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Removal of sodium dodecyl benzene sulfonate from water by means of a new tannin-based coagulant: Optimisation studies through design of experiments

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ABSTRACT

A new tannin-based coagulant and flocculant agent has been tested on the removal of sodium dodecyl benzene sulfonate (SDBS), a dangerous and pollutant anionic surfactant. It is called *Tanfloc* and consists of a chemically modified tannin extract from *Acacia mearnsii de Wild*. In order to study the interaction between pH and initial surfactant concentration (ISC), a design of experiments procedure has been carried out. The influence of these two variables has been evaluated. Increasing pH level leads to a loss of efficiency in surfactant removal, while increasing ISC allows the system to enhance the efficiency of the removal process. ANOVA test reported significativity for four of the five involved variables and the influence of pH was similar to the influence of ISC. An optimum q of 0.96 mg mg^{-1} was found at pH 4.9 and ISC equal to 103.2 mg L^{-1}.

1. Introduction

Surfactants have become a very important group of compounds in modern life. They are present in a large variety of usual and normal products like soaps, detergents, pharmaceuticals or personal care products. They are used in chemical industry, “hi-tech” devices, paints, leather [1]. As it can be appreciated, surfactants have achieved a main position in human activity. More than 12 M tonnes per year [2] are produced, according to the latest statistical data, so surfactants can be considered as a first importance chemical group.

Surfactants dumping into the environment represent a harmful and noxious practice [3]. They may be useful and needed compounds, but they are also considered dangerous and undesirable substances because of their impact on water fauna and vegetal life [4]. The main aspects in which surfactants modify on environmental equilibrium involve [5] groundwater and lakes pollution, pharmaceutical products binding (so pollution activity of these kinds of chemical compounds is considerably increased), animal and human toxicity and biopersistence [6].

Due to these reasons, removing surfactants from water flows has become a priority of a large number of researchers. Nowadays, surfactants can be removed by several mechanisms, most of them imply adsorption on activated carbon [7] or onto other materials [8], biological degradation [9,10], chemical oxidation [11–15] or electrochemical removal [16]. Recuperation of these products is also a challenge and a scope of several investigations [17]. However, new removal methods should be researched because surfactants and tensioactives impact is high enough. Specifically, the risk of bioaccumulation of sulfonated surfactants, such as sodium dodecyl benzene sulfonate (SDBS), has been fully characterized [18,19]. Taking these risks into account, the investigation we have developed has been focused on this surfactant.

Under *tannins* denomination there are lots of chemical families. Tannins have been used traditionally for tanning animal skins, but it is possible to find several products that are distributed as flocculants. Tannins come from secondary vegetal metabolites [20] that are present in bark, fruits or leaves. Tannin-rich barks come from trees such as *Acacia*, *Castanea* or *Schinopsis*. However, it is not needed to search for tropical species: *Quercus ilex*, *suber* or *robur* have also tannin-rich bark.

Tanfloc is a trademark that belongs to TANAC (Brazil). It is a tannin-based product, which is modified by a physico-chemical process, and has a high flocculant power. Some previous papers have researched on this particular coagulation agent [21]. It is obtained from *Acacia mearnsii de Wild* bark. This tree is very common in Brazil and it has a high concentration of tannins. Production process is under intellectual patent law, but similar procedures are widely reported as Mannich base reaction [22]. Specific industrial process for *Tanfloc* is referred by US patent number 6,478,986 B1 [23]. It involves tannin polymerization by the addition of formaldehyde (37%), ammonium chloride and commercial hydrochloric acid. The product so obtained under certain temperature conditions has a viscous appearance with 36% of active material.

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Several references have been found regarding these kinds of chemical processes [24–26]. Most of them are patents, including the specific process for *Tanfloc*, which is reported [23]. 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.

Similar products have been studied as general flocculants previously [21]. *Tanfloc* has been tested as flocculant in wastewater [27,28] and its results are promising.

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 remediation processes such as surfactants removal. This investigation focus its interest in advancing in surfactant removal by means of a new process that is (a) cheaper than others such as electrocoagulation; (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. Taking care of environmental subjects may include these and other considerations that make the possibility of becoming clean a universal chance.

SDBS long molecule (Fig. 1) presents a benzene ring and a large linear chain on one side; and a sulfonate negative-charged group on the other side. This charged group and the large organic chain make SDBS a rather-expected molecule to be removed by a cationic coagulant agent, such as *Tanfloc*. pH and initial surfactant concentration (ISC) are presumed to be very important variables that might affect surfactant removal percentage in a severe way. To point out the relative influence of these variables and their interaction and to optimize the surfactant removal process by a design of experiments is the aim of this investigation.

2. Materials and methods

2.1. Sodium dodecyl benzene sulfonate

Surfactant was provided by FLUKA (CAS number 25155-30-0). 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.

2.2. Buffered solution

All assays were done in a pH-stable medium. A pH 7-buffered solution was prepared by mixing 1.2 g of NaH_2PO_4 and 0.885 g of Na_2HPO_4 in 1-L flask. Assays with different pH were carried out by adjusting this buffered solution to the specific pH by using HCl 0.5 M and NaOH 0.5 M. All reagents were supplied by PANREAC in analytical purity grade.

2.3. General surfactant removal assay

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 soft blade-stirring agitation was applied for 2 h, until equilibrium was achieved. Kinetic studies of our specific research (Fig. 2) and previous studies carried out [29] reported this period was enough for guarantee equilibrium. Then, a sample was collected and it was centrifuged. Surfactant removal was determined by visible spectrophotometry.

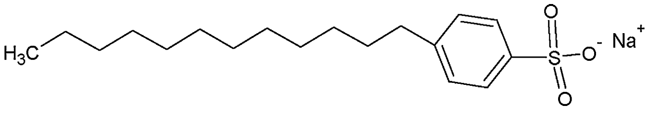

Fig. 1. Structure of sodium dodecyl benzene sulfonate molecule.

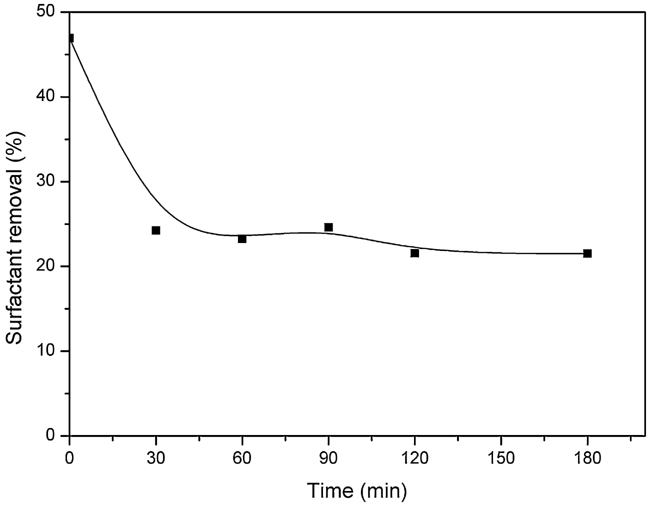

Fig. 2. Kinetic evolution on surfactant removal.

2.4. Surfactant analysis

In order to analyse surfactant concentration, a method based on methylene blue–anionic surfactant association was used [30]. 5 mL of clarified sample was put into a separation funnel. 25 mL of trichloromethane (PANREAC) and 25 mL of methylene blue solution (PANREAC) were added and funnel was shaken vigorously. Organic fraction was taken out and put into another separation funnel, in which 50 mL of cleaning solution was added. Funnel was shaken again, and the resultant organic fraction was put into a 25-mL flask. It was filled up to the mark with trichloromethane and methylene blue concentration was determined by visible spectrophotometry at 652 nm, with zero made with pure trichloromethane by using a HEλIOS spectrophotometer.

2.5. Mathematical and statistical procedures

Section 3.2 was statistically analyzed by using *StatGraphics Plus for Windows 5.1*. A factorial central composite orthogonal and rotatable design was used with 8 replicates of central point, so the total number of experiments was 16.

3. Results and discussion

3.1. Preliminary evaluation of Tanfloc dosage

Experimental series were made in order to determine flocculant dosage influence on surfactant removal. A fixed dose of 50 mg L^{-1} of surfactant was evaluated to be removed with different doses of *Tanfloc*. As it can be appreciated in Fig. 3, final surfactant concentration tends to decrease as *Tanfloc* dose increases. However, it is observed that process effectiveness arrives to a maximum, and higher doses of extract does not achieve lower surfactant concentrations. There is a residual surfactant concentration that is not possible to remove through this flocculation process and seems to be about 10 mg L^{-1}. This can be due to the existence of an 'equilibrium surfactant concentration' which is highly difficult to remove, as it has been reported previously [31].

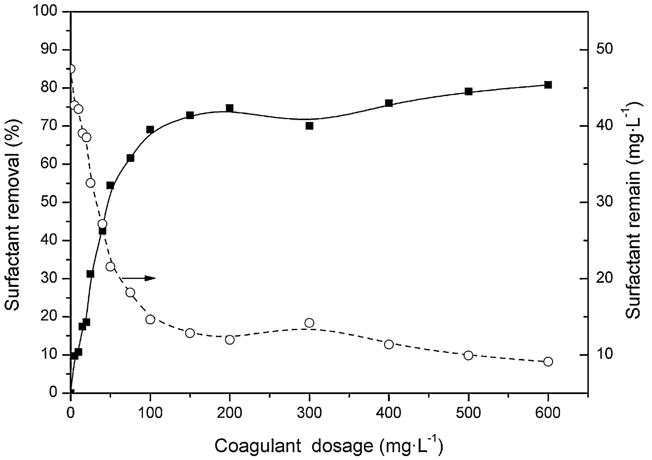

Fig. 3. Preliminary surfactant removal by *Tanfloc*.

3.2. Design of experiments

The traditional experimental method, one factor at a time approach, can hardly be used to establish relationships among all the experimental input factors and the output responses. Even though 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 the minimum number of experiments [32].

The design of experiments is a common methodology in order to improve industrial and economical production processes [33]. By means of this mathematical procedure a lower number of experiments is needed and the results that are obtained from the investigation have the consistency of a statistical process. In fact, it has been used thoroughly in many related research, such as those reported by Bhatia et al. [34] or Sabio et al. [35].

Using design of experiments based on response surface methodology (RSM), the aggregate mix proportions can be arrived with the 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.

In order to determine if there exist a relationship between the factors and the response variables investigated, the data collected must be analyzed in a statistical manner using regression. In developing the regression equation, the test factors were coded according to Eq. (1):

$$\chi_i = \frac{X_i - X_i^x}{\Delta X_i} \tag{1}$$

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 (Eq. (2)):

$$Y = b_0 + \sum_{j=1}^{k} b_j \chi_j + \sum_{i,j=1}^{k} b_{ij} \chi_i \chi_j + \sum_{j=1}^{k} b_{jj} \chi_j^2 \tag{2}$$

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 classes 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

$$N = 2^k + 2 \cdot k + n \tag{3}$$

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

3.3. Determination of working region

One of the most important tasks in designing a plan of experiments inside a CCD is determining the variables that are going 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 to carry out a previous analysis of the effect of several variables in order to select two or more among them.

In the case of surfactant removal by *Tanfloc* three variables have been tested in a step-by-step procedure: pH, initial surfactant concentration (ISC) and temperature. Target parameter was *q* capacity, that is, the relationship between the amount of surfactant that is removed and the flocculant mass. Eq. (4) defined *q*:

$$q = \frac{(C_0 - C_l) \cdot V}{W} \tag{4}$$

where C_0 is initial surfactant concentration (mg L^{-1}), C_l is equilibrium surfactant concentration in bulk solution (mg L^{-1}), *V* is the volume of solution (L), and *W* is *Tanfloc* mass (mg).

The effect of temperature was evaluated and it was found not to be very interesting. Series of experiments were carried out with a ISC equal to 50 mg L^{-1} and *Tanfloc* dosage equal to 50 mg L^{-1} at 10, 20, 30 and 40 °C. A decrease in *q* values was reported (around 40%), so temperature was not selected to work on. This is in agreement with previous investigations and surfactant characterizations [36].

On the contrary, series of experiments involving ISC and pH were carried out. The initial conditions were equal to those adopted in the evaluation of temperature (50 mg L^{-1} of *Tanfloc* and surfactant). The study of pH was carried out with a fixed ISC equal to 50 mg L^{-1} and the series of ISC were carried out with a pH equal to 7. Both series were performed at 20 °C.

Fig. 4 represents the results of these experiments. As it can be appreciated, by increasing pH level the efficiency of *Tanfloc* decreases dramatically, while the increment of ISC leads to an improvement in flocculant effectiveness. This is the reason we have selected these two factors to work on. The specific study involves a range of 40–160 mg L^{-1} in initial surfactant concentration (ISC) and 4–10 in pH. Consequently, step is equal to 60 mg L^{-1} and 3 pH units; central value is equal to pH 7 and 100 mg L^{-1}. In Fig. 4 the filled box marks the study region.

Taking into account all the previous considerations, Table 1 shows the experiments we have carried out.

3.3.1. ANOVA report

In a first approach, we should refer the ANOVA analysis that shows us the significance of the different parameters. According to the RSM, five factors are considered. Four of them have a *p*-value below 0.05 (significativity limit), so they are statistically significative. As we are working on *q* and not on the surfactant removal, the fact that *q* capacity may be improved as ISC increases is not obvious. Non-linear polynomic regression is carried out taking into account

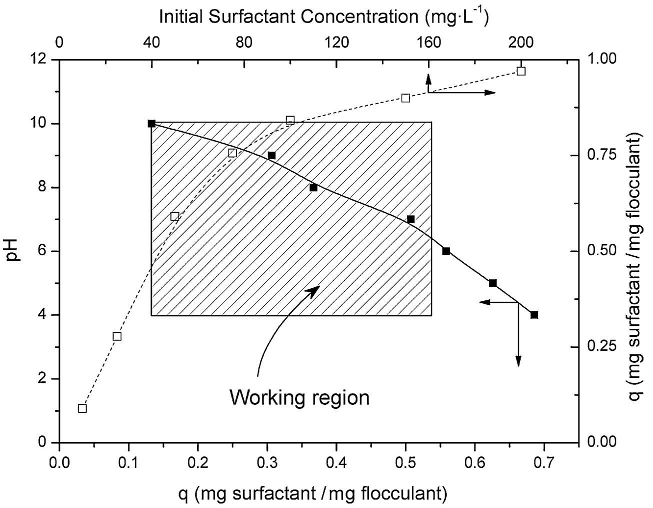

Fig. 4. Determination of the study region.

Eq. (2). In this sense, this regression is the following expression (Eq. (5)):

$$q = 0.89 - 0.20 \cdot P + 0.09 \cdot C + 0.08 \cdot P \cdot C - 0.14 \cdot P^2 - 0.30 \cdot C^2 \quad (5)$$

where the values of C (initial surfactant dosage) and P (pH) should be coded according to Eq. (1). q values are given in mg of removed surfactant per mg of flocculant. The adjusted correlation factor r^2 is equal to 0.91. This regression leads to an optimum q (0.96 mg mg^{-1}) at pH equal to 4.9 and a initial surfactant concentration of 103.2 mg L^{-1}.

ANOVA test also gives us the value of Durbin–Watson statistic, which has a value equal to 2.54, with a p-value of 0.12. As this p-value is higher than 0.05, there are no evidence of correlation in the residuals series. This means the random order of experiments has been effective in order to avoid any systematic error. Fig. 5 is the graphical representation of this aspect. For each experiment, the difference between experimental q and calculated q (according to Eq. (5)) is represented versus the specific run number. As no correlation can be appreciated (residuals are located in a random order to both the sides of the 0 axis), the randomization of the design is fully working and no accumulation of experimental error is observed.

3.3.2. Significant graphics

Modelization is made on the basis of five factors which correspond to Eq. (5). A graphical expression of the ANOVA test results may be the Pareto graphic (Fig. 6). Bars represent the standardized effects of each involved factor, considering them as the pH, the ISC and combinations of both. Nonfilled bars are a graphical representation of negative-affecting factors, such as pH and the squared ISC and pH. That means that these factors appear in the expression (5) behind a negative sign. On the other hand, filled bars represent positive-affecting factors, such as ISC and the combination of ISC–pH. 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.

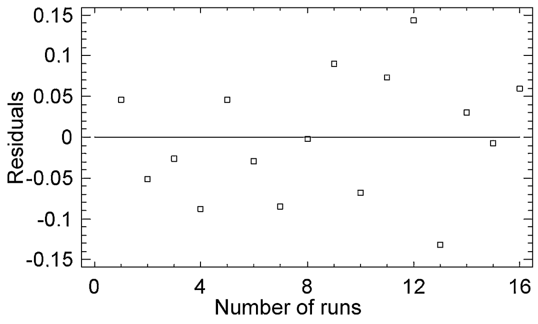

Fig. 5. Residual correlation: $q_{\text{experimental}} - q_{\text{calculated}}$.

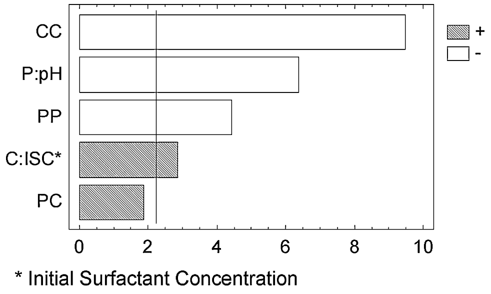

Fig. 6. *Pareto* graphic: standardized effects.

Pareto graphic also gives us an idea of how factors influence on the final response q. Positive bars indicate that by varying the variable q increases. Negative bars indicate the contrary. As it can be shown, as pH level raises q decreases and as ISC raises q increases. This is reported in other similar investigations [37,38].

Table 1
Experimental planning in DOE.

Random run	Real pH	Real ISC [a] (mg L^{-1})	Coded pH	Coded ISC	Surfactant removal (%)	q (mg · (mg of flocculant)$^{-1}$)
1	7	100	0	0	46.9	0.94
2	7	100	0	0	42.1	0.84
3	7	100	0	0	43.3	0.87
4	4	40	−1	−1	69.4	0.55
5	7	100	0	0	46.9	0.93
6	7	100	0	0	43.2	0.86
7	11.24	100	1.41	0	11.6	0.23
8	7	15.14	0	−1.41	49.6	0.15
9	7	100	0	0	49.2	0.98
10	7	100	0	0	41.3	0.82
11	10	40	1	−1	17.1	0.13
12	2.75	100	−1.41	0	52.1	1.04
13	4	160	−1	1	16.5	0.53
14	10	160	1	1	13.9	0.44
15	7	100	0	0	44.3	0.88
16	7	184.85	0	1.41	12.8	0.47

[a] Initial surfactant concentration.

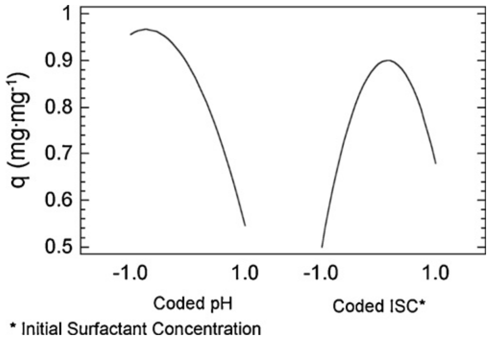

Fig. 7. Main effects of ISC and pH.

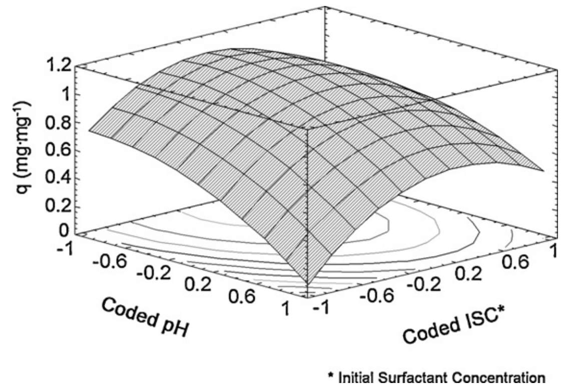

Fig. 9. Response surface of the CCD model.

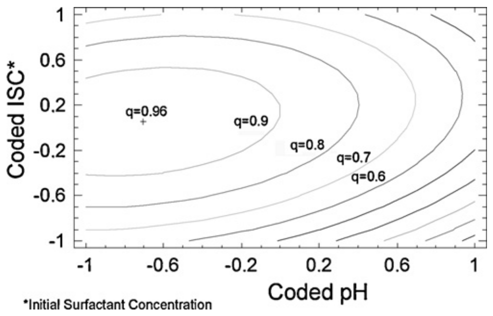

Fig. 10. Contour plot of the response surface. Optimum marked by a cross. q in mg mg^{-1}.

3.3.3. *Main effects*

The evaluation of the CCD model leads also to the study of the main effects of the involved variables. This can be appreciated in Fig. 7. Two curves are drawn representing the effect of varying each variable while the other one keeps constant. As it is reported, pH and ISC present similar effects, in the sense that their variation imply similar modifications on q. The dependency of it is linked to both variables, and each one present a maximum: in the first part of the curve in the case of pH and in the middle in the case of ISC. This will be clearly appreciated in the response surface and in the optimum point.

3.3.4. *Interaction between variables*

The fact that interaction appears between the two studied variables is evident in the Fig. 8. The two curves represent the evolution of q by varying pH in the extremes of the CCD model, that is, with ISC equal to 1 (upper value) and equal to −1 (low value). As the curves do not present a parallel behaviour, it may be assumed that there is interaction and the modification of one of the variables affects to the other one.

3.3.5. *Response surface and contour plot*

The most important graphical representation in the RSM is the surface graphic (Fig. 9). It plots Eq. (5) and allows to evaluate from a qualitative point of view how is the behaviour of the whole studied system. As it can be appreciated, the response is a quite convex surface inside the studied region. Both variables have similar affection on the target variable q and an optimum is presented: that is, a maximum.

The contour plot, which is drawn in Fig. 10, is almost more clear in order to identify the maximum point. It appears in the negative part of the coded pH values and around the center of the ISC. Quantitatively, a statistical analysis of the model yields to an optimum in the point −0.7 for pH and 0.05 for ISC, which is equivalent to pH 4.9 and 103.2 mg L^{-1}. As both factors are inside the significant region of the model (that is, both are statistically significative as their p-values are under 0.05), this optimum may be considered as statistically different from other near points. Maximum value of q is equal to 0.96 mg of removed surfactant per mg of *Tanfloc*.

Table 2 reports the q values that are obtained in other investigations. As it can be appreciated, q reached in the current research is near to the most interesting values, those that correspond to polymeric resins and ion-exchange resins. Apart from other advantages, such as the contact time, which is much lower in the case of tannin-based coagulants, optimum q is higher than those obtained with other natural raw materials. Coal, activated carbon, alumina, montmorillonite, sepiolite and some kinds of polymeric resins and ion-exchange resins are less efficient than the coagulation/flocculation process we are focused on.

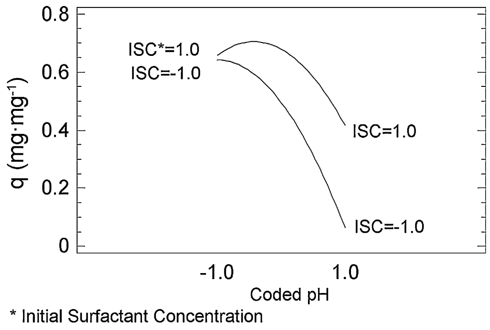

Fig. 8. Interaction graphic for ISC and pH.

Table 2
Comparison between optimum q and other literature values.

Adsorbent	q capacity (mg · (mg of flocculant)$^{-1}$)	Reference
Coal	0.03	[39]
Activated carbon	0.15–0.53	[8]
Activated carbon	0.40	[31]
Activated carbon	0.17–0.61	[40]
Alumina	0.06	[41]
Montmorillonite	0.06	[42]
Sepiolite	0.02	[43]
Polymeric resins, ion-exchange resins	0.87	[44]
Polymeric resins, ion-exchange resins	4.18–5.23	[45]
Polymeric resins, ion-exchange resins	0.42–0.66	[46]
Ion-exchange resins	0.42–1.21	[8]

4. Conclusions

This investigation has revealed the following conclusions:

- *Tanfloc* has been tested as an anionic surfactant coagulant that may be used in the removal of these dangerous pollutants. It presents a high efficiency as high values of q capacity are obtained with little doses of *Tanfloc*.
- Although *Tanfloc* presents a more than acceptable coagulant activity in a wide operating region regarding pH and ISC, increasing pH level leads to low q values while increasing ISC leads to a higher efficiency in surfactant removal.
- An orthogonal, rotatable factorial central composite design of experiments was carried out. It showed that the importance of the ISC is similar to pH. An optimum q was found in pH 4.9 and 103.2 mg L^{-1}.

Acknowledgments

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