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Removal of Alizarin Violet 3R (anthraquinonic dye) from aqueous solutions by natural coagulants

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ABSTRACT

In this paper the ability of two natural products in removing dyes has been tested. After a preliminary screening for dye removal capacity, a tannin-based coagulant called *ACQUAPOL C-1* and a vegetal protein extract derived from *Moringa oleifera* seed have been fully studied. The influence of several parameters such as pH, temperature or initial dye concentration (IDC) have been tested and the behavior of both coagulants has been compared. pH results to be an interesting variable and dye removal decreases as pH increases. This effect is higher in *ACQUAPOL C-1* than in *M. oleifera* seed extract. Temperature seems not to be so affecting parameter, while IDC appears to be a very important variable in q_c capacity, which is higher as IDC increases. Langmuir isotherm model fits very well in both cases of *ACQUAPOL C-1* and *M. oleifera* seed extract dye removal.

1. Introduction

Dyestuff is one of the largest industries all over the world, and its implications to economic and social conditions in many countries are quite important, mainly in India and China [1]. Depending on several factors as fiber class, color or industrial procedure, there is a quite large variety of dye substances that might be highly pollutant if dumped.

Over 50,000 tons of dye are discharged into environmental effluent annually, so they are risky hazardous substances because they damage aquatic and vegetal life [2]. For many years researchers have been working on several ways of removing dyes from wastewater and different procedures have been developed: adsorption onto materials such activated carbon [3,4], physical and chemical degradation [5,6] and a large number of other techniques: Fenton's oxidation, electrochemical degradation, ozonization, etc. [7,8].

Dyes may be classified into several different groups, according to their usage in dyestuff. Consequently, there are acidic, basic, disperse, direct dyes, etc. (family names that have to do with when and how dyes are used). Regarding, on the other hand, to their chemical structure, lots of compounds are included as dye. In the present work we have considered five kinds of dyes: azo-dyes (Chicago Sky Blue 6B, Acid Red 88 and Palatine Fast Black WAN), anthraquinonic (Alizarin Violet 3R), triphenylmethane (Eriochromecyanine), indigoid (Indigo carmine) and thiazinic (Methylene Blue). Apart from this last one, they are anionic dyes. A preliminary screening of *Moringa oleifera* and *ACQUAPOL C-1* ability in removing dyes were done on these five types of dye. Then, we have centered the investigation on Alizarin Violet 3R.

Alizarin Violet 3R is a synthetic dye which is characterized by a high chemical/biological oxygen demand, suspended solids in some cases and intense violet color [9]. These aspects make industrial effluents of this dye highly toxic and extremely injurious to both aquatic and land life forms. The difficulty to degrade or remove this dye has been thoroughly reported previously [10] and it is mainly caused by the five aromatic rings and the two sulfonated groups that make this dye a persistent and carcinogenic agent.

The remediation of several pollution problems is a target of many researchers nowadays. Technical ways of solving environmental concerns and menaces such as the dumping of surfactants, dyes, pharmaceuticals and other hazards are available long time ago, but making them cheaper and sustainable is still a challenge. A possible source of low-cost materials that could provide a successful solution are natural raw materials [11,12].

In this sense, we are researching on *M. oleifera* as a water treatment agent for several years. As a tropical multi-purpose tree, *M. oleifera* is very interesting from the point of view of developing cooperation, as it is a widespread, easy-available water treatment method. Using *M. oleifera* for water treating can imply two different ways: (a) One concerning its usage as a primary source of activated carbon [13,14] and (b) Another one through seed extraction, which

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product works as a coagulant/flocculant agent [15–17]. 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 maintain and it presents not an external dependency of reagents, as it would happen with other products ($Al_2(SO_4)_3$, $FeCl_3$, etc.). Because of that reason, it has been recommended by the Food and Agricultural Organization (FAO) as a proper and advisable way of treating water [18].

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 are presented in traditional coagulant and flocculant agents (that have not a natural origin), as many health implications. This is the reason it is important to keep on researching about *Moringa*'s properties.

On the other hand, we have worked on tannin-derived coagulants. 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 vegetal secondary metabolites [19]: bark, fruits, leaves, etc. 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.

ACQUAPOL is a trademark that belongs to ACQUACHIMICA (Brazil). It is a tannin-based product, which is modified by a physicochemical process, and has a high flocculant power. 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 [20–24]. Most of them are patents, including the specific process for an industrial product as *ACQUAPOL C-1* (*TANFLOC*), which is reported [25]. 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. *ACQUAPOL* is presented as powder (*ACQUAPOL C-1*) or liquid (*ACQUAPOL S5T*).

M. oleifera and *ACQUAPOL C-1* are natural coagulant agents among others. There are rather interesting previous studies about coagulant capacity or turbidity removal ability of natural-based products [26,27]. Concretely, previous studies have reported that *M. oleifera* has as a very significative ability in removing azo dyes [28], surfactants [29] or even heavy metals [30]. Tannin-derived coagulants have also been tested previously in polluted water treatment [31]. Because of that, and due to the fact that all of these substances fit well in the considerations about sustainability and accuracy for developing countries made before, it is needed to research on other properties of biological and organic natural raw materials.

First of all, we have tested different natural agents to remove Alizarin Violet 3R. We have tested *M. oleifera* and *ACQUAPOL* ability for dye removal with several kinds of dye. Then, we have studied the specific characterization of both coagulants by evaluating the influence of several parameters.

2. Materials and methods

2.1. 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.

2.2. Natural coagulant products preparation

Apart from *M. oleifera* and *ACQUAPOL C-1*, five kinds of natural coagulant products were tested in a preliminary screening. They were prepared in the following ways:

- *Cationic starch* was supplied by CARGILL (USA). It is used as an authorized alimentary supplement. It is presented as powder.
- *Other modified tannin* was supplied by TANAC, S.A. (Brazil). Its name is *TANFLOC* and consists also of tannins from *A. mearnsii* that have been modified chemically in order to introduce a quaternary nitrogen that confers *TANFLOC* its cationic character. Other product with the same nature were supplied by SILVATEAM, S.A. (Italy), in case of *SILVAFLOC*, and ACQUAQUIMICA SETA, S.A. (Brazil) in case of *ACQUAPOL S5T*. Differences between *SILVAFLOC*, *ACQUAPOL* C-1 and S5T and *TANFLOC* lay on tannin nature (*A. mearnsii* for *ACQUAPOL* and *TANFLOC* and *Quebracho* for *SILVAFLOC*) and on chemical modification, which is under patent law. *TANFLOC* and *ACQUAPOL C-1* are presented as powder, while *SILVAFLOC* and *ACQUAPOL S5T* are presented as a dense, sticky solution.
- *Chitosan* was supplied by FLUKA.
- *Aluminium sulphate* $Al_2(SO_4)_3 \cdot 18H_2O$ was supplied by PANREAC.

2.3. Moringa oleifera seed extraction

Dry seeds were obtained from SETROPA, Holland. The extraction process was carried out in the following ways: 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 were 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 time 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 clear, milky-like liquid.

Moringa stock solution prepared in this way was used the same day it was produced, although there are references that point the stability of the extract [32].

2.4. General dye removal assay

An Alizarin Violet 3R (SIGMA) 1000 mg L^{-1} solution was prepared by adding 0.295 g in 250 mL. Different volumes of this initial solution were put into 100 mL-flask, and certain quantities of coagulant were added. Final volume was reached with distilled water. 30 rpm stirring was applied for 1 h (NAHITA 686/1 motor stirrer), until equilibrium was achieved. Then, a sample was taken and it was centrifuged. Photometric analysis was carried out in a 1-cm glass cell. The maximum absorbance wavelength was 549 nm and a linear relationship of absorbance versus dye concentration was checked at this wavelength in the concentration range of this experimental work. An HEL λ IOS UV/VIS spectrophotometer was used for photometric measures.

2.5. Removal of other dyes

Stock solutions of 1000 mg L^{-1} for each six dyes were prepared (percentual dye content was considered). A screening of *M. oleifera* extract and *ACQUAPOL C-1* interaction with these products was done by carrying out different assays: 5 mL of *M. oleifera* seed extract or 100 mg L^{-1} of *ACQUAPOL C-1* and 10 mL of each dye solution into a 100 mL-flask, and then it was filled to the mark. Then, a similar treatment as described before (see Section 2.4) was carried out. Photometric analysis was developed at appropriate wavelength for each compound. These data are shown in Table 1.

Table 1
Dyes main characteristics

Product	Chemical formula	Molecular weight (g/mol)	Wave length analysis (nm)	Color index number	CAS number	Dye content	Supplier
Indigo Carmine	$C_{16}H_8N_2Na_2O_8S_4$	466.36	612	73015	482-89-3	90%	SIGMA
Chicago Sky Blue 6B	$C_{34}H_{24}N_6Na_4O_{16}S_4$	992.8	618	24410	2610-05-1	85%	SIGMA
Acid Red 88	$C_{20}H_{13}N_2NaO_4S$	400.4	505	15620	1658-56-6	75%	ALDRICH
Palatine Fast Black WAN	$C_{60}H_{36}N_9Na_3O_{21}S_3 \cdot Cr_2$	1488	565	15711	5610-64-0	90%	ALDRICH
Alizarin Violet 3R	$C_{28}H_{20}N_2Na_2O_8S_2$	622.6	549	61710	6408-63-5	90%	ALDRICH
Eriochromecyanine R	$C_{23}H_{15}Na_3O_9S$	536.4	437	43820	3564-18-9	90%	PANREAC
Methylene Blue	$C_{16}H_{18}ClN_3S \cdot 3H_2O$	373.9	665	52015	61-73-4	99%	PANREAC

3. Results and discussion

3.1. Preliminary screening of dye removal

Several assays of Alizarin Violet 3R removal were carried out with different natural agents, as well as with alum. Most of these were based on polysaccharides (starch or chitosan) or proteins (vegetal extracts such as *M. oleifera*) and others were tannin-based flocculant agents (*TANFLOC*, *SILVAFLOC* and both *ACQUAPOL*). Some previous research papers were found referring the ability of gums and vegetal proteins to remove dyes [33,34]. Dye removal by tannin-based coagulants is mentioned just in one previous work [28]. A preliminary screening was needed to search for an efficient and operative dye removal mechanism which would be comparable with alum coagulation efficiency [35].

The structure of Alizarin Violet 3R has five phenol rings, two ketone groups, two negative charged sulfonate groups and two amine links between the extreme phenol rings. The long and aromatic organic chain and the sulfonate groups make Alizarin Violet 3R a molecule which was expected to be removed by cationic coagulant agents, such as *M. oleifera* seed extract or tannin-based coagulants, as well as with synthetic and common coagulant products (polyaluminium chloride or sulphate).

Fig. 1 shows dye removal percentages that have been carried out by using different agents. A standard dosage of 100 mg L^{-1} of dye and 100 mg L^{-1} of coagulant agent was fixed and experiments were carried out at pH 7 at 20 °C. As Fig. 1 shows, every product exhibits a slight removal activity, with *ACQUAPOL* products and *M. oleifera* seed extract showing the highest dye removal efficiency and alum and cationic starch the lowest one. This result differs from the bibliographic data, especially those data referred to by Blackburn [36], but it is clear that the dosages are rather different (100 versus 10,000 mg L^{-1}). With regard to tannin-based flocculants, it is observed that *TANFLOC* and *SILVAFLOC* work rather well, removing more than 50% of dye concentration.

In spite of its polysaccharide nature, chitosan presents a significative low dye removal activity (ca. 10%). Further studies must be done with this product in order to improve this property.

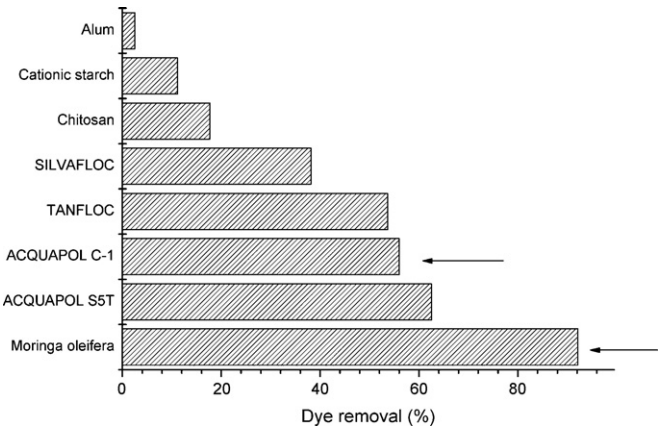

Fig. 1. Preliminary screening of Alizarin Violet 3R removal by several coagulant agents.

Clearly, *M. oleifera* and *ACQUAPOL* family products are the coagulant agents that present a high efficiency as dye removal products, therefore this study is focused on their activity. Aluminium sulphate was used to compare results from nature and synthetic coagulant agents. Without pH adjustment and with the mentioned dosage alum does not present a significant dye removal ability. Other drawbacks and risks linked to aluminium usage as a primary coagulant agent (environmental bioaccumulation, implications with Alzheimer's disease [37]) make this product not recommended for this scope.

3.2. Removal of other dyes

In order to test the ability of both selected coagulant agents to remove other dyes, several assays were performed on other six dyes with different natures, structures and usages. The results of these experiments are shown in Fig. 2. Bearing in mind their chemical structures (supplementary data), some aspects of dye removal as a result of the coagulation process can be discussed.

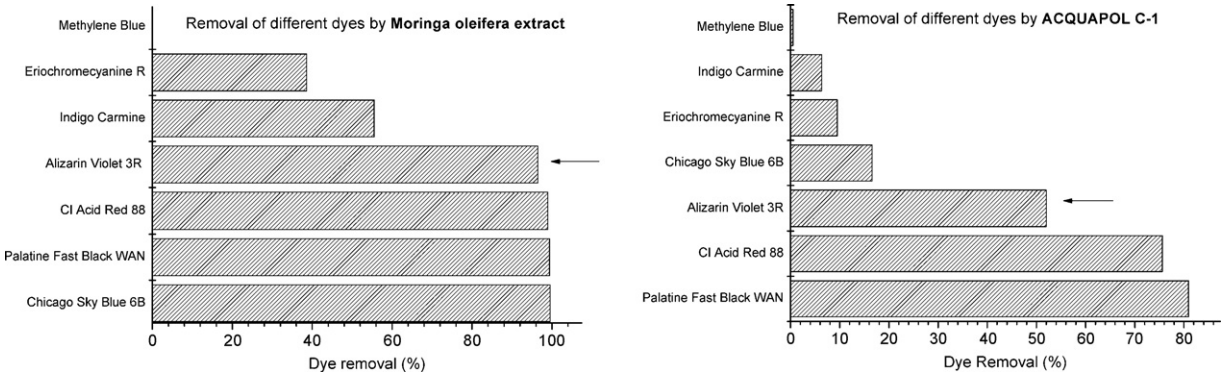

Fig. 2. Preliminary screening on several dye removal.

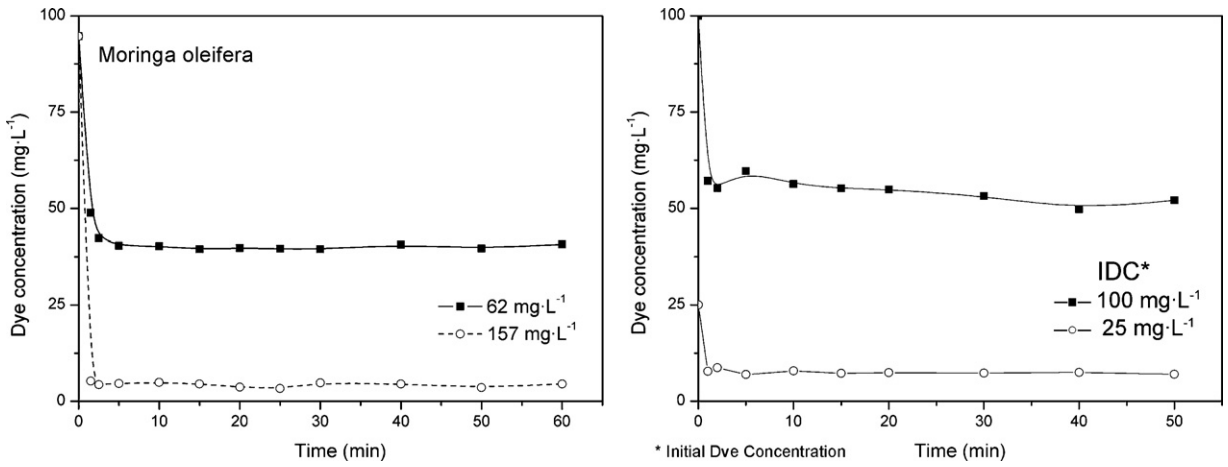

Fig. 3. Kinetic evolution on dye removal.

As a first approach, it is clear that the capacity of *M. oleifera* is higher than *ACQUAPOL C-1* in removing almost every type of dye. Just in the case of Methylene Blue, although both products have a very low removing ability due to the cationic character of this dye, *ACQUAPOL C-1* has a slightly higher efficiency. Azo dyes are easily removed by *M. oleifera* seed extract (Chicago Sky Blue 6B, Palatine Fast Black WAN and Acid Red 88), while Alizarin Violet 3R, an anthraquinonic dye, is slightly less removable than azo dyes, but also near 100%. In the case of *ACQUAPOL C-1*, the removal of azo dyes and Alizarin Violet 3R is more graduated and has to do with the amphoteric behavior of the tannin source. Eriochromecyanine R is the most persistent dye in the case of *M. oleifera* seed extract, while Indigo Carmine is the most difficult to remove in the case of *ACQUAPOL C-1*. The reason of this behavior may has to do with the non-linear structure of both Indigo Carmine and Eriochromecyanine R that may cause steric difficulties and the coagulation process may prefer linear molecules rather than other space distributions.

Bearing in mind previous papers [28], where azo dye removal by *M. oleifera* has been thoroughly studied, we have focused our investigation on Alizarin Violet 3R, as an example of anthraquinonic dye.

3.3. Kinetics of dye removal

As a first step in the research process, a kinetic study was carried out for both coagulant agents. In the case of *M. oleifera* seed extract, two different dosages (62 and 157 mg L^{-1}) of seed extracts were applied to a initial dye concentration of 100 mg L^{-1}. These assays were represented in the first graphic of Fig. 3. In the case of *ACQUAPOL C-1* a unique dosage of 100 mg L^{-1} of coagulant was applied to two different initial dye concentrations of 25 and 100 mg L^{-1}. This corresponds to the second graphic of the mentioned figure. As it is shown, in both cases the coagulation process is very fast, with equilibrium dye concentration (i.e. that which remains after the depletion of the corresponding coagulant agent) being achieved in the first 5 min. This is probably because of complex coagulation mechanisms that may involve a net-like structure formation, which does not need a very long contact time. This gives a great advantage comparing with other processes like sorption, in which contact times seem to be longer.

According to these kinetic data, further experiments were carried out for the duration of 1 h in total to guarantee the chemical equilibrium was achieved.

3.4. Coagulant dosage

A series of experimental data were made to determine the coagulant dosage influence on dye removal for each case. A fixed dose of 100 mg L^{-1} of dye was evaluated to be removed with different doses of seed extract and *ACQUAPOL C-1*. These doses varied between 6.28 and 314.3 mg L^{-1} in the case of *M. oleifera* and between 1 and 600 mg L^{-1} in the case of the tannin coagulant. As can be seen in Fig. 4, dye removal tends to be gradually higher while q_c capacity (see Section 3.8) tends to decrease. Almost 100% dye removal is easily reached with not so high coagulant doses, but effectiveness of *M.*

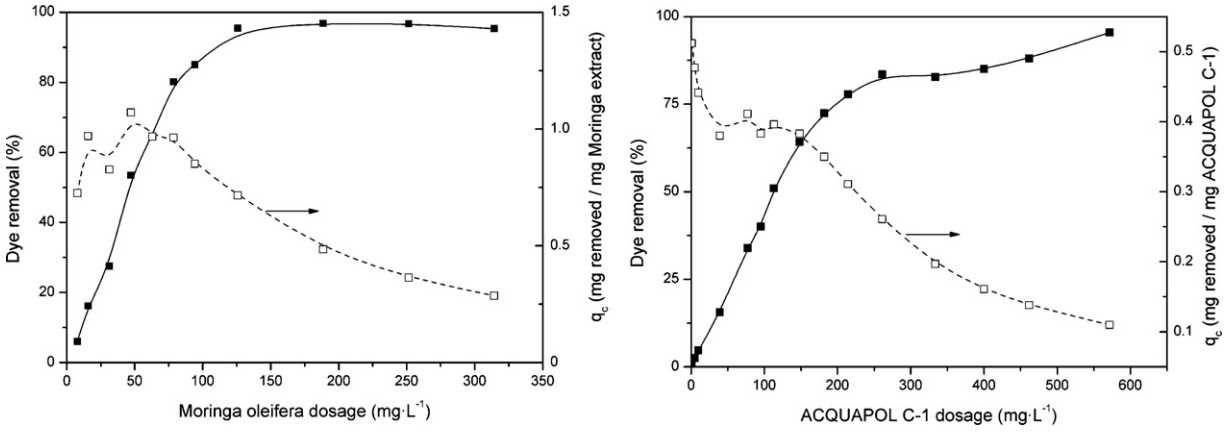

Fig. 4. General assay of dye removal.

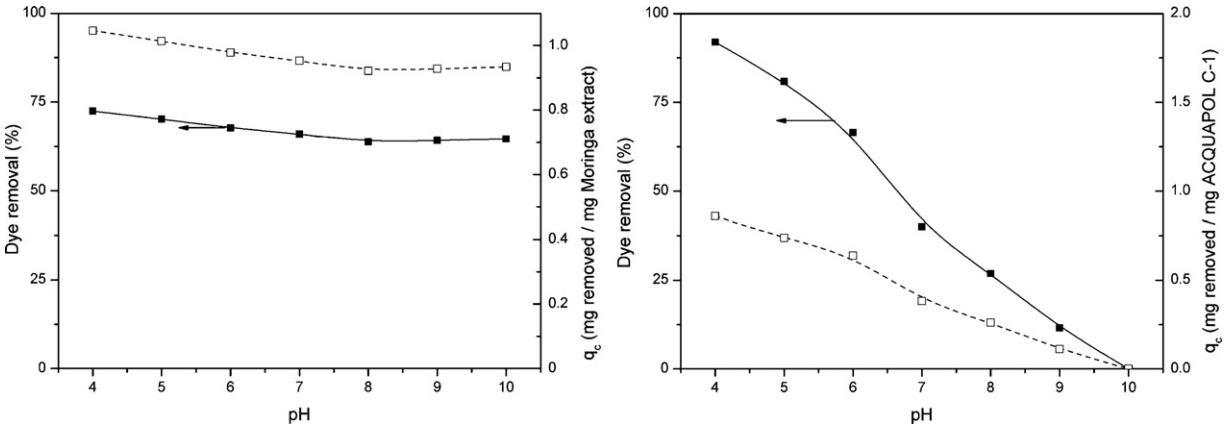

Fig. 5. Influence of pH level on dye removal.

oleifera seems to be significatively higher. Doses of ca. 100 mg L^{-1} achieves over than 80% of dye removal. For this same dye removal doses of ca. 400 mg L^{-1} are needed in the case of *ACQUAPOL C-1*.

No flocculant additive or pH variation was used in these assays, thus tested coagulants offer another advantage over inorganic traditional coagulant agents such as alum [38](apart from its lack of effectiveness). No health or pollutant risks are observed because of the natural origin of *M. oleifera* and because of the biodegradability of *ACQUAPOL C-1* that is properly indicated by SETA S.L.

It is also important to point out that most of the proposed processes for dyestuff wastewater treatment recommend a two-step procedure (adsorption and coagulation) either as just one step is not so effective in removing enough dye concentration or a large amount of coagulant agent is needed [39].

3.5. pH influence

Previous papers have shown that pH has an important role in the coagulation process [40,41]. Because of this, several assays with different pH values have been carried out, varying the pH between 4 and 10, with an initial charge of dye of 100 mg L^{-1} and with fixed doses of 62.86 mg L^{-1}(*M. oleifera* seed extract) and 100 mg L^{-1} (*ACQUAPOL C-1*). No differences were observed in the analytical wavelength value for Alizarin detection at different pH values (supplementary data). Fig. 5 shows the experimental results as a percentage of dye removal versus pH. As it is reported, increasing pH values leads to a dramatic loss of efficiency in the case of the tannin-based coagulant, while *M. oleifera* seed extracts undergoes a very slight decreasing tendency. q_c values also report the same behavior. pH seems to have different effects on the nature of these two coagulants: on one hand *M. oleifera* has proteinic, cationic nature that may imply enhancement of the coagulant activity at low pH; on the other hand tannin-based coagulants are rather known to be much affected by a pH increase that may lead to the denaturation of the chemical polyphenolic structure. Although this loss of effectivity was acute, pH range must be observed to be wide and this parameter can be easily fit into the operating values that are, in every case, more flexible than those reported in other investigations [42], where pH is more influential and changes along the assay.

3.6. Temperature influence

During our investigation, it appeared that temperature did not seem to be a very important factor in the coagulant process as it is reported previously [43]. A series of assays were performed to confirm this. Temperatures were varied between 20 and 40 °C, with a pH level of 7 and a dye initial concentration of 100 mg L^{-1}. The results are shown in supplementary data. No significant variations in treatment efficiency were observed: a high dye removal was achieved in all cases, not under 80% in the case of seed extract and 35% in the case of *ACQUAPOL C-1*. This flexibility in working temperature represents an advantage over other methods [7,44], allowing the treatment of several kind of industrial effluent.

3.7. Initial dye concentration influence

A high efficiency in dye removal has been confirmed by all the experiments carried out previously. However, it was considered important to research on how significant initial dye concentration was with reference to the percentage of dye removal in each case.

A series of experiments were carried out by varying only the initial dye concentration between 40 and 400 mg L^{-1} in the case of *M. oleifera* seed extract and 25 and 150 mg L^{-1} in the case of *ACQUAPOL C-1*. The difference in the operating range has to do with the different efficiency of each product. Fixed doses of 62.87 mg L^{-1} of seed extract or 100 mg L^{-1} of tannin-based coagulant were used. The percentage of dye removal and q_c capacity are shown in Fig. 6. Increasing the initial dye concentration leads to a loss of the percentage of dye removal, which is more acute in the case of *M. oleifera* than in the case of the tannin-based coagulant. In spite of this difference, q_c is rather more stable in the case of the seed extract than in the case of *ACQUAPOL C-1*. This fact may be caused by the higher efficiency of the *M. oleifera* seed extract, which allows a higher initial dye concentration before coagulant agent tends to be exhausted.

3.8. Theoretical adsorption modeling

In order to characterize even more the coagulation phenomenon, it is pretended to propose a theoretical model which explains the dye removal by the action of these two products. Coagulation and flocculation processes are rather difficult to model mathematically, due to two main reasons: (a) the complex nature of the phenomenon, which implies molecule physico-chemical interaction (van der Waals and hydrogen bridges forces) [45] and (b) the fact that the intrinsic composition of the organic functional groups that form the flocculant active principle in the both products is not completely known. We have worked on the hypothesis that dye removal by coagulation and flocculation process may involve two stages. A first destabilization of colloids, that may be ruled by chemical interactions between coagulant molecules (cationic, positive charged) and dye molecules (anionic, negative charged). Then, when the complex coagulant–dye is formed, flocs begin to grow by sorption mechanisms. This should be the controlling stage, so the

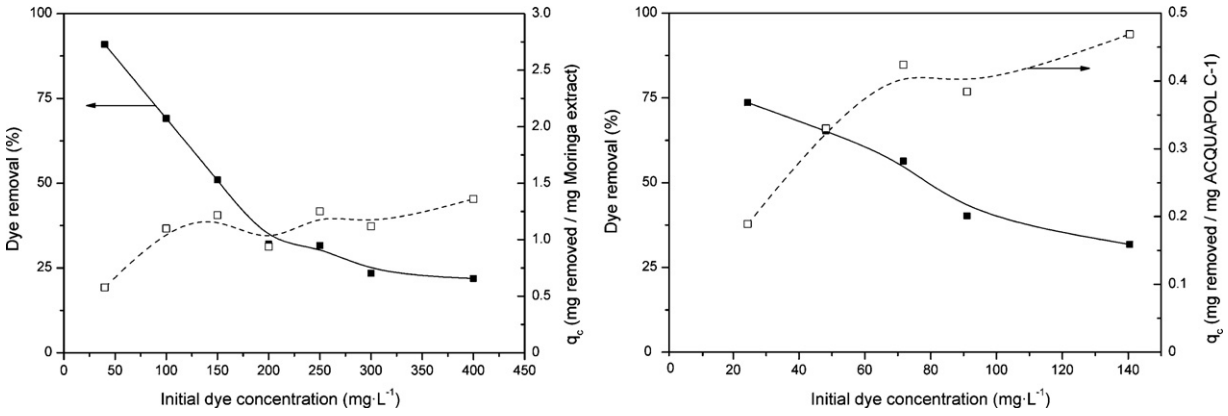

Fig. 6. Influence of initial dye concentration on dye removal.

whole process can be simulated as an adsorption phenomenon. The possible coagulation mechanisms [46] and the fact that *M. oleifera* is known to form bridges and netlike structures [47] adsorption and coagulation processes may be considered in this theoretical model. Other similar conjectures are made and applied previously with similar processes [48].

Firstly, adsorption capacity (q_c) has been determined, defined as:

$$q_c = \frac{(C_0 - C_l) \cdot V}{W} \quad (1)$$

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

Two main adsorption models have been considered in the present work: 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 number of molecules desorb and adsorb at any time. The probabilities are related to the strength of the interaction between the adsorbent surface and the adsorbate [49]. That is the physical meaning of Eq. (2):

$$q_c = k_{l1} \frac{C_l}{1 + k_{l2} \cdot C_l} \quad (2)$$

where k_{l1} is the first Langmuir adsorption constant (L[mg of coagulant]$^{-1}$) and k_{l2} is the second Langmuir adsorption constant (L[mg of removed dye]$^{-1}$).

Freundlich model was derived from empirical data [50] and assumes that q_c capacity is a power function of the equilibrium dye concentration (C_l). That is what Eq. (3) express:

$$q_c = k_f \cdot C_l^{n_f} \quad (3)$$

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

By combining data series of Sections 3.4, 3.5 and 3.7 it is possible to look for a theoretical model that fits rather well to experimental data. This is shown in Figs. 7 and 8. Both figures represent the experimental data versus predicted ones (according to the two mentioned models). As it can be appreciated, the curve fit is reasonably well with the two proposed equations. However, linear expressions of Freundlich and Langmuir models (supplementary data) gives a cri-

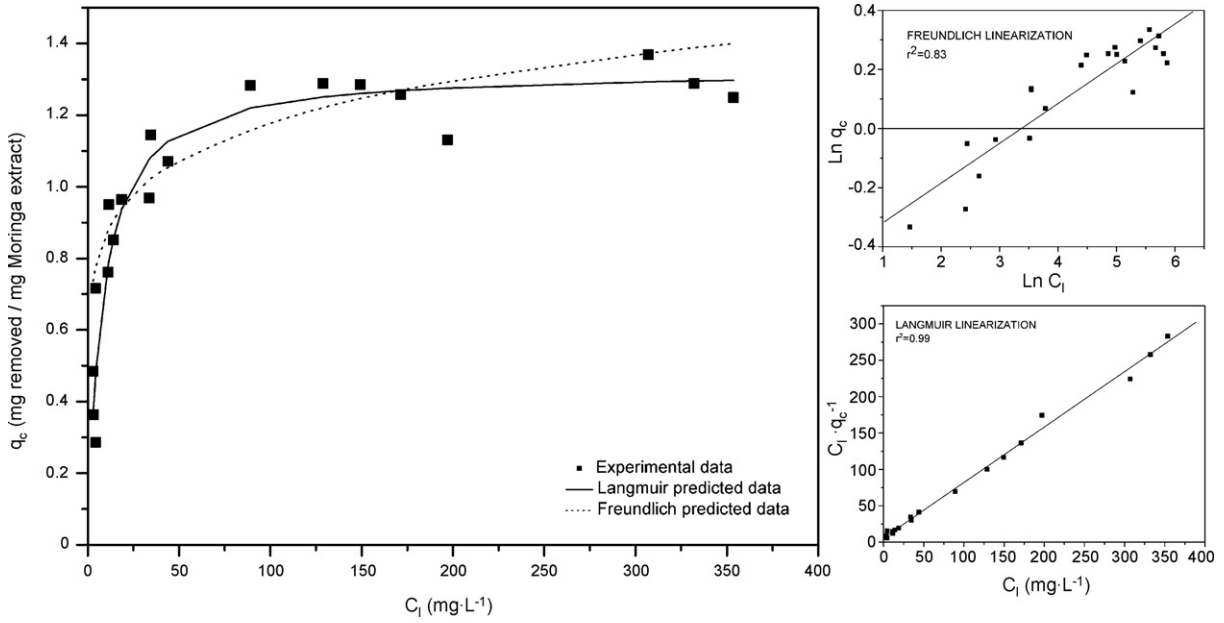

Fig. 7. Theoretical model of dye removal by *Moringa oleifera*.

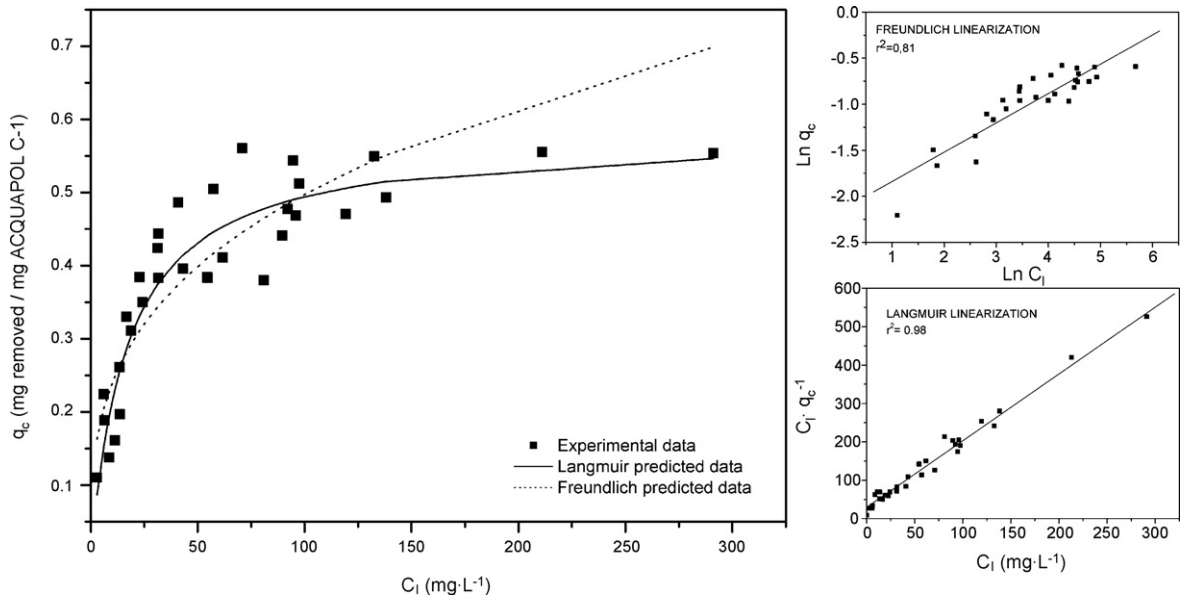

Fig. 8. Theoretical model of dye removal by *ACQUAPOL C-1*.

Table 2
Theoretical models parameters. Units in text.

Coagulant	Langmuir data adjustment	Freundlich data adjustment
Moringa oleifera seed extract	$k_{l1} = 1.71 \times 10^{-1}$; $k_{l2} = 1.29 \times 10^{-1}$	$k_f = 6.35 \times 10^{-1}$; $n_f = 1.35 \times 10^{-1}$
ACQUAPOL C-1	$k_{l1} = 3.42 \times 10^{-2}$; $k_{l2} = 5.88 \times 10^{-2}$	$k_f = 1.15 \times 10^{-1}$; $n_f = 3.18 \times 10^{-1}$

terion to discriminate the adequacy of these data adjustments. Linear fitting graphics are included in Figs. 7 and 8.

The first considered case is the removal of Alizarin with *M. oleifera* seed extract. Through linearization method it is shown that Langmuir equation fits better to experimental data than Freundlich's proposal, according to r^2 values. These are equal to 0.99 in the case of Langmuir and 0.83 in the case of Freundlich.

Regarding the second case (*ACQUAPOL C-1*), the adequacy of Langmuir model is evident according to the low r^2 value of Freundlich data adjustment, which is equal to 0.81. Instead, Langmuir r^2 is equal to 0.98, similar than in the case of *M. oleifera* seed extract. In Fig. 8 it can be seen the fact that Freundlich's proposal goes far from experimental data in the last part of the curve. Saturation phenomenon in a monolayer sorption process is not considered by this theoretical model.

The values of the different parameters involved in these two models in each case are referred in the table 2. It is observed that they are significatively higher in the case of *M. oleifera* dye removal, according to the higher q_c obtained by this coagulant agent.

4. Conclusions

This investigation has revealed the following conclusions:

- Among several natural products, *M. oleifera* and *ACQUAPOL C-1* have been found to be highly effective in removing dye through a coagulation process. In the studied case of Alizarin Violet 3R removal, up to 95% and 80% dye removal is easily achieved by seed extract or tannin-based coagulant, respectively.
- *M. oleifera* and *ACQUAPOL C-1* were fully effective with other kind of dyes, such as azo dyes, not only anthraquinonic dyes.
- As the pH level increases, efficiency of the process decreases, almost certainly because of the cationic character of both coagulant products and because, at acidic pH levels, hydrophobic links are enhanced. The affection of the pH level is higher in the case of the tannin-based coagulant than in *M. oleifera* seed extract protein.
- Temperature does not significantly affect the dye removal process.
- The initial dye concentration affects negatively the percentage of dye removal, although complete removal increases with a higher initial dye concentration.
- Langmuir and Freundlich theoretical models have been tested and the first of them results to be more accurate to the mechanism of dye removal.

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Appendix A. Supplementary Data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.04.131.

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