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Study of Rhodamine B Retention by Polyurethane Foam from Aqueous Medium in Presence of Sodium Dodecylsulfate

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Abstract: This work reports a study about the adsorption of Rhodamine B (RB) by unloaded polyether type polyurethane foam (PUF) in a medium containing sodium dodecylsulfate (SDS). The adsorption process was based on the formation of an ionic-pair between RB and SDS, which presented high affinity by PUF. Adsorption was characterized in relation to equilibrium, kinetic, and thermodynamic aspects and the results obtained showed that the ratio between the SDS and RB concentrations played an important role on the adsorption efficiency. A maximum adsorption capacity of $6.85 \times 10^{-6}\,\mathrm{mol\,RB\,g^{-1}}$ was observed at established experimental conditions. The adsorption process was spontaneous (negative ΔG) and presented an endothermic characteristic (positive ΔH). Also, its rate was regulated by an intraparticle diffusion process. Sequential extraction experiments were carried out by changing PUF plugs in 30 and 60 min time intervals, resulting in removal rates higher than 95%.

Keywords: Cationic dyes, polyurethane foam, Rhodamine B, solid-phase extraction

INTRODUCTION

The intense development of industrial activities is responsible for the disposal of a large variety of harmful toxic pollutants to the environment. Several of these pollutants are not degraded by natural process. In this

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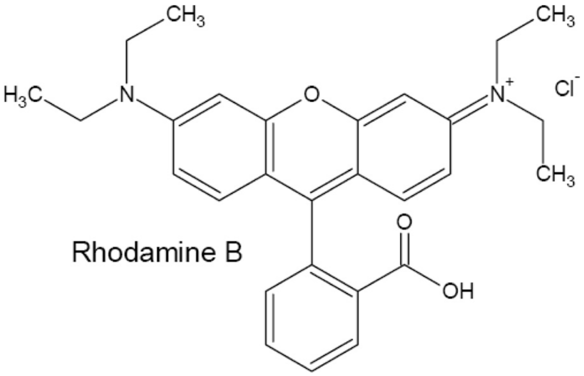

Figure 1. Structure of Rhodamine B.

context, the discharge of dyes represents a serious problem because of their persistence and non-biodegradable characteristics (1). Moreover, highly colored effluents containing dyes can affect aquatic life present in natural water bodies by decreasing sunlight penetration and/or even leading to direct poisoning of living organisms (2–4). Although photochemical degradation of dyes can be applied in some cases (5–8), several dyes are difficult to degrade since they are stable in front of light and resistant to chemical or anaerobic digestion (9).

Rhodamine B (RB), Fig. 1, is a cationic (or basic) dye widely used in food and textile industries as a colorant. It has been also employed as fluorescent water tracer to characterize the migration of natural water bodies (10). Nowadays, it is well known that RB can cause several adverse effects on humans like skin, gastrointestinal, and respiratory tract irritation (11). According to current literature, RB is considered to be potentially both genotoxic and carcinogenic (12–13). In front of this scenario, the study and development of suitable methods for RB removal from aqueous medium are required.

The application of solid adsorbents for the removal of chemical substances from water has assumed remarkable importance, because their use has increased considerably in the last few years. Solid-phase extraction techniques can be considered an interesting alternative for the treatment of contaminated waters and effluents, especially if the sorbent employed presents low cost and does not require any treatment before utilization (14). Polyurethane foams (PUF) are an interesting alternative for this purpose since they meet these requirements and, besides, present excellent chemical and thermal resistance, high efficiency, and can be easily found in the market (15).

The use of polyurethane foams for the retention of chemical substances from aqueous medium was first described by Bowen (16). According to his study, polyurethane foams can be employed for the sorption of two classes of substances:

(i) Free molecules with high polarizability such as aromatic compounds and metallic dithizonates and
(ii) Large anions with high polarizability.

The presence of polar and non-polar groups in the structure of the polyurethane foams makes them very versatile to retain organic substances with different characteristics. Some papers document the use of unloaded polyurethane foams for the adsorption of organic compounds through a mechanism similar to a liquid–liquid solvent extraction (17–21). However, only few research papers were published reporting a full characterization of the adsorption process of organic and inorganic substances onto unloaded and loaded PUF (22–26).

Recently, several solid materials have been employed for the adsorption of various cationic dyes (1,4,14,27–35) through different experimental approaches. Since current literature does not address any work regarding the use of polyurethane foam for the adsorption of RB, the aim of this work was to study and develop a methodology for this task. Additionally, this work presents a new experimental arrangement for extraction with PUF where a cylindrical plug of foam is adapted to the arm of an overhead stirrer. This approach presents several advantages over existing methodologies such as the possibility to renew the adsorbent surface just changing the PUF plug and the elimination of a filtration step to separate the sorbent from the solution.

EXPERIMENTAL

Apparatus

Spectrophotometric measurements of solutions containing RB and SDS were carried out with an UV-Vis spectrophotometer, model 800 XI, supplied by Femto (Brazil, São Paulo). All absorbance measurements were performed with a standard 10-mm optical path quartz cuvette, furnished by Hellma (Germany) at 554 nm, which was the wavelength where maximum absorbance was observed for the SD-RB ionic-pair.

An overhead stirrer with digital adjustment of rotation speed, model RW 20 DZM supplied by Ika (Germany), was employed for the stirring of solutions with PUF. Cylinders of PUF were adjusted to the stirrer arm (made of stainless steel) of the apparatus in order to perform the extraction of RB from solutions containing SDS using the set-up previously described (26).

Reagents

All reagents were of analytical grade and used as received. The solutions were prepared with purified water obtained with a Simplicity Milli-Q System (Millipore, Saint-Quentin Yvelines, France).

A $1.0 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ RB stock solution was prepared by dissolving 0.2392 g of the reagent (chloride form) provided by Vetec (Rio de Janeiro, Brazil) in 100 mL of water. After total dissolution of the solid, the mixture was transferred to a 500 mL volumetric flask and the volume was made up to mark with water. This solution was stable for one week, at least.

A $1.0 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ SDS stock solution was prepared by simple dissolution of 0.144 g SDS (Vetec, Rio de Janeiro, Brazil) in 100 mL water. The mixture was transferred to a 500 mL volumetric flask and the volume was made up to mark.

Working solutions were prepared daily from adequate dilution of RB and SDS stock solutions according to the desired concentration of each component.

Open cell polyether type polyurethane foam with $0.017\,\mathrm{g\,cm^{-3}}$ density (Ortobom, Brazil) was used throughout the experimental work. It was employed without any chemical treatment for cleaning. PUF cylinders adjustable to the arm of the overhead stirrer were obtained by employing a leather cutter with 3 cm diameter (26).

General Procedure

The experiments were carried out by stirring 200 mL of a solution containing known concentrations of RB and SDS with a cylinder of 200 ± 10 mg of PUF adapted to the arm of the overhead stirrer (26). The concentration of RB in solution was determined by spectrophotometry at 554 nm in time intervals previously established. The percentage of RB retained on PUF was calculated according to the Eq. (1):

$$\mathrm{R}(\%) = 100 - \left(\frac{\mathrm{C_t}}{\mathrm{C_0}} \times 100\right) \qquad (1)$$

where R is the percentage of removal, $\mathrm{C_0}$ is the initial concentration of RB in the solution, and $\mathrm{C_t}$ is the RB concentration in the solution at time t.

The stirring velocity was 200 rpm, a value established during experimental work. All experiments were carried out at laboratory ambient temperature (25 ± 2°C) except otherwise mentioned.

RESULTS AND DISCUSSION

The working strategy adopted in this study was divided into two steps:

(i) Establishment of chemical and instrumental conditions in order to achieve maximum extraction of RB by PUF and;
(ii) Equilibrium, kinetic, and thermodynamic characterization of the adsorption process.

The first step was developed through the evaluation of the influence of several extraction parameters on the removal percentage of RB, as an ionic-pair with SDS, by the PUF. The second step was developed by the application of adsorption isotherms (Langmuir and Freundlich) and kinetic models (Lagergren, second-order, Morris-Weber and Reichenberg) to the obtained data as well as the determination of thermodynamic parameters.

Effect of SDS Concentration on RB Retention

In this study, the influence of the SDS concentration on the retention of RB was evaluated. It was performed taking into consideration that the substance adsorbed onto the PUF is the ionic-pair formed from the reaction between the cationic dye and the anionic surfactant SDS, according to the equilibrium shown below:

$$\mathrm{SD^- + RB^+ \rightleftarrows SD\text{-}RB\ (ionic\text{-}pair)}$$

$$\mathrm{SD\text{-}RB\ (ionic\text{-}pair) + PUF\ (s) \rightleftarrows SD\text{-}RB\text{-}PUF\ (s)}$$

where SD^- is the anion (dodecylsulfate) yielded from the SDS dissociation, RB^+ is the cationic dye Rhodamine B, and PUF is the solid polyurethane foam.

Once SD-RB ionic-pair presents lower solubility in water than RB, it is preferentially adsorbed onto PUF, probably through a solvent extraction-like mechanism. Therefore, in order to establish experimental conditions to enhance SD-RB formation and, consequently, RB

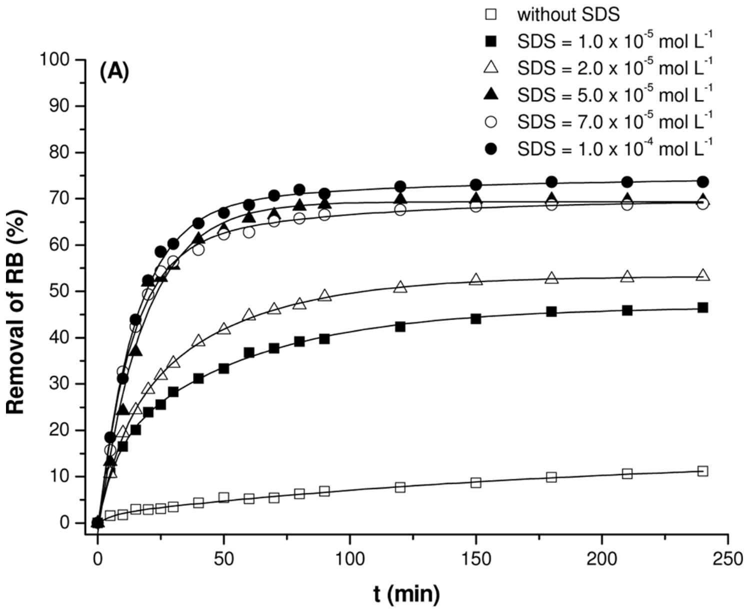

Figure 2. Effect of the concentration of SDS added on the removal of RB from aqueous solution (RB concentration was 1.0×10^{-5} mol L^{-1}).

retention, the influence of the SDS concentration added to the medium was evaluated. For this purpose, a RB concentration of 1.0×10^{-5} mol L^{-1} was maintained constant in the experiments and the concentration of SDS added was varied between 0 and 1.0×10^{-4} mol L^{-1}. Obtained results are shown in Fig. 2.

As expected, the increase in SDS concentration resulted in a strong increase of the amount of dye retained by PUF up to SDS concentration of 5.0×10^{-5} mol L^{-1}. This occurred because the increase of SDS concentration enhanced the conversion of RB into ionic-pair by shifting the equilibrium to the right side (SD-RB formation). It is important to remark that even in the absence of SDS some amount of dye was adsorbed onto PUF (around 11%), probably due to the formation of hydrogen bonds between OH group present in the RB molecule and nitrogen atoms present in the structure of foam. For concentrations higher than 5.0×10^{-5} mol L^{-1}, the percentage of RB removed from solution was practically constant, indicating that the process became independent of SDS concentration in solution. In all further experiments a concentration of SDS seven times higher than RB (7.0×10^{-5} mol L^{-1}) was employed in order to ensure maximum formation of the ionic-pair.

Evaluation of Adsorption Conditions

In order to evaluate the removal rate of RB (as ionic-pair with SDS) from solution, the effects of stirring time and the initial concentration of the dye were investigated. For this task the retention of RB by PUF from solutions containing solute concentrations in a range of $5.0 \times 10^{-6} - 2.0 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ was tested. In all experiments the concentration of SDS added was seven times higher than the RB concentration and a constant adsorbent dose (200 mg PUF/200 mL solution) was applied. In all experiments, a 240 min stirring time was employed.

As can be seen in Fig. 3, the highest removal percentages were verified for solutions containing the highest concentrations of the dye, evidencing that the initial concentration of the solute affects the adsorption process. The same behavior was already reported in the removal of the cationic dye methylene blue by zeolites (36). The equilibrium was attained after 60 min of stirring time, independently of the initial concentration of the dye.

In this work, the adsorption process was evaluated taking into consideration three steps. The first one was the solute transportation

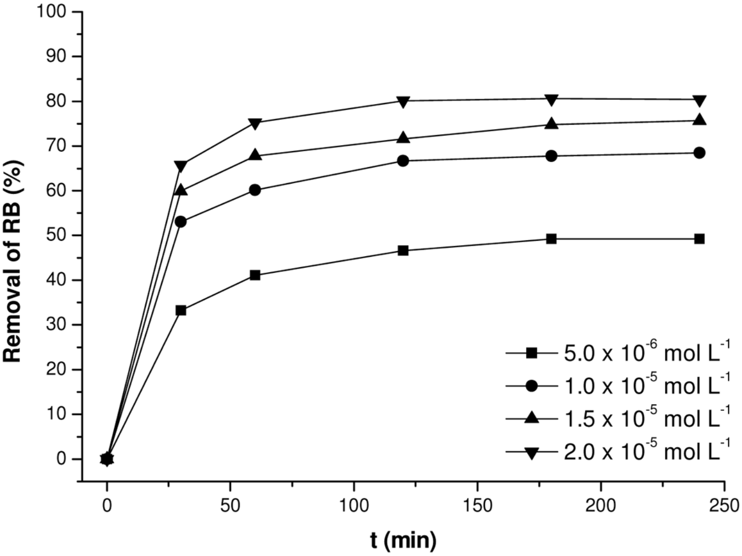

Figure 3. Effect of initial concentration of the solute on the removal percentage of RB by PUF as ionic-pair with SDS. SDS concentration was always seven times higher than of dye.

from the bulk solution until the boundary layer film present on the sorbent surface (solution-sorbent interface). This process was considered extremely dependent of the stirring of solution because, in this situation, effective collisions between RB molecules (in fact SD-RB ionic-pair) and the sorbent occur with the highest probability. The second step considered was the diffusion of solute molecules through the boundary layer film. After migration through the boundary layer film, the solute molecules achieve the sorbent surface being retained by PUF. This process is usually called film diffusion. In the last step, the solute then migrates into the porous structure of the PUF, leaving its more external sites free for the adsorption of other molecules. This process is called intraparticle diffusion. The time required to complete the whole adsorption process depends on the time required to complete each step and the slower process is the rate limiting process of the adsorption. Curves observed for the SD-RB uptake by PUF presented a single, smooth, and continuous profile, indicating that the equilibrium between the solute in the solid and the liquid phases is achieved after only 60 min of stirring.

As mentioned before, the first process is dependent on the stirring of the solution in the presence of the sorbent, which is controlled, in the present case, by the rotation speed of the overhead stirrer. Therefore, the influence of this parameter was investigated by testing the removal efficiency when the rotation speed of the overhead stirrer was varied in the range of 100–400 rpm. Although the increase of stirring speed could increase the number of effective collisions between the solute and the solid phase, no remarkable differences were observed among the retention percentages obtained in all of the tested range. This fact can indicate that even for lower rotation speed the concentration gradient in the solution is broken, enhancing the mass transfer of the solute from the solution to interfacial film. Therefore, in all further experiments, a rotation speed of 200 rpm was utilized.

Application of Adsorption Isotherms

Solid phase extraction systems can be conveniently modeled by the application of equilibrium adsorption isotherms, which provide a mathematical description of the adsorption capacity at equilibrium conditions. Besides, they allow the comparison of different adsorption systems operated at different experimental conditions. A number of different isotherms are reported in the current literature. Undoubtedly, the most employed for this purpose are the Langmuir and Freundlich isotherms.

The Langmuir isotherm takes into account some conditions:

(i) adsorption occurs on a uniform surface containing sites with equivalent adsorbing capacity in relation to the solute and
(ii) adsorption occurs on a monolayer (30).

For a system in which only the solute is significantly sorbed onto the solid surface, the Langmuir isotherm can be written as shown in Eq. (2):

$$\frac{C_e}{q_e} = \frac{1}{Q \cdot b} + \frac{C_e}{Q} \tag{2}$$

where C_e is the concentration of the solute in the solution after equilibrium is achieved (mol L^{-1}), q_e is the amount of the solute retained on the adsorbent (mol g^{-1}) at equilibrium, Q is the maximum adsorption capacity (mol g^{-1}) of the monolayer, and the term b can be assumed as an apparent adsorption equilibrium constant (L mol^{-1}).

The application of the Langmuir isotherm to the adsorption of RB dye by PUF yielded a linear fit when C_e was plotted against C_e/q_e ($C_e/q_e = -5.65 \times 10^5\ C_e + 2.39$) with a correlation coefficient $r = 0.9580$. However, a negative slope was obtained for the straight line, which resulted in the derivation of negative values for the parameters Q and b. This result can indicate that the system does not follow the Langmuir isotherm, probably because one of the conditions previously stated was not satisfied. In the present case, it seems that the adsorption does not occur on the monolayer, which could explain that increasing initial concentrations of the solute resulted in increasing extraction percentage. In this situation there is no limitation of the number of active sites on the adsorbent because the solute can be adsorbed on multiple layers. Thus, the Langmuir isotherm was considered invalid to describe the behavior of the present system.

Then, the Freundlich isotherm, which does not present such restrictions, was tested for the system. The Freundlich isotherm is an empirical equation commonly employed to model heterogeneous systems. It has been successfully utilized to model the adsorption processes in solution (37). The Freundlich isotherm can be expressed as Eq. (3):

$$q_e = K_F C_e^{1/n} \tag{3}$$

or in its linearized form (Eq. (4)),

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

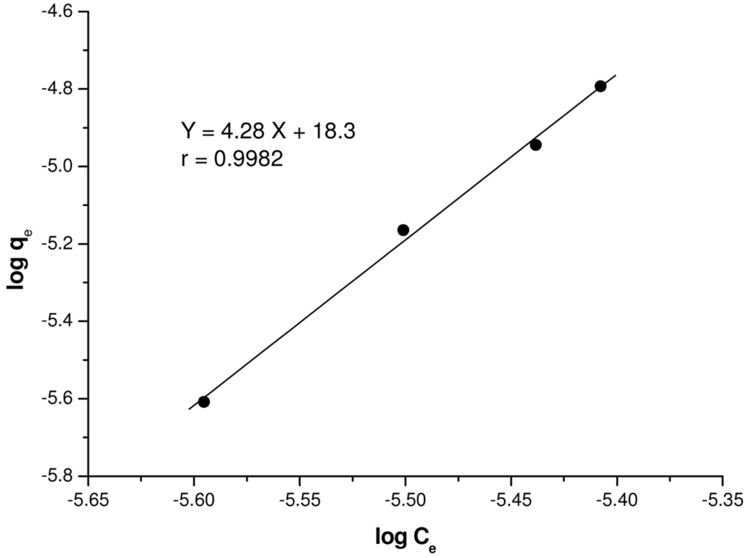

Figure 4. Plot of Freundlich isotherm in the linearized form.

where q_e is the amount of solute retained on the adsorbent at equilibrium ($\text{mol}\,g^{-1}$), C_e is the solute concentration in solution after equilibrium is reached ($\text{mol}\,L^{-1}$), and K_F and $1/n$ are isotherm parameters related to the adsorption extension and the degree of nonlinearity between the solution concentration and adsorption, respectively.

As expected, a linear fit with excellent correlation ($r = 0.9982$) was verified (Fig. 4) when log C_e was plotted against log q_e ($\log q_e = 4.28 \log C_e + 18.3$), indicating that the system can be conveniently modeled by the Freundlich isotherm. The related adsorption parameters K_F and $1/n$ were found to be $2.00 \times 10^{18}\,\text{mol}\,g^{-1}$ and 4.28, respectively.

As can be seen from data presented previously, it is clear that the system fits better to the Freundlich model, which gave a plot with a correlation coefficient higher than 0.99. The experimental value of $1/n$ was higher than unity, which evidenced a favorable adsorption of the SD-RB ionic-pair by PUF (38). According to Singh et al. (39), when the parameter $1/n$ presents a value higher than unity (n value lower than 1) a cooperative adsorption can be occurring among active sites with different adsorption capacities (energies). In these cases, there are significant interactions among solute molecules, increasing the adsorption efficiency with the increase of solute concentration in solution. Therefore, the better adjustment of data to the Freundlich isotherm and the observation of a value higher than unity for the parameter $1/n$ reinforce the idea that adsorption probably occurs on multiple layers, which is a clear evidence of primarily a physical adsorption mechanism.

Kinetic Characterization of the Adsorption

As mentioned before, in previous experiments it was verified that the equilibrium for the system under study was reached after 60 min stirring time. In this context, an appropriate kinetic model was required to quantify the changes in the adsorption rate of SD-RB with time. For this task two models were tested. First, the Lagergren equation (pseudo first-order) (Eq. (5)) was applied (23):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{5}$$

where q_e is the amount of solute adsorbed at equilibrium (mol g^{-1}), q_t is the amount of solute adsorbed at time t (mol g^{-1}) and k_1 is the overall rate constant.

The application of this model to the data obtained for the adsorption of RB (as ionic-pair) by PUF provided a plot with a correlation coefficient lower than 0.90. Besides, the model presented a poor predictive capacity for the values of q_t and q_e, indicating that it can not be applied to describe the adsorption kinetics of the solute by PUF. It was also verified that, in the application of the pseudo first-order model, experimental data deviated from linearity only after 25 min stirring time, a behavior already reported in the literature for the retention of cationic dyes by other adsorbents (30,32,39). Therefore, a pseudo second-order model (40) was tested. This model can be described by Eq. (6):

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} t \tag{6}$$

where q_e and q_t represent the same amounts (mol g^{-1}) previously described and k_2 is the overall pseudo-second order rate constant.

According to this model, if the adsorption process follows a pseudo second-order kinetics a linear relationship between t and t/q_t should be verified. As can be seen in Fig. 5, a linear fit with excellent correlation ($r = 0.9998$) was obtained by applying a pseudo second-order kinetics model to the present case. Also, the value of q_e predicted by the model was only 4.3% higher than that observed in the experimental work, which confirmed the satisfactory predictive capacity of the pseudo second-order model. The pseudo second-order rate constant, calculated from linear fit

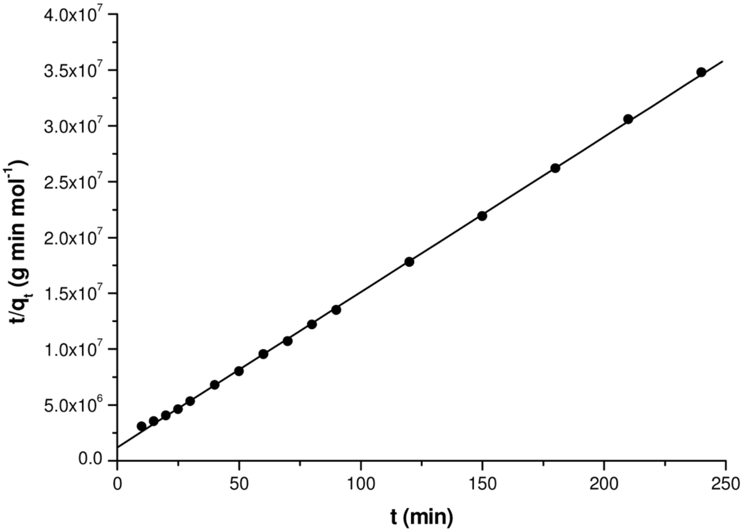

Figure 5. Pseudo-second order plot for the kinetic modeling of SD-RB adsorption by PUF. RB $= 1.0 \times 10^{-5}$ mol L^{-1} and SDS $= 7.0 \times 10^{-5}$ mol L^{-1}.

parameters, was equal to 1.60×10^4 L min^{-1} mol^{-1}. Analyzing the results obtained in the kinetics study, it was possible to conclude that the whole adsorption process was governed by a pseudo second-order kinetics.

A mechanistic study was also carried out by testing the Morris-Weber and Reichenberg models for the system under study. According to Morris-Weber model (Eq. (7)), if a straight line passing through the origin is obtained when plotting $t^{1/2}$ against q_t, a diffusion process (intraparticle or film diffusion) can be assumed as the rate controlling step of the adsorption process (41). The model considers that there is a linear relationship between the uptake and the square-root of time and that the slope of the linear plot is the diffusion rate constant, as follows:

$$q_t = k_d\ t^{1/2} + C \tag{7}$$

where q_t (mol g^{-1}) is the amount of solute sorbed at time t (min), K_d is the rate constant of intraparticle transport (mol g^{-1} min$^{-1/2}$), and C (mol g^{-1}) is the intercept.

Once verified if a diffusion process controls the adsorption rate, the application of the Reichenberg model (Eq. (8)) allow the verification of intraparticle or film diffusion (or both) as rate-limiting processes in the adsorption of the solute (42).

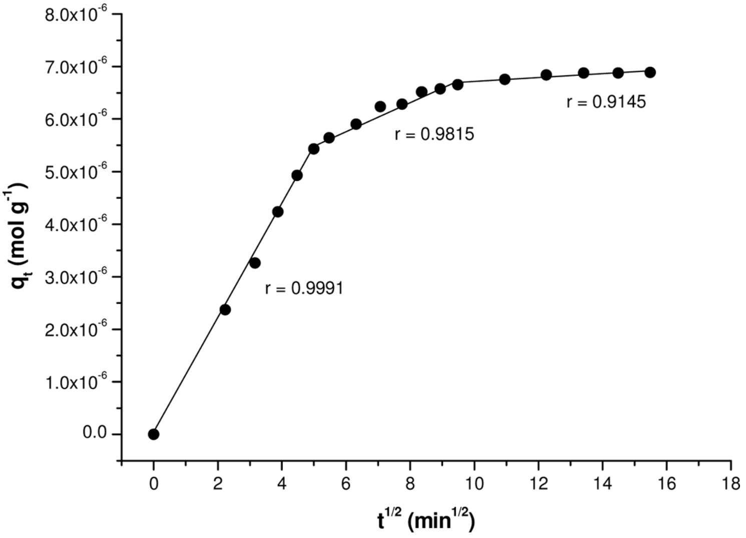

Figure 6. Morris-Weber plot for the SD-RB adsorption by PUF. RB = 1.0×10^{-5} mol L^{-1} and SDS = 7.0×10^{-5} mol L^{-1}.

$$Bt = -2.303 \log(1 - F) - 0.4977$$

where Bt is the Reichenberg parameter and F represents the ratio qt/qe.

As can be seen in Fig. 6, the application of the Morris-Weber model to the data obtained for the adsorption of SD-RB by PUF provided a multilinear plot with three well-defined regions. It is important to notice that similar behavior has been observed in several studies about the adsorption of cationic dyes by other solid phases (14,34,43–45). This result proved that a diffusion process regulates the adsorption rate of RB (in fact SD-RB ionic-pair) by PUF. The Reichenberg equation was then employed to check that adsorption proceeds via film diffusion or intraparticle diffusion mechanism (Fig. 7).

In the first region, which comprises the time interval between 0 and 25 min, the adsorption rate seems to be controlled only by an intraparticle diffusion process, since straight lines passing through the origin were verified in the application of both Morris-Weber (r = 0.9991) and Reichenberg models (r = 0.9976). Such observation can be assumed as a natural behavior for the system, since in the beginning of the adsorption process the amount of solute on the solid surface is low, resulting in a low velocity for the intraparticle diffusion.

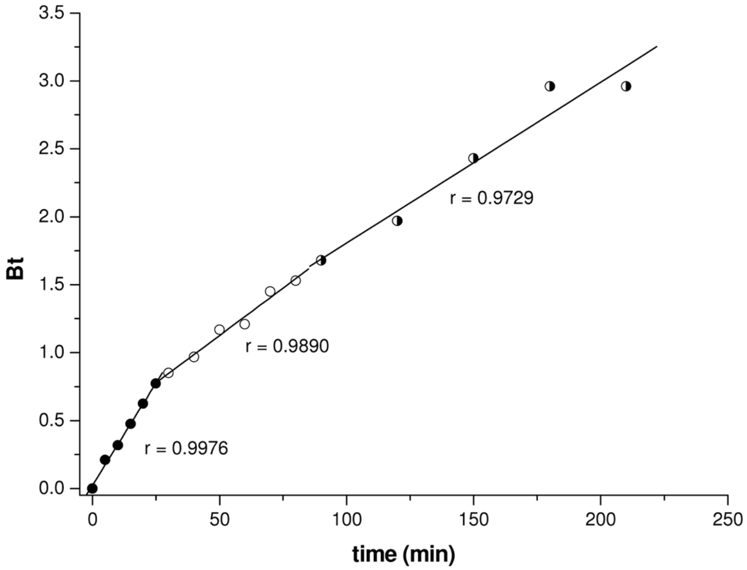

Figure 7. Reichenberg plot for the SD-RB adsorption by PUF. $RB = 1.0 \times 10^{-5}\,mol\,L^{-1}$ and $SDS = 7.0 \times 10^{-5}\,mol\,L^{-1}$.

The application of the Morris-Weber model to the time range of 25–90 min also yielded a good linear fit (r = 0.9815). However, the slope of the straight line decreased and the line did not pass through the origin anymore, indicating that, although intraparticle diffusion could be still active in the control of the adsorption rate, other processes like film diffusion could also play an important role. This hypothesis was confirmed by the application of the Reichenberg model to the data. In this case, a straight line (r = 0.9885) was obtained, confirming that intraparticle diffusion occur. However, in the same way as the Morris-Weber plot, the straight line did not pass through the origin, evidencing that film diffusion also contributes to the regulation of the adsorption rate.

Finally, from 90 to 240 min, an equilibrium region was verified, which was characterized by the occurrence of a linear plot almost parallel to $t^{1/2}$ axis. In this region, the intraparticle diffusion process was considered less active, probably due to the low solute concentration in the liquid phase and the film diffusion seems to be the most important mechanism. This was confirmed by the application of the Reichenberg model to the data of this region. Again, a linear plot (r = 0.9729) that does not pass through the origin was obtained. This fact indicated that intraparticle diffusion was still regulating the adsorption rate but together with film diffusion process.

Thermodynamic Characterization of Adsorption

Temperature plays an important role on the adsorption processes. Therefore, its influence on the adsorption of SD-RB by PUF was evaluated. The study consisted in the stirring, for 240 min, of 200 mL of a 1.0×10^{-5} mol L^{-1} dye solution containing 2.5×10^{-4} mol L^{-1} SDS between 25 and 60°C. The results obtained in this experiment (Fig. 8) indicated that the increase of temperature resulted in an increase of the adsorption efficiency, probably due to the increase of kinetic energy of the solute molecules, which increased the number of effective shocks between such molecules and the solid phase. From data obtained in this experiment, it was possible to characterize the adsorption process from the thermodynamic point of view. For this purpose, the Vant'Hoff equation (Eq. (9)) was applied in order to derive enthalpy and entropy variations (ΔH and ΔS, respectively). The equilibrium constant, K_c, was calculated for each temperature experimented by using Eq. (10).

$$\log K_c = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \quad (9)$$

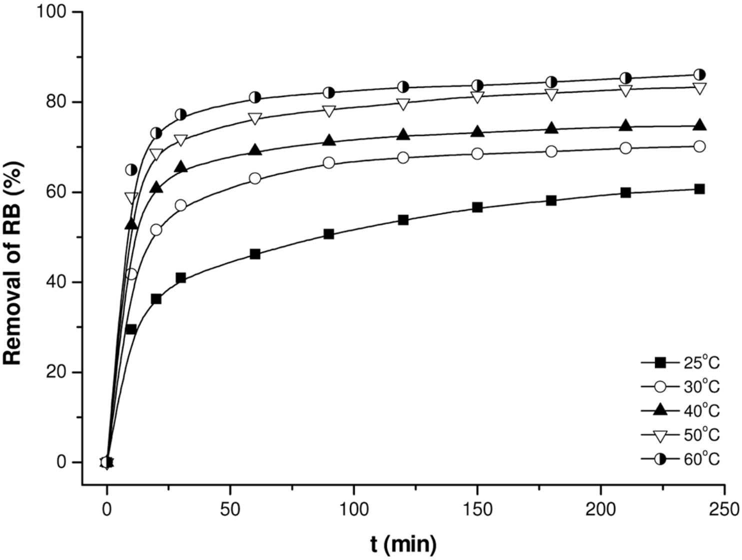

Figure 8. Effect of the temperature on the extraction of SD-RB by PUF. In all cases, RB and SDS concentrations were 1.0×10^{-5} and 7.0×10^{-5} mol L^{-1}, respectively.

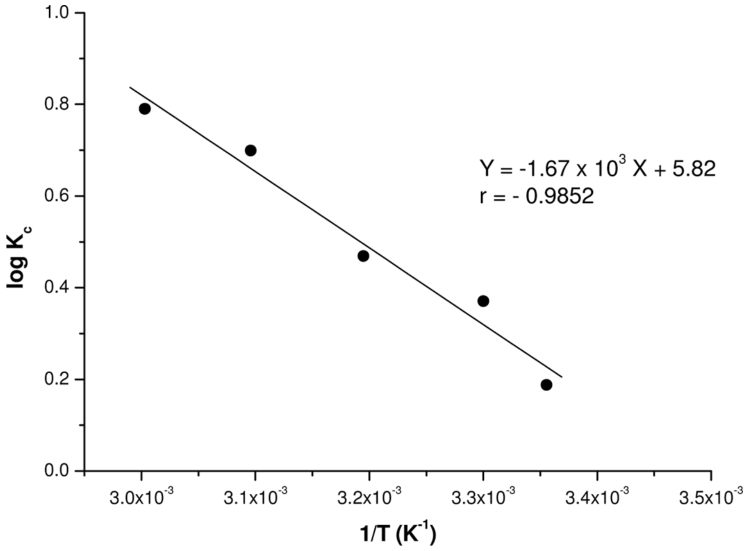

Figure 9. Plot of Vant' Hoff equation for the system under study using experimental data obtained in the evaluation of the effect of temperature. K_c was always calculated employing C_e and q_e at 240 min.

$$K_c = C_{ads}/C_e \tag{10}$$

where C_{ads} is the amount of solute adsorbed onto PUF at equilibrium ($mol\,g^{-1}$) and C_e is the concentration of the solute in solution ($mol\,L^{-1}$) in the same condition.

Enthalpy and entropy variations for the adsorption were estimated from angular and linear coefficients of the linear fit obtained from the plot of 1/T (T in K) versus log K_c (Fig. 9). The equation obtained was $\log K_c = -1.67 \times 10^3 \ 1/T + 5.82$ with a correlation coefficient $r = -0.9852$. Afterwards, a variation of the Gibbs free energy (ΔG) for the adsorption process was calculated by using Eq. (11):

$$\Delta G = \Delta H - T\Delta S \tag{11}$$

where T is the absolute temperature (in K).

The estimated values of ΔH and ΔS were $32.0 \pm 3.1\,kJ\,mol^{-1}$ and $111 \pm 10\,J\,mol^{-1}\,K^{-1}$, respectively. Substituting these values in Eq. (10) and taking into consideration a temperature of 298 K, a ΔG of $-1.08\,kJ\,mol^{-1}$ was obtained. The negative value of ΔG (at 298 K) indicated that the adsorption process is spontaneous, while the positive value of ΔH showed that it is endothermic. This behavior was compatible with the experimental observation, since increasing the adsorption efficiency of SD-RB was noted with the increase of temperature. Also, the magnitude of ΔH indicates that the adsorption of SD-RB ionic-pair by PUF is carried out through a physical process (45), corroborating the hypothesis raised when the Freundlich isotherm was applied to the system. The positive value of ΔS evidenced an entropy increase for the adsorption process. Although this behavior has not been expected, since the adsorption process involves a considerable loss of degrees of freedom, it can be explained by the increase of the kinetic energy of the molecules which remained in solution with increasing temperature. This phenomenon probably compensated the entropy decreasing due to adsorption.

Sequential Extraction

Another approach evaluated with the system was to perform color removal in multiple consecutive steps, similarly to a liquid-liquid extraction process. For this purpose, a solution containing $1.0 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ RB and $7.0 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ SDS was stirred with PUF cylinders, sequentially. The changes of the PUF cylinders were performed in 30 and 60 min time intervals and the results obtained in this experiment are shown in Fig. 10. As can be seen in Fig. 10a, an adsorption percentage of 95.8% was obtained after six consecutive extractions of 30 min with foam cylinders, which corresponds to an extraction procedure of 3 h. In turn, by changing the PUF plugs in a 60 min time interval it was possible to remove 95.4% after 4 h experiment, which corresponds to four changes of the adsorbent.

Sequential extraction was modeled in order to allow the prediction of the adsorption percentage in relation to the number of extractions. For this task, the number of extractions was plotted versus $-\log C_N$, for different step times. In this case, a straight line passing through $-\log C_o$ was obtained (Fig. 10b). Then, the model equation was assumed as shown in Eq. (12):

$$-\log C_N = K_N N - \log C_o \qquad (12)$$

where C_o is the initial concentration of the solute in solution, C_N is the concentration of the solute in solution after N extractions, and K_N is a constant dependent on the time interval of each step.

For the present case K_N was determined for 30 and 60 min time intervals and it presented values of 0.234 and 0.330, respectively. Additionally,

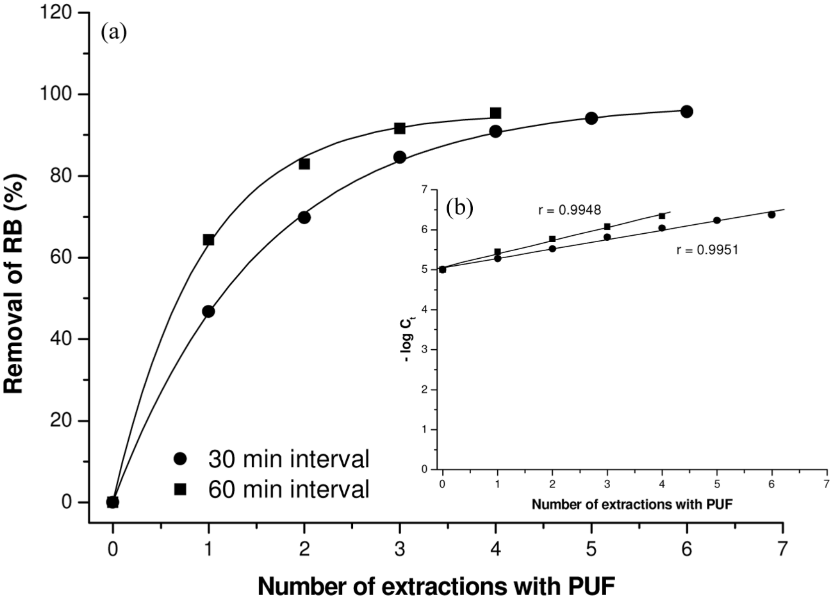

Figure 10. Adsorption of RB employing sequential extraction approach by changing PUF cylinders in 30 and 60 min time interval. (a) Adsorption efficiency in relation to the number of extraction steps employed and (b) Modeling of the sequential extraction approach.

substituting Eq. (10) in Eq. (1) and rearranging, we have Eq. (13):

$$\log(100 - \mathrm{R}(\%)) = \mathrm{K_N N} + 2 \tag{13}$$

Using Eq. (13) it is possible to predict the percentage of adsorption as a function of the number of extractions carried out with PUF cylinders and the time passed between each change of adsorbent.

CONCLUSIONS

The results obtained in this study proved that polyether type polyurethane foam can be employed as an effective sorbent for the removal of Rhodamine B from waters. In this case, the formation of the hydrophobic ionic-pair between dye and surfactant, which have high affinity by PUF, showed to be essential for the adsorption process. Higher removal efficiency was verified when the SDS molar concentration was seven times higher than RB because, in this situation, the formation of the ionic-pair is enhanced. The maximum adsorption capacity of 6.85×10^{-6} mol RB g^{-1} was observed at 25°C when the adsorption was performed in 200 mL of a solution containing 1.0×10^{-5} mol L^{-1} RB. However, the increase of the initial concentration of the dye in solution caused an increase in the removal efficiency, being possible to retain 1.61×10^{-5} mol RB g^{-1} when 200 mL of a 2.0×10^{-5} mol L^{-1} RB solution was tested. The adsorption kinetics followed a pseudo-second order model and, according to the Morris-Weber and the Reichenberg models, film diffusion and intraparticle diffusion processes were active in the control of the adsorption rate. The amount of dye sorbed increased with the increase of temperature, indicating that adsorption is an endothermic process.

Sequential extraction experiments showed that it is possible to achieve enhanced removal efficiency of the dye only by changing the polyurethane foam cylinders before the equilibrium is reached. Around 96% of the dye present in 200 mL of a 1.0×10^{-5} mol L^{-1} RB solution was removed after six consecutive step extractions of 30 min with 200 mg PUF cylinders or after four consecutive extraction steps of 60 min.

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