



Removal of sodium lauryl sulphate by coagulation/flocculation with *Moringa oleifera* seed extract

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ABSTRACT

Among other natural flocculant/coagulant agents, *Moringa oleifera* seed extract ability to remove an anionic surfactant has been evaluated and it has been found to be very interesting. Sodium lauryl sulphate was removed from aqueous solutions up to 80% through coagulation/flocculation process. pH and temperature were found to be not very important factors in removal efficiency. Freundlich (F), Frumkin–Fowler–Guggenheim (FFG) and Gu–Zhu (GZ) models were used to adjust experimental data in a solid–liquid adsorption hypothesis. Last one resulted to be the most accurate one. Several data fit parameters were determined, as Freundlich order, which was found to be 1.66, Flory–Huggins interaction parameter from FFG model, which was found to be 4.87; and limiting *Moringa* surfactant adsorption capacity from GZ model, which was found to be 2.13×10^{-3} mol/g.

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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, 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. Attending to last statistical data, more than 15 million tonnes per year [2] are used, so surfactants can be considered as a first important chemical group.

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

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 [4], chemical association [5] or electrochemical removal [6]. However, new removal methods should be researched on because surfactants and tensioactives impact is high enough.

In this sense, we have been researching on *Moringa oleifera* as a water treatment agent for several years. As a tropical multipurpose tree, *M. oleifera* is very interesting from the point of view of developing cooperation, as it is a wide-spread, easy-available water treatment method. The use of *M. oleifera* as water treatment can imply two different ways: (a) one concerning its usage as a primary source of activated carbon [7,8] and (b) another one through seed extraction, whose product works as a coagulant/flocculant agent [9–11]. Last method is rather more effective and accurate, and it replies better to its application in developing countries. Its power lays on the fact that it is not technologically difficult to operate by non-qualified personal, it is easy to work with and it presents not a external dependency of reagents, as it would happen with other products ($\text{Al}_2(\text{SO}_4)_3$, FeCl_3 , etc.). Because of those reasons, it has been recommended by the Food and Agricultural Organization (FAO) as a proper and advisable way for treating water [12].

But *M. oleifera* presents not only this kind of advantages that make it interesting just for developing countries: as a natural coagulant, it has not several disadvantages that arise with traditional coagulant and flocculant agents (that have not a natural origin), as many health implications [13]. This is the reason it is important to keep on researching on *Moringa*'s properties.

M. oleifera is a natural coagulant agent among others like starch, modified tannins, mucilages or several vegetal extracts (for

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example *Caesalpinia spinosa*). There are rather interesting previous studies about coagulant capacity or turbidity removal ability of these products [14,15]. Because of that, and due to the fact that all of these substances fit well in the previous definition of sustainability and accuracy for developing countries, it is needed to research on other properties of starches and biological and organic natural matters.

After a preliminary screening on surfactant-removal ability of several natural agents, this paper aims to characterize another interesting capacity *Moringa oleifera* seems to present: that is surfactant removal. Due to its proteinic nature and flocculant activity it works very well removing surfactants from surface water.

2. Materials and methods

2.1. Natural coagulant products preparation

Apart from *M. oleifera*, seven kinds of natural coagulant products were tested in a preliminary screening. They were prepared in the following way:

Cationic starch was supplied by Cargill (USA). It is used as an authorized alimentary supplement. It is presented as powder.

Anionic starch solution was supplied by Alcochemical (USA). It is presented as a dense, viscous, sticky solution.

Opuntia ficus-indica mucilage was obtained as it was described previously [16,17]: pods of *Opuntia ficus-indica* were cut and external layer was removed manually. Internal fraction was milled in a domestic blender (Braun). 200 g of the resultant juice were put into a beaker and it was filled up to 1 L with distilled water. Then it was kept at 60 °C for 24 h. After this period, the mixture was filtered and concentrated by vacuum evaporation to one-third of the initial volume. Then, it was precipitated with ethanol twice, in order to achieve a clean impurities-free mucilage. The resultant mix of ethanol and mucilage was dried in a heater at 60 °C for 12 h. Final product presents a green, crystal aspect.

C. spinosa seeds, also known as *Tara*, were obtained from Cajamarca (Peru). Seeds were separated from pods manually. They were milled with a domestic blender (Braun) and 5 g of seed powder were mix with 100 mL of distilled water. After 30 min of stirring, the extract was filtered and liquid fraction was kept.

Modified tannin was supplied by Tanac, S.A. (Brazil). Its name is TANFLOC and consists of tannins from *Acacia mearnsii* that have been chemically modified in order to introduce a quaternary nitrogen that confers TANFLOC its cationic character. Other three products with the same nature were supplied by Silvateam, S.A. (Italy), in the case of SILVAFLOC, and Aquachimica Seta, S.A. (Brazil) in the case of AQUAPOL C1 and AQUAPOL S5T. Differences between SILVAFLOC, AQUAPOL C1 and S5T and TANFLOC lay on tannin nature (*A. mearnsii* for AQUAPOL and TANFLOC and *Quebracho* for SILVAFLOC) and on chemical modification, which is under copyright law. TANFLOC and AQUAPOL C1 are presented as powder, while SILVAFLOC and AQUAPOL S5T are presented as a dense solution.

Guar and Karaya gums were supplied by Sigma. They are presented as powder.

Aluminium sulphate $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ was supplied by Panreac.

2.2. *M. oleifera* seed extraction

Seeds were obtained from Setropa (Holland). The extraction process was carried out in the following way: seeds were reduced into powder by a domestic mill. A 1-M NaCl (Panreac) solution was prepared and 5 g of powder were put into 100 mL of it. The NaCl solution with powder was stirred for 30 min time at room temperature (around 25 °C). No pH modification was needed, as natural pH

7 was achieved. Then, the extract was filtered twice: once through commercial filter paper on Büchner funnel and once again through a fine filtering millipore system (0.45 µm glass fiber). The result is a clear, milk-like liquid.

2.3. General surfactant removal assay

A sodium lauryl sulphate ($\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$) (Aldrich) 500 ppm 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 distilled water. A vigorous magnetic agitation was applied for 6 h, until equilibrium was achieved. Several kinetic studies reported this period was enough for guarantee equilibrium (constant concentration of surfactant in bulk solution, results not showed in the present paper). Then, a sample was taken and it was centrifuged. Surfactant removal was determined by visible spectrophotometry.

2.4. Surfactant analysis

In order to analyse surfactant concentration, a method based on methylene blue-anionic surfactant association was used [18]. 5 mL of clarified sample were 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 were 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 625 nm, with zero made with pure trichloromethane by using a HELIOS spectrophotometer.

Reagents were prepared in the following way:

Cleaning solution: 43.5 g of NaH_2PO_4 (Aldrich) were taken and they were diluted into 500 mL of distilled water. 6.6 mL of H_2SO_4 (Panreac) 98%, w/w were added and dilution was raised up to 1 L.

Methylene blue solution: 30 mg of methylene blue (Aldrich) were added to 1 L of cleaning solution.

3. Results and discussion

3.1. Preliminary screening on surfactant removal

Several assays of surfactant removal were performed with different natural agents. Most of them were based on polysaccharides (starches, mucilage and gums) or proteins (vegetal extracts), and others were tannin-based flocculant agents (TANFLOC, SILVAFLOC and AQUAPOL). Some previous research papers have been found out referring polysaccharides and proteins capability to remove surfactants from aqueous solutions [19–21], so a preliminary screening was needed in order to search for an efficient and operative surfactant removal mechanism by a natural product.

Fig. 1 shows surfactant removal percentages that have been carried out by using different agents. Standard dosage of 100 ppm of flocculant agent and 30 ppm of surfactant was fixed. Experiments were carried out at pH 7 and 20 °C. As it can be seen, every product presents a slight removal activity. Polysaccharides as starches (anionic and cationic starches) and guar gum present a surfactant removal capacity of around 15%. Obviously, cationic starch works much better than the anionic one, as surfactant has anionic character.

Referring to tannin-based flocculant, it is observed that SILVAFLOC works rather well, it removes almost 50% of surfactant. Nevertheless, the efficiency of TANFLOC and both AQUAPOL products just arrives up to 5 or 10%.

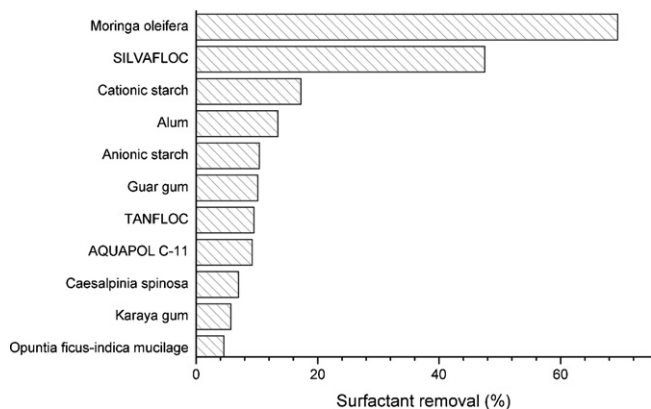


Fig. 1. Preliminary screening on surfactant removal with several natural products.

In spite of its proteinic nature, tara (*C. spinosa*) extract does not present a significant surfactant removal activity, although *M. oleifera* seed extract does. It is clearly appreciated that this last natural agent is highly efficient as a surfactant removal product, so this paper will focus on its activity.

Aluminium sulphate was used in order to compare results from natural and from synthetic coagulant agents. As it can be seen, alum presents certain surfactant removal activity (around 17%), but SILVAFLOC, cationic starch and above all *M. oleifera* are clearly more effective.

3.2. *M. oleifera* dosage

Experimental series was made in order to determine extract dosage influence on surfactant removal. A fixed dose of 25 ppm of surfactant was evaluated to be removed with different doses of *Moringa* extract: from 5 to 80 mL/L. These doses are equivalent to 15.7–251.8 mg/L in w/v (determined by the total solids content in extract, excluding NaCl content). As it can be appreciated in Fig. 2, final surfactant concentration tends to decrease as *Moringa* seed extract dose increases. However, it is observed that process efficiency arrives to a maximum, and higher doses of extract do not achieve lower surfactant concentrations. There is a residual surfactant concentration that is not possible to remove through *M. oleifera* seed extract and seems to be about 5 ppm. This can be due to the existence of an “equilibrium surfactant concentration” which

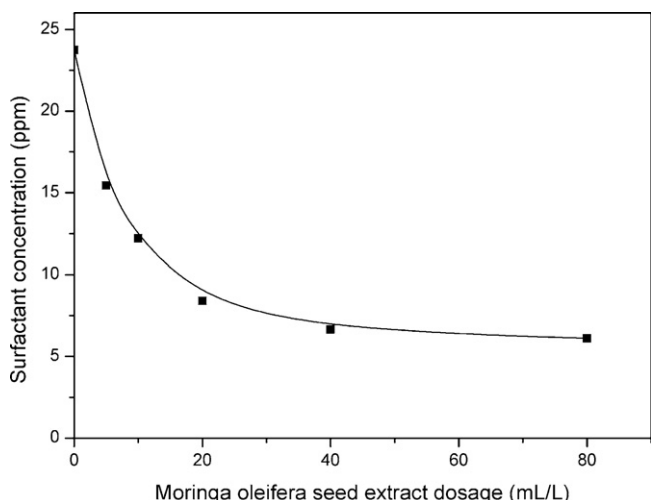


Fig. 2. Surfactant removal by *Moringa oleifera* seed extract.

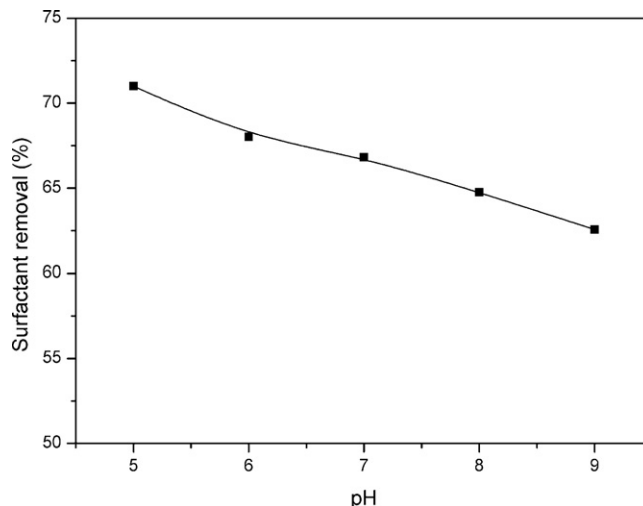


Fig. 3. pH influence on surfactant removal.

is highly difficult to remove, as it has been reported previously [22].

3.3. pH

pH values were varied between 5 and 9, in order to determine its influence on surfactant removal. Experimental data series is shown in Fig. 3. As it can be appreciated a fixed dose of 40 mL/L of *M. oleifera* seed extract with a surfactant dose of 25 ppm tends to be less effective as pH becomes higher. Surfactant anionic character should not be dramatically reduced by lowering pH, while proteinic nature of *M. oleifera* [23] makes this extract to be cationic, and its cationic form would be higher at acidic pH. Electrostatic attraction between *M. oleifera* cationic proteins and negative-charge surfactant active centers is reinforced. In addition, links to hydrophobic chains would be enhanced [22]. So both effects should explain this behaviour by modifying pH.

3.4. Temperature

In order to appreciate temperature influence on surfactant removal process, a series of experiments was carried out over a range of temperatures. Experiments at 10, 20, 30 and 40 °C were performed. The influence of temperature on the percentage of surfactant removal is minimum with removal efficiencies in the range of 67–69%. In a general way, temperature does not seem to be significantly important if it is fixed to room temperature or higher, as the only different data in surfactant removal appears at 10 °C, with a slightly lower surfactant removal. It is a common effect in coagulation/flocculation process [24].

3.5. Surfactant dosage

Initial surfactant dosage was varied between 1 and 130 ppm. In this range we are working below critical micellar concentration (CMC), which is determined to be 2364 ppm [25]. A fixed dosage of 40 mL/L of *M. oleifera* seed extract was applied in order to evaluate the effect of increasing initial surfactant dosage. Results can be seen in Fig. 4. There it is represented as removal efficiency (%) versus initial surfactant concentration (ppm). This percentage tends to be higher up to 100 ppm, then it begins to decrease. Although CMC has not arrived yet, it is obvious that *M. oleifera* presents limits on treatment ability. It is clearly referred below

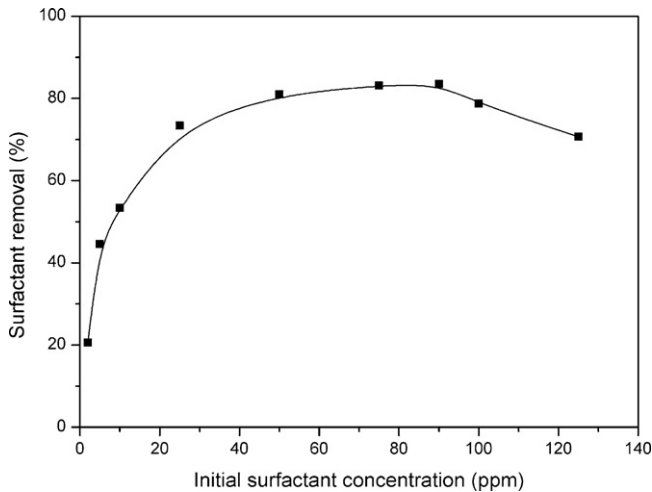


Fig. 4. Initial surfactant concentration influence on surfactant removal.

(see Section 3.6.3) and that is the main reason why from 100 to 130 ppm surfactant removal tends to be lower. In addition, it is known that increasing the total amount of surfactant (and particularly anionic one) may lead to a denaturation of proteins [26].

3.6. Theoretical adsorption modeling

Interaction between surfactants and natural polymers (polysaccharides, proteins, etc.) has been studied for many years because it is important to succeed in product formulations in many areas (pharmaceuticals, cosmetics, food processing, etc.). Although the basic mechanisms of surfactant–polymer interaction are reasonably well understood, researchers still disagree at molecular level. It is generally accepted that their interactions may occur between individual surfactant molecules and the polymer chain, or in the form of surfactant–polymer aggregate complexes (micellar or hemimicellar interactions).

The basic forces controlling surfactant–polymer interactions are van der Waals and dispersion forces, hydrophobic effects, dipolar and acid–base interactions and electrostatic interactions. The importance of each type will vary with the nature of the surfactant and the polymer.

By combining data series from Sections 3.2 and 3.5 it is possible to look for a theoretical model that should explain *Moringa*–surfactant interaction phenomena.

Firstly, adsorption capacity (q) has been determined, defined as

$$q = \frac{(C_0 - C_1)V}{W} \quad (1)$$

where C_0 is initial surfactant concentration (mol/L), C_1 is equilibrium surfactant concentration in bulk solution (mol/L), V is the volume of solution (L), and W is *Moringa* mass (g).

Fig. 5 shows adsorption capacity values versus equilibrium surfactant concentration for those experiments carried out varying the *M. oleifera* extract dosage and initial surfactant concentration, at same temperature (20 °C) and pH 7. As it is observed, a S-shaped curve is presented, with a slight increasing of q at low values of C_1 . q values raise up rather fast along the intermediate range of C_1 (between 2×10^{-5} and 6×10^{-5} mol/L), and they arrive to an asymptotic maximum from 6×10^{-5} mol/L and ahead, which corresponds to q_∞ as it is explained below. This kind of curve has been thoroughly studied by researchers [27].

When a polymer is added to a surfactant solution, it is often observed that processes such micellization appear to begin at surfactant concentration below the critical micellar concentration (CMC) of the surfactant in the absence of polymer. In many cases, a complex aggregate structure is formed in association with the polymer at lower concentration of surfactant. This concentration is known as critical aggregation (or association) concentration (CAC) and varies with the nature of the polymer. The difference between both concentrations may vary by a factor of 10–1000 in some cases.

For sodium lauryl sulphate, the critical micellar concentration in water is 8.3 mmol/L [25] and the critical aggregation concentration, determined from Fig. 5 is around 1.0×10^{-5} mol/L. So the ratio CMC/CAC takes an approximated value of 830 for the surfactant–protein system studied in the present work.

A simple model that has been used to describe the adsorption of surfactants is the regular behaviour model [28]. For dilute solutions, this model simplifies to the Frumkin–Fowler–Guggenheim (FFG) equation [29,30]

$$\frac{\theta_l}{1 - \theta_l} = C_1 k_{12} \exp(x_{12} \theta_l) \quad (2)$$

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

$$\theta_l = \frac{q}{q_\infty} \quad (3)$$

C_1 is the equilibrium surfactant concentration in bulk solution (mol/L), k_{12} is the adsorption constant, being a measure of the interaction between surfactant and polymer surface, and x_{12} is the Flory–Huggins parameter [31], defined as

$$x_{12} = \frac{N_A z}{RT} [(\varepsilon_{12} - 0.5(\varepsilon_{11} + \varepsilon_{22}))] \quad (4)$$

where N_A is the Avogadro's number, z is the number of the nearest neighbours to a central surfactant molecule, and ε_{11} , ε_{12} and ε_{22} are the pairwise interaction potential.

In this model k_{12} and x_{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 (GZ) [32] 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

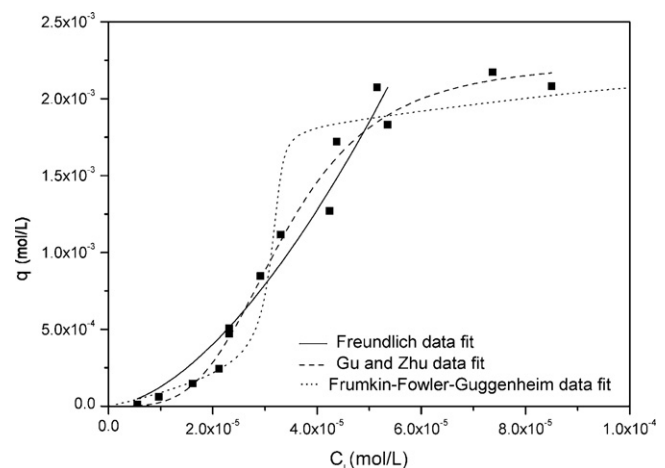


Fig. 5. Experimental data and models adjustment.

Table 1
Fitting models parameters

Parameter	Model	Symbol	Units	Expression	Reference
Equilibrium surfactant concentration in bulk solution	F, GZ, FFG	C_1	mol/L		
Initial surfactant concentration	F, GZ, FFG	C_0	mol/L		
Adsorbate amount	F, GZ, FFG	W	g		
Total volume	F, GZ, FFG	V	L		
Adsorption capacity	F, GZ, FFG	Q	mol/g	$\frac{(C_0 - C_1)V}{W}$	[36]
Freundlich adsorption order	F	n_f	None		[36]
Freundlich adsorption constant	F	k_f	$\frac{L^n}{g \text{ moles}^{n-1}}$		[36]
Limiting adsorption ratio	FFG	θ_l	None	$\theta_l = \frac{q}{q_\infty}$	[37]
Flory–Huggins interaction parameter	FFG	x_{12}	None		[34]
Adsorption constant	FFG	k_{12}	None		[34,37]
Limiting adsorbed surfactant	FFG, GZ	q_∞	mol/g		[27,34]
Gu and Zhu adsorption constant	GZ	k_g	None		[27]
Gu and Zhu adsorption order	GZ	n_g	None		[27]

the surface. This model leads to the following equation [5]:

$$\frac{\theta_l}{1 - \theta_l} = k_z C_1^{n_g} \tag{5}$$

where n_g is the number of monomers in the surfactant aggregate. Taking into account the definition of θ_l (5) becomes

$$q = q_\infty k_z \frac{C_1^{n_g}}{1 + k_z C_1^{n_g}} \tag{6}$$

This equation is reduced to the Langmuir equation for $n_g = 1$.

Eqs. (2) and (6) lead to three models that have been studied: Freundlich (F), Frumkin–Fowler–Guggenheim (FFG) and Gu and Zhu (GZ) models. Parameter values and statistics summary for the three models are shown in Table 2. Table 1 shows different parameters that have been used in these modelizations.

3.6.1. Freundlich model

In Eq. (6), if the term $k_z C_1^{n_g}$ is much lower than 1, the derived expression is known as the Freundlich equation

$$q = k_f C_1^{n_f} \tag{7}$$

where k_f is the Freundlich adsorption constant and its value is given by the following equation:

$$k_f = k_g q_\infty \tag{8}$$

As it is observed in Fig. 5, Freundlich model does not work well when the curve presents a final zone of saturation, as it occurs in the last two points of the curve. That is, this model just explains the first part of adsorption phenomena. Due to this reason, it is possible to fit almost every obtained data and to find a rather well-fit curve by excluding last points that correspond to adsorption saturation [33]. In order to prove the validity of Freundlich model, a plot of $\ln q$ versus $\ln C_1$ was carried out and showed in Fig. 6. Taking into account this consideration, linear data fit according to this scheme seems to be very accurate, giving a r^2 determination coefficient of 0.936.

Considering points below 6.0×10^{-5} mol/L, Freundlich equation fits rather well, conducting to a value of 2.6×10^4 ($L^{1.66} \text{ mol}^{-0.66} \text{ g}^{-1}$) for k_f and 1.66 for n_f ($r^2 = 0.956$).

3.6.2. Frumkin, Fowler and Guggenheim model

FFG model [29] is used when adsorption from dilute solution is being studied. With this condition, surfactant concentration usually appears far from critical micellar concentration (CMC) [34]. It is considered a simplification from a general model [28] in which several parameters are included. FFG equation is presented in Eq. (2).

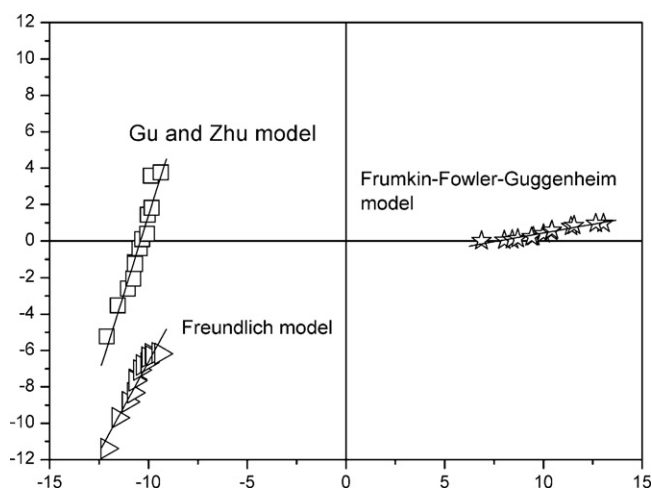


Fig. 6. Linearization of the three studied models (see Table 2 for axis components in each case).

By carrying out a non-linear fit, it is possible to determine values of x_{12} , k_{12} and q_∞ , this last parameter needed for θ_l calculation. This non-linear fit conducts to a x_{12} value of 4.87, k_{12} value of 2.63×10^3 L/mol and q_∞ value of 2.16×10^{-3} mol/g.

Taking the logarithms of both sides of Eq. (2) and then rearranging the terms yield:

$$\ln \frac{\theta_l/(1 - \theta_l)}{C_1} = \ln k_{12} + x_{12} \theta_l \tag{9}$$

Eq. (9) is a linear expression, so it is possible to correlate data from q and C_1 into a linear model. As it can be seen in Table 2, r^2 determination coefficient is high enough again, so it is possible to conclude this model fits well to present situation. It can be appreciated also in Fig. 6, where $\ln(\theta_l)/(1 - \theta_l)/C_1$ is represented versus θ_l . As it can be seen, a 0.940 r^2 determination coefficient is achieved.

3.6.3. Gu and Zhu model

Gu and Zhu [27,35] proposed a two-step adsorption model for various types of S-shaped adsorption non-Langmuir isotherms. First step implies adsorption of surfactant molecules as individual molecules or ions. Second step leads to an adsorption increasing as surface aggregates form through interaction of the hydrophobic chains of the surfactant molecules with each other.

The physical meaning of this theoretical model may be found in the fact that adsorption process appears accompanied of some

Table 2
Parameter values and statistical summary

Model	Expression	Parameters values	r^2	Linearization	Linear expression r^2
F	$q = k_f C_1^{n_f}$	$k_f = 2.6 \times 10^4$, $n_f = 1.66$	0.956	$\ln q = n_f \ln C_1 + \ln k_f$	0.936
FFG	$\frac{\theta}{1-\theta} = C_1 k_{12} \exp(x_{12} \theta_1)$	$k_{12} = 2.63 \times 10^3$, $q_\infty = 2.16 \times 10^{-3}$, $x_{12} = 4.87$	0.940	$\ln \frac{\theta_1/(1-\theta_1)}{C_1} = \ln k_{12} + x_{12} \theta_1$	0.940
GZ	$q = q_\infty k_g \frac{C_1^{n_g}}{1 + k_g C_1^{n_g}}$	$q_\infty = 2.13 \times 10^{-3}$ $k_g = 9.6 \times 10^{17}$, $n_g = 3.98$	0.979	$\ln \frac{q}{q_\infty - q} = n_g \ln C_1 + \ln k_g$	0.934

kind of flocculation process, as floc formation is observed in the experimental assay. This may be due to the hemimicellar formation hypothesis [1,34].

Mathematically, GZ model is expressed by Eq. (6). Fig. 6 shows non-linear experimental data fit and it is possible to observe a very good r^2 determination coefficient in Table 2 (0.979).

4. Conclusions

This investigation has revealed the following conclusions:

Among several natural products, *M. oleifera* derived extract has been found to be an anionic surfactant-removal agent in aqueous solutions. 80% of elimination was reached for sodium lauryl sulphate (one of the most common surfactants) in the most cases. For other surfactants this elimination could be different.

Inside the operational values of pH, temperature and flocculant dosage, it has been reported that:

- As pH increases, efficiency of the process decreases, due surely to the cationic character of the *Moringa* protein and to the fact that at acid pH hydrophobic links are enhanced.
- Temperature does not affect significantly to surfactant removal process.
- *M. oleifera* surfactant removal process presents a limit on its working, it is not possible to remove a residual surfactant concentration of about 5 ppm.
- Freundlich, Frumkin–Fowler–Guggenheim and Gu–Zhu adsorption models fit rather well to experimental data, so surfactant removal phenomena can be explained through adsorption hypothesis. Experimental series fits better to Gu–Zhu hypothesis, secondly to Freundlich's and last to Frumkin–Fowler–Guggenheim, according to r^2 determination parameter value. It is possible to prove the goodness of this fitting by showing linearized graphics.

Numerical values may differ in other operational conditions or working with different surfactant or flocculant products.

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