



## Employment of polyurethane foam for the adsorption of Methylene Blue in aqueous medium

Eliene E. Baldez, Nicolle F. Robaina, Ricardo J. Cassella\*

Departamento de Química Analítica, Universidade Federal Fluminense, Outeiro de São João Batista s/n, Niterói/RJ 24020-150, Brazil

### ARTICLE INFO

#### Article history:

Received 3 January 2008

Received in revised form 8 February 2008

Accepted 19 February 2008

Available online 23 February 2008

#### Keywords:

Methylene Blue  
Polyurethane foam  
Adsorption

### ABSTRACT

This work presents a detailed study about the adsorption of Methylene Blue (MB) onto polyether type polyurethane foam (PUF). The adsorption process is based on the formation of a hydrophobic ionic-pair between cationic dye MB and dodecylsulfate anion (SDS), which present high affinity by PUF. Set-up employed in the study was built up by adjusting a 200 mg cylinder of PUF to the arm of an overhead stirrer. The system was characterized in relation to equilibrium, kinetic and thermodynamic aspects and it was modeled by employing Langmuir and Freundlich isotherms. Obtained results showed that the ratio between SDS and MB concentrations plays an important role on the adsorption process. According to Langmuir isotherm, a maximum adsorption capacity of  $7.20 \times 10^{-5}$  mol MB g<sup>-1</sup> was achieved when optimized operational conditions were employed. The adsorption rate seems to be regulated by an intraparticle diffusion mechanism. Adsorption process was spontaneous (negative  $\Delta G$ ) at ambient temperature and presented an endothermic characteristic (positive  $\Delta H$ ). Sequential extraction experiments were carried out by changing PUF plugs in 30 min time intervals and around 96% of the MB present in solution could be removed through consecutive extractions with six 200 mg PUF cylinders.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

Nowadays, the removal of chemical substances from aqueous medium is an important subject under industrial and environmental point of view. The application of the adsorption technique has assumed remarkable importance in the treatment of contaminated waters and effluents, especially if the adsorbent employed presents low cost and does not require any treatment before its utilization [1]. In this scenario, polyurethane foams (PUFs) can be considered suitable adsorbents for the retention of chemical substances, since they are cheap and can be used without any previous treatment. Besides, polyurethane foams present excellent chemical and thermal resistance, high efficiency and are easily found in the market [2].

Polyurethane foams are able to retain different classes of substances because of the presence of polar and non-polar groups in their structures. According to Bowen [3], polyurethane foams can be applied for the retention of free molecules with high polarizability such as aromatic compounds, metallic dithizonates or iodine, and large anions also with high polarizability. 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 [4–9]. Although the utilization of polyurethane foams in separation and/or preconcentration procedures has increased since the pioneering work of Bowen, only few research works report a full characterization of the adsorption process of organic and/or inorganic substances onto unloaded and/or loaded PUF [10–14].

From environmental point of view, the discharge of dyes into natural water bodies represents a serious problem because of their persistence and non-biodegradable characteristics [15]. 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 [16–18]. In order to avoid these problems, effluents containing dyes must be treated for their removal before disposal. For this task some processes can be employed like: (i) photochemical degradation, which is not an efficient process due to the high stability of most dyes in front of light and (ii) chemical or anaerobic digestion, which are not suitable for dyes elimination because their intrinsic resistance [19]. Therefore, the development of suitable adsorption techniques for the removal of dyes from aqueous medium becomes an interesting approach. Several solid materials have been recently used for the adsorption of basic (cationic) dyes [1,15,18,20–34] including MB [25–34]. Different experimental conditions were employed in these works as well as different cationic dyes were evaluated.

Methylene Blue is a basic (or cationic) dye employed in several industrial fields. Although its low toxicity, it can cause some specific

\* Corresponding author. Tel.: +55 21 2629 2222; fax: +55 21 2629 2143.  
E-mail address: [cassella@vm.uff.br](mailto:cassella@vm.uff.br) (R.J. Cassella).

harmful effects in humans such as heartbeat increase, vomiting, shocks, cyanosis, jaundice and tissue necrosis [35]. Once current literature does not cite any work regarding to the use of PUF for the adsorption of any cationic dye, including MB, this work aimed to develop and study a methodology for the adsorption of this dye using a monolithic plug of polyurethane foam. Also, a kinetic and thermodynamic characterization of the process was performed. 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 is advantageous since it eliminates the necessity of a filtration step to separate adsorbent from solution for measurement and allows the easy change of adsorbent plugs.

## 2. Materials and methods

### 2.1. Apparatus

Spectrophotometric measurements of MB–SDS solutions were performed with a Femto 800xi UV–vis spectrophotometer equipped with a 10-mm optical path quartz cuvette. The spectrophotometer was set at 664 nm, which is the wavelength where maximum absorption was observed for the MB–SDS ionic-pair.

An Ika RW 20 DZM overhead stirrer with digital adjustment of velocity was employed for adsorption experiments. It was equipped with a stirrer arm made of stainless steel furnished by the own manufacturer. Cylinders of PUF were adjusted to this stirrer arm in order to perform extraction of MB from solutions containing SDS (Fig. 1).

### 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).

A  $1.00 \times 10^{-3} \text{ mol L}^{-1}$  MB stock solution was prepared by dissolving 0.160 g of the reagent 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. This solution was stable for 1 week, at least.

A  $1.00 \times 10^{-3} \text{ mol L}^{-1}$  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

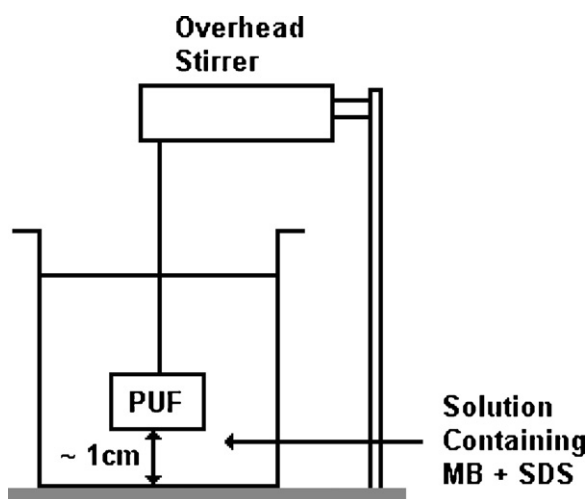


Fig. 1. Manifold employed for the adsorption studies of MB onto polyurethane foam in a medium containing sodium dodecylsulfate.

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.

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

Open cell polyether type polyurethane foam with  $0.017 \text{ g cm}^{-3}$  density (Ortobom, Brazil) was used throughout the experimental work. It was employed without previous treatment. PUF cylinders with 3 cm diameter were cut with a leather cutter [14].

### 2.3. General procedure

The experiments were carried out by stirring 200 mL of a solution containing known concentrations of MB and SDS with a cylinder of  $200 \pm 10 \text{ mg}$  of PUF adapted to the arm of the overhead stirrer. Concentration of MB in solution was determined by spectrophotometry at 664 nm in time intervals previously established. The percentage of MB retained on PUF was calculated according to the following equation:

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

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  $t$ . The stirring velocity was adjusted to 200 rpm, a value established during experimental work. All experiments were carried out at laboratory ambient temperature ( $25 \pm 2 \text{ }^\circ\text{C}$ ) except otherwise mentioned.

## 3. Results and discussion

The main goal of this work was to establish experimental conditions (chemical and instrumental) for maximum extraction of MB by PUF and to characterize the adsorption process. In order to achieve this goal, the influence of several extraction parameters on removal efficiency of MB (as ionic-pair with SDS) by PUF was investigated. The application of adsorption (Langmuir and Freundlich) and kinetic (Lagergren, second-order and Morris–Weber) models to the obtained data was performed as well as the determination of thermodynamic parameters.

### 3.1. Effect of SDS concentration

In this study, the effect of SDS concentration added to the solution on the removal of the dye was evaluated. It was performed taking into account that the substance sorbed onto PUF is the ionic-pair formed from the association of the cationic dye MB with the anionic surfactant SDS, according to the equilibria shown in Fig. 2. In the experiment a MB concentration of  $5.0 \times 10^{-5} \text{ mol L}^{-1}$  was maintained constant while the concentration of SDS was varied from 0 to  $5.0 \times 10^{-4} \text{ mol L}^{-1}$ , which caused a variation of the ratio  $[\text{SDS}]/[\text{MB}]$  from 0 to 10. As can be seen in Fig. 3A, a strong increase in the percentage of dye extracted from solution was observed when SDS concentration was increased to  $2.5 \times 10^{-4} \text{ mol L}^{-1}$ . For SDS concentrations higher than this value the percentage of MB removed from solution was practically constant, indicating that the process became independent of SDS concentration in solution. These observations are summarized in Fig. 3B that was built up taking into consideration the percentage of dye retained after 240 min agitation. The explanation for this behaviour is probably associated to the equilibrium between MB and MB–SDS species in the aqueous medium. For lower SDS concentrations, the conversion of hydrophilic MB into its respective hydrophobic ionic-pair is not favoured, while the increase of SDS concentration enhances

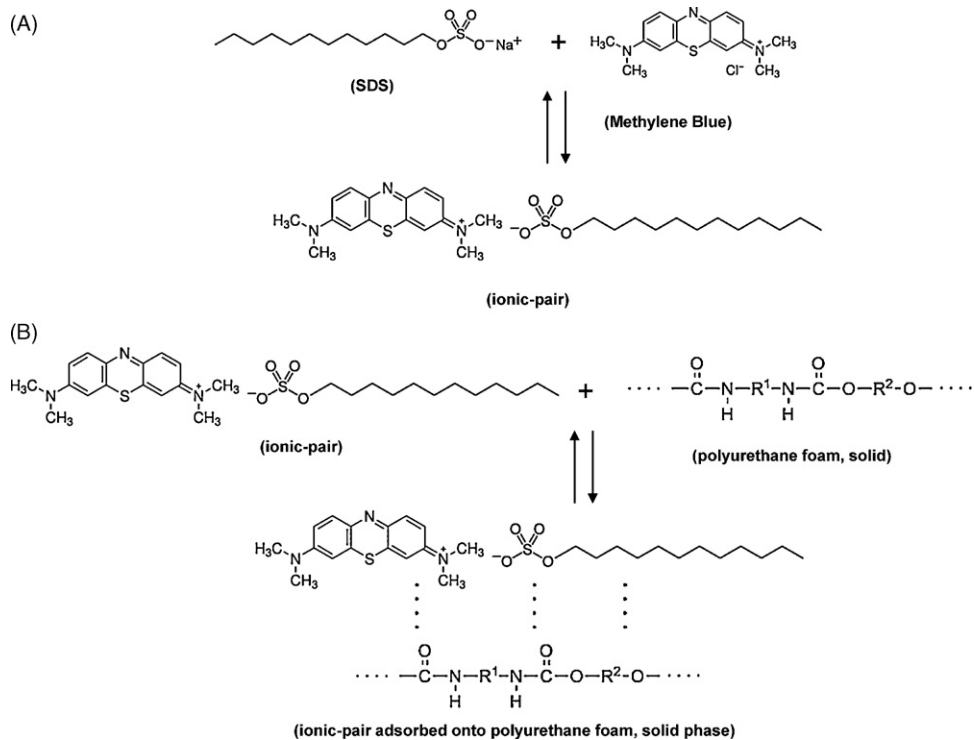


Fig. 2. Scheme of the equilibria involved in the adsorption process studied. (A) Formation of the ionic-pair and (B) adsorption.

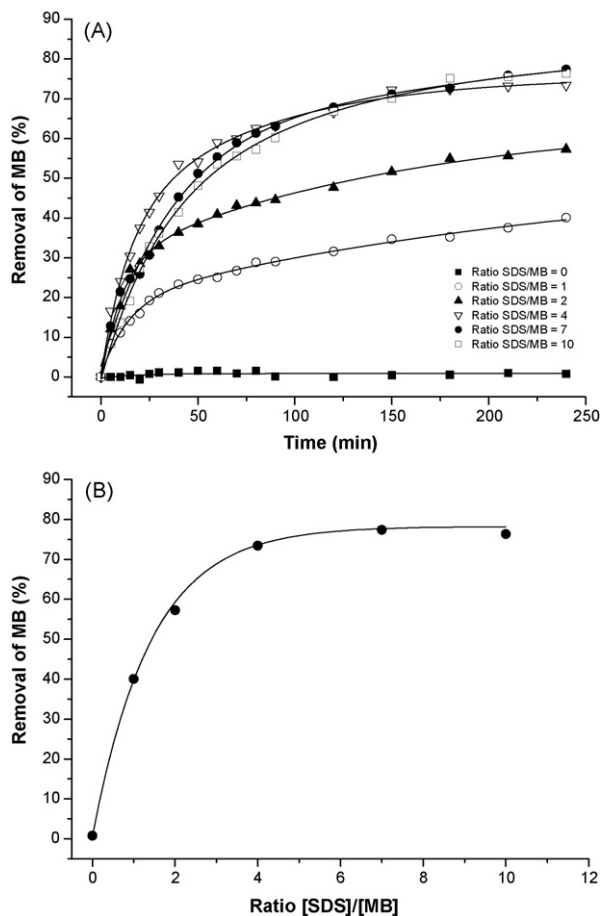


Fig. 3. Effect of the ratio between SDS and MB concentrations on the removal of MB from aqueous solution (MB concentration was  $5.0 \times 10^{-5} \text{ mol L}^{-1}$ ). Stirring time = 240 min.

this conversion by displacing the equilibrium in the direction of MB–SDS formation. Once PUF is able to retain, preferentially, more hydrophobic species [3], the percentage of removal is increased. It is important to remark that the adsorption of MB alone was null, which evidenced that adsorption process was strongly dependent on the formation of the ionic-pair and must follow a solvent-like extraction mechanism with the PUF acting as a polymeric extractant. This behaviour was already reported for PUF [36–40]. A SDS concentration five times higher than MB concentration was established for all further experiments in order to achieve maximum retention of the solute by PUF.

### 3.2. Equilibrium studies

The relation between removal of MB as ionic-pair and stirring time was investigated in order to evaluate the removal rate of MB from solutions containing different concentrations of the solute. This experiment was carried out for MB concentrations in a range of  $2.5 \times 10^{-5}$ – $1.0 \times 10^{-4} \text{ mol L}^{-1}$ . In all experiments SDS concentration added was five times higher than MB concentration and a fixed adsorbent amount (200 mg/200 mL) in the test solution was applied for 240 min stirring time. Highest removal percentages were obtained (Fig. 4) for solutions containing lower concentrations of MB, evidencing that the adsorption efficiency of PUF decreased with the increase of initial MB concentration. In spite of this fact, the amount of MB adsorbed per unit of mass of adsorbent increased with the increase of MB concentration in the test solution (Fig. 5). For solute concentrations of  $2.5 \times 10^{-5}$  and  $5.0 \times 10^{-5} \text{ mol L}^{-1}$ , maximum removal was observed after 180 min stirring time. On the other hand, for MB concentrations of  $7.5 \times 10^{-5}$  and  $1.0 \times 10^{-4} \text{ mol L}^{-1}$  equilibrium was attained only at 240 min stirring time.

Three steps were taken into consideration for the adsorption mechanism of MB–SDS ionic-pair by PUF. In the first step, it is necessary that MB–SDS ionic-pair present in solution achieve the

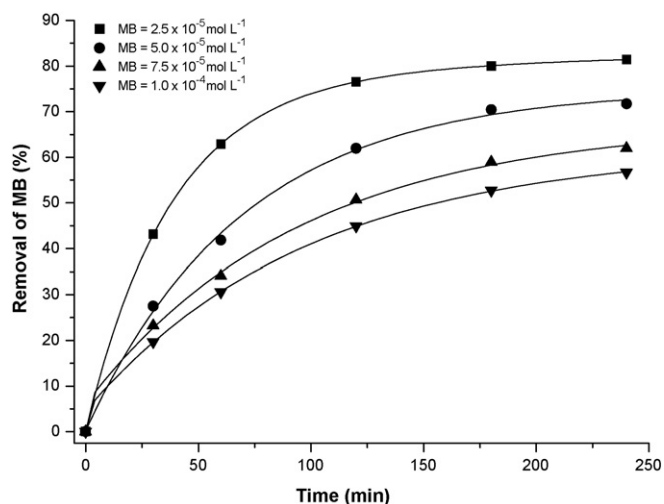


Fig. 4. Effect of initial concentration of MB on the removal percentage. SDS concentration was always five times higher than that of dye.

boundary layer film onto PUF surface. This process can be considered highly dependent on the effective shock between solute molecules and the adsorbent, being greatly enhanced by convenient agitation, which breaks the concentration gradient along the solution, increasing the probability of solute molecules to encounter the adsorbent surface. Secondly, the solute adsorbed onto film must diffuse through boundary layer film until the adsorbent surface, in a process called film diffusion. Finally, the last step considered was the diffusion of the solute into the porous structure of the PUF, in a process called intraparticle diffusion. In order to complete this whole process, in most cases, relatively long contact times are required.

As mentioned before, the first process is dependent on the agitation speed, which is controlled by the rotation of the overhead stirrer. Therefore, the influence of this parameter was investigated by varying the rotation speed of the overhead stirrer between 100 and 400 rpm. An increase of 32% in the removal efficiency of MB was verified when stirring speed was increased from 100 to 200 rpm and remained almost constant for values higher than 200 rpm. Similar behaviour was reported by Crini et al. [23] in the adsorption of the cationic dye Malachite Green by a cyclodextrin-based adsorbent. According to them, the increase in agitation speed causes a reduction in the number of particles surrounding film boundary layer,

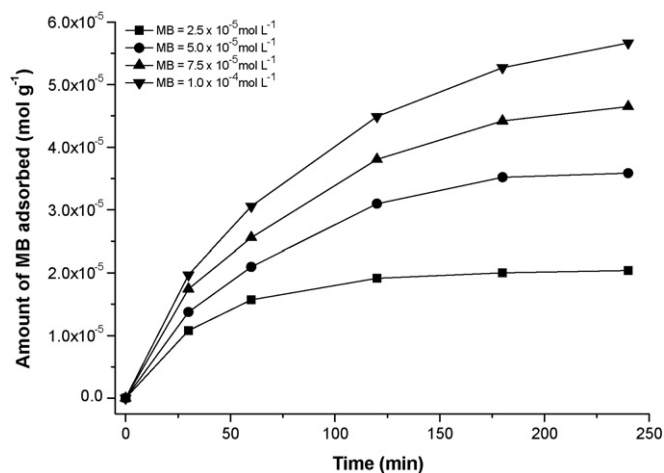


Fig. 5. Effect of the initial concentration of MB on the amount of dye removed from solution. SDS concentration was always five times higher than that of dye.

which increases the external film transfer coefficient, and hence the adsorption capacity. Obviously, this process is limited by adsorption capacity of the material, which could explain the stabilization of the removal efficiency for agitation velocities higher than 200 rpm. Therefore, a stirring speed of 200 rpm was utilized in all further experiments.

### 3.3. Adsorption isotherms

Adsorption systems can be modeled by application of equilibrium adsorption isotherms, which provide a convenient mathematical description of the adsorption capacity after equilibrium is reached. Also, the equations of such isotherms allow the comparison of different adsorption systems operated at different experimental conditions. A number of different isotherms are reported in the current literature. However, the most employed are Langmuir and Freundlich isotherms.

Langmuir isotherm takes into consideration that adsorption occurs on uniform surface containing sites with equivalent adsorbing capacity in relation to solute. This isotherm also considers that adsorption occurs on a monolayer [22]. Therefore, for a system in which only the solute is significantly adsorbed onto the solid surface, the Langmuir isotherm can be written as

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (2)$$

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

The application of the Langmuir isotherm to the present system yielded a linear fit when  $C_e$  was plotted against  $C_e/C_{ads}$ . The equation obtained was  $C_e/C_{ads} = [1.39 \times 10^4 \pm 1.12 \times 10^3] C_e + [0.185 \pm 0.030]$ ,  $r = 0.9979$ . From this equation it was possible to calculate the parameters  $Q$  and  $b$  that were  $7.20 \times 10^{-5} \text{ mol g}^{-1}$  and  $2.57 \times 10^3 \text{ L mol}^{-1}$ , respectively. From  $Q$  value in  $\text{mol g}^{-1}$  it was possible to estimate a maximum adsorption capacity of MB by PUF as  $20.4 \text{ mg g}^{-1}$ , which is in the capacity range reported for other materials [27–34].

Freundlich isotherm is an empirical equation commonly employed to model heterogeneous systems. It has been successfully utilized to model adsorption processes in solution [41]. The equation of Freundlich isotherm can be written as

$$C_{ads} = K_F C_e^{1/n} \quad (3)$$

where  $C_{ads}$  is the amount of solute retained on the adsorbent,  $C_e$  is the solute concentration in solution after equilibrium is reached and  $K_F$  and  $1/n$  are isotherm parameters related to adsorption extension and the degree of nonlinearity between solution concentration and adsorption, respectively. Freundlich isotherm is usually applied in its linearized form:

$$\log C_{ads} = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

For the present case, a linear fit ( $\log C_{ads} = [0.454 \pm 0.021]$ ,  $\log C_e - [2.26 \pm 0.10]$ ,  $r = 0.998$ ) was verified when  $\log C_e$  was plotted against  $\log C_{ads}$ , indicating that the system can be conveniently modeled by Freundlich isotherm. The related adsorption parameters  $K_F$  and  $1/n$  were found to be  $5.46 \times 10^{-3} \text{ mol g}^{-1}$  and 0.454, respectively.

### 3.4. Kinetic characterization of the adsorption

As mentioned before, in previous experiments it was verified that the adsorption equilibrium for the system under study was reached after 180 min stirring time when solute was found at low concentrations. In this context, an appropriate kinetic model was required to quantify the changes in the adsorption rate of MB–SDS with time. For this task two models were tested. Firstly, the first-order Lagergren equation (Eq. (5)) was applied to adsorption kinetics [10]:

$$\log(q_e - q_t) = \log q_e - \frac{k}{2.303}t \quad (5)$$

where  $q_e$  is the concentration of the solute adsorbed at equilibrium ( $\text{mol g}^{-1}$ ),  $q_t$  is the concentration of solute adsorbed at time  $t$  ( $\text{mol g}^{-1}$ ) and  $k$  is the overall rate constant.

It was observed that the adsorption of MB–SDS followed the Lagergren equation in the first 40 min ( $\log(q_e - q_t) = [-1.22 \times 10^{-2} \pm 4.55 \times 10^{-4}]t - [4.44 \pm 0.01]$ ,  $r = -0.9958$ ) with an overall rate constant of  $-0.0281 \text{ min}^{-1}$ . Negative signal indicates that solute concentration in solution decreases with increasing time. After elapsed this time, the order of the adsorption process changed and experimental data could not be adjusted to Lagergren equation. This behaviour could indicate that the first stage of the adsorption process (external transport of solute from solution until adsorbent surface) follows a pseudo-first-order kinetics while the posterior processes (film diffusion and intraparticle diffusion) do not follow the same order.

A second-order kinetics was also tested for the system under study. This model can be described by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

According to this model, if the adsorption process follows a pseudo-second-order kinetics a linear relationship between  $t/q_t$  is verified. In the present case, a straight line ( $t/q_t = [2.40 \times 10^4 \pm 2.63 \times 10^2]t + [6.03 \times 10^5 \pm 2.86 \times 10^4]$ ) with excellent correlation ( $r = 0.9991$ ) was obtained by applying a second-order kinetics model. The pseudo second-order constant  $k_2$  calculated for the system was  $958 \text{ g min}^{-1} \text{ mol}^{-1}$ .

Analyzing the results obtained in the kinetics study, it was possible to conclude that the first step of the process (mass transport from solution until adsorbent) followed a pseudo-first-order kinetics and the whole adsorption process is governed by a pseudo-second-order kinetics.

A mechanistic study was also carried out by testing the Morris–Weber model 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  $q_t$ , an intraparticle diffusion process can be assumed as the rate controlling step of the adsorption process [42]. When the plot does not pass through origin it is possible to conclude that a boundary layer effect occurs at a given degree and thus the intraparticle diffusion process is not the unique rate controlling step [23]. 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 rate constant of intraparticle transport, as follows:

$$q_t = K_d t^{1/2} + C \quad (7)$$

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

As can be seen in Fig. 6, the application of the intraparticle diffusion model to the data obtained for the adsorption of MB–SDS by PUF yielded a plot with three well defined regions. The first region

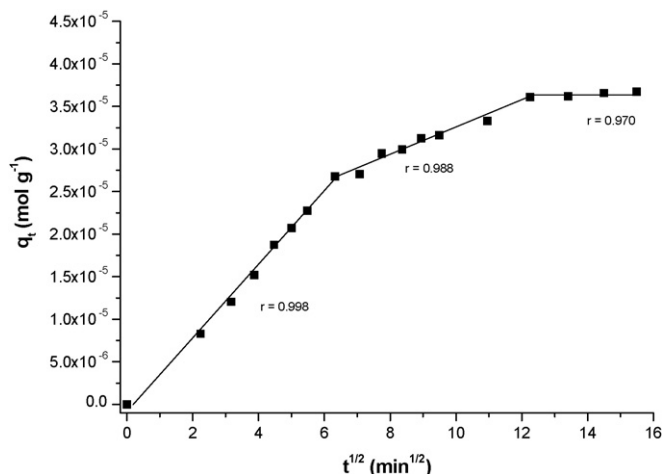


Fig. 6. Morris–Weber plot for the kinetic modeling of MB–SDS system adsorption onto PUF.

of the graph (first 40 min) presented a linear relationship between  $t^{1/2}$  and  $q_t$  with a straight line ( $r = 0.998$ ) passing through origin. This behaviour evidenced that an intraparticle diffusion process was controlling the adsorption rate. Also, it is important to note that this behaviour only occurred during the external transport of the solute from solution until boundary layer. The application of Morris–Weber model to the second region (between 40 and 120 min) also provided a good linear fit ( $r = 0.978$ ). Nevertheless, in this case, the straight line did not pass through origin and its slope decreased. This behaviour indicated that although intraparticle diffusion still contributes to the control of the adsorption rate, the film diffusion process can also play important role during this period of time. Finally, in the third stage (after 180 min), the equilibrium is achieved, which can be noted by the occurrence of a straight line almost parallel to  $t^{1/2}$  axis. In this stage, the intraparticle diffusion starts to slow down, probably due to the low concentration of solute in the liquid phase. Similar multilinearity was already reported for the adsorption of other cationic dyes by other adsorbents like iron humate [1] and cyclodextrin-based adsorbent [23].

### 3.5. Thermodynamic characterization of adsorption

A thermodynamic characterization of the adsorption of MB–SDS by PUF was performed by evaluating the extraction efficiency at different temperatures. The study consisted in the agitation for 240 min of aliquots of 200 mL of a  $5.0 \times 10^{-5} \text{ mol L}^{-1}$  dye solution containing  $2.5 \times 10^{-4} \text{ mol L}^{-1}$  SDS at 25, 30, 40, 50 and 60 °C. The equilibrium constant,  $K_C$ , was calculated for each temperature tested using the following equation:

$$K_C = \frac{C_{\text{ads}}}{C_e} \quad (8)$$

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

According to Vant'Hoff equation (Eq. (9)) a linear fit must be obtained when  $1/T$  ( $T$  in K) is plotted versus  $\log K_C$  over the entire range of temperature investigated. As can be seen, the angular and linear coefficients contain quantitative information about the values of  $\Delta H$  and  $\Delta S$  of adsorption, respectively:

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

$$\Delta G = -RT \ln K_C \quad (10)$$

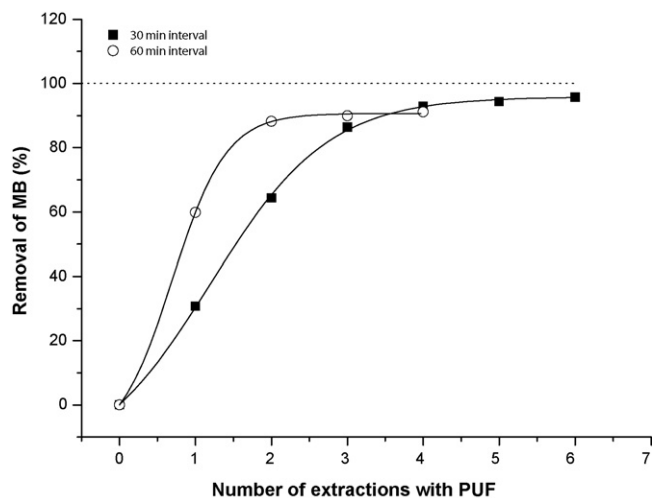


Fig. 7. Adsorption of solute by employing successive extractions in 30 and 60 min time intervals.

where  $T$  is the absolute temperature (K) and  $R$  is the ideal gas constant ( $\text{J K}^{-1} \text{mol}^{-1}$ ).

A linear fit with an equation of  $\log K_C = [-1.75 \times 10^3 \pm 2.20 \times 10^2] / T + [6.46 \pm 0.70]$  ( $r = -0.9770$ ) was obtained in this experiment and the values of  $\Delta H$  and  $\Delta S$  were estimated as  $33.4 \pm 4.2 \text{ kJ mol}^{-1}$  and  $124 \pm 13 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. The value of  $\Delta G$  was derived directly from  $K_C$  using Eq. (10) and it was  $-2.88 \text{ kJ mol}^{-1}$  at 298 K. The negative value of  $\Delta G$  and positive value of  $\Delta H$  indicated that the adsorption process is spontaneous and endothermic. This behaviour is compatible with the experimental observation, since an increase of the MB–SDS adsorption was noted with the increase of temperature. Also, the endothermic character of the adsorption process indicates that it is related to a physical process, reinforcing the idea raised before that a solvent-like extraction mechanism is involved.

In terms of thermodynamic characteristics (negative  $\Delta G$  and positives  $\Delta H$  and  $\Delta S$ ) and order of magnitude, the values obtained in this work are similar to those reported elsewhere for the adsorption of MB onto different materials [27–29]. The main exception was the work published by Gürses et al. [30], which reported an exothermic adsorption of MB onto a clayish material.

### 3.6. Sequential extraction

A sequential extraction approach, similar to a liquid–liquid extraction process, was tested to perform MB–SDS extraction by PUF. For this purpose, a solution containing  $5.0 \times 10^{-5} \text{ mol L}^{-1}$  MB and  $2.5 \times 10^{-4} \text{ mol L}^{-1}$  SDS was stirred with various PUF cylinders, sequentially. The changes of PUF cylinders were done in 30 and 60 min time intervals and the results obtained in this experiment are shown in Fig. 7.

As can be seen in Fig. 7, 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. The same procedure was tested by replacing PUF cylinders at 60 min intervals. In this condition, it was possible to remove 91.1% after a 4 h extraction (four changes of PUF plugs).

Sequential extraction was modeled in order to allow the prediction of percentage adsorption 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  $-\log C_0$  was obtained. Then, the model equation

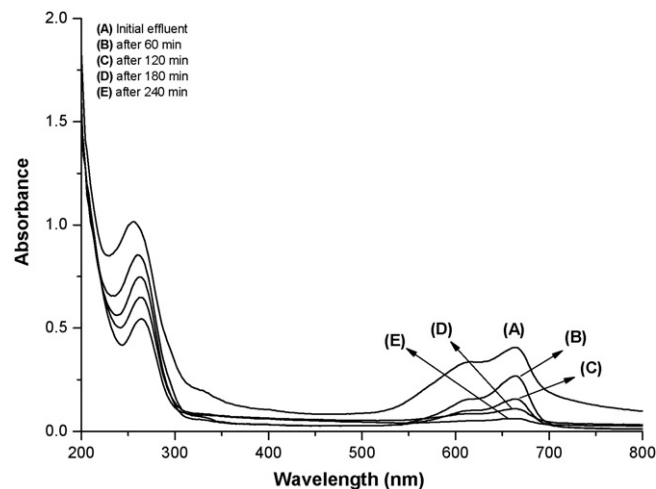


Fig. 8. Spectra obtained during removal of MB from a real sample of industrial effluent employing four consecutive extractions of 60 min with 200 mg PUF.

was assumed as

$$-\log C_N = K_N N - \log C_0 \quad (11)$$

where  $C_0$  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 studied system  $K_N$  was determined for 30 and 60 min time intervals and the values of 0.250 and 0.271 were verified, respectively. Substituting Eq. (1) into Eq. (11) and rearranging, the following equation can be obtained:

$$\log(100 - R(\%)) = -K_N N + 2 \quad (12)$$

Eq. (12) can be employed to predict the percentage of adsorption in relation to the number of extractions carried out with PUF cylinders and the time interval of each extraction step.

In order to verify the applicability of the developed procedure, it was applied to a real sample of industrial effluent containing MB. Four step extractions of 60 min were applied and a removal percentage of 85% was attained. It is possible to note that the removal efficiency of MB in the real effluent decreased in relation to that obtained in model experiments. This decrease probably occurred due to interference of matrix components. The evolution of MB removal is presented in Fig. 8 that shows the spectra recorded during extraction procedure. A remarkable decrease of the intensity of MB absorption band at 664 nm was noted, evidencing that the dye was removed from effluent by action of PUF.

## 4. Conclusions

Unloaded polyether type polyurethane foam can be used as an effective adsorbent for the removal of MB from waters in a medium containing SDS due to the formation of the hydrophobic ionic-pair between dye and surfactant. Better results can be achieved when SDS molar concentration is five times higher than MB because, in this situation, the formation of ionic-pair is enhanced. According to Lagmuir isotherm, a maximum adsorption capacity of  $7.20 \times 10^{-5} \text{ mol MB g}^{-1}$  was observed at  $25^\circ \text{C}$  from 200 mL of a solution containing  $5.0 \times 10^{-5} \text{ mol L}^{-1}$  MB. In these conditions, the adsorption kinetics followed a pseudo-second-order model and, according to Morris–Weber model, an intraparticle diffusion process is active in the control of adsorption rate. The amount of dye adsorbed increased with the increase of temperature, indicating that adsorption is an endothermic process.

Sequential extraction experiments showed that is possible to enhance the removal rate of dye by replacing PUF cylinders before equilibrium is achieved. Results obtained in this experiment demonstrated that is possible to remove around 96% of the MB present in 200 mL of a solution containing  $5.0 \times 10^{-5} \text{ mol L}^{-1}$  in around 3 h, using six consecutive step extractions of 30 min with 200 mg PUF cylinders.

### Acknowledgements

The authors are grateful to CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brazil) and FAPERJ (Fundação Carlos Chagas de Amparo a Pesquisa do Estado do Rio de Janeiro) for the grants and fellowships and for financial support.

### References

- [1] P. Janos, V. Smidova, Effects of surfactants on the adsorptive removal of basic dyes from water using an organomineral sorbent—iron humate, *J. Colloid Interface Sci.* 291 (2005) 19–27.
- [2] T.D. Braun, J.D. Navratil, A.B. Farag, *Polyurethane Foam Sorbents in Separation Science*, CRC Press Inc., Boca Raton, USA, 1985.
- [3] H.J.M. Bowen, Absorption by polyurethane foams—new method of separation, *J. Chem. Soc. A* 7 (1970) 1082–1085.
- [4] H.S. Rathore, I. Ali, T. Begum, Solid phase preconcentration and spectrophotometric determination of carbaryl traces in water, *Microchem. J.* 51 (1995) 393–397.
- [5] A.B. Farag, A.M. El-Wakil, M.S. El Shahawi, Collection and separation of some organic insecticides on polyurethane foam columns, *Fresenius J. Anal. Chem.* 328 (1986) 59–60.
- [6] M.S. El-Shahawi, Preconcentration and separation of some organic-water pollutants with polyurethane foam and activated carbon, *Chromatographia* 363 (1993) 318–322.
- [7] M.S. El-Shahawi, Retention profiles of some commercial pesticides, pyrethroid and acaricide residues and their application to tomato and parsley plants, *J. Chromatogr. A* 760 (1997) 179–192.
- [8] R.J. Cassella, S. Garrigues, R.E. Santelli, M. de la Guardia, Retention of carbaryl by polyether type polyurethane foam: a critical study, *Analyst* 125 (2000) 257–261.
- [9] R.J. Cassella, S. Garrigues, R.E. Santelli, M. de la Guardia, Spectrophotometric determination of carbaryl by on-line elution after its preconcentration onto polyurethane foam, *Talanta* 52 (2000) 717–725.
- [10] S.M. Hasany, M. Mufazzal, M. Ahmed, Adsorption isotherms and thermodynamic profile of Co(II)-SCN complex uptake on polyurethane foam, *Sep. Sci. Technol.* 35 (2000) 379–394.
- [11] O.D. Sant'Ana, L.S. Jesuino, R.J. Cassella, M.S. Carvalho, R.E. Santelli, Solid phase extraction of Cu(II) as diethyldithiocarbamate (DDTC) complex by polyurethane foam, *J. Braz. Chem. Soc.* 14 (2003) 728–733.
- [12] O.D. Sant'Ana, L.S. Jesuino, R.J. Cassella, M.S. Carvalho, R.E. Santelli, Solid-phase extraction of Cd(II) as diethyldithiocarbamate complex by polyurethane foam: kinetic and thermodynamic characterization, *Sep. Sci. Technol.* 39 (2004) 2695–2709.
- [13] O.D. Sant'Ana, L.S. Jesuino, R.J. Cassella, M.S. Carvalho, R.E. Santelli, Determination of lead by electrothermal atomic absorption spectrometry employing a novel sampling strategy of polyurethane foam impregnated with thiazolylazop-cresol (TAC), *J. Braz. Chem. Soc.* 15 (2004) 96–102.
- [14] G.N. Almeida, L.M. Sousa, A.D. Pereira Netto, R.J. Cassella, Characterization of solid-phase extraction of Fe(III) by unloaded polyurethane foam as thiocyanate complex, *J. Colloid Interface Sci.* 315 (2007) 63–69.
- [15] S.T. Ong, C.K. Lee, Z. Zainal, Removal of basic and reactive dyes using ethylene-diamine modified rice hull, *Bioresour. Technol.* 98 (2007) 2792–2799.
- [16] S. Srivastava, R. Sinha, D. Roy, Toxicological effects of malachite green, *Aquat. Toxicol.* 66 (2004) 319–329.
- [17] S.J. Culp, F.A. Beland, Malachite green: a toxicological review, *J. Am. Coll. Toxicol.* 15 (1996) 219–238.
- [18] A.A. Attia, B.S. Girgis, N.A. Fathy, Removal of methylene blue by carbons derived from peach stones by  $\text{H}_3\text{PO}_4$  activation: batch and column studies, *Dyes Pigments* 76 (2008) 282–289.
- [19] G. McKay, A.G. Sweeney, Principles of dye removal from textile effluent, *Water Air Soil Pollut.* 14 (1980) 3–11.
- [20] R. Jain, M. Mathur, S. Sikarwar, A. Mittal, Removal of the hazardous dye Rhodamine B through photocatalytic and adsorption treatments, *J. Environ. Manage.* 85 (2007) 956–964.
- [21] B.S. Inbaraj, J.T. Chien, J. Yang, B.H. Chen, Equilibrium and kinetic studies on sorption of basic dyes by a natural biopolymer poly( $\gamma$ -glutamic acid), *Biochem. Eng. J.* 31 (2006) 204–215.
- [22] S. Wang, H. Li, L. Xu, Application of zeolite MCM-22 for basic dye removal from wastewater, *J. Colloid Interface Sci.* 295 (2006) 71–78.
- [23] G. Crini, H.N. Peindy, F. Gimbert, C. Robert, Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: kinetic and equilibrium studies, *Sep. Purif. Technol.* 53 (2007) 97–110.
- [24] W.-T. Tsai, H.-C. Hsu, T.-Y. Su, K.-Y. Lin, C.-M. Lin, T.-H. Dai, The adsorption of cationic dye from aqueous solution onto acid-activated andesite, *J. Hazard. Mater.* 147 (2007) 1056–1062.
- [25] M.I. El-Khaiari, Kinetics and mechanism of adsorption of methylene blue from aqueous solution by nitric-acid treated water-hyacinth, *J. Hazard. Mater.* 147 (2007) 28–36.
- [26] V.J.P. Vilar, C.M.S. Botelho, R.A.R. Boaventura, Methylene blue adsorption by algal biomass based materials: biosorbents characterization and process behaviour, *J. Hazard. Mater.* 147 (2007) 120–132.
- [27] Y. Bulut, H. Aydın, A kinetics and thermodynamics study of methylene blue adsorption on wheat shells, *Desalination* 194 (2006) 259–267.
- [28] G. Atun, G. Hisarli, W.S. Sheldrick, M. Muhler, Adsorptive removal of methylene blue from colored effluents on fuller's earth, *J. Colloid Interface Sci.* 261 (2003) 32–39.
- [29] S. Wang, Z.H. Zhuh, Characterisation and environmental application of an Australian natural zeolite for basic dye removal from aqueous solution, *J. Hazard. Mater.* 136 (2006) 946–952.
- [30] A. Gürses, S. Karaca, Ç. Dogar, R. Bayrak, M. Açıkyıldız, M. Yalçın, Determination of adsorptive properties of clay/water system: methylene blue sorption, *J. Colloid Interface Sci.* 269 (2004) 310–314.
- [31] O. Hamdaoui, Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick, *J. Hazard. Mater.* 135 (2006) 264–273.
- [32] W.T. Tsai, K.J. Hsien, J.M. Yang, Silica adsorbent prepared from spent diatomaceous earth and its application to removal of dye from aqueous solution, *J. Colloid Interface Sci.* 275 (2004) 428–433.
- [33] R. Dhodapkar, N.N. Rao, S.P. Pande, S.N. Kaul, Removal of basic dyes from aqueous medium using a novel polymer: Jalshakti, *Bioresour. Technol.* 97 (2006) 877–885.
- [34] C.A. Basar, Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared waste apricot, *J. Hazard. Mater.* 135 (2006) 232–241.
- [35] A.T. Paulino, M.R. Guilherme, A.V. Reis, G.M. Campese, E.C. Muniz, J. Nozaki, Removal of methylene blue dye from an aqueous media using superabsorbent hydrogel supported on modified polysaccharide, *J. Colloid Interface Sci.* 301 (2006) 55–62.
- [36] L. Schumack, A. Chow, Extraction of aromatic organic compounds by polyurethane foam, *Talanta* 34 (1987) 957–962.
- [37] P. Fong, A. Chow, Extraction of aromatic acids and phenols by polyurethane foam, *Talanta* 39 (1992) 497–503.
- [38] M.S. El-Shahawi, S.M. Al-Daheri, Preconcentration and separation of acaricides by polyether based polyurethane foam, *Anal. Chim. Acta* 320 (1996) 277–287.
- [39] M.S. El-Shahawi, A.M. Kiwan, S.M. Al-Daheri, M.H. Saleh, The retention behaviour and separation of some water-soluble organophosphorus insecticides on polyester-based polyurethane foams, *Talanta* 42 (1995) 1471–1478.
- [40] A. Proctor, J.F. Toro-Vazquez, The Freundlich isotherm in studying adsorption in oil processing, *J. Am. Oil Chem. Soc.* 73 (1996) 1627–1633.
- [41] F.C. Wu, R.L. Tseng, R.S. Juang, Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan, *Water Res.* 35 (2001) 613–618.