximum, which is near to 80 mg·L^{-1}, that probably has to do with the Critical Micellation Concentration (CMC). The behaviour of q is radically different before and after CMC point is crossed. Once it has happened, the original increasing path of q turns dramatically into a decreasing way. It is surely caused by the general appearence of micelles inside the bulk solution, which have a particularly different sorption way onto flocs [28,31]. In the first stages of the *charge* evaluation, the coagulant is not completely efficient since there is excessive amount of it. As the *charge* increases, the coagulant tends to be exhausted and the capacity of the system tends to grow, being more efficient therefore. This capacity become almost null once the CMC is tresspassed.

pH is known to play an important role in coagulation processes [32]. Because of this fact, several trials with different pH values have been carried out, varying pH between 4 and 9 with fixed concentrations of surfactant (ca. 60 mg·L^{-1}) and 160 mg·L^{-1} of coagulant. As can be appreciated in subfigure (3), the same coagulant dose tends to be less effective as pH becomes higher. This fact has to do with the cationic form of the coagulant, which should be higher at acidic pH and lower at basic level. Electrostatic attraction between coagulant cationic chains and negatively-charged active centers in the surfactant molecules is reinforced. In addition, links to hydrofobic chains would be enhanced [30]. However, this coagulant presents a high efficiency since q capacity varies between 0.20 and 0.30 mg·g^{-1}, both variables high enough.

Finally, this coagulant seems to present stability along the studied temperature range (10-40°C). An initial surfactant concentration of 60 mg·L^{-1} was treated with a fixed coagulant dose of ca. 160 mg·L^{-1}, pH 7 and different temperatures. As can be observed in subfigure (4), no differences can be stated from these experimental series. In a general way, temperature does not seem to be significatively important. This stability add a new advantage to the studied coagulant, since it allows the treatment of wastewater under thermal contamination, e.g. lakes or ponds, which is a desirable characteristic [33].

2.3. *Design of experiments*

The previous section does not show any interaction between variables. It is not possible to predict the combined influence of the different variables on the final response unless specific experimentation is carried out. Although some theoretical approaches can be done, the empir-

ical evidence of the real influence of the operative conditions can be established only through the experimentation. Design of experiments is a statistical procedure focused on detecting these links between the working variables and can reduce significantly the number of experiments, keeping however the reliability of the conclusions at a high standard.

Traditionally, researchers have used the experimental method called *one factor at a time*. Through this approach, it is very difficult to establish the corresponding relationships among all the input factors and the output responses. Instead, it is usually accepted this method can be useful in finding predominant variables, but afterwards a desing of experiments is mandatory to obtain a probable optimum response. It offers a better alternative to study the effect of variables and their response with minimum number of experiments [34]. This methodology was widely used in these kinds of chemical processes [35] and offers a powerful tool for evaluating the intrinsic relationships between variables properly.

As we have reported in previous works [35], the data collected must be analyzed in a statistically manner using regression. Accordingly, the test factors must be coded as equation 2 shows:

$$\chi_i = \frac{X_i - X_i^x}{\Delta X_i} \tag{2}$$

where χ_i is the coded value of the *i*th independent variable, X_i the natural value of the *i*th independent variable, X_i^x the natural value of the *i*th 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. 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. 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, that is the case of section 2.2. The most influent variables are, according to these results, the coagulant dosage and the initial surfactant concentration (ISC). Therefore, the working region was established taking into account these trials. Figure 5 presents this area graphically. As can be appreciated, two squares are presented, one concerning the real working region (that is, where statistically significant conclusions can be obtained) and the limits of the design, where the extreme points are placed for obtaining the tendency. The particular design consists of 16 experimental points that are referred in table 1

Figure 5. Working region fo the design of experiments.
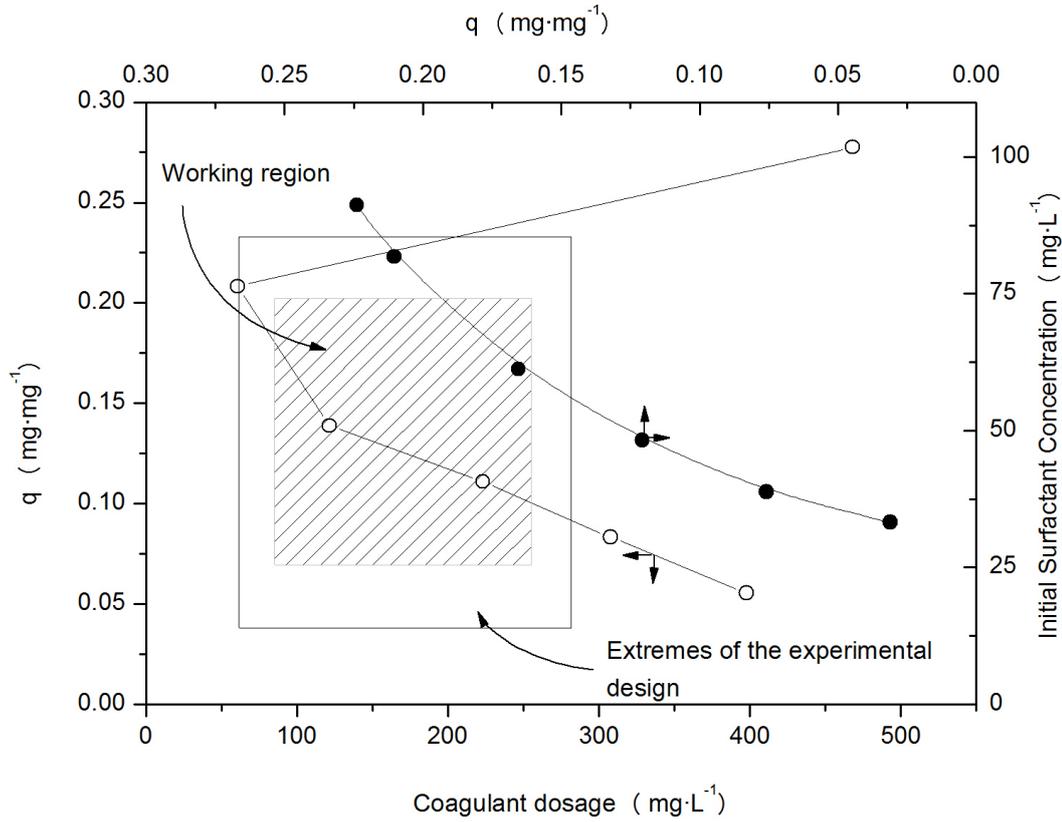
Analytical results

ANOVA analysis is the first approach to the DOE result. It shows the significance of the different parameters under an analytical point of view and it is important to state the significance of the design. According to the RSM, five factors are considered in this particular case and all of them are statistically significant, attending to each p-value in the ANOVA test. It presents a very high correlation factor (up to 0.97), which implies the system is correctly explained through these two variables and their interactions. Non-linear polynomic regression is carried out by taking into account the coded variables. This regression is given by equation 3:

$$q = 0.20 + 0.02 \cdot D + 0.03 \cdot C - 0.03 \cdot D^2 - 0.03 \cdot C^2 + 0.04 \cdot D \cdot C \qquad (3)$$

where D is the coded coagulant dosage and C is the coded *charge*, initial surfactant concentration.

Moreover, ANOVA results gave a Durbin-Watson factor equal to 2.2, which is higher than 0.05 and, consequently, it is non significative. This means there is no evidences of autocorrelation and therefore the randomization in the experimental sample was effective.

Analytically, an optimum combination of ISC and coagulant dosage is presented at 1 and 0.85 coded levels respectively. This point corresponds to 76 mg·L^{-1} of surfactant and 234

mg·L^{-1} of coagulant. With these experimental conditions, a q capacity of 0.23 mg·mg^{-1} is achieved, which is a quite high value if compared with other results from previous works as it is indicated below. This theoretical capacity was experimentally confirmed.

Graphical analysis

Graphical tests are made on the basis of five factors which correspond to equation 3. These are presented in figure 6. For example, subfigure (1) presents the *Pareto* graphic. Bars represent the standarized effects of each involved factor, considering them as coagulant dosage, ISC and the combinations of both. Nonfilled bars are a graphical representation of positive-affecting factors, such as ISC. This means that this factor appears in the 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.

Figure 6. Design of experiments. 1) Pareto graphic, 2) Main effects, 3) Interaction of variables, 4) Response Surface Graphic. * Initial Surfactant Concentration.
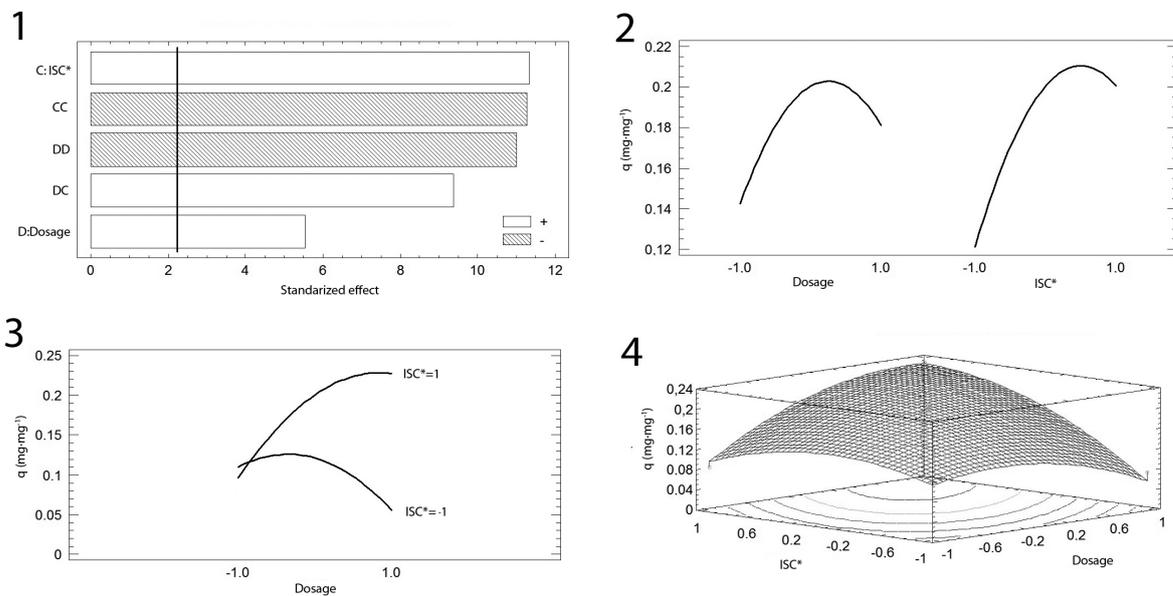
Pareto graphic also gives us an idea of how factors affect on the final response of percentage removal. Positive bars indicate that by varying the variable the response increases. Negative bars indicate the contrary. As can be shown, as ISC increases the response is increased as well. This is consistent with the results presented in section 2.2.

The evaluation of the CCD model also drives to the study of the main effects of the involved variables. This can be appreciated in subfigure (2). Two curves are drawn representing the effect of varying each variable while the other one keeps constant. The effect of both variables is quite

similar since both lines present not relevant differences. An optimum combination appears in the two curves of the studied system, this will drive us to the optimum combination of both variables.

Consequently, the fact that interaction does appears between the two studied variables is evident from subfigure (3). The two curves represent the evolution of the response by varying temperature in the extremes of the CCD model, that is, with coagulant dosage equal to 1 and equal to -1. Since the curves are crossed, it may be assumed that there is effective interaction and the modification of one of them affects the other one. Evidently, this result is valid only inside the working region, out of it the behavior of the system may differ.

Finally, the most important graphical representation in the RSM is the surface graphic, which is presented in subfigure (4). It plots equation 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 with both variables ruling the response q. Contour plots are drawn beneath it as well for a better comprehension of the surface. The maximum appears, as said before, around 1 and 0.85 for ISC and coagulant dosage respectively.

2.4. Theoretical model

Once adsorption hypothesis is accepted, the coagulation phenomenon can be explained by the classical theoretical models. Specific coagulation models are rather difficult to apply and they are not very used in scientific literature because the nature of the phenomenon is quite complex (it implies molecule physico-chemical interaction such as van der Waals and hydrogen bridges forces [36]). Moreover, it is even more difficult if one deals with natural products such as *Moringa oleifera* seed extract, whose intrinsic composition is not completely known. However, the importance of a theoretical argument is more than evident in order to make easier further studies [37].

According to the hypothetical interactions between surfactants and natural polymers, three models have been established for explaining this particular coagulation phenomenon. The basic interaction mechanisms are reasonably well understood, but researchers still disagree at molecular level. It is generally accepted that these interactions may occur between individual surfactant molecules and the polymer chain, or in the form of surfactant-polymer aggregate complexes (micellar or hemimicellar interactions).

It is important to keep in mind that the behavior of surfactant solutions may change radically once the Critical Micelation Concentration (CMC). In addition, there also exists a lower concentration (called Critical Aggregation Concentration, CAC [38]) that induces the formation of a complex aggregate structure. CAC usually appears below CMC, the difference between both concentrations may vary by a factor of 10-1000 in some cases [2]. CAC is identified in surfactant-polymer systems with the concentration where coagulation starts, while CMC is clearly established when the models are not useful any more. The specific behavior of every

particular system will vary with the nature of the surfactant and the polymer. For modelling the surfactant removal, we will attend to the first stage of detergent adsorption, that is, the one that occurs below CMC, as the second one refers to a completely different mechanism, as said before. According to this, the following arguments are referred just to the first stage of the process, that is, up to CMC.

Three theoretical models were considered in this work. The first of them was proposed by Freundlich [39] and was derived from empirical data. It assumes that q capacity is a power function of the equilibrium dye concentration (C_l). Equation 4 express this mathematically:

$$q = k_f \cdot C_l^{n_f} \tag{4}$$

where

n_f is the Freundlich adsorption order (dimensionless)

and k_f is the Freundlich adsorption constant ($[L^{n_f}] \cdot [\text{mg of coagulant}]^{-1} \cdot [\text{mg of removed surfactant}^{n_f-1}]$).

A simple model that has been used to describe the adsorption of surfactants is the regular behaviour model [40]. For dilute solutions, this model simplifies to the Frumkin-Fowler-Guggenheim (FFG) equation [41,42].

$$\frac{\theta_l}{1 - \theta_l} = C_l \cdot k_{12} \cdot \exp(\chi_{12} \cdot \theta_l) \tag{5}$$

where θ_l is the ratio between the adsorption and the maximum adsorption:

$$\theta_l = \frac{q}{q_\infty} \tag{6}$$

k_{12} is the adsorption constant, being a measure of the interaction between surfactant and polymer surface,

and χ_{12} is the Flory-Huggins parameter [43].

In this model k_{12} and χ_{12} should be considered as adjustable parameters expressing the affinity for the surface and the lateral interactions in the adsorbed layer, respectively.

Zhu and Gu [44] proposed a very simple model for adsorption of surfactant assuming that the adsorbed layer is composed of surfactant aggregates. A surfactant aggregate is formed on the surface before stable aggregates are formed in solution. The model considers that these aggregates are stabilized by the presence of the surface. This model leads to the following equation 7:

$$\frac{\theta_l}{1 - \theta_l} = k_g \cdot C_l^{n_g} \tag{7}$$

where n_g is the number of monomers in the surfactant aggregate,

and k_g is the Gu and Zhu constant for the studied model.

Taking into account the definition of θ_l, equation 7 becomes

$$q = q_\infty \cdot k_g \frac{C_l^{n_g}}{1 + k_g \cdot C_l^{n_g}} \qquad (8)$$

This equation is reduced to the Langmuir equation for $n_g = 1$. In addition, if the term $k_g \cdot C_l^{n_g}$ is much lower than 1, the derived expression is known as the Freundlich equation 4.

Equations 4, 5 and 8 lead to three models that have been studied: Freundlich (F), Frumkin-Fowler-Guggenheim (FFG) and Gu and Zhu (GZ) models.

Figure 7. Theoretical model.
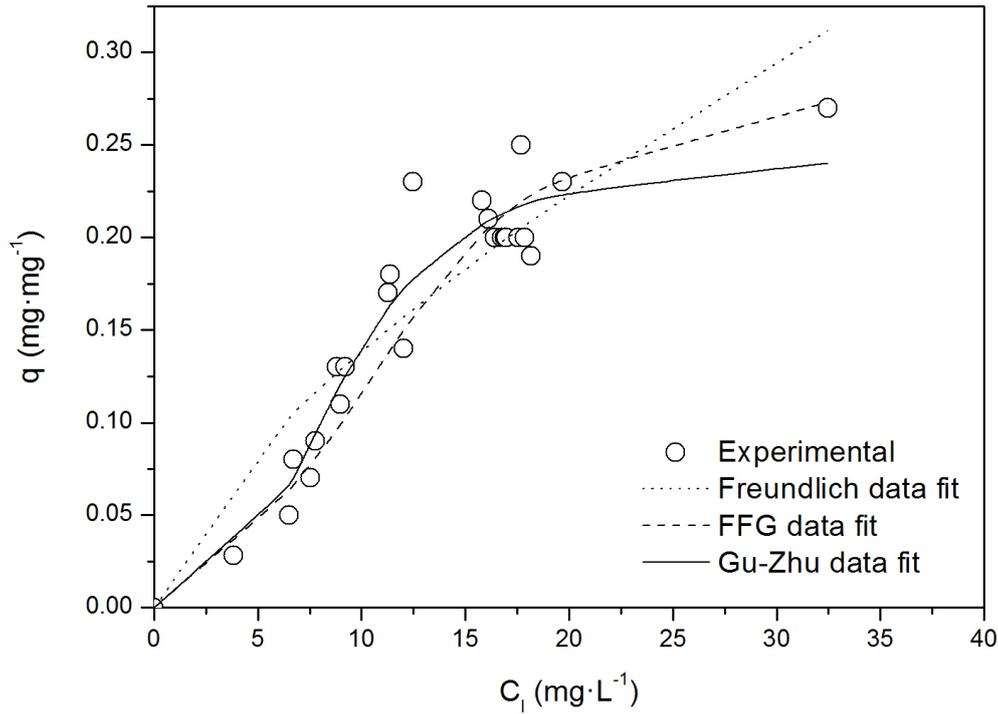
By combining data series of previous sections and other more especifically carried out, it is possible to look for theoretical models that fits rather well to experimental data. This is showed in figure 7, where experimental and predicted values are presented. As can be observed, a S-shape curve is presented, with a slight increasing of q at low values of C_l. q values raise up rather fast along the intermediate range of C_l between 5 and 15 mg·L^{-1}. Then, they keep on increasing and presumably they arrive to an asymptotic value, which corresponds to q_∞. These kinds of curves have been thoroughly studied by researchers [45].

The specific parameter values and the statistic summary for both systems and for each corresponding model are shown in table 2. It is remakable that non-linear adjustment fits accurately

for the three models (r^2 above 0.8) but the most reliable model is the Gu and Zhu hypothesis. Non linear adjustment is presumed to be more accurate than linear fits, since no homocedasticity assumptions are needed [46,47]. According to Gu and Zhu adjustment, q_∞ is quite near to maximum q predicted by RSM in section (0.23 mg·mg^{-1}).

To the best of our knowledge, no previous works were published regarding the specific removal of this particular surfactant. However, similar studies were carried out addressing the removal of other detergents. Perhaps the most interesting one was presented by Ayranci and Duman [30] where several surfactants were removed by adsorption with activated carbon. The maximum q capacities were there very similar to those obtained in the current paper. Other similar studies reached to q values of the same magnitude order, as presented in table 3. The efficacy of *Moringa oleifera* seed extract in removing SLES is placed inside the adsorption range of these different products.

3. Experimental Section

3.1. *Buffered solution*

The trials with added dye were performed with pH-stable media according to preliminary data [21]. 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.

3.2. *Model compounds*

Polyoxyethylene (3.5) sodium lauryl ether sulfate (SLES) was purchased to CHEM SERVICE Inc. It is a long-chain anionic surfactant with one sulfate group as hydrophylic extreme whose composition is $C_{12}H_{25}(OCH_2CH_2)_{3.5}OSO_3Na$. Chemical structure is shown in figure 8 and responds to a CAS number of 32612-48-9. Its appearence is as a dense and sticky gel.

Figure 8. Chemical structure of SLES

Other surfactants were used in the preliminary screening (section 2.1). They were the following ones:

- Sodium dodecyl benzene sulfonate (SDBS) $C_{18}H_{29}SO_3Na$.

- Sodium dodecyl diphenyl ether disulfonate (SDDED) $C_{35}H_{56}S_2O_7Na_2$.

- Sodium triethanolamine lauryl sulfate (TEA-LS) $C_{18}H_{40}NSO_4Na$.

- Sodium dioctyl sulfosuccinate (SDSS) $C_{20}H_{37}SO_7Na$.

- Sodium lauryl sulfoacetate (SLSA) $C_{14}H_{27}SO_5Na$.

- POE Sodium sulfated nonylphenol (SSN) $C_{17}H_{28}SO_5Na$.

3.3. *Moringa oleifera seed extract and other cogulants*

Dry seeds were obtained from SETROPA, Holland. The extraction process were carried out as referred elsewhere [17,18]. The result is a clear, milky-like liquid. *Moringa* stock solution prepared in this way was used the same day it was producted, although there are references that point the stability of the extract [22].

Regarding the rest of coagulant agents, modified tannin extracts were supplied by different commercial trademarks. Tanfloc (from TANAC, Brazil) consists of tannins from *Acacia mearnsii* that have been modified chemically in order to introduce a quaternary nitrogen. This confers Tanfloc its cationic character. Other three products with the same nature were suplied by SILVATEAM, S.A. (Italy), in case of Silvafloc, and ACQUACHIMICA SETA, S.A. (Brazil) in case of Acquapol C1 and Acquapol S5T. Differences between Silvafloc, Acquapol C1 and S5T and Tanfloc lay on tannin nature (*Acacia mearnsii* for Acquapol and Tanfloc and *Schinopsis balansae* for Silvafloc) and on chemical modification, which is under copyright law. Tanfloc and Acquapol C1 are presented as powder, whereas Silvafloc and Acquapol S5T are presented as a solution.

The traditional and common aluminium sulfate for coagulant purpose was supplied by PANREAC ($Al_2(SO_4)_3.18H_2O$) with analytical purity grade.

3.4. *Surfactant removal trials and analysis*

A surfactant solution of 500 mgL^{-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 [23] reported 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 [24]. The spectrophotometer used was a HEλIOS UV/VIS.

3.5. *Mathematical and statistical procedures*

A factorial Central Composite (CCD) orthogonal and rotatable design was used for the optimization of the quantitative variables such as coagulant dosage and initial surfactant concentration. The CCD analysis was carried out under Response Surface Methodology. Design of experiments section was statistically analyzed by using *StatGraphics Plus for Windows 5.1* [25].

Other statistical considerations, such as non-linear adjustment or replicability tests (section) were performed with SPSS 15.0.1 for Windows [26].

Acknowledgements

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Table 1. Experimental planning in the design of experiments.

Number of run	Coded coagulant dosage	Coded ISC [a]	Real coagulant dosage	Real ISC[a]
1	0	-1.41	165	15
2	-1	-1	82	25
3	-1	1	82	75
4	0	0	165	50
5	0	0	165	50
6	1.41	0	280	50
7	0	0	165	50
8	0	0	165	50
9	0	0	165	50
10	0	1.41	165	85
11	0	0	165	50
12	-1.41	0	48	50
13	0	0	165	50
14	1	-1	246	25
15	0	0	165	50
16	1	1	246	75

[a]Initial Surfactant Concentration

Table 2. Theoretical models adjustment parameters for surfactant removal. Units in text.

	Parameter values	r^2
Freundlich	k_f=0.028; n_f=0.69	0.83
FFG	k_{12}=2.31$\cdot$ 10^{-2}; q_∞=0.320; χ_{12}=0.24	0.83
Gu and Zhu	k_g=1.14$\cdot10^{-3}$; n_g=3.09; q_∞=0.245	0.91

Table 3. Other studies on surfactant removal from aqueous effluents.

Surfactant	q_{max}[a]	Treatment agent	Reference
SLS	0.61	*Moringa oleifera* coagulant	[18]
SDBS	1.15	Silvafloc	[48]
SDBS	1.36	Tanfloc	[28]
LAS[b]	0.49-1.21	IEx resins	[49]
LAS[b]	0.027-0.53	Activated carbon	[49]

[a]mg$\cdot$mg^{-1}
[b]Linear alkylbenzene sulfonate