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ORIGINAL CONTRIBUTION

The adsorption of dyes used in the textile industry on mesoporous materials

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Abstract An adsorbent material made with a silica lamellar mesoporous material treated with chitosan has been proved to be useful to adsorb both anionic and cationic dyes used in the textile industry. The two tested dyes Tectilon Blue (anionic) and Rhodamine B (cationic) have different adsorption kinetics reflecting a complex mechanism of the phenomenon. Furthermore, the adsorption capacity and interaction strength of Tectilon Blue is higher than those of Rhodamine B. Tectilon Blue molecules are situated with the molecular plane perpendicular to the adsorbent surface, whilst that of the Rhodamine B molecule is flat and parallel to the surface. The differences may be attributed to the different regions of the adsorbent surface on which the dyes are adsorbed because of their different electric charge.

Keywords Textile industry · Textile dyes · Adsorption · Mesoporous material · Chitosan · Rhodamine B · Tectilon Blue

Introduction

The textile industry has a major impact in the economy but also on the environmental quality of life in many communities. Textile industry requires the use of vast amounts of water and chemicals, and the effluents have important effects on environmental quality in textile-manufacturing regions [1–3].

Between the numerous processes applied to textile fibres, dyeing originates serious problems because the residual waters remained colored and having high organic content. When these effluents are discharged in surface waters, they are highly colored and covered by foam because dyes are generally surface active. Foam reduces the oxygen diffusion through the water surface thus limiting the depuration by natural oxidation. Moreover, dyes can be toxic to the aquatic flora and fauna.

To eliminate dye pollution in wastewater, the adsorption on different substances is currently investigated by studying different adsorbents: powdered activated carbon [4–6], chitosan- [7, 8], alumina- [9], formaldehyde- and sulphuric acid-treated sawdust [10], surfactant-modified sepiloite [11] and bentonite [12] among others. We studied the use of mesoporous silica materials because they have a high specific surface, and adsorption is a surface process. Because silica surface is negative, we also tried to employ a chitosan-treated mesoporous silica material because chitosan is a cationic polyelectrolyte, and then the composed material may be capable of adsorbing both cationic and anionic dyes. Literature reports [7, 8] indicate that chitosan has a good dye adsorption capacity under both acidic and basic conditions.

Experimental

Chemicals

Hexadecyltrimethylammonium bromide (CTAB) was from Fluka (>98%), and tetramethylorthosilicate (TEOS, 99%) was from Aldrich. Sodium silicate was from Sigma (aqueous solution 27% SiO_2 in 14% NaOH). Chitosan was obtained from crustacean chitin in the Laboratory of

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Basic and Applied Investigation on Chitin, Universidad Nacional del Sur, Bahía Blanca. Chitin was isolated from shrimp (*Pleoticus mülleri*) waste. The raw material was homogenized and triturated in an industrial triturator (Westinghouse model DASO6). To remove all organic materials, the product was rinsed at room temperature with water, as required. The clean residue was treated with 9% (w/w) NaOH (Lab Chem) at 65 °C for 90 min, to remove proteins, then demineralized by 10% (v/v) HCl (Merck) at 20 °C for 15 min, washed with water at room temperature and finally air dried. Chitosan was prepared directly by heterogeneous deacetylation of chitin at 136 °C with 50% (w/w) NaOH for 1 h. Its characteristics were: 88% deacetylation degree, 0.78% ash, 6.0% moisture, viscosity 130 mPa s measured in 1% acetic acid solution, with a Brookfield model DV-IV+ viscosimeter.

The tested dyes were an anionic one: Anthraquinone Blue (Tectilon Blue), whose structure is shown in Fig. 1a, and the other cationic: Rhodamine B, whose structure is shown in Fig. 1b. Both dyes were selected because they are employed in the textile industry and were kindly provided by Torello Hnos, a textile industry of Bahía Blanca, Argentina. To follow the variation of the dyes' concentration in the supernatant, the following wavelengths were used in a UV-Vis spectrophotometer GBC Cintra 20: 609 (Tectilon Blue) and 526 nm (Rhodamine B). Concentration vs absorbance calibration curves were made for both dyes giving straight lines. The maximum dye concentration was 0.24 g% because this is the concentration of the dyeing bath in the industry as informed by Torello Hnos. It is presumably that the effluents must have a dye concentration below this value.

Adsorbents preparation

MCM-41 (hexagonal) silica material was prepared by adding 6.2 g of sodium silicate to 13.3 ml of water and 0.2 ml of H_2SO_4 (98%, Baker). The gel was agitated for 40 min, and then a solution of 5.59 g of CTAB in 16.75 ml water was added and agitated for 30 min. Then, 6.6 ml of water were added, and the system was agitated for 30 min. The sample was autoclaved at 120 °C for 48 h, filtered and washed with distilled water. Finally, the material was calcined at 540 °C for 1 h.

MCM-48 (lamellar) silica material was prepared by mixing 11.6 ml of TEOS with 2 ml water with 2 min of agitation. Then, a solution of 1.1 g of NaOH in 20 ml water was added drop to drop while stirring. Then a solution of 7.65 g CTAB in 38 ml water was added 1 min after the addition of the NaOH solution. The resulting gel was agitated for 5 min and then autoclaved at 100 °C for 48 h. The gel was filtered and washed with distilled water and left to dry at room temperature. Finally, it was calcined at 540 °C for 1 h.

Both mesoporous materials (0.2 g each) were immersed in 4 ml of a solution of 0.9 g% of chitosan in 1% aqueous acetic acid and left for 48 h. Then, the material was filtered and left to dry at room temperature. The materials treated in this way are designated MCM-41Ch and MCM-48Ch.

A third material (N3M) was prepared by adding 6.2 g of sodium silicate to 13.3 ml of water with 0.2 ml acetic acid and stirred for 40 min. Then, a solution of 5.59 g in 16.75 ml of water was added to the formed paste and stirred for 30 min, and 17 ml of chitosan solution (0.85% in 1% aqueous acetic acid) was added, followed of 6.6 ml of water. The system was agitated for 30 min, and then it was autoclaved at 120 °C for 48 h. The obtained material was filtered and washed.

Dye adsorption experiments

Qualitative dye adsorption tests were performed by immersion of 50 mg of each adsorbent in two tubes, each containing 5 ml of either the anionic or the cationic dye solution of 0.05 mM. Then, the solutions were left by 24 h at room temperature, and the adsorption of the dye was verified visually.

Both MCM-41 and MCM-48 materials only adsorbed the cationic dye. N3M, MCM-41 and MCM-48 treated with

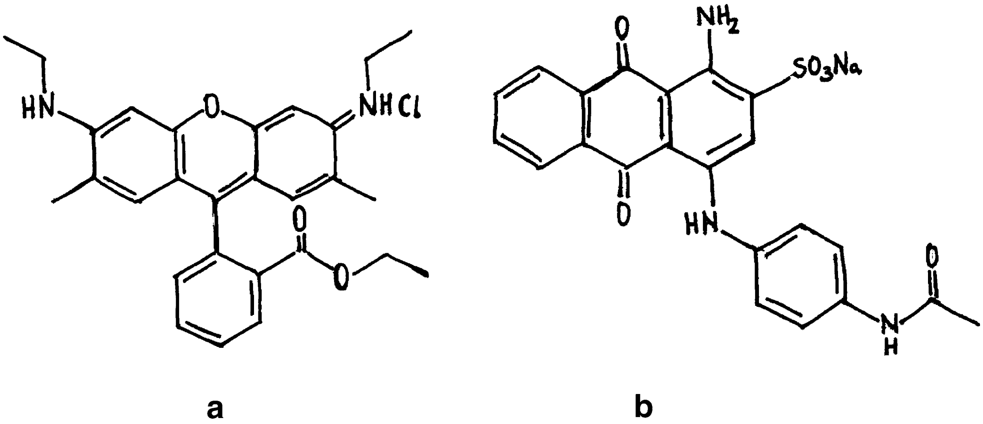

Fig. 1 The structure of **a** Rhodamine B and **b** Tectilon Blue

chitosan (MCM-41Ch and MCM-48Ch) adsorbed both the anionic and the cationic dyes. Then, the following experiments were performed with the materials that adsorb both dyes.

To determine the best adsorbent material, 50 mg of each material was placed in a tube with 5 ml of 0.05 mM dye solution, and the absorbance was measured at different times. MCM-48 treated with chitosan (MCM-48Ch) was the more effective adsorbent.

It may be seen in Figs. 2 and 3 that for both dyes, the MCM-48Ch is the most effective adsorbent. For Tectilon Blue, the MCM-41 material treated with chitosan (MCM-41Ch) is slightly less effective, and N3M is much less effective. However, for Rhodamine B, N3M is marginally more effective than MCM-41Ch.

To determine the adsorption capacity of MCM-48Ch, the quantity of adsorbed dye per gram of adsorbent (Γ_e) was determined. The dye absorbance in the supernatant liquid of tubes containing a 50 mg of adsorbent and 5 ml of dye solution was determined. The samples had different initial concentrations (0.066, 0.112, 0.156, 0.200 and 0.223 mM for Rhodamine B and 0.061, 0.101, 0.142, 0.183 and 0.203 mM for Tectilon Blue). Measurements were performed at different times up to reach the equilibrium. Temperature was maintained at 298.1±0.1 K with a water circulation thermostat.

Adsorption kinetics

Runs were performed starting with dye solutions having different initial concentration C_0 between 0.077 and 1.00 mM (Tectilon Blue) and between 0.06 and 0.200 mM (Rhodamine B) at 298.1 K using a water circulating thermostat, giving straight lines (not shown). These straight lines were fitted by the least-squares method obtaining the slope and intercept and their variances (s). For each dye, the differences between the values of slopes (or between intercepts) were not statistically significant with a confidence level of 0.90. Then, the different values were averaged with the minimum variance unbiased weighed method [13], which assigns a statistical weight equal to $1/s^2$. Thus, while all the data are used in the average, the method gives the higher statistical weight to the datum having the minimum variance. The variance of the resulting average is smaller than the minimum variance of the original data. Then, errors were computed with the Student's t method.

Nitrogen adsorption studies

Nitrogen adsorption studies were made with a Micrometrics Model ASAP (Accelerated Surface Area and Porosimetry System) 2020 instrument at 77 K.

Results and discussion

Nitrogen adsorption

Because the MCM-48Ch was the more effective adsorbent, the study was centered on this material. To characterize the material, nitrogen adsorption studies were realized on this material and its precursor MCM-48. The adsorption isotherm on MCM-48Ch (not shown) was a type IV one with a *H4* hysteresis loop. This kind of isotherm is associated with a capillary condensation in mesopores. The initial part of the isotherm is attributed to a mono-layer–multi-layer adsorption. The *H4* hysteresis loop is

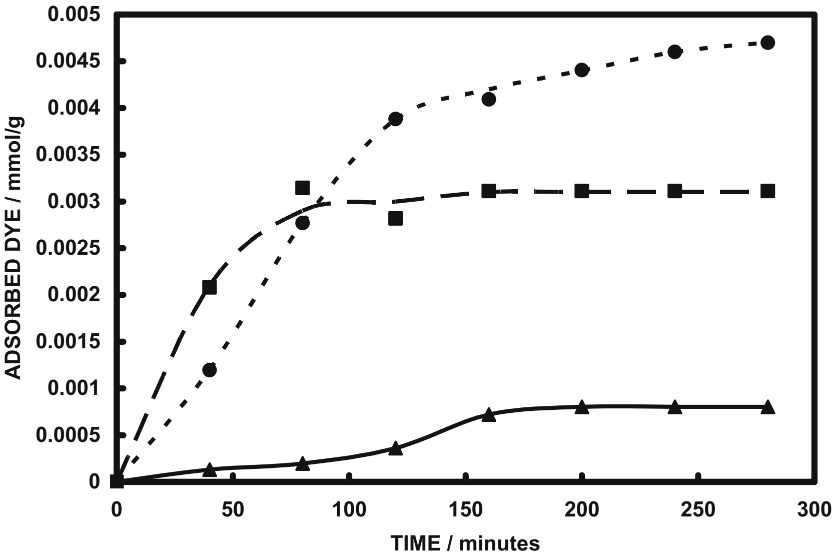

Fig. 2 Adsorption isotherms of Tectilon Blue on: *circles*, MCM-48Ch, *triangles*, MCM-48Ch, *squares*, N3M. *Curves* are eye guides

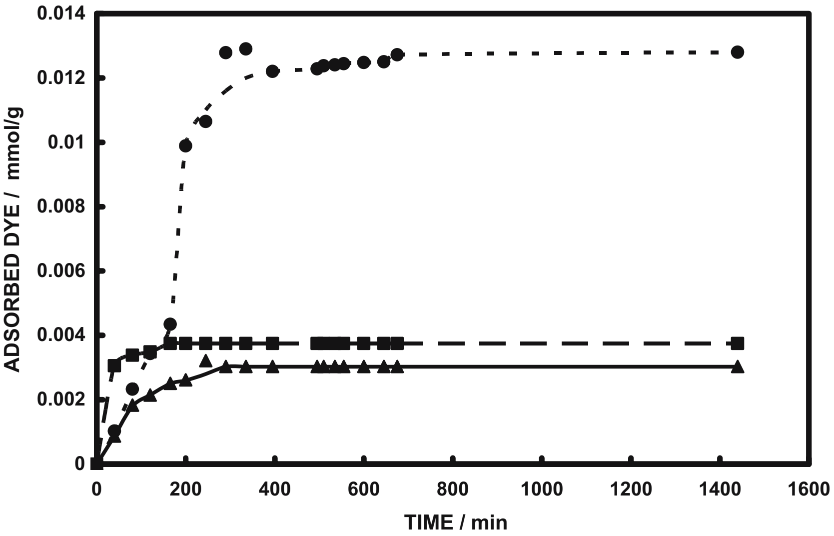

Fig. 3 Adsorption isotherms of Rhodamine B on: *circles*, MCM-48Ch, *triangles*, MCM-48Ch, *squares*, N3M. *Curves* are eye guides

associated with narrow slit-like pores [14]. This kind of isotherm is commonly shown by industrial mesoporous adsorbents.

Figure 4 shows the *t* plot for MCM-48Ch, which is typical of mesoporous materials with slit-like pores. Consequently, the pore radius must be taken as the half of the distance between adjacent lamellae. The negative value of the micropore volume, which can be deduced from Fig. 4, is due to the absence of micropores, probably because they were filled or sealed by chitosan molecules. Therefore, the intercept is almost zero, and a small negative intercept is inside the experimental error.

Figure 5 shows the pore radius distribution of the MCM-41Ch material. The zone above 0.7 nm means that the slit pores are not of constant width, but there is a broad distribution as expected because the material is mainly a superposition of independent lamellae. There are some small pores indicated by the maxima at 0.55 and 0.65 nm.

Plots of the precursor MCM-48 material are similar to those of MCM-48Ch and are not shown. The Brunauer–Emmett–Teller (BET) area for MCM-48 was A_{BET}= 689.4 $\mathrm{m}^2\ \mathrm{g}^{-1}$, and that for MCM-48Ch was A_{BET}= 759.6 $\mathrm{m}^2\ \mathrm{g}^{-1}$.

Adsorption isotherms

The equilibrium adsorption data were treated with both the Langmuir and the Freundlich isotherms. The used Langmuir isotherm was:

$$\frac{1}{\Gamma}=\frac{1}{\Gamma_{\mathrm{mx}}}+\frac{1}{K_{\mathrm{L}}\Gamma_{\mathrm{mx}}}\times\frac{1}{C_{\mathrm{e}}} \qquad (1)$$

where $\Gamma_{\mathrm{e}}=(C_0-C_{\mathrm{e}})V/m$ is the amount of dye adsorbed (mmol/g of adsorbent) at the equilibrium, C_0 and C_{e} being the initial and equilibrium concentration of dye in the

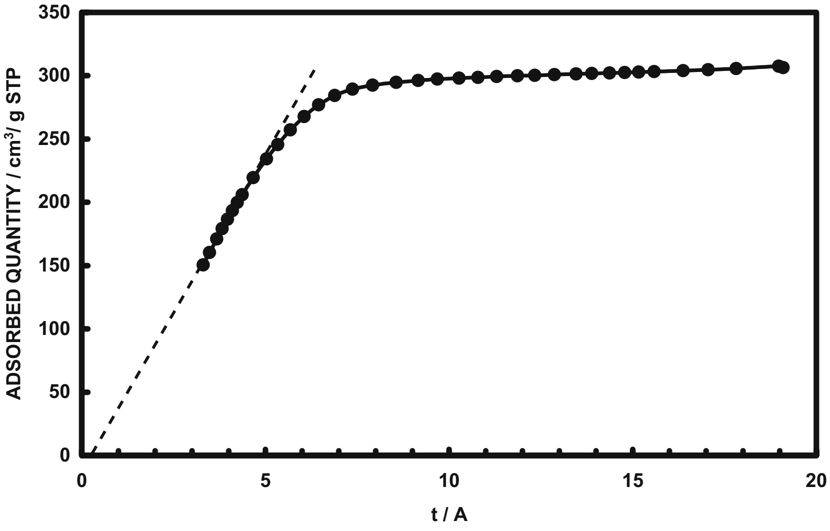

Fig. 4 *t* plot for the adsorption of nitrogen on MCM-48Ch material

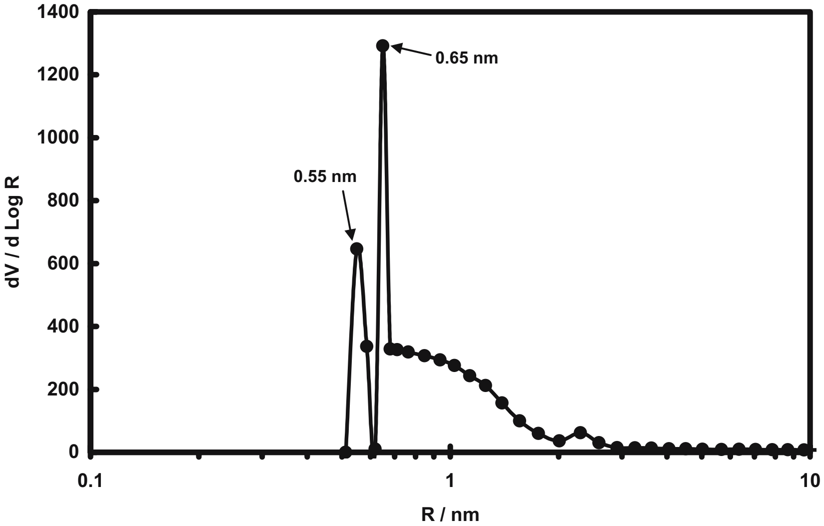

Fig. 5 The pore size distribution of the MCM-48Ch material

supernatant, V is the volume of solution, m the mass of adsorbent, K_L the Langmuir constant and Γ_{mx} the maximum amount of adsorbed dye forming a mono-layer on the adsorbent surface.

The representation of the Langmuir isotherm for the dyes on MCM-48Ch gave straight lines (not shown) whose least squares fitting equations are:

For Rhodamine B:

$$1/\Gamma_e = (9.921 \pm 0.063)(1/C_e) + 1.25 \pm 0.62 \quad (C_e \text{ in mM}) \quad r = 0.99996 \tag{2}$$

giving Γ_{mx}=0.80±0.02 mmol/g, i.e. 0.350±0.009 g of dye per gram of adsorbent, and K_L=0.126±0.062. From the value of Γ_{mx} and the BET area per gram of adsorbent (A_{BET}= 760 m^2 g^{-1}) obtained from the nitrogen adsorption measurements, the area occupied by an adsorbed dye molecule can be obtained by:

$$A_{molec} = A_{BET}/N_A \Gamma_{mx} \tag{3}$$

N_A being the Avogadro's number. For Rhodamine B, the experimental value of A_{molec}=157±51 Å^2. To interpret this value, a model of the surfactant molecule was made using the size of the different atoms and the bond length and angles. From this model, the area occupied by a Rhodamine B molecule with its plane parallel to the adsorbent surface (A_{para}) is 101.3 Å^2, and the area occupied by a molecule with its plane perpendicular to the adsorbent surface and the polar group pointing to the adsorbent (A_{perp}) is 39.7 Å^2. By comparing the experimental and theoretical areas, it may be concluded that adsorbed Rhodamine B molecules are placed with its plane parallel to the adsorbent surface of MCM-48Ch.

For Tectilon Blue:

$$1/\Gamma_e = (9.999 \pm 0.036)(1/C_e) + 0.20 \pm 0.36 \; (C_e \text{ in mM}) \quad r = 0.9999 \tag{4}$$

giving Γ_{mx}=5.0±1.8 mmol/g, i.e. 2.6±0.9 g of dye per gram of adsorbent, and K_L=0.020±0.036. The value of A_{molec}=25.2±9 Å^2. The values computed with the molecular model are A_{para}=63.8 Å^2 and A_{perp}=27.8 Å^2. By comparison of the different areas, it may be concluded that the adsorbed Tectilon Blue molecules are placed perpendicular to the adsorbent surface.

Examples of both orientations of dye molecules on the adsorbent surface may be found in the literature. Graham [15] found an apparent molecular area of 197 Å^2 for methylene blue on Graphon, which is larger than the actual molecular area of 175 Å^2, which may indicate that the plane of the molecule is parallel to the surface. However, on the oxidized surface of Spheron, a partially graphitized carbon black, the area was about 105 Å^2, indicating a possible tilt of the molecule plane with respect to the surface [16]. Sheppard et al. [17, 18] studying the adsorption of cyanine dyes on silver halides also found that the saturation layers were formed by a close-packed mono-layer of essentially planar cations, with the plane of the molecules essentially perpendicular to the adsorbent surface.

The orientation of adsorbed molecules depends both on the nature of the interaction between the adsorbent surface and these molecules and the nature of the interactions of molecules comprising the bulk solution. The adsorption of dyes generally follows the Langmuir equation but can be multi-layered [19]. Furthermore, association of dyes at interface or in solution can produce problems of interpretation [20]. Because adsorption from solution is a competitive adsorption, some portions of the surface will remain occupied by solvent molecules. Then, it is improbable that the whole liquid/solid interface at any point of the isotherm is covered with a dense unimolecular film of the solute while the solvent is totally excluded [21]. Then, the interpretation of dye adsorption data from solution cannot be considered free of systematic error. Nevertheless, taking into account the possible sources of error, the interpretation of the above results for the orientation of Tectilon Blue and Rhodamine B on MCM-48Ch seems to be quite reasonable.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor of equilibrium parameter RL, which is defined by the equation [22]:

$$\mathrm{RL} = 1/(1 + K_\mathrm{L} C_0) \tag{5}$$

When RL>1, the type of isotherm is unfavourable to adsorption, RL=1 indicates a linear adsorption, 0<RL<1 indicates a favourable adsorption and RL=0 indicates an irreversible one. The obtained values were RL=0.997±0.001 for Tectilon Blue and 0.980±0.006 for Rhodamine B, irrespective of the initial dye concentration, which indicates a favourable and almost linear adsorption.

The Freundlich isotherm equation was also used:

$$\log \Gamma_\mathrm{e} = \log K_\mathrm{F} + \frac{1}{n} \log C_\mathrm{e} \tag{6}$$

giving straight lines whose least squares fitting equations are:

For Rhodamine B:

$$\begin{aligned} &\log \Gamma_\mathrm{e} = (0.968 \pm 0.014) \log C_\mathrm{e} - 1.037 \pm 0.015 \\ &r = 0.9998 \end{aligned} \tag{7}$$

giving K_F=0.0918±0.0031.

For Tectilon Blue:

$$\begin{aligned} &\log \Gamma_\mathrm{e} = (0.9979 \pm 0.0046) \log C_\mathrm{e} - 1.032 \pm 0.0044 \\ &r = 0.9999 \end{aligned} \tag{8}$$

giving K_F=0.0993±0.0010.

To verify if the values of $1/n$ and K_F for both dyes are significantly different from a statistical point of view, a test of difference of averages was performed using the Student's t probability distribution. For the difference in $1/n$ values, the resulting critical t value was t_c=4.058±0.005 and for difference between K_F values, 4.605±0.001. Both t_c values have a significance level of ~1; that is, the probability that both compared values were two independent estimations of the same value is about zero. Then, the Freundlich characteristics of adsorption for the two dyes are significantly different. Because the slope $1/n$ is roughly interpreted as the intensity of adsorption ([19], pp. 388–389), it may be concluded that Tectilon Blue adsorption is more intense than that of Rhodamine B. Because K_F is interpreted as measure of the adsorbent capacity ([19], pp. 388–389), it may be concluded that the adsorbent capacity for Tectilon Blue is also higher than that for Rhodamine B. Both results agree with those obtained from Langmuir isotherms.

Both treatments fitted well to the data, with a slight advantage to the Langmuir one, but that has not any statistical significance. However, the fact that the Freundlich isotherm also fits well the data is in agreement with the fact that the adsorbent surface is not homogeneous (it is actually formed by silica and chitosan, whose structure is not univocally defined and may vary from one to other part of the biopolymer). The Freundlich equation can be shown to result from a modification to the Langmuir derivation in which the affinity of the surface sites varies continuously ([19], pp. 388–389).

The different adsorption characteristics of both dyes are probably associated with different sites of adsorption: Tectilon Blue, being anionic, is probably adsorbed on chitosan, and the cationic Rhodamine B on negative sites of silica.

Adsorption kinetics

To study the adsorption kinetics, the differential method was used:

$$v = -\mathrm{d}C/\mathrm{d}t = kC^n \tag{9}$$

in which $v=-\mathrm{d}C/\mathrm{d}t$ is the velocity of reduction of the dye concentration C, k is the kinetic constant and n the kinetic order of the adsorption process. The value of v can be computed between two consecutive dye concentrations

Table 1 Kinetic data for the adsorption of Tectilon Blue and Rhodamine B on the chitosan-treated mesoporous material (MCM-48Ch)

Dye	N	n_average	e_n	Log k_average	$e_{\log\ k}$	k_average	e_k
Tectilon Blue	61	1.4418±	0.0004	−1.5589±	0.0009	0.02751±	0.00006
RhodamineB	17	1.295±	0.001	−3.530±	0.003	0.000295±	0.000002

N Number of original points, $n_{average}$ average order of the adsorption kinetics, e_n error of the n_average estimation, $k_{average}$ average value of the kinetic constant in Eq. 9, e_k error in the k_average estimation

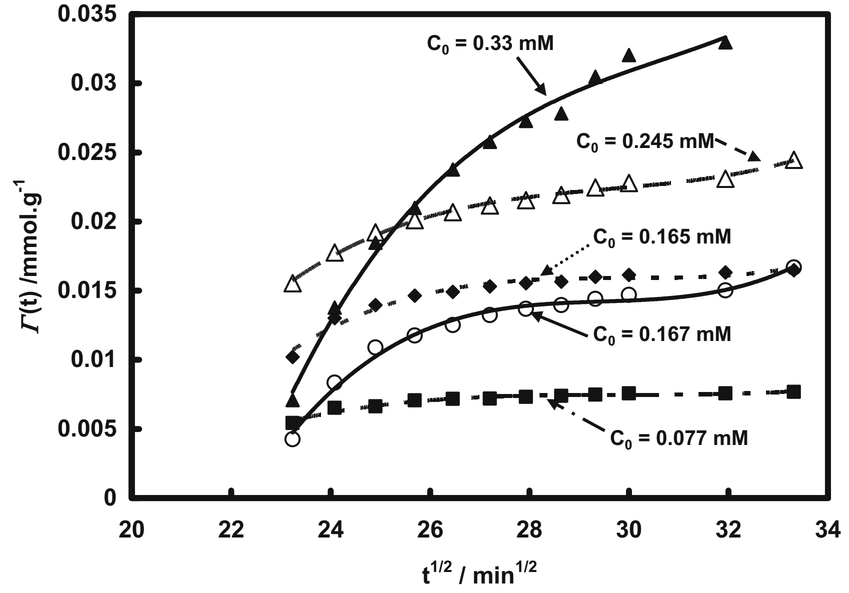

Fig. 6 Representation of Tectilon Blue adsorption on MCM-48Ch as a function of the square root of time. The different initial concentration of the dye is indicated. *Lines* are polynomial fitting curves

(determined by spectrophotometry) C_1 and C_2, corresponding to two consecutive times of measurement t_1 and t_2:

$$v_{12} = -(C_2 - C_1)/(t_2 - t_1) \tag{10}$$

which is plotted at the intermediate concentration C_{12}= (C_1+C_2)/2. Then, by applying logarithms to Eq. 9:

$$\log\ v = n.\log\ C + \log\ k \tag{11}$$

and plotting log v as a function of log C, the value of k can be obtained from the intercept and that of n from the slope.

The rate of adsorption from solution depends on many factors. Of primary importance here are: size and structure of the adsorbed molecules, nature of solvent and porosity of the adsorbent.

Adsorption from the solution on a solid surface being an exchange process, its rate is determined not only by transport to the surface and attachment of the component to be adsorbed but also by the rate of detachment of adsorbed other components. Hence, when one speaks of a rate of adsorption, this implies a combination of an adsorption and a desorption rate. When the residence time of adsorbate at the interface is relatively short, the kinetics is governed by the rate of supply. If this supply is diffusion controlled and the concentration of adsorbate on the adsorbent surface at time t=0 is zero, then the initial part of the adsorption follows the relationship [23]:

$$\Gamma(t) = 2D_a^{1/2}C_a t^{1/2}/\pi^{1/2}(\Gamma(t) << \Gamma_{\mathrm{mx}}) \tag{12}$$

showing the typical $t^{1/2}$ dependence of diffusion- controlled processes. This equation applies to diffusion-controlled processes on flat adsorbent surfaces from quiescent solutions.

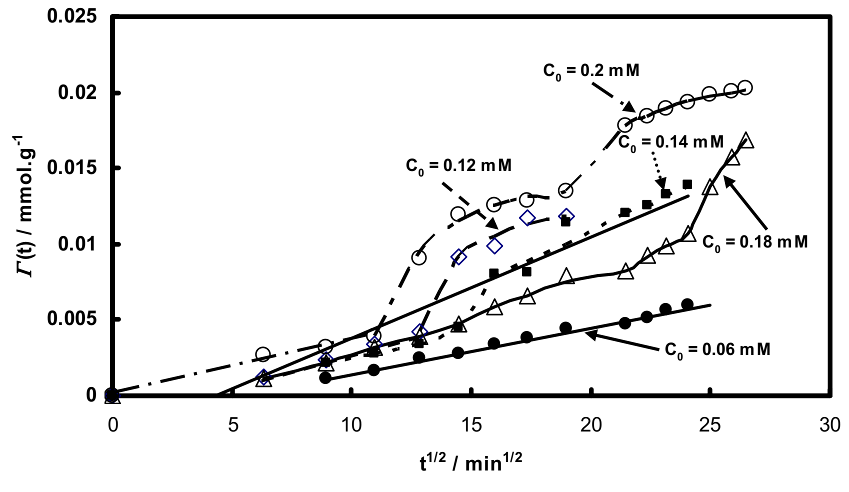

Fig. 7 Representation of Rhodamine B adsorption on MCM-48Ch as a function of the square root of time. The different initial concentration of the dye is indicated. *Lines* are eye guides

A second step in the adsorption process may be related to re-arrangements on the surface and diffusion into pores and channels in porous adsorbents (internal diffusion). Furthermore, heterogeneity of the surface may cause re-arrangement of adsorbate molecules once they are primarily adsorbed.

According to Poulchly and Erdös [24], the process of adsorption itself is so rapid that it is difficult to determine its time of duration, but the adsorption equilibrium takes a long time to establish. Adsorption kinetic results are given in Table 1.

On the other hand, the values of adsorbed dye per gram of adsorbent at different times $\Gamma(t)$ (mmol g^{-1}) were plotted as a function of the square root of time (Figs. 6 and 7). As it can be seen in Fig. 6, the kinetics of adsorption of Tectilon Blue is not governed only by diffusion, as the graphs are not straight lines. The fitting curves are all three order polynomials. Figure 7 shows the plot for Rhodamine B. The kinetics is different to that of Tectilon Blue: The lowest C_0 curve shows diffusion-controlled kinetics (i.e. follows a straight line), while the other curves with higher C_0 have a first step, which is diffusion controlled followed by non-diffusion kinetics.

The factionary value of n for the adsorption kinetics of both dyes indicates a complex mechanism, as it is expected from the above discussion. A glance on Figs. 6 and 7 indicates that the adsorption kinetics of both dyes is qualitatively different. Rhodamine B seems to be initially diffusion governed, but in some point of the adsorption, the kinetic law changes, while Tectilon Blue did not show a distinguishable diffusion-governed step.

Conclusions

The adsorbent material made with a silica lamellar mesoporous material treated with chitosan has been proved to be useful to adsorb both anionic and cationic dyes used in the textile industry. The two tested dyes Tectilon Blue (anionic) and Rhodamine B (cationic) have adsorption kinetics with a factionary order reflecting a complex mechanism of the phenomenon, which is different for both adsorbates. Furthermore, the adsorption capacity and interaction of Tectilon Blue is higher than those of Rhodamine B. Tectilon Blue molecules are probably situated with the molecular plane perpendicular to the adsorbent surface, whilst that of the Rhodamine B molecule is flat and parallel to the surface. Because the surface of the adsorbent is complex with negative regions arising from silica and positive ones appertaining to the previously adsorbed chitosan, whose composition is variable, the differences in the adsorbent/adsorbate interaction may be attributed to the different regions of the adsorbent surface on which the dyes are adsorbed because of their different electric charge.

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