

Contents lists available at ScienceDirect

Journal of Hazardous Materials



journal homepage: www.elsevier.com/locate/jhazmat

Polyurethane foam loaded with SDS for the adsorption of cationic dyes from aqueous medium: Multivariate optimization of the loading process

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ARTICLE INFO

Article history: Received 13 November 2008 Received in revised form 6 January 2009 Accepted 7 January 2009 Available online 19 January 2009

Keywords: Polyurethane foam Adsorption Cationic dyes Multivariate optimization

ABSTRACT

This paper reports the development of a new procedure for the adsorption of four cationic dyes (Rhodamine B, Methylene Blue, Crystal Violet and Malachite Green) from aqueous medium employing polyurethane foam (PUF) loaded with sodium dodecylsulfate (SDS) as solid phase. PUF loading process was based on the stirring of 200 mg PUF cylinders with acidic solutions containing SDS. The conditions for loading were optimized by response surface methodology (RSM) using a Doehlert design with three variables that were SDS and HCl concentrations and stirring time. Results obtained in the optimization process showed that the stirring time is not a relevant parameter in the PUF loading, evidencing that the transport of SDS from solution to PUF surface is fast. On the other hand, both SDS and HCl concentrations were important parameters causing significant variation in the efficiency of the resulting solid phase for the removal of dyes from solution. At optimized conditions, SDS and HCl concentrations were 4.0×10^{-4} and 0.90 mol L⁻¹, respectively. The influence of stirring time was evaluated by univariate methodology. A 20 min stirring time was established in order to make the PUF loading process fast and robust without losing efficiency. The procedure was tested for the removal of the four cationic dyes from aqueous solutions and removal efficiencies always better than 90% were achieved for the two concentrations tested (2.0×10^{-5} and 1.0×10^{-4} mol L⁻¹).

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1. Introduction

Discharge of dyes into natural water bodies represents a serious problem, since highly colored effluents can disturb aquatic life present in this compartment by decreasing sunlight penetration and/or even leading to direct poisoning of living organisms [1-3]. This problem is enhanced because some dyes cannot be degraded by chemical or photochemical processes and presents intrinsic non-biodegradability [4,5]. So that, in these cases, alternative procedures must be employed for the elimination of such dyes before disposal. Undoubtedly, in this field, the study and development of adsorption techniques is a very interesting approach, especially when solid adsorbents are cheap and commercially available. Because of their intense use in several industrial areas, cationic dyes can be considered an important class of compounds to be studied from this point of view. This statement is reinforced by the verification that current literature reports several works regarding the application of solid materials for the adsorption of cationic (or basic) dyes present in aqueous solutions [6-16]. Different materials have been applied for the adsorption of different cationic dyes. In this universe, only one work, developed by our research group, relates the application of polyurethane foams (PUF) for this purpose [17]. However, in such work, a surfactant is added to the effluent solution instead of using modified PUF, a more adequate approach.

According to Bowen [18], PUF can be applied for the solid phase extraction of different substances because of the presence of polar and non-polar groups in their structures. Some few papers describe the use of untreated polyurethane foams for the adsorption of hydrophobic substances through a mechanism similar to a liquid–liquid solvent extraction [19–24]. On the other hand, the use of loaded PUF has provided extraction procedures with higher velocity and selectivity. In fact, this approach has mostly been employed for the solid phase extraction of metallic cations in analytical procedures with PUF being used as solid support for organic reagents [25–27].

The optimization of experimental procedures has suffered a remarkable change in last few years. Nowadays, most times, researchers prefer to employ multivariate procedures instead of laborious univariate processes. The main advantages of the use of multivariate methods are the necessity of fewer experiments, reducing cost and time, and the possibility to obtain information about interaction between variables, which is not possible in univariate optimization. Most popular multivariate strategies are based on response surface methodology (RSM), which is a

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^{0304-3894/\$ -} see front matter © 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2009.01.033

multivariate technique that fits, mathematically, the experimental domain in the theoretical design by use of a response function [28,29]. In this field, second-order designs like Central Composite, Box–Behnken or Doehlert matrix have been employed to establish the mathematical relationship (model) among factors (experimental variables in the levels tested) and experimental response [30]. As mentioned before, a great advantage of these designs is the small number of experiments required to build the models.

Doehlert designs are characterized by their high efficiency value. It means that, by applying this design, a low number of experiments is required to obtain an equation (model) with high number of coefficients. [31]. Because of this feature, Doehlert designs have been extensively used in the optimization of diverse chemical procedures like sample preparation for analysis [32,33], establishment of operational conditions in electrothermal atomic absorption spectrometry [34–36], solid phase extraction of metallic cations [37,38] and establishment of chromatographic conditions [39,40]. However, any work about the optimization of solid phase preparation using Doehlert or any other design was not found.

The aim of this work was to perform the multivariate optimization of the loading process of PUF with sodium dodecylsulfate (SDS) for its use in the adsorption of cationic dyes from aqueous solution.

2. Materials and methods

2.1. Apparatus

Spectrophotometric measurements of all dye solutions were performed with a Femto 800XI UV-Vis spectrophotometer (São Paulo, Brazil) equipped with a 10-mm optical path quartz cuvette. The spectrophotometer was set at maximum absorption wavelength for each cationic dye evaluated (Methylene Blue, MB, at 664 nm; Crystal Violet, CV, at 586 nm; Malachite Green, MG, at 620 nm and Rhodamine B, RB, at 549 nm) and analytical curves were employed to determine dyes concentrations in solutions.

An Ika RW 20 DZM (Staufen, Germany) overhead stirrer with digital adjustment of speed was employed for loading and adsorption experiments. It was equipped with a stirrer arm made of stainless steel furnished by the manufacturer. Cylinders of PUF loaded with SDS were adjusted to this stirrer arm, as reported previously [41], in order to perform extraction of cationic dyes from aqueous solutions. The same setup was used for the loading of PUF by stirring the foam cylinders with SDS solutions.

2.2. Reagents

All reagents were of analytical grade and used without further purification. The solutions were always prepared with water purified in a Simplicity Milli-Q System (Millipore, Bedford, USA).

Stock solutions of the four cationic dyes with 1.00×10^{-3} mol L⁻¹ concentration were prepared by dissolving appropriate masses of each dye (all reagents were of analytical grade and provided by Vetec, Rio de Janeiro, Brazil) in around 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 the mark with water. These solutions were used for only one week, being discarded after this time. Solutions used in the experiments were prepared just before use by adequate dilution of the stock solutions.

A 1.00×10^{-3} mol L⁻¹ SDS stock solution was prepared by simple dissolution of 0.144 g SDS (Vetec, Rio de Janeiro, Brazil) in around 100 mL water. After total dissolution of the solid and decrease of the foam formed during this process, the mixture was transferred to a 500 mL volumetric flask and the volume was made up to the mark. Solutions employed in the optimization of the loading procedure were prepared just before use by dilution of the stock solution according to desired concentration.

Open cell polyether type polyurethane foam with 0.017 g cm⁻³ density (Ortobom, Brazil) was used throughout the experimental work. It was employed without previous treatment. PUF cylinders had 3 cm diameter and 2 cm thickness and they were cut with a leather cutter [41].

2.3. Procedure for PUF loading with SDS

The loading procedure consisted of the stirring (at 200 rpm) of a PUF cylinder $(200 \pm 10 \text{ mg})$ with a SDS solution containing known concentrations of HCl during a time previously established. The concentrations of SDS and HCl as well as the stirring time were those established in the experimental planning built up following a Doehlert design. Just after stirring with acidic SDS solutions, all cylinders were squeezed between two filter paper sheets in order to eliminate the excess of liquid retained by the foam and dried at room temperature by 24 h. The conditions of each experiment are shown in Table 1. All experiments were carried out at laboratory ambient temperature, which was always maintained around 23 ± 1 °C, and a stirring speed of 200 rpm.

2.4. Procedure for the adsorption of cationic dyes

Methylene Blue was the cationic dye selected for the optimization of the loading procedure. The percentage of MB retained from a 5.00×10^{-5} mol L⁻¹ solution was the parameter used in the evaluation of the removal efficiency of each PUF cylinder loaded with SDS obtained in each experiment listed in Table 1. For the adsorption of MB, PUF cylinders loaded with SDS were stirred with 200 mL of MB solution using the same setup employed for loading process. The stirring speed was also maintained at 200 rpm. Concentrations of MB in solution were determined by spectrophotometry at 664 nm in time intervals previously established using analytical curve approach and the percentage of MB retained on PUF was calculated according to the following equation:

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

where *R* is the percentage of removal, C_0 is the initial concentration of MB in the solution and C_t is the MB concentration in the solution at time *t*. All these experiments were also carried out at laboratory ambient temperature and total stirring time of 240 min. Afterwards, PUF cylinders were loaded at optimized conditions and used for the adsorption of three other cationic dyes from aqueous solutions using the same strategy.

2.5. Optimization strategy

The optimization was performed using a response surface methodology. A Doehlert design was employed for the optimization of three experimental variables involved in the loading process of PUF with SDS: SDS concentration (S), HCl concentration (A) and stirring timer (t). According to the experimental design, SDS concentration was evaluated at five levels while HCl concentration and time were evaluated at seven and three levels, respectively. Response function (Y) was the removal efficiency of MB. The Doehlert design for these three variables is shown in Fig. 1, which resulted in the experiments described in Table 1. Experimental data were processed by using Excel for Windows software using a spreadsheet prepared exclusively for this purpose. All experiments were carried out in triplicate, being that the three values obtained in the central point were used to estimate experimental variance.

As usual, the experimental design is expressed in terms of coded values. In the case of the Doehlert for three variables, the coded values vary regularly from -0.817 to 0.817 for the variable with three levels, from -1 to 1 for the variable with five levels and from -0.866

Table 1

Experiments planned by Doehlert design for the optimization of the loading process of PUF with SDS and results obtained. Results are expressed as mean \pm standard deviation for three individual experiments, except in the central point, where individual results are shown.

| Experiment | Stirring time (min) | HCl concentration (mol L^{-1}) | SDS concentration (mol L ⁻¹) | MB removal efficiency (%) |
|------------|---------------------|-----------------------------------|--|---------------------------|
| 1 | 120(0) | 2.5 (0.866) | $3.5 	imes 10^{-4}$ (0.5) | 88.0±1.9 |
| 2 | 120 (0) | 1.3 (0) | $4.5 	imes 10^{-4}$ (1) | 91.3 ± 0.8 |
| 3 | 120 (0) | 0.10 (-0.866) | $3.5 	imes 10^{-4} (0.5)$ | 85.7 ± 1.4 |
| 4 | 120 (0) | 0.10 (-0.866) | $1.5	imes 10^{-4} \ (-0.5)$ | 52.9 ± 3.3 |
| 5 | 120 (0) | 1.3 (0) | $5.0 	imes 10^{-5} (-1)$ | 48.5 ± 4.8 |
| 6 | 120 (0) | 2.5 (0.866) | $1.5 	imes 10^{-4} \ (-0.5)$ | 80.3 ± 3.7 |
| 7a | 120 (0) | 1.3 (0) | $2.5 	imes 10^{-4}$ (0) | 86.2 |
| 7b | 120 (0) | 1.3 (0) | $2.5 	imes 10^{-4}$ (0) | 84.7 |
| 7c | 120 (0) | 1.3 (0) | $2.5 	imes 10^{-4}$ (0) | 84.4 |
| 8 | 210 (0.817) | 2.1 (0.577) | $2.5 	imes 10^{-4}$ (0) | 81.8 ± 3.9 |
| 9 | 210 (0.817) | 0.90 (-0.289) | $3.5 	imes 10^{-4} (0.5)$ | 88.2 ± 1.0 |
| 10 | 210 (0.817) | 0.90 (-0.289) | $1.5 	imes 10^{-4} \ (-0.5)$ | 79.4 ± 1.6 |
| 11 | 30 (-0.817) | 1.7 (0.289) | $1.5 	imes 10^{-4} \ (-0.5)$ | 78.9 ± 4.6 |
| 12 | 30 (-0.817) | 1.7 (0.289) | $3.5 	imes 10^{-4} (0.5)$ | 87.5 ± 1.0 |
| 13 | 30 (-0.817) | 0.50 (-0.577) | $2.5 	imes 10^{-4}$ (0) | 81.1 ± 3.4 |

Coded values of variables are shown between parentheses.

to 0.866 for the variable with seven levels [42]. The codification for the present work is also shown in Table 1. The relation between coded (C_i) and real values (X_i) can be obtained from the following expression:

$$C_i = \left(\frac{2(X_i - X_i^0)}{\Delta X_i}\right) \times \alpha$$

where X_i^0 is the real value at the center of the experimental domain, ΔX_i is the amplitude of variation of the real value, and α is equal to 0.866, 1 and 0.817 for the first (seven levels), second (five levels) and third factor (three levels), respectively.

2.6. Determination of the critical point

Second-order models like Doehlert design – when are built up with three experimental factors $(X_1, X_2 \text{ and } X_3)$ – can be represented by the following equation, which describes mathematically the response function (*Y*) [43]:

$$\begin{aligned} (Y) &= a + b(X_1) + c(X_2) + d(X_3) + e(X_1)^2 + f(X_2)^2 + g(X_3)^2 \\ &+ h(X_1)(X_2) + i(X_1)(X_3) + j(X_2)(X_3) \end{aligned}$$

where (Y) is the experimental response to be optimized, (a) is the constant term, (b), (c) and (d) are coefficients of the linear terms,



Fig. 1. Doehlert design with three variables for the optimization of SDS and HCl concentrations and stirring time of the PUF loading process.

(e), (f) and (g) are coefficients of the quadratic terms and (h), (i), and (j) are coefficients of interaction between the three factors.

In order to characterize the response function obtained and establish the second derivatives of this function, which made possible the calculation of the critical point coordinates (X_1^c, X_2^c, X_3^c), the Lagrange criterion was applied. According to this criterion, the response surface will present different characteristics depending on the values of Δ_1 , Δ_2 and Δ_3 , which are the determinants of the matrices obtained by derivation of the function *Y* according to the following:

$$\Delta_{3} = \begin{vmatrix} \left(\delta^{2}Y/\delta A^{2}\right) & \left(\delta^{2}Y/\delta B\delta A\right)^{2} & \left(\delta^{2}Y/\delta C\delta A\right)^{2} \\ \left(\delta^{2}Y/\delta A\delta B\right)^{2} & \left(\delta^{2}Y/\delta B^{2}\right) & \left(\delta^{2}Y/\delta C\delta B\right)^{2} \\ \left(\delta^{2}Y/\delta A\delta C\right)^{2} & \left(\delta^{2}Y/\delta B\delta C\right)^{2} & \left(\delta^{2}Y/\delta C^{2}\right) \end{vmatrix}$$
$$\Delta_{2} = \begin{vmatrix} \left(\delta^{2}Y/\delta A^{2}\right) & \left(\delta^{2}Y/\delta B\delta A\right)^{2} \\ \left(\delta^{2}Y/\delta A\delta B\right)^{2} & \left(\delta^{2}Y/\delta B^{2}\right) \end{vmatrix}$$
$$\Delta_{1} = \left| \left(\delta^{2}Y/\delta A^{2}\right) \right|$$

When $\Delta_2 = 0$, there is no information about the presence of relative maximum or minimum in the surface. On the other hand, relative maximum and minimum can be observed when $\Delta_1 < 0$, $\Delta_2 > 0$, $\Delta_3 < 0$ and $\Delta_1 > 0$, $\Delta_2 > 0$, $\Delta_3 > 0$, respectively. A saddle point is observed when none of the previous situations occur. Saddle point is defined as the critical point of a response surface that presents maximum response for levels of some variables and simultaneously minimum response for levels of other variables of the system [43].

Some preliminary evidence about the presence of maximum and minimum points in the response surface could be verified by analyzing the signals of the quadratic coefficients (e, f and g) in the polynomial function. When all these coefficients are negative, the function can show a maximum. On the other hand, when the coefficients are positive, the function can show a minimum. A saddle point is generally observed when some of them are positive and others are negative. Nevertheless, it is always necessary to verify these conclusions by applying the Lagrange criterion, which was done in this work [43].

The coordinates of the critical point (X_1^c, X_2^c, X_3^c) were calculated by solving the equations system: $\delta Y/\delta X_1 = 0$; $\delta Y/\delta X_2 = 0$ and $\delta Y/\delta X_3 = 0$. In the present case, since the response surface presented a maximum point, the levels of the variables found for the critical point were considered the optimum values for loading PUF with SDS in order to obtain maximum retention of MB. The same condi-

tions were used for loading PUF with SDS for retention of the others cationic dyes investigated.

3. Results and discussion

3.1. Optimization of PUF loading process with SDS

The use of polyurethane foam for the removal of cationic dyes from aqueous solutions containing SDS has already been described by our research group [17]. In that work, the formation of an ionicpair between dye and surfactant was of fundamental importance for successful extraction. However, the addition of SDS to solutions containing dye cannot be considered an adequate strategy for dye removal due to remaining surfactant concentration in solution. Therefore, as mentioned before, the present work aimed to develop a procedure for the removal of cationic dyes from aqueous solutions with foams loaded with SDS, avoiding the surfactant addition to solutions. The method is based on the loading of PUF with SDS in acidic medium. In this case, the formation of HSDS in acidic medium makes possible the extraction of SDS by PUF and its immobilization on solid phase surface. Subsequently, the treated foam can be agitated with aqueous solutions containing dyes and the formation of the ionic-pair between them and the surfactant takes place directly on the PUF surface.

In order to optimize the PUF loading process, SDS concentration, HCl concentration and stirring time employed for PUF loading were varied in the ranges of 5.0×10^{-5} – 4.5×10^{-4} mol L⁻¹, 0.1–2.5 mol L⁻¹ and 20–210 min, respectively, according to the experiments indicated by Doehlert design. Each PUF cylinder obtained was applied for the removal of MB from aqueous solutions containing 5.0×10^{-5} mol L⁻¹ of the dye and the removal efficiency was estimated in terms of percentage of dye extracted. This parameter was taken as response and maximum values for it were desired. Results obtained in the experiments are shown in Table 1. The data obtained were treated and resulted in the following equation for the model that describes the dependence of response (removal efficiency of MB) in relation to variables studied:

$$\begin{split} Y &= -0.619 + 3.74 \times 10^5 [\text{SDS}] - 3.80 \times 10^8 [\text{SDS}]^2 + 30.8 [\text{HCI}] \\ &- 3.17 [\text{HCI}]^2 + 0.076t + 1.54 \times 10^{-4}t^2 - 5.22 \times 10^4 [\text{SDS}] [\text{HCI}] \\ &- 2.26 \times 10^2 [\text{SDS}]t - 4.04 \times 10^{-2} [\text{HCI}]t. \end{split}$$

As can be noted, negative quadratic coefficients were verified for SDS and HCl concentrations and a positive one was obtained for stirring time. This result indicated that a surface without a defined maximum was obtained in the experimental design. As expected, the application of the Lagrange criterion indicated the occurrence of a surface with a saddle point. Although this behaviour, the coordinates of the critical point were identified, providing the values of 4.11×10^{-4} mol L⁻¹, 0.60 mol L⁻¹ and 135 min for SDS concentration, HCl concentration and stirring time, respectively.

The effect of each variable on the response was evaluated by analyzing the Pareto chart (Fig. 2), which shows the normalized effect of each variable. The effects must be always normalized because of the very different magnitude of the values set for each factor. As can be seen in Fig. 2, the effect of both SDS and HCl concentrations was statistically significant at a 95% confidence level, while the stirring time did not show any effect on the MB removal efficiency in the range of 30–210 min. This result could explain the appearance of a saddle point in the response surface, since the presence of the variable *stirring time* can distort the model because it does not present significant effect on response. The model obtained presented a correlation coefficient of 0.960 for the relation between predicted and observed values.



Effect Estimate (Absolute Value)

Fig. 2. Pareto chart of effects for the Doehlert design with three variables (SDS concentration, HCl concentration and stirring time).

In view of this result, a new calculation was run for the system but only taking into consideration the variables SDS and HCl concentration as shown in Fig. 3. The values used in this new design were those already obtained in the experiments for the first design. Stirring time considered for this new design was 120 min as set for the experimental planning initially considered. The equation obtained was then:

$$\begin{split} Y &= 4.78 + 3.63 \times 10^5 [\text{SDS}] - 3.80 \times 10^8 [\text{SDS}]^2 + 27.5 [\text{HCl}] \\ &- 3.17 [\text{HCl}]^2 - 5.22 \times 10^4 [\text{SDS}] [\text{HCl}]. \end{split}$$

This time, by applying the Lagrange criterion, it was verified that the response surface had a critical point with a well-defined maximum (Fig. 4). Also, excellent correlation coefficient was observed (0.999) for the new model, evidencing that it had a high predictive capacity. The optimum values of SDS and HCl concentrations indicated by calculation were 4.14×10^{-4} and 0.92 mol L^{-1} , respectively. Therefore, SDS and HCl concentrations used in all further experiments were 4.0×10^{-4} and 0.90 mol L^{-1} , respectively, and a new univariate experiment was performed in order to establish a convenient stirring time taking into consideration the velocity and robustness of the methodology.



Fig. 3. Doehlert design with two variables for the optimization of SDS and HCl concentrations in the PUF loading process. Stirring time was 120 min.



Fig. 4. Response surface for the relation between SDS and HCl concentrations.

The optimization of stirring time was carried out in a wider range by changing its value from 1 to 135 min. As can be seen in Fig. 5, the MB removal efficiency was almost constant (around 90%) from 10 to 135 min, indicating that the transport of SDS from liquid phase to PUF surface was really fast. Some decrease in the MB removal efficiency was noted only when the stirring time was lower than 10 min because, in this case, there was no enough time to promote the retention of remarkable amounts of SDS by PUF. As consequence, the formation of the ionic-pair on the foam surface was lower, which led to the verification of poorer removal efficiency. Therefore, in order to make the loading procedure faster and robust without losing efficiency, a stirring time of 20 min was established for the PUF loading process with SDS.

3.2. Use of PUF loaded with SDS for the removal of cationic dyes from aqueous medium

Once optimized conditions for PUF loading were established, the developed methodology was tested for the possible removal



Fig. 6. Removal efficiency obtained with unloaded PUF and SDS loaded PUF for solutions containing 2.0×10^{-5} mol L⁻¹ of dye.

of other cationic dyes from aqueous medium. This study was performed by using PUF cylinders already loaded with SDS for the extraction of Malachite Green, Crystal Violet, Rhodamine B and, again, Methylene Blue in aqueous medium containing dyes with 5.00×10^{-5} mol L⁻¹ concentration. The results were compared with those obtained after extraction with an unloaded PUF cylinder. As shown in Fig. 6, it was virtually impossible to achieve noticeable extraction efficiency of all cationic dyes tested with unloaded PUF. This occurred probably because there were no suitable interactions between PUF and the dyes. Also, it is important to consider that all cationic dyes evaluated present high solubility in water, which makes difficult their transfer to the hydrophobic PUF. Nevertheless, when PUF cylinders loaded with SDS were employed, extremely high removal efficiencies were achieved after 240 min stirring time. Removal rates varied between 94.1% for CV and 99.6% for RB. As explained previously, this probably occurred due to the formation of ionic-pairs between dves and SDS on PUF surface. How these ionic-pairs present low solubility in water, their retention by hydrophobic PUF was enhanced probably due to the formation of strong hydrophobic interactions between foam and solute. Results obtained also showed that the extraction of cationic dyes by loaded PUF is fast. Although the extraction experiments were carried out for 240 min, for all dyes maximum retention (equilibrium) was



Fig. 5. Influence of stirring time employed in the loading process on the removal efficiency of SDS loaded PUF. SDS and HCl concentrations in the loading were 4.0×10^{-4} and $0.90 \text{ mol } \text{L}^{-1}$, respectively. Adsorption experiments were performed with a $5.0 \times 10^{-5} \text{ mol } \text{L}^{-1}$ MB.



Fig. 7. Amount of each dye retained by unloaded and SDS loaded PUF from solutions containing different initial concentrations. RB = triangles, CV = circles, MB = squares and MG = diamonds.

Table 2

Mass of each dye adsorbed from solution with a 200 mg cylinder of PUF loaded with SDS after 240 min stirring time.

| Cationic dye | Mass of dye retained from solution (mg) | | |
|-----------------|--|----------------------------------|--|
| | $2.0 \times 10^{-5} \text{ mol } L^{-1}$ | $1.0\times 10^{-4}\ mol\ L^{-1}$ | |
| Rhodamine B | 1.8 | 8.7 | |
| Crystal Violet | 1.4 | 6.7 | |
| Methylene Blue | 1.1 | 5.1 | |
| Malachite Green | 1.3 | 6.4 | |

achieved after 60 min stirring, being that for some dyes like RB and MG, it was possible to reach this point just after 30 min stirring.

In order to evaluate the capacity of loaded PUF cylinders, the developed procedure was tested for the extraction of the dyes from solutions containing increased amounts of them. For this task, individual solutions of each dye containing $1.0 \times 10^{-4} \text{ mol } \text{L}^{-1}$ were submitted to the developed extraction procedure. As can be seen in Fig. 7, which compares the amount of solute retained per gram of PUF in the two different concentrations tested, even when dyes were present in concentrations as high as $1.0\times 10^{-4}\,mol\,L^{-1}$ it was possible to retain almost all solute present in the solution. It is important to remark that the amounts (in molg⁻¹) of each dye adsorbed onto SDS loaded PUF were proportional to initial dye concentration. This behaviour indicated that SDS loaded PUF presents great availability of active sites for the adsorption of this class of compounds. Table 2 presents the mass of each dye retained by the PUF cylinder from individual solutions containing 2.0×10^{-5} and 1.0×10^{-4} mol L⁻¹ of each dye.

4. Conclusions

The Doehlert design approach proved to be a rapid, economical, and efficient way of optimizing the experimental conditions for the PUF loading with SDS aiming the adsorption of cationic dyes from aqueous medium. Among variables studied, both SDS and HCl concentrations and the interaction between them presented remarkable effect on the SDS loaded PUF preparation. Removal efficiency was higher when SDS concentration was 4.0×10^{-4} mol L⁻¹ in a medium containing 0.90 mol L⁻¹ HCl. The PUF loading process with SDS showed to be very fast, being completed just after 10 min stirring, at optimized conditions.

After optimizing loading process, the procedure was applied to the extraction of four cationic dyes (Rhodamine B, Crystal Violet, Methylene Blue and Malachite Green) from aqueous solutions. It was tested with individual solutions containing 2.0×10^{-5} and 1.0×10^{-4} mol L⁻¹ of each dye, being obtained, always, removal efficiencies higher than 90%. The maximum removal of dyes from solution was attained just after 60 min stirring of each solution with treated foam cylinders. It is important to remark that unloaded PUF was not able to retain tested dyes, proving that the loading process is fundamental to achieve acceptable removal efficiencies in the adsorption of the cationic dyes chosen.

Acknowledgements

The authors are grateful to Fundação Carlos Chagas Filho de Apoio à Pesquisa do Estado do Rio de Janeiro (FAPERJ) and to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for providing grants, fellowships and financial supports.

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