

Removal of Disperse Blue 56 from synthetic textile effluent using ionic flocculation

R. P. F. Melo, S. K. S. Carmo, E. L. B. Barros, A. G. Câmara, S. K. S. Nunes and E. L. Barros Neto

ABSTRACT

The textile industry is one of the main generators of industrial effluent due to the large volumes of water containing a wide variety of pollutants, including dyes. Thus, the present study aimed to remove the Disperse Blue 56 dye present in synthetic textile effluent using ionic flocculation through surfactant flocs produced from animal/vegetable fat, assessing the system at different surfactant concentrations and temperatures. The process kinetics, adsorption mechanism and equilibrium were evaluated. The results show that the kinetics was better described by the Elovich model when compared to pseudo-first order and pseudo-second order models, indicating that chemical adsorption occurs during the process. The study of the adsorption mechanism obtained lower outer layer diffusivities than their intra-particle counterparts, demonstrating that the dye transport to the surfactant floc is controlled through the outer layer. The Langmuir isotherm was suitable for equilibrium data and the separation factor calculated showed that the isotherm is classified as favorable. Dye removal efficiency reached 87% after 360 minutes of contact between the effluent and the surfactant flocs, indicating that ionic flocculation is an efficient alternative in the treatment of textile effluent containing disperse dye.

Key words | adsorption mechanism evaluation, environmentally friendly surfactant, ionic flocculation, kinetics and equilibrium adsorption, textile effluent treatment

HIGHLIGHTS

- Ionic flocculation was studied for removal of a disperse dye from water.
- Surfactants obtained from animal/vegetable fat are used for wastewater treatment.
- Kinetic, diffusion mechanism and equilibrium were evaluated.
- Temperature does not have considerable influence on the process.
- The proposed methodology allows a removal efficiency of 87%.

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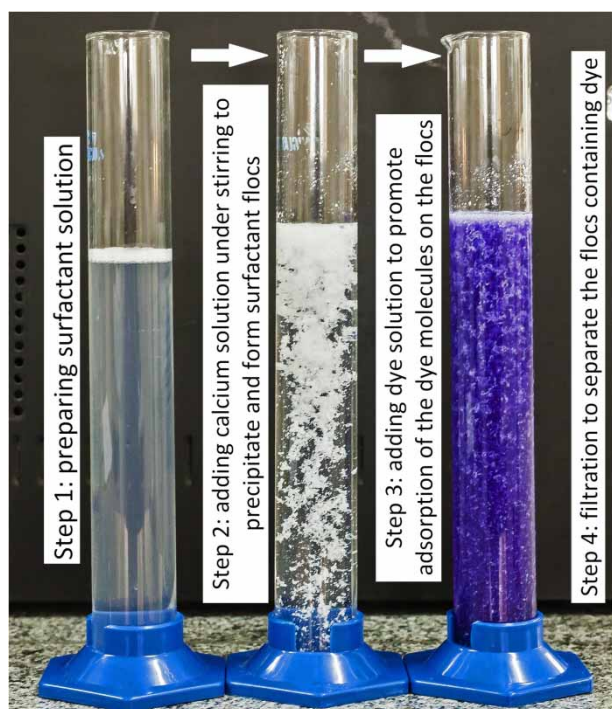
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GRAPHICAL ABSTRACT



INTRODUCTION

The textile industry is one of largest polluters in the world, since it generates significant amounts of aqueous effluents containing numerous additives used during the dyeing process. These include dyes, detergents, solvents and salts (Behera *et al.* 2021). The ‘wet’ processes, which involve chemical baths and require washing and rinsing stages, generate significant amounts of effluent, as do dyeing processes (Verma *et al.* 2012). Most chemicals used in textile production and processing are not very environmentally toxic; however, some materials, such as dyes, may have long-term toxic effects (Mojtabavi *et al.* 2020).

Disperse dyes are among the most important in the textile sector, since they are involved in the dyeing process of synthetic fiber materials, such as polyester. They are insoluble in water and colloids in aqueous medium. Disperse dyes usually result in 80–92% fixation (Berradi *et al.* 2019) and in relation to the environment, disperse dyes are not biodegradable and may be bioaccumulative, due to their hydrophobicity (Hunger 2003).

As such, several studies have been carried out to obtain efficient textile effluent treatment processes, such as

coagulation–flocculation (Dotto *et al.* 2019), advanced oxidative processes (Asgar *et al.* 2015), electrochemical processes (Samsami *et al.* 2020) and adsorption (Li *et al.* 2019). In addition, processes that involve the use of surfactants in the treatment of textile effluents have proven to be efficient: cloud-point extraction (Mortada 2020), microemulsions (Petcu *et al.* 2016) and micellar ultrafiltration (Zaghbani *et al.* 2009).

Surfactants, widely used in separation processes (Scamehorn & Harwell 1989; Yazdi 2011; Yamini *et al.* 2020), are classified into four types: anionic, cationic, nonionic and amphoteric. Of these, anionic surfactants stand out, accounting for 70 to 75% of world consumption. The oldest anionic surfactants are formed from the neutralization of a carboxylic acid by sodium or potassium hydroxide (Myers 2006). However, these surfactants are unstable in aqueous medium containing calcium ions, forming a precipitate, since the Krafft point of calcium surfactants is above 100 °C (Zapf *et al.* 2003). When subjected to agitation, the precipitate aggregates to form hydrophobic flocs, which are capable of adsorbing organic compounds, such as textile effluent dyes, in solution. The flocs can then be separated by

filtration or flotation, thereby removing the organic material from the aqueous medium. This precipitation process is called ionic flocculation when applied to the treatment of effluent containing organic compounds. Ionic flocculation applied to the treatment of effluents containing dye is a new process. Normally, the separation processes that use surfactants work with micellar systems as separation agents, and in ionic flocculation, the separation agent is in the form of flocs. There are therefore many aspects to investigate in the behavior of flocs as an adsorbent surface. Given that the process depends on the surface interaction between the dye in the medium and the surfactant floc surface, factors such as adsorption capacity, temperature, kinetics, diffusion mechanism and equilibrium need to be assessed. In addition, an attractive factor for ionic flocculation application is the use of low surfactant concentrations, which are obtained from renewable low-cost raw materials (animal/vegetable fat).

The present study proposed to treat a synthetic textile effluent containing disperse dye as a pollutant model, in order to evaluate the efficiency of ionic flocculation using surfactant flocs obtained through the interaction between calcium and an anionic surfactant based on a mixture of animal/vegetable fat. Kinetics, the mass transfer mechanism and equilibrium were also analyzed.

MATERIALS AND METHODS

Materials

The Disperse Blue 56 (DB56) dye used in this study ($\lambda_{\max} = 550$ nm, CAS 12217-79-7, molecular mass = 349.14 g/mol, $C_{14}H_9BrN_2O_4$) was provided by TMX (Brazil), and the surfactant was base soap (molecular mass = 292 g/mol and c.m.c. = 1.35×10^{-3} M), a mixture (weight/weight %) composed of carboxylate anionic surfactants with different alkyl chain lengths, produced in the laboratory from animal/vegetable fat. The base soap was obtained from a mixture of beef tallow (95%) and coconut oil (5%), whose composition is presented in Table 1 (Melo *et al.* 2015). The calcium was obtained from an analytical grade calcium chloride ($CaCl_2$) solution. The experiments were performed in a thermostatic bath (Water Separability Tester, Koehler Instrument Company, Inc., USA) and dye concentration was determined by UV-Vis spectrophotometer (Varian Analytical Instruments, Cary 50 Conc, USA).

Table 1 | Composition of the oils used to obtain the surfactant

Acid, Carbon number	Coconut oil (wt. %)	Animal fat (wt.%)
C10	6	–
C12	47	–
C14	18	5
C16	9	29
C18	3	25
C18 =	6	36
C18,2 =	2	1.5
C16 =	6	3

Methods

Experimental procedure

The experiments were carried out in 100-mL graduated test tubes with added distilled water and taken to the thermostatic bath. The surfactant was then added to adjust its concentration to 650 ppm, and dissolved at a stirring rate of 600 rpm. A calcium solution (3,600 ppm) was added to adjust the calcium concentration to 325 ppm and form flocs with the surfactant. This concentration was sufficient to ensure complete surfactant precipitation. The mixture was stirred at 140 rpm for the flocs to remain more evenly distributed in the medium. After floc formation, the dye solution was added to produce an initial concentration of 100 ppm. In this process, flocs act as a dye adsorbent.

Contact time and kinetic model

The first step of this study was to determine the time required to reach equilibrium. The experimental procedure adopted is described in the previous section and the samples were collected at time intervals between 15 and 420 minutes to evaluate dye removal efficiency. The kinetic pseudo-first order, pseudo-second order and Elovich models were tested to describe the experimental data.

The pseudo-first order model is based on the fact that the adsorption rate is proportional to the number of free sites (Hameed *et al.* 2008; Loganathan *et al.* 2014). The linearized form of the pseudo-first order model is given by Equation (1):

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (1)$$

where q_t and q_e are the adsorption capacities at time t and equilibrium, respectively, and k_1 the rate constant of the

pseudo-first order model. The value of q_e was considered the maximum value of q_t from the experimental data. Thus, a linear fit of $\ln(q_e - q_t)$ vs t can be used to obtain the k_1 constant of the model, which is useful in predicting whether the model is suitable for the experimental data.

The pseudo-second order model considers that the process probably involves chemical interactions (Loganathan *et al.* 2014) and is based on the fact that the rate is linearly related to the square of the number of free sites. The linearized form of the pseudo-second order model is given by Equation (2), and the k_2 constant can be obtained by linear regression of the experimental data: (t/q_t) vs t :

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \left(\frac{1}{q_e} \right) t \quad (2)$$

The Elovich model was the third applied in the kinetics study. This model considers that solid surfaces are energetically heterogeneous and that neither desorption nor interactions between the adsorbed species can affect the adsorption kinetics in a low surface coverage (Gupta & Bhattacharyya 2011), in addition to being applicable over an extensive range during the slow stage, failing at the end of the process, where it becomes excessively slow (Low 1960). The linearized form of the Elovich model is given by Equation (3):

$$q_t = \left(\frac{1}{b} \right) \ln(t) + \left(\frac{1}{b} \right) \ln(a \cdot b) \quad (3)$$

where a and b are the constants for the model, and a is associated with the initial adsorption rate. In order to evaluate model applicability, a plot of q_t vs $\ln(t)$ is used, which can determine constants a and b using linear regression.

To determine the most adequate model to describe process kinetics, the authors used Equation (4), which represents root mean square error (RMSE):

$$RMSE = \sqrt{\sum_{i=1}^N \frac{[(q_{exp} - q_{mod})/q_{exp}]^2}{N}} \quad (4)$$

where q_{exp} and q_{mod} are the experimental and calculated adsorption capacities, respectively, and N the number of experimental points.

Evaluation of the adsorption mechanism

Given that different mass transfer resistances are present in adsorption, a detailed analysis of the process is necessary to identify the controlling step, since this cannot be done by analyzing the kinetic models. The intra-particle diffusion model was used to understand the diffusion mechanism of the dye molecules for the surfactant flocs. The expression for this model is given by Equation (5):

$$q_t = k_{ip} t^{1/2} + C \quad (5)$$

where k_{ip} ($\text{mg/g} \cdot \text{min}^{0.5}$) is the intra-particle diffusion rate constant and C a constant that provides a measure of the thickness of the outer layer, i.e., the larger the C , the greater the thickness of the outer layer (Hameed & El-Khaiary 2008; Hameed *et al.* 2008).

To determine diffusivity in the outer layer and inside the particle, the diffusion models proposed by Crank (Crank 1975) were used (Equations (6) and (7)), following the methodology applied by Dotto & Pinto (2011):

$$\frac{q_t}{q_e} = 6 \left(\frac{D_f}{\pi r_p^2} \right)^{0.5} t^{0.5} \quad (6)$$

$$\frac{q_t}{q_e} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1) \exp(-D_p q_n^2 t / r_p^2)}{9 + 9\alpha + q_n^2 \alpha^2} \quad (7)$$

$$\alpha = \frac{C_e}{C_o - C_e} \quad (8)$$

$$tg(q_n) = \frac{3q_n}{3 + \alpha q_n^2} \quad (9)$$

where D_f and D_p are the diffusivities in the outer layer and the particle, α and q_n the variables defined by Equations (8) and (9), and r_p the average radius of the adsorbent particles. C_o is the initial dye concentration and C_e the equilibrium dye concentration in the aqueous phase. The values of q_n used in Equation (7) are obtained from the non-zero roots of Equation (9).

Adsorption isotherm

The experiments to evaluate adsorption equilibrium were carried out using surfactant concentrations varying from 260 to 780 ppm, maintaining dye concentration at 100 ppm. The experiments were performed at three different temperatures: 30, 40 and 50 °C. The results obtained were

tested in the Langmuir model, whose linearized expression is given by Equation (10):

$$\frac{C_e}{q_e} = \frac{1}{q_m n} + \frac{C_e}{q_m} \quad (10)$$

where q_m is the maximum adsorption capacity and n the adsorption equilibrium constant. Both q_m and n are obtained from the equation of the line on the C_e/q vs C_e graph.

In the equilibrium study, the separation factor (R_L) that classifies the Langmuir isotherm was also evaluated and calculated by Equation (11):

$$R_L = \frac{1}{1 + nC_0} \quad (11)$$

RESULTS AND DISCUSSION

Kinetic and contact time

To determine the equilibrium time of the system, samples with dye and surfactant concentration of 100 and 650 ppm, respectively, were analyzed. Dye adsorption on the surfactant precipitate (floc) was evaluated at temperatures of 30, 40 and 50 °C to observe its effect on the equilibrium. The process operating time was evaluated up to 420 minutes. The results obtained are shown in Figure 1.

Figure 1 shows that the equilibrium time of the process is reached in approximately 360 minutes, obtaining

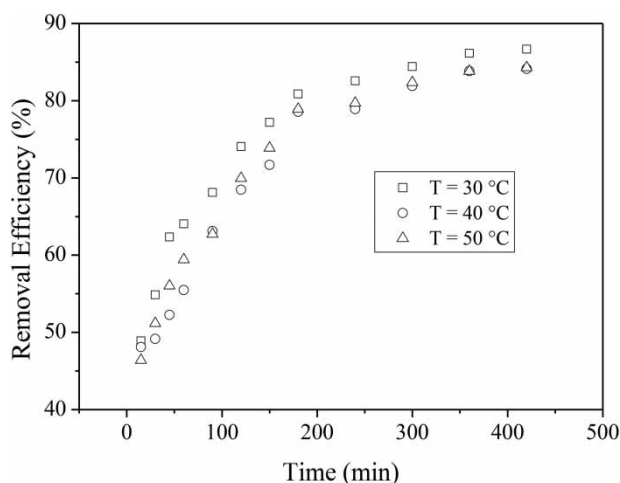


Figure 1 | Dye removal efficiency vs time, t (min) at different temperatures. Dye concentration = 100 ppm.

approximately 87% removal efficiency. However, at 180 minutes it reached 80%, corresponding to favorable dye adsorption on the floc, confirmed in the evaluation of process equilibrium. Furthermore, temperature did not have a significant influence on removal efficiency. This result corroborates that of another study that assessed the effect of temperature on removal efficiency, in which ionic flocculation was used to remove Direct Yellow 27 (Melo *et al.* 2017).

The removal results obtained were used to determine the most appropriate kinetic model to describe the experimental data. The linearized equation of each kinetic model was used to determine the constants of the models. Table 2 shows the values of the constants. As shown in Table 3, the pseudo-second order and Elovich models are adequate for all temperatures, according to the coefficient of determination; however, the latter exhibited the smallest error, indicating a chemical adsorption process (Wu *et al.* 2009). This result is in line with other studies (Table 4), in which the Elovich model proved to be adequate in representing the adsorption processes of pollutants from aqueous solutions.

The model constants were used to determine the adsorption capacities and compare them with the experimental data (Figure 2). As presented in the figure, the experimental adsorption capacity is closer to that determined by the

Table 2 | Kinetic model constants for dye adsorption at different temperatures

Temperature (°C)	Pseudo-second order		Elovich		Pseudo-first order
	q_e (mg/g)	k_2 (g/mg.min)	a (mg/g.min)	b (g/mg)	k_1 (1/min)
30.0	136.86	$3.2 \cdot 10^{-4}$	66.15	0.054	$9.90 \cdot 10^{-3}$
40.0	138.31	$2.4 \cdot 10^{-4}$	33.56	0.050	$9.83 \cdot 10^{-3}$
50.0	137.55	$2.7 \cdot 10^{-4}$	39.62	0.051	$9.82 \cdot 10^{-3}$

Table 3 | Coefficient of determination and error for each temperature studied

Models	Temperature (°C)	R ²	Error
Pseudo-first order	30	0.835	0.3468
	40	0.842	0.3174
	50	0.843	0.3297
Pseudo-second order	30	0.998	0.0842
	40	0.997	0.1241
	50	0.997	0.1034
Elovich	30	0.988	0.0195
	40	0.951	0.0561
	50	0.976	0.0334

Table 4 | Studies in which the Elovich kinetic model was adequate in describing the adsorption process and the constant values obtained in each of them

Reference	Adsorbate	Adsorbent	<i>a</i> (mg/g.min)	<i>b</i> (g/mg)
Luz-Asunción <i>et al.</i> (2020)	RR2	GQD-1	24.88	0.243
Pérez-Calderón <i>et al.</i> (2020)	Reactive Red 195	cross-linked chitosan/oxalic acid hydrogels	64.00	0.040
Assis <i>et al.</i> (2020)	Indosol Blue	rGO-Co ₃ O ₄	62.34	0.011
Mittal <i>et al.</i> (2021)	Crystal Violet dye	XG-HNC	65.57	0.014

Elovich model. The pseudo-second order model provides good approximations after a prolonged contact time (after 180 min), but have been weak for short contact times

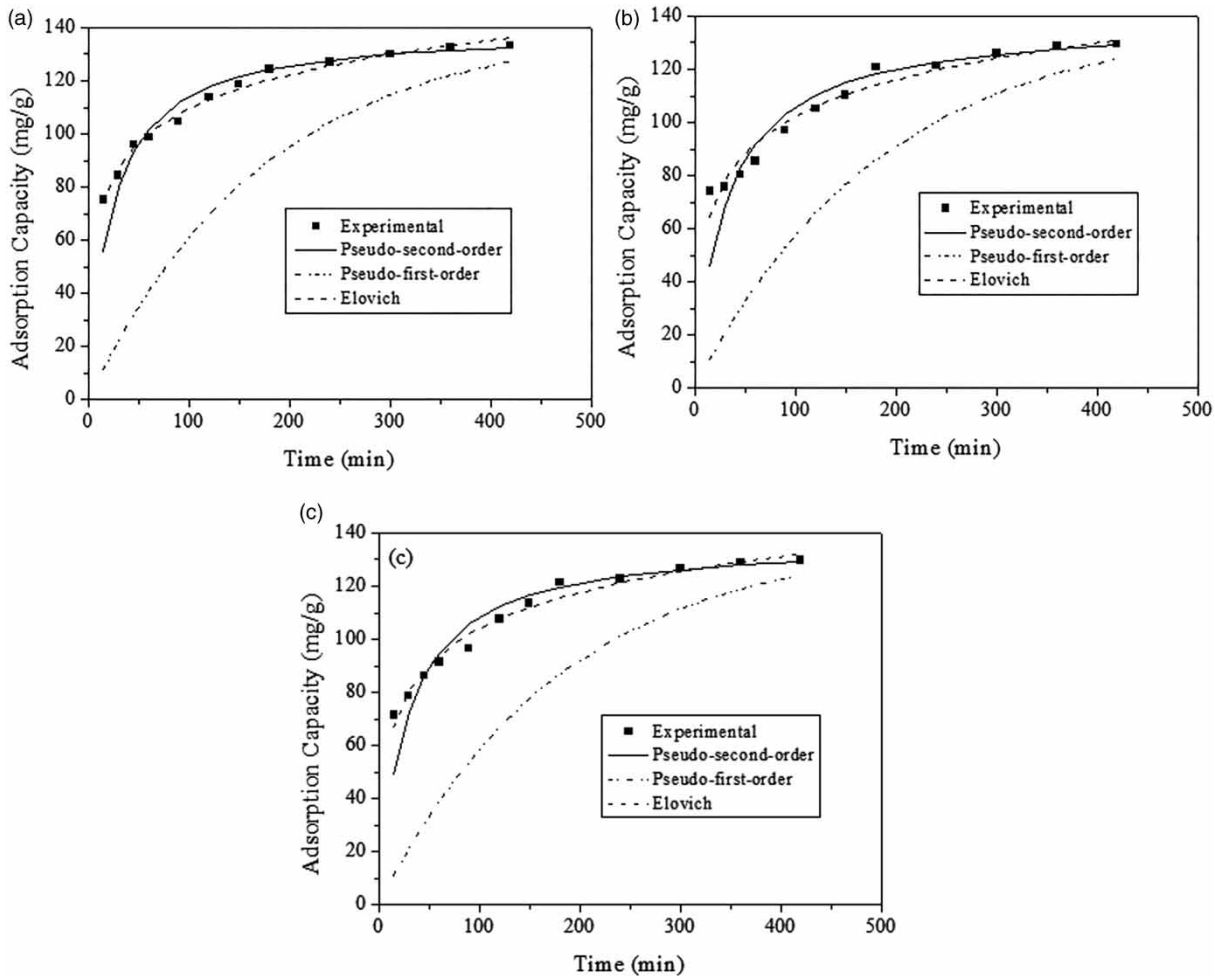
(before 180 min). The first order model exhibited significant deviations throughout the range studied, except for prolonged periods.

The equilibrium approximation factor (Equation (12)) (R_E), defined by Wu *et al.* (2009) for the Elovich model was calculated to describe the behavior of the dye adsorption kinetics curve:

$$R_E = \frac{1}{q_{ref}b} \quad (12)$$

where q_{ref} is the adsorption capacity at the longest operation time.

According to the R_E value, the kinetic curve is classified as slow rising ($R_E > 0.3$), mild rising ($0.3 > R_E > 0.1$), rapid rising ($0.1 > R_E > 0.02$) and instant approaching equilibrium ($R_E < 0.02$). The R_E values were around 0.15 for all the temperatures evaluated. Thus, the kinetic curve displays

**Figure 2** | Adsorption capacities obtained experimentally and by the models, (a) $T = 30\text{ }^{\circ}\text{C}$, (b) $T = 40\text{ }^{\circ}\text{C}$ and (c) $T = 50\text{ }^{\circ}\text{C}$.

mild rising behavior, which corresponds to a process where chemical adsorption can be observed (Wu *et al.* 2009).

Determination of diffusion mechanism

In order to identify the diffusion mechanism, the intra-particle diffusion model (Equation (5)) was applied to the experimental dye removal data as a function of time. The purpose of this analysis was to determine the diffusion-controlling step: diffusion in the outer layer or intra-particle. In the intra-particle model, the plot of q_t vs $t^{1/2}$ may be multi-linear throughout the time interval studied (Hameed *et al.* 2008; Abramian & El-Rassy 2009; Tang *et al.* 2012). This behavior indicates that two or more stages are involved in the diffusion of dye particles onto the adsorbent (Sun & Yang 2003; Dotto & Pinto 2011; Tang *et al.* 2012). The first linear section of the intra-particle model corresponds to adsorbate transport from the solution to the outer surface of the

adsorbent and the second stage to adsorbate transport from the outer surface into the pores of the adsorbent. In the final equilibrium stage, intra-particle diffusion decreases due to the very low adsorbate concentration in the solution (Wu *et al.* 2009; Noroozi *et al.* 2007).

The results obtained for the intra-particle model are presented in Figure 3, showing only two linear segments, corresponding to the first two stages of the diffusion process using the intra-particle model. Figure 1 demonstrates that disperse dye adsorption on the surfactant is very slow, and longer times should be evaluated to identify equilibrium time. If the third stage could be verified in the intra-particle model, it would occur at times greater than 420 minutes, which would make the study long and impractical.

Figure 3 shows that none of the lines crosses the origin, indicating that intra-particle diffusion is not the only controlling stage, but that another mechanism is involved (Kiran *et al.* 2006; Hameed *et al.* 2008; Abramian & El-Rassy 2009).

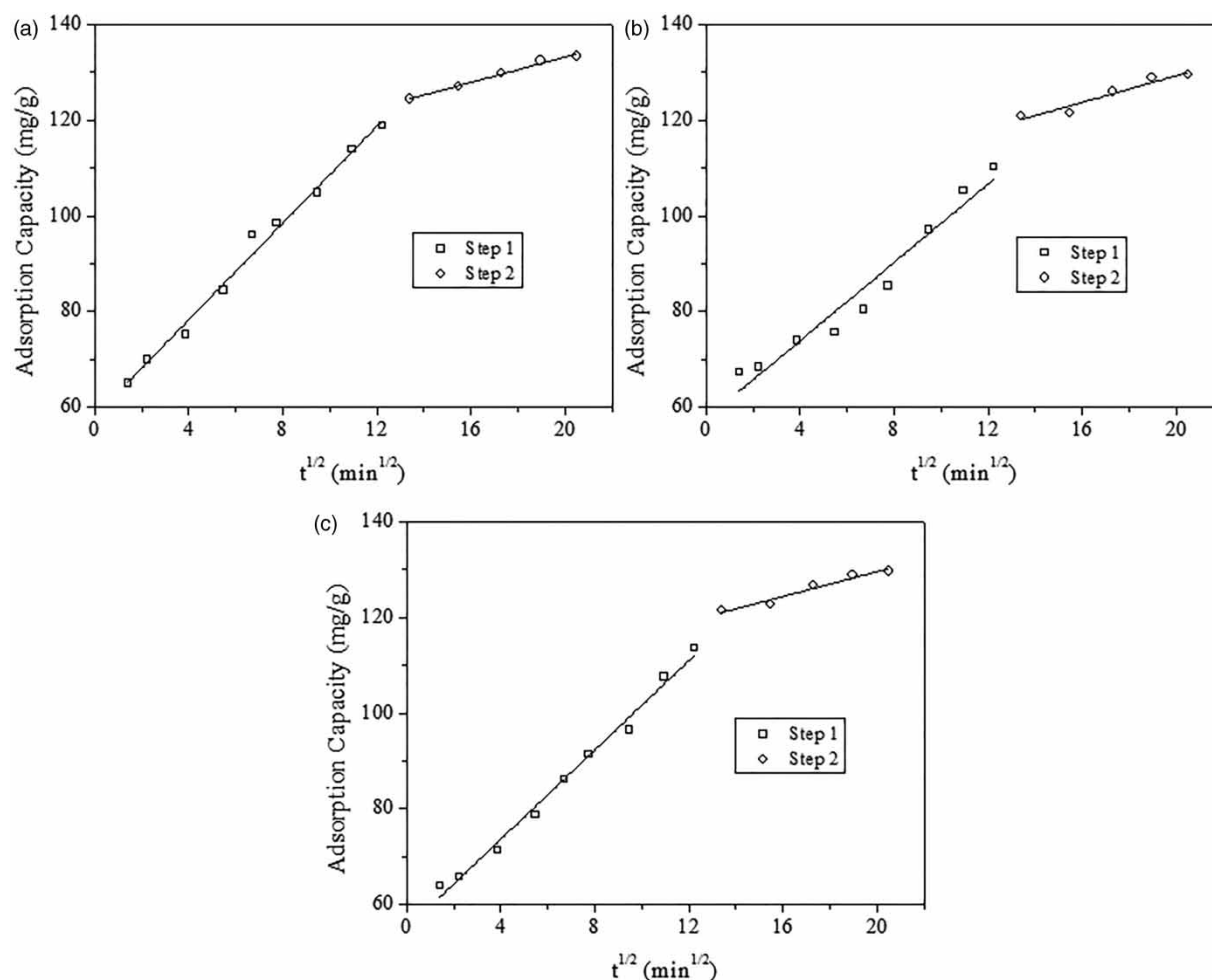


Figure 3 | Adsorption capacity of the disperse dye in the calcium surfactant floc (mg/g) vs $t^{1/2}$ ($\text{min}^{1/2}$), (a) $T = 30^\circ\text{C}$, (b) $T = 40^\circ\text{C}$ and (c) $T = 50^\circ\text{C}$.

Dotto & Pinto (2011) demonstrated that the diffusivity of the outer layer and the intra-particle diffusivity of the stages identified can be determined by fitting Equations (6) and (7) to the experimental data, corresponding to the first and second steps, respectively.

The diffusivity value in the outer layer (D_f/r_p^2) is obtained through the angular coefficient adjusted by the linear regression of the experimental data of the plot of q_t/q_e vs t , using Equation (6). The intra-particle diffusivity value (D_p/r_p^2) is obtained by the angular coefficient of line $\ln(1 - q_t/q_e)$ vs t obtained by the linearization of Equation (7), with the series approximating the first term, since the other terms become negligible for very long periods. The results obtained from the diffusivities of the outer and intra-particle layer are presented in Table 5 along with the coefficients of determination for linearized Equations (6) and (7).

Table 5 shows that the diffusivities in the outer layer are always smaller than those in the particle. This indicates that dye transport to the outer layer is the step controlling the diffusion mechanism. In addition, diffusivity values do not vary appreciably with temperature, indicating that it does not significantly influence the process over the range studied.

Adsorption equilibrium

To determine if the behavior of the experimental data fits the Langmuir model, the process was evaluated at a surfactant concentration range of 325–780 ppm for the three temperatures studied. The contact time between the dye solution and the adsorbent was established as 180 minutes. The results obtained are shown in Figure 4.

Figure 4 demonstrates that temperature had a negligible influence on equilibrium, since the corresponding points at different temperatures overlap. The linear relationship between C_e/q vs C_e was used to determine the Langmuir isotherm constants, as shown in Table 6. The coefficient of determination and the separation factor were also obtained.

Table 6 shows that the coefficients of determination obtained for the equilibrium data are very close to unity, indicating that the Langmuir model is adequate to describe the equilibrium between the adsorbent and the dye solution.

Table 5 | Diffusivities in the outer layer and in the particle, and coefficients of determination at each of the temperatures assessed

Temperature (°C)	D_f/r_p^2	R^2	D_p/r_p^2	R^2
30	$1.19 \cdot 10^{-4}$	0.990	$1.32 \cdot 10^{-3}$	0.984
40	$9.50 \cdot 10^{-5}$	0.969	$8.70 \cdot 10^{-4}$	0.934
50	$1.01 \cdot 10^{-4}$	0.990	$8.35 \cdot 10^{-4}$	0.961

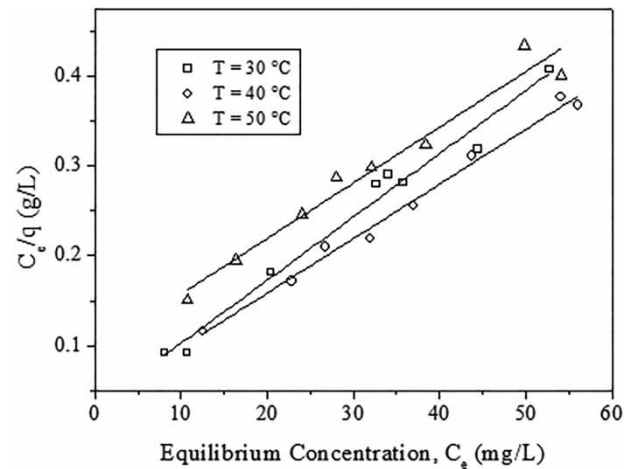


Figure 4 | Isotherms obtained for dye adsorption at different temperatures.

Table 6 | Constants obtained for the Langmuir model, separation factor and coefficient of determination

Temperature (°C)	q_m (mg/g)	n (L/g)	R_L	R^2
30	142.86	0.215	0.044	0.981
40	163.93	0.164	0.057	0.990
50	161.30	0.065	0.133	0.964

Table 6 also shows the separation factor (Equation (11)), which classifies the isotherm as unfavorable if $R_L > 1$; favorable if $0 < R_L < 1$; linear if $R_L = 1$; and irreversible if $R_L = 0$. According to the values obtained for R_L , adsorption is favorable at all the temperatures assessed.

CONCLUSIONS

In the present study, ionic flocculation was evaluated for the treatment of a synthetic textile effluent, using a disperse dye as pollutant, and the adsorbent was the surfactant floc obtained through the reaction between an animal-/plant-derived surfactant and calcium. The following conclusions can be drawn:

- Kinetic evaluation showed that the process can be described according to the Elovich model, and that the time required to reach equilibrium was 180 minutes.
- Since diffusivity inside the particle is greater than that in the outer layer, diffusion is controlled by transport of the solution molecules to the particle surface.
- The Langmuir model was adequate to describe the equilibrium of the process and the separation factor showed that the behavior of the isotherm is favorable.

An important conclusion is that surfactant flocs represent a new interface for adsorption, providing a separation process based on surfactant action in the form of flocs without the need for micelles. In addition, high dye removal efficiency (87%) was achieved. Thus, an innovative methodology can be studied through ionic flocculation. Further studies using ionic flocculation should evaluate the effects of carbonic chain length and type of carbonic chain (branched, saturated or unsaturated) to achieve better dye removal efficiency.

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DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

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