ORIGINAL ARTICLE

Performance and characterization of a new tannin-based coagulant

J. Beltrán-Heredia · J. Sánchez-Martín · C. Gómez-Muñoz

Abstract Diethanolamine and formaldehyde were employed to cationize tannins from black wattle. This novel coagulant called *CDF* was functionally characterized in removing sodium dodecylbenzene sulfonate (anionic surfactant) and Palatine Fast Black WAN (azoic dye). Refined tannin-derived commercial coagulants exhibited similar efficiency, while CDF presented higher coagulant ability than alum, a usual coagulant agent. Low doses of CDF (ca. 100 mg L^{-1}) were able to remove more than 70 % of surfactant and more than 85 % of dye (initial pollutant concentration of ca. 100 mg L^{-1}) and it presented no temperature affection and worked at a relatively wide pH range. Surfactant and dye removal responded to the classical coagulant-and-adsorption models, such as Frumkin–Fowler–Guggenheim or Gu and Zhu in the case of surfactant, and Langmuir and Freundlich in the case of dye.

Keywords Tannins · Coagulation · Natural coagulants · Dye removal

Introduction

Since the mid 1950s, the development of industrial areas has grown exponentially in the so-called First World and emerging countries. In this scenario, the need to implement new and cheaper water treatment technologies has arisen to keep the aquatic environment clean and safe from pollution concerns (García-Serna et al. 2007). This is an urgent task to take care of regarding especially two main pollution sources: dyes and surfactants.

On the one hand, it is well known that coloured water can destroy environmental equilibrium. The need for advising about the toxicity of such compounds is widely reported in scientific literature and seems not to decrease in the recent years (Beltrán-Heredia et al. 2011c). As it is generally accepted, many dyes are toxic and present even carcinogenic effects. Some of them are used in the pharmaceutical production, but the large exposure to them can cause several harmful effects. Effluents containing those persistent contaminants can be highly toxic and extremely injurious to both aquatic and terrestrial life forms (Cabaço et al. 2008). The difficulty of removing or degrading these kinds of wastewater effluents is well documented (Khataee et al. 2011). Palatine Fast Black WAN (structure showed in Fig. 1) is the dye selected in the current investigation. We have selected this dye as a model compound due to its implications presented elsewhere (Beltrán-Heredia et al. 2011c).

On the other hand, surfactants have arosen as a main pollutant group that has to be taken care of. According to previous literature, detergents and other tensioactives may modify environmental equilibrium by contaminating lakes and groundwater (Cserháti et al. 2002). Moreover, they usually present a synergistic binding effect on pharmaceuticals, and hence the impact of such chemicals and their toxicity for both humans and animals has considerably increased (Clara et al. 2007). There already exist several methods for removing surfactants from aqueous effluents. The main ones may involve chemical association (Rosu et al. 2007), electrochemical removal (Önder et al. 2007) or adsorption on activated carbon (Basar et al. 2004). However, there is still a challenge in developing new removal

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Fig. 1 Chemical structures of model compounds. **a** Palatine Fast Black WAN, anionic dye; **b** Sodium dodecylbenzene sulfonate, anionic surfactant
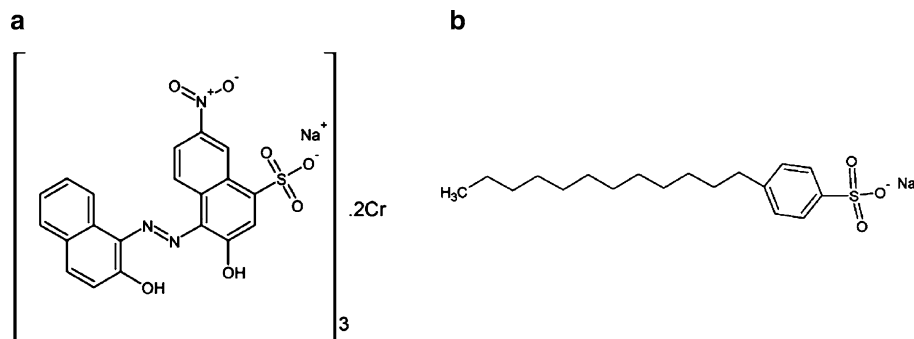
methods that may be even cheaper and easier to apply. Nowadays, the great impact of surfactants have claimed more research efforts. Particularly, anionic tensioactives enter into the aquatic ecosystems together with polluted waters because they are widely used in many industries, including petroleum, oil refining, petrochemical and gas industries. They are also used in pest control in aquaculture for combating pathogenic organisms for fish (Ostroumov 2006). We have selected *sodium dodecylbenzene sulfonate* (SDBS) whose structure is presented in Fig. 1.

Tannin-derived coagulants (Beltrán- Heredia et al. 2011a) represent a new and feasible source of treatment agents and because of that we have fully researched on them previously. The ability of these new products in several fields is more than evident: removing turbidity (Sánchez-Martín et al. 2009), surfactants (Beltrán- Heredia et al. 2009d) to heavy metals (Beltrán-Heredia and Sánchez-Martín 2008). Apart from ours, the large majority of the previous studies about these kinds of coagulants only considered commercially available products (Graham et al. 2008a, b). Our preliminary study already published (Beltrán-Heredia et al. 2010) opens the line of working directly with raw tannin extracts and proceeds with the cationization through formaldehyde at the laboratory scale. The optimum coagulant was obtained with *Acacia mearnsii* de Wild tannin extract (*Clarotan*), diethanolamine (DEA) and formaldehyde. The probable structure of this tannin-derived coagulant has been presented and it is supposed to follow a *Mannich* base reaction mechanism. We have also performed this cationization with other nitrogenous agents, such as glycidyltrimethylammonium chloride, with relevant results (Beltrán- Heredia et al. 2011c).

From these preliminary studies, the current paper will be focused on the characterization of the optimum coagulant obtained from *Clarotan*, a commercial extract from Black Wattle bark, and DEA in the removal of dye and surfactant. After a preliminary evaluation and comparison with other coagulants, the influence of variables such as temperature, pH or initial pollutant concentration is evaluated for both systems (*Palatine Fast Black WAN* and SDBS) and the experimental data are adjusted for the corresponding

theoretical models. These characterization data are mandatory prior to implementing the corresponding scale-up in real installation plants, since the behavior of the system has to be known if one wants to present these novel agents as a real depuration choice. After these preliminary studies, further research must be done, particularly those regarding the treatment of real wastewater samples and the implementation in a large-scale installation.

Materials and methods

Tannin-based coagulant synthesis

The reagents involved in the cationization process are :

1. Tannin extract from *Acacia mearnsii* de Wild. The commercial trademark was *Clarotan* and it was supplied by TANAC Inc. (Brazil).
2. *Diethanolamine* and *formaldehyde*. Both products were supplied by SIGMA in commercial purity grade.

The cationization process was conducted as referred elsewhere (Beltrán-Heredia et al. 2010). As much as 2.5 g of *Clarotan* was diluted in distilled water at room temperature and the sample was thermostated at 30 °C; 10.8 g of DEA was added to the mix and the cationization began when a peristaltic pump (MASTERFLEX, ColeParmer) added sequentially 1.5 g of formaldehyde. The coagulant was then aged for 24 h and put in a 50-mL flask that was filled up to the mark with distilled water.

This coagulant is the optimal category of a factorial design that involves the cationization with DEA, NH$_4$Cl and glycidyltrimethylammonium chloride. The three types of tannins are Weibull Black (*Acacia*), Clarotan (*Acacia*) and Quebracho (*Schinopsis balansae*). This study was performed in our previous work (Beltrán-Heredia et al. 2010).

Other coagulants

Apart from the optimum tannin-based coagulant, naturally obtained from *Clarotan Acacia mearnsii* de Wild tannin, five

kinds of natural or inorganic coagulant products were tested in a preliminary screening for dye or surfactant removal:

- **Guar gum** was presented as a powder by SIGMA (USA).
- **Cationic starch** was supplied by CARGILL (USA). It is used as an authorized alimentary supplement. It was presented as a powder.
- **Other modified tannin**s commercially available were supplied by TANAC, S.A. (Brazil). *Tanfloc* also consists of tannins from *Acacia mearnsii* that have been modified chemically to introduce a quaternary nitrogen conferring *Tanfloc* its cationic character. A similar product called *Acquapol C1* is supplied by ACQUACHIMICA, S.A. (Brazil). Lastly, another coagulant with the same nature was supplied by SILVATEAM, S.A. (Italy) named *Silvafloc*. Differences between *Tanfloc*, *Acquapol C1* and *Silvafloc* lay in the nature of tannin: while *Acacia mearnsii* was used for the two first ones, *Quebracho* was the tannin source for *Silvafloc*. The chemical modification, which is under patent law, may be taken into account. *Silvafloc* may be produced involving monoethanolamine, while the others are from ammonium chloride nitrogenation. All of them presumably underwent an ulterior chemical purification to enhance their efficiency. *Tanfloc* and *Acquapol C1* are presented as powder, while *Silvafloc* is presented as a dense, sticky solution.
- ***Moringa oleifera*** seed extract was produced as described elsewhere (Beltrán-Heredia and Sánchez-Martín [2008]). Dry seeds were obtained from SETRO-PA (The Netherlands). Shelled seeds were reduced into powder by a domestic mill (Braun). A 1 M NaCl (PANREAC) solution was prepared and 5 g of *Moringa* seed powder was put into 100 mL of it (stock solution was so considered 5 % w/w). The NaCl solution with powder was vigorously stirred at pH 7 and room temperature for 30 min with magnetic agitation. 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 white, milky-like liquid. *Moringa* stock solution prepared in this way was used the same day it was produced, although there have been references that point out to the stability of the extract (Katayon et al. [2006]).
- **Aluminium sulphate** $Al_2(SO_4)_3 \cdot 18H_2O$ was supplied by PANREAC.

Buffered solution

The trials were performed with pH-stable media. To this end, a pH 7 buffer solution was prepared of 1.2 g of NaH$_2$PO$_4$ and 0.88 g of Na$_2$HPO$_4$ in 1 L of distilled water. The pH was then adjusted to 7 with HCl 1 M or NaOH 1M. All reagents were of analytical grade from PANREAC.

Model compounds

Palatine Fast Black WAN, an azoic dye ($C_{60}H_{36}N_9Na_3O_{21}S_3Cr_2$) with molecular weight equal to 1,488 g mol^{-1}, was selected as a model compound. It was provided by Aldrich. Sodium dodecyl benzene sulfonate ($C_{18}H_{29}SO_3Na$) has a molecular weight equal to 348.48 g mol^{-1} and it was supplied in analytical grade as powder by Fluka.

The chemical structures of both compounds are shown in Fig. [1].

General contaminant removal trials

A 100 mg L^{-1} of pollutant solution was prepared. Different volumes of this initial solution were put into 100-mL flask, and a certain amount of coagulant was added. The final volume was reached with buffered solution. 30 rpm blade-stirring was applied for 1 h until equilibrium was achieved. Then, a sample was taken and centrifuged. Although some authors have pointed out to the need of rapid mixing stage in treating surface river water (Rossini et al. [1999]), our previous own works evidenced that the coagulant test reached equilibrium without this stage (Beltrán-Heredia et al. [2009b]) because these trials dealt with the destabilization of microcolloids that were almost dissolved in the aqueous matrix.

Photometric analysis was carried out in a 1-cm glass cell for dye determination. The maximum absorbance wavelength was 565 nm and a linear relationship of absorbance versus dye concentration was checked at this wavelength in the concentration range of this experimental work. An HEλIOS UV/VIS spectrophotometer was used for photometric measures. In the case of the surfactant, a similar procedure was followed. Surfactant removal was determined by visible spectrophotometry according to previous literature (Tôei and Fujii [1977]). Kinetic studies of our specific research such as those presented in Fig. [2] confirmed that this period was enough for reaching equilibrium. These data agreed with other previous studies (Beltrán-Heredia et al. [2009b]; Chen et al. [2007]).

Results and discussion

Preliminary screening

Several trials of contaminant removal were performed with different natural and inorganic coagulant agents. These

Fig. 2 Kinetics of pollutant removal. **a** Removal of SDBS. **b** Removal of Palatine Fast Black WAN. Dye initial concentration: 100 mg L^{-1}; surfactant initial concentration: 50 mg L^{-1}; coagulant dose: 100 mg L^{-1}
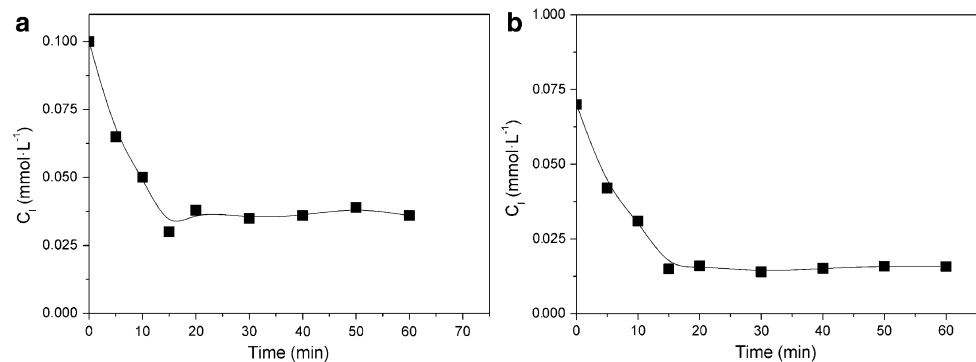
should confirm the feasibility of the new coagulant in removing azoic dye and anionic surfactant. Starch and guar gum were based on vegetal polysaccharides and *Moringa oleifera* seed extract, which are well-known coagulant agents for the two model compounds with a proteinaceous nature (Gassenschmidt et al. 1995). Some previous studies have referred to the capability of polysaccharides and proteins to remove either surfactants (Merta and Stenius 1999; Fijan et al. 2007; Blanco et al. 2007) or dyes (Sanghi et al. 2006, 2007), so a preliminary screening is needed to search for the real position of this coagulant inside the range of natural and commercial products.

The complete comparison test should include the determination of the optimal coagulant conditions for each product. This could be achieved through design of experiments or by constructing the corresponding equilibrium isotherm (see "Theoretical modelization" below). However, an initial approach can be made if one replicates similar conditions in each system: 100 mg L^{-1} of coagulant and 50 mg L^{-1} of surfactant or 100 mg L^{-1} in the case of dye. The experiments were carried out according to the general removal process described in "General contaminant removal trials". Figure 3 depicts the percentual removal of each contaminant depending on the particular coagulant that was applied. As can be seen, the best one is *Moringa oleifera* seed extract, which was able to remove almost 100 % of dye and near 95 % of the surfactant. This has to do with the proteinic nature of this coagulant and was observed previously (Beltrán-Heredia et al. 2009a), but some problems arose with this product, such as the build-up of organic matter (Ndabigengesere and Narasiah 1998), so other possible agents for this wastewater remediation should be searched for.

The main and most relevant aspect in Fig. 3 is CDF belongs to the intermediate group of coagulants that give an appropriate response to surfactant and dye removal. This group could be formed by the tannin-based coagulants: *Silvafloc*, *Tanfloc*, *Acquapol C1* and CDF itself. The efficiency of this coagulant is expected to be higher once the purification takes place; therefore, this product may be

considered an feasible coagulant compared with those derived from *Quebracho colorado* (*Schinopsis balansae*, *Silvafloc*) or those produced from NH$_4$Cl, such as *Tanfloc* and *Acquapol C1*. This product in the optimum category resulted from a design of experiments which revealed the most favourable synthesis process for these kinds of coagulants (Beltrán-Heredia et al. 2010).

Alum was included for knowing how competitive tannin-derived coagulants are. As can be appreciated, alum presented a reasonably high effectiveness in dye removal, but its ability with surfactant was actually low (around 35 %). This fact and the undesirable effect of aluminium intake [which is a health risk suspect (Flaten 2001) derived from its usage as primary coagulant and its environmental bioaccumulation] confirm that tannin-derived coagulants can be a real alternative to inorganic metal salts.

Finally, polysaccharide gums such as cationic starch or guar gum presented a slight Palatine Fast Black WAN dye and SDBS removal ability, but not high enough. Further studies should be performed to optimize the real coagulant action of these agents.

Influence of variables

Several operating variables were selected in order to characterize the functionality of this coagulant: the coagulant dosage, coagulating temperature, pH level and the initial pollutant concentration (so-called *charge*). Different experiments were carried out in each case to evaluate the behavior of the system when the studied variable was changed.

Coagulant dosage

To evaluate the efficiency of CDF in removing both types of pollutants, a fixed initial pollutant concentration underwent a progressive decrease when increasing doses of coagulant were applied. The surfactant seemed to present a residual concentration of ca. 0.03 mmol L^{-1} not

Fig. 3 Preliminary screening for dye and surfactant removal by coagulation with different natural and commercial coagulants

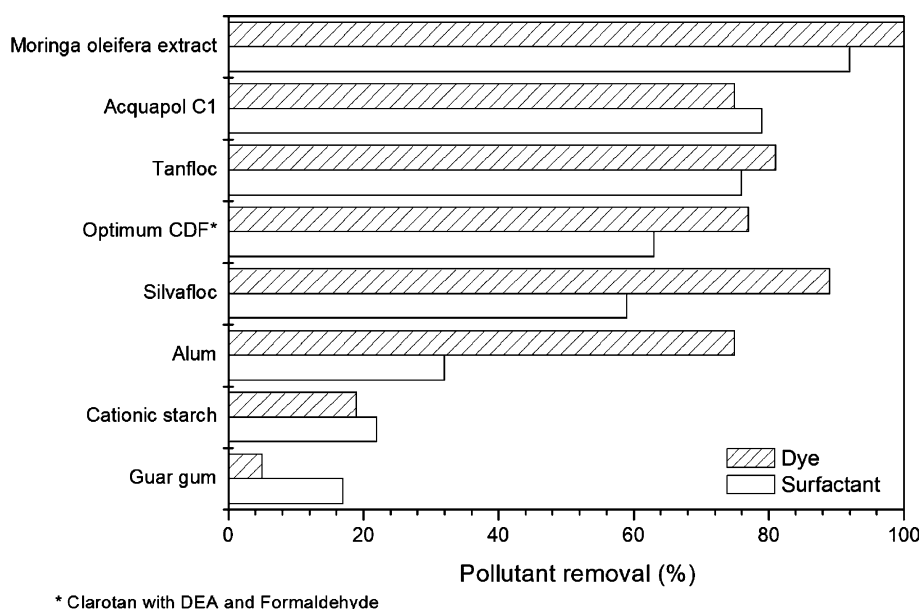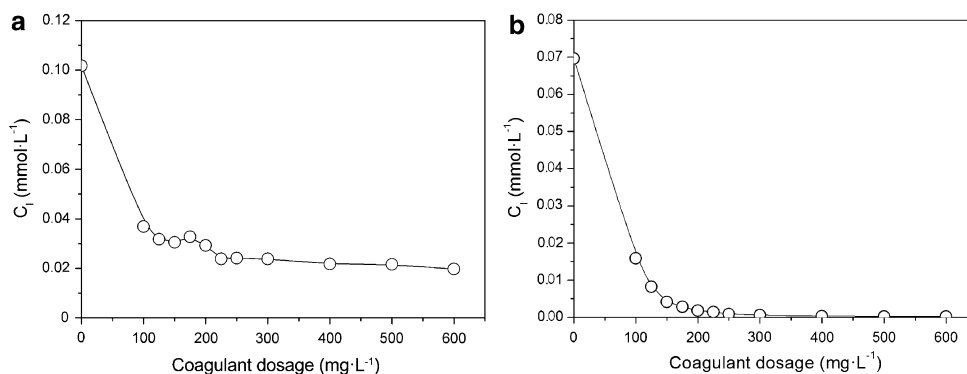* Clarotan with DEA and Formaldehyde

Fig. 4 Influence of the coagulant dosage. **a** Removal of SDBS; **b** removal of Palatine Fast Black WAN

removable by coagulation (Fig. 4b). In the case of dye, an initial concentration of ca. 0.07 mmol L^{-1} reached significantly low levels after the application of 100 mg L^{-1}, while almost a total removal was obtained beyond 200 mg L^{-1}. In any case, a high efficiency of the coagulant is easily reached with reasonably low CDF dosages and the response of the system is very similar to that observed by previous researchers (Ayranci and Duman 2007).

Temperature

Both systems (surfactant and dye) seem to present stability along the studied temperature range (10–40°C). An initial surfactant concentration of 0.1 mmol L^{-1} or dye concentration of 0.07 mmol L^{-1} was treated with a fixed coagulant dose of 100 mg L^{-1}, pH 7 and different temperatures. As can be observed in Fig. 5, no differences can be stated from these experimental series. In a general way, temperature does not seem to be significatively important. This stability adds 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 (Mohan et al. 2002).

pH

pH is known to play an important role in coagulation processes (Shi et al. 2007). Because of this fact, several trials with different pH values have been carried out, varying pH between 5 and 10 with fixed concentrations of pollutant (0.1 mmol L^{-1} of surfactant, 0.07 mmol L^{-1} of dye) and 100 mg L^{-1} of coagulant. As can be appreciated in Fig. 6, 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 dye and surfactant molecules is reinforced. In addition, links to hydrophobic chains would be enhanced (Ayranci and Duman 2007). This effect is more evident in the case of dye removal (Fig. 6a), while pH over 7 reduces the percentual removal of surfactant to 25 %.

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Fig. 5 Influence of coagulation temperature. **a** Removal of SDBS; **b** removal of Palatine Fast Black WAN
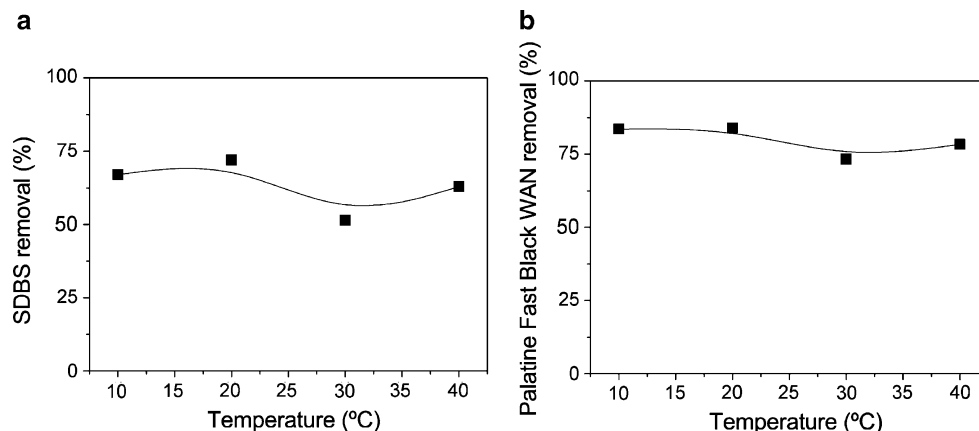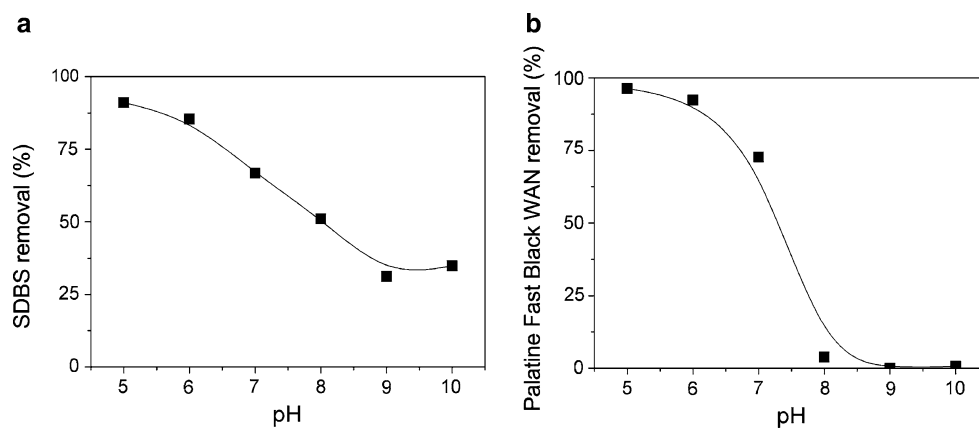

Fig. 6 Influence of pH level. **a** Removal of SDBS; **b** removal of Palatine Fast Black WAN

Initial pollutant concentration (charge)

If initial pollutant concentration (also called *charge*) is varied, the efficiency of the coagulation systems tends to differ from standard conditions. Two target variables should be taken into account in the evaluation of this last factor. Not only percentual removal but also q capacity (see below "Theoretical modelization") should be observed in this step. A fixed amount of coagulant (ca. 100 mg L^{-1}) was applied to different initial concentrations of surfactant and dye. As Fig. 7 depicts, increasing initial pollutant concentrations leads to a loss of percentual removal and the coagulant tends to be exhausted. However, q capacity, which is indicative of the efficiency of the product, tends to grow in both cases.

Theoretical modelization

Coagulation phenomenon can be modeled considering as an adsorption-like process. We have already pointed out the difficulties of modeling coagulation itself (Beltrán-Heredia et al. 2011c). We assumed the working hypothesis that the dye (and similarly with surfactant) may be destabilized in a two-step process: a coagulation following the

traditional coagulant formation, and then a growth process of the flocks by sorption mechanisms, as presented elsewhere by other researchers (Miller et al. 2008).This should be the controlling stage and the whole process can be modeled as adsorption.

Consequently, adsorption capacity (q) has been determined and defined as:

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

where C_0 is initial pollutant concentration (mmol L^{-1}), C_1 is equilibrium pollutant concentration in bulk solution (mmol L^{-1}), V is the volume of solution (L), and W is coagulant mass (g).

Dye removal model

Two main adsorption models have been considered in the present work regarding dye removal: Langmuir and Freundlich model. The first of them assumes that the molecules striking the surface have a given probability of adsorbing. Molecules already adsorbed similarly have a given probability of desorbing. At equilibrium, equal numbers of molecules desorb and adsorb at any time. The

Fig. 7 Influence of initial contaminant concentration (*charge*). **a** Removal of SDBS; **b** removal of Palatine Fast Black WAN
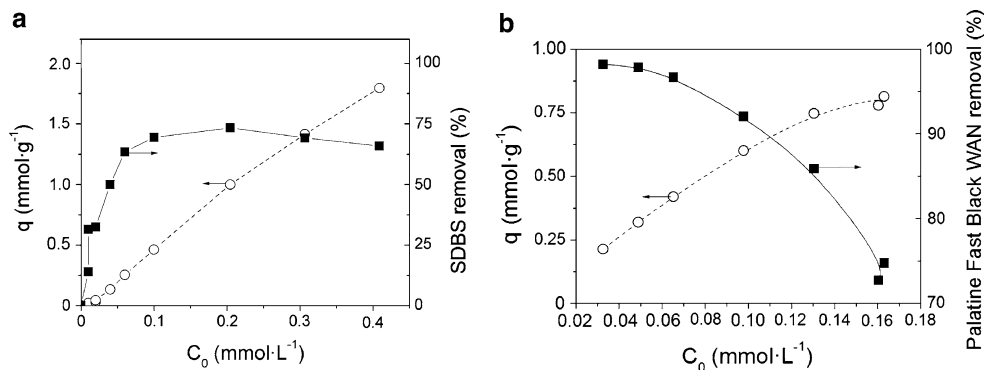
probabilities are related to the strength of the interaction between the adsorbent surface and the adsorbate (Langmuir 1916). That is the physical meaning of the Eq. 2:

$$q = k_{11} \frac{C_1}{1 + k_{12}C_1} \qquad (2)$$

where k_{11} is the first Langmuir adsorption constant (L [mg of coagulant]$^{-1}$) and k_{12} is the second Langmuir adsorption constant (L [mmol of removed dye]$^{-1}$) .

On the other hand, Freundlich model was derived from empirical data (Freundlich 1906) and assumes that q capacity is a power function of the equilibrium dye concentration (C_1).

$$q = k_f C_1^{n_f} \qquad (3)$$

where n_f is the Freundlich adsorption order (dimensionless) and k_f is the Freundlich adsorption constant ([L^{n_f}] [mg of coagulant] [mmol of removed dye$^{n_f - 1}$])

Surfactant removal model

Once the 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 (Wilkinson et al. 1997)). 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 (Sarkar and Bandyopadhyay 2011).

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 the 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) is reached. In addition, there also exists a lower concentration [called critical aggregation concentration, CAC (Rosen 2004)] that induces the formation of a complex aggregate structure. CAC usually appears below CMC, and the difference between both concentrations may vary by a factor of 10-1000 in some cases (Myers 2006). CAC can be established by identifying the exact point where the coagulation starts in the surfactant-polymer system, while CMC is clearly established when the models are not useful any more. The specific behavior of a particular system will vary with the nature of the surfactant and the polymer. For modeling 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 stated earlier. According to this, the following arguments are referred just to the first stage of the process, that is, up to CMC.

Apart from Freundlich model (Eq. 3), two theoretical models were considered in this work for surfactant removal.

A simple model that has been used to describe the adsorption of surfactants is the regular behavior model (Hildebrand et al. 1970). For dilute solutions, this model simplifies to the Frumkin–Fowler–Guggenheim (FFG) equation (Fowler and Guggenheim 1939; Frumkin 1925).
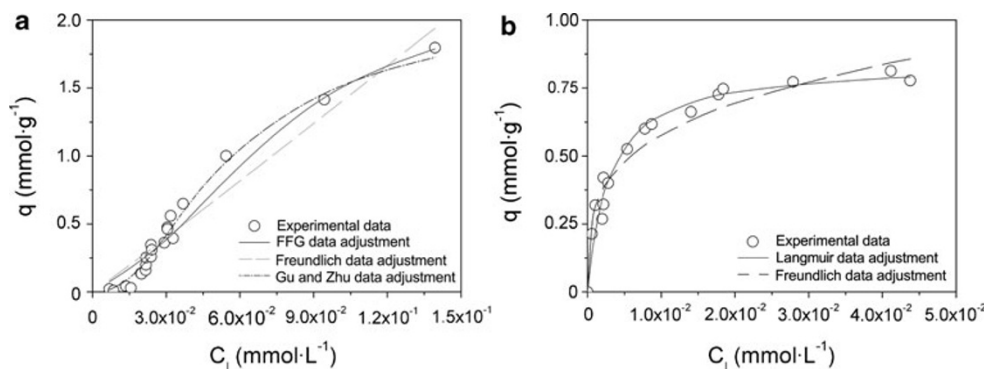
$$\frac{\theta_1}{1 - \theta_1} = C_1 k_{12} \exp(\chi_{12}\theta_1), \qquad (4)$$

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

$$\theta_1 = \frac{q}{q_\infty} \qquad (5)$$

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 (Flory 1953).

Fig. 8 Theoretical modelization of both systems. **a** SDBS-CDF; **b** Palatine-CDF

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 (1991) 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 Eq. 6:

$$\frac{\theta_1}{1 - \theta_1} = k_g C_1^{n_g}, \tag{6}$$

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_1, Eq. 6 becomes

$$q = q_\infty k_g \frac{C_1^{n_g}}{1 + k_g C_1^{n_g}}. \tag{7}$$

This equation is reduced to the Langmuir equation for $n_g = 1$. In addition, if the term $k_g C_1^{n_g}$ is much lower than 1, the derived expression is known as the Freundlich Eq. 3.

Eqs. 3, 4 and 7 lead to three models that have been studied: Freundlich (F), Frumkin–Fowler–Guggenheim (FFG) and Gu and Zhu (GZ) models.

By combining the data series of previous sections and other more especifically carried out studies, it is possible to look for theoretical models that fits rather well to experimental data. This is shown in Fig. 8, where the experimental and predicted values of each system are presented. Figure 8a presents the SDBS-CDF interaction system, and according to previous considerations three models were applied. As observed, an S-shape curve is presented, with a slight increase of q at low values of C_1. q values increase rather fast along the intermediate range of C_1 between 0.015 and 0.03 mmol L^{-1}. Then, they keep on increasing and presumably arrive at an asymptotic value, which corresponds to q_∞. This kind of curve has been thoroughly

Table 1 Theoretical model adjustment parameters for dye and surfactant removal

	Parameter values	r^2
Surfactant		
Freundlich	$k_f = 14.71$; $n_f = 1.03$	0.93
FFG	$k_{12} = 4.63$; $q_\infty = 2.22$; $\chi_{12} = 2.29$	0.97
Gu and Zhu	$k_g = 918.3$; $n_g = 2.31$; $q_\infty = 1.90$	0.98
Dye		
Freundlich	$n_f = 0.26$; $k_f = 1.97$	0.92
Langmuir	$k_{11} = 293.1$; $k_{12} = 348.1$	0.95

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studied by researchers (Somasundaran and Krishnakumar 1997).

Regarding Palatine Fast Black WAN-CDF interaction system, the experimental data fit reasonably well with the two proposed equations, with average r^2 above 0.92.

The specific parameter values and the statistic summary for both systems and for each corresponding model are shown in Table 1. These values are rather comparable to those obtained in previous works. For example, the elimination of Palatine Fast Black WAN by means of a commercially available tannin-based coagulant such as TANFLOC reached a maximum rate of 0.61 mmol L^{-1} (Beltrán-Heredia et al. 2011b), lower than that of the current work. Regarding the specific surfactant SDBS, our previous works (Sánchez-Martín et al. 2011) showed 1.46 mmol L^{-1} with another tannin-based coagulant (Weibull Black). These and other similar results (Beltrán-Heredia et al. 2009b, c) confirmed the feasibility of this coagulant in the context of natural products for wastewater treatment.

Conclusions

Tannin-derived optimum coagulant called CDF in the present investigation stands as a real alternative to traditional inorganic metal coagulants in the removal of dyes

and surfactants according to the high coagulant performances in both dye and surfactant contaminants. It presents the functional working advantages that may encourage further studies with regard to purifying and refining the active coagulant principal. Its ability to remove anionic dyes such as Palatine Fast Black WAN and surfactants such as sodium dodecylbenzene sulfonate was confirmed in a wide range of experimental conditions: temperature did not affect the coagulant process, while acidic pH enhanced the removal of pollutants. Theoretical models for coagulation systems (CDF-Palatine and CDF-SDBS) were adequately applied with significantly high r^2 levels. Further works must be carried out to examine the feasibility of this coagulant in large-scale installations.

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