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Removal of Reactive Black 5 from water using carboxylic acid-grafted SBA-15 nanorods

Sakine Habibi[a], Leila Hajiaghababaei[a,*], Alireza Badiei[b], Marzieh Yadavi[b], Shiva Dehghan Abkenar[c], Mohammad Reza Ganjali[d], Ghodsi Mohammadi Ziarani[e]

[a]*Department of Chemistry, Yadegar-e-Imam Khomeini (RAH), Shahre Rey Branch, Islamic Azad University, Tehran, Iran, Tel. +98 9125017614; Fax: +98 21 33999022; email: lhajiaghababaei@yahoo.com (L. Hajiaghababaei), Tel. +98 9378240629; email: sarohhabibi110@gmail.com (S. Habibi)*
[b]*School of Chemistry, College of Science, University of Tehran, Tehran, Iran, Tel. +98 9127907837; email: abadiei@khayam.ut.ac.ir (A. Badiei), Tel. +98 9126191842; email: marziyadavi@yahoo.com (M. Yadavi)*
[c]*Department of Chemistry, Savadkooh Branch, Islamic Azad University, Savadkooh, Iran, Tel. +98 9111174767; email: dehghan54@yahoo.com*
[d]*Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran, Tel. +98 9121384440; email: ganjali@khayam.ut.ac.ir*
[e]*Department of Chemistry, Alzahra University, Tehran, Iran, Tel. +98 9378240629; email: gmohammadi@alzahra.ac.ir*

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ABSTRACT

SBA-15 mesoporous silica was grafted with carboxylic acid groups and evaluated as a novel solid phase adsorbent for removing Reactive Black 5 (RB5) from aqueous media. The adsorbent was prepared based on a procedure described in the literature, and characterized using Fourier transform infrared spectroscopy, Raman, thermogravimetric analysis and X-ray diffraction, and nitrogen physisorption techniques. The different adsorbents were evaluated for removing RB5 and were found to possess adsorption capacities in the order of: SBA-15/tricarboxylic acid groups > SBA-15/dicarboxylic acid groups > SBA-15/tetracarboxylic acid groups. The adsorption of RB5 on the adsorbent based on electrostatic attraction and hydrogen bonding has been described; the results of batch studies conducted to evaluate the optimal adsorption conditions and operating parameters, for example, pH, amount of adsorbent, contact time and analyte concentration, have been reported. The data were evaluated using the Langmuir adsorption model. Further, the thermodynamic parameters and the desorption process were monitored and evaluated.

Keywords: Dye removal; Reactive Black 5; Carboxylic acid-functionalized SBA-15 nanorods

1. Introduction

Treating wastewaters, which are known to contain various dyes, is an important issue. These dyes fall into three different structural categories, which include (1) cationic dyes (i.e., basic dyes mainly used for acrylic fibers), (2) anionic dyes (i.e., acidic, direct and reactive dyes used in the case of wool, silk and nylon); and (3) non-ionic dyes (i.e., disperse dyes improved against water, light and perspiration) [1,2]. Among the different classes, reactive dyes are azo compounds that are widely used (about 45% of all dyes annually produced for textile industry are from this family), and are also very difficult to remove [3]. These compounds are further used in rubber, cosmetics, leather, paper, pharmaceutical and food industries [4,5], and this can lead to their emission water sources. These unfortunate, yet common phenomena have become a serious environmental issue due to the harm it causes on aqueous ecosystem and humans [6]. At high

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* Corresponding author.

concentrations, textile dyes may be toxic and more difficult to remove. A wide range of dyes are resistant against thermal and/or photo-degradation [7]. Also, measures intended for making these compounds resistant to different factors make them hard to remove, through water treatment processes.

Various chemical and physical procedures have been developed and used for treating textile wastewaters [3,8]. Adsorption processes have been found to be alternatives for eliminating reactive dyes, and mesoporous silica compounds, for example, SBA-15, MCM-41, SBA-3 and MCM-48, are considered as promising adsorbents for this purpose, given their large surface area, high pore volumes and ordered structures [9–11]. The applications of these structured compounds for eliminating heavy metal ions, organic dyes and other organic compounds have been recently studied and found to be very promising adsorbents [12–20]. In the light of the fact that adsorption is very much dependent on the surface of the adsorbent, the presence of functional groups on the surface of such compounds can have more important effects, as opposed to the surface area of the material. Consequently, a great deal of effort has been directed to modify the surface of mesoporous silica through grafting certain functional groups as a means of enhancing the adsorption properties of sorbents. As a result, a range of sorbent grafted with organic small molecules have been prepared and used for adsorbing organic and inorganic pollutants from aqueous media. Some examples include synthesis of mesostructured SBA-15, HMS and MCM-41 grafted with sulfonic acid [21–25]. Corriu et al. [26] also reported the preparation of SBA-15 modified with phosphonic acid groups. Pan et al. [27] synthesized cyanide- and carboxylate-functionalized SBA-1, and Chen et al. [28] prepared multicarboxylic-modified SBA-15 for the adsorption of cationic dyes and copper ions from aqueous media. In another work, Ho et al. [29] synthesized functional MCM-41 modified with amino or carboxylic groups for removing acid blue 25 and methylene blue dyes from water, and the results showed large adsorption capacity and high selectivity. Mesoporous materials modified with carboxylic groups have also been found to have pH-dependent delivery and controlled release of drug molecules containing free amino functional groups [30].

Carboxylic groups act as good ligands towards organic or inorganic species and can also form hydrogen bonds, and hence the present work was focused on grafting SBA-15 nanorods with di-, tri- and tetracarboxylic acid groups (S-C1, S-C2 and S-C3). The resulting adsorbents were characterized and used for removing Reactive Black 5 (RB5) from water samples, and the effects of solution pH, amount of the adsorbent concentration of the pollutant and contact time on the adsorption efficiency of the sorbents were evaluated and optimized.

2. Experimental setup

2.1. Instrumentation

The small angle X-ray scattering (SAXS) patterns were recorded with a model Hecus S3-MICROpix SAXS diffractometer with a one-dimensional position sensitive detector using Cu Kα radiation (50 kV, 1 mA) at the wavelength of 1.542 Å. The SEM images were taken using Oxford LEO 1455V STEM. Nitrogen physisorption isotherms were obtained on a BELSORP-miniII at liquid nitrogen temperature (77 K). The specific surface areas were measured using multiple point Brunauer–Emmett–Teller (BET) method. The pore size distributions were calculated using desorption branches of the isotherms by Barrett–Joyner–Halenda (BJH) method. The Fourier-transform infrared (FTIR) spectra were recorded using Equinox 55 spectrometer in the range between 400 and 4,000 cm^{-1}.

The pH was controlled by Metrohm pH meter model 713 and Varian Cary 100 double beam spectrophotometer was used for the detection of dye concentration in the solution.

2.2. Reagents and solutions

Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol), P123, ($EO_{20}PO_{70}EO_{20}$, M_W = 5,800 g/mol) was obtained from Sigma-Aldrich (St. Loius, MO, USA) and tetraethyl orthosilicate (TEOS), hydrochloric acid (35%), ethanol, N,N′-dimethylformamide, succinic anhydride, 3-aminopropyltriethoxysilane (APS) and N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AAPS) were from Merck (Darmstadt, Germany). 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (AEPS) was also obtained from Sigma-Aldrich. None of the chemicals were subjected to any treatment. C.I. Reactive Black 5 (Fig. 1) was procured from Bayer (Germany), and double distilled water (DDW) was used in all experiments. The pipettes and vessels were kept in dilute nitric acid for at least 1 d after repeatedly washing with DDW.

The dye solutions were prepared through dissolving the RB5 powder in DDW to form a stock solution and then diluting it to desired concentrations.

2.3. Synthesis of SBA-15 nanorods

SBA-15 nanorods were synthesized according to the procedure that is described in our previous work [31–33]. Briefly, 23.4 g of nonionic triblock copolymer (Pluronic P123) was dissolved in the mixture of deionized water (606.8 g) and hydrochloric acid (146.4 g, 35%). Then, 50 g of TEOS was added to this clear solution dropwise within 15 min under stirring at 55°C. The obtained mixture was stirred for 5 min at the rate of 500 rpm. The obtained mixture was stirred for

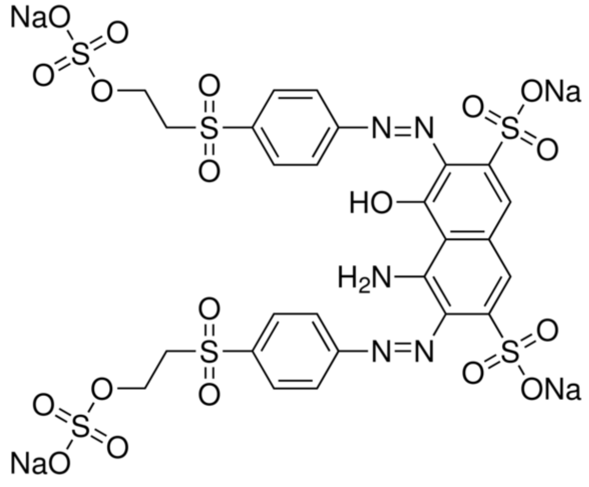

Fig. 1. Molecular structure of Reactive Black 5 dye.

5 min at the rate of 500 rpm. The reaction batch was maintained at static conditions for 24 h (hydrolysis time) at 55°C temperature and then for another 24 h at 100°C for further condensation. The precipitate was obtained after filtration and ethanol extraction through a Soxhlet extractor was used for removing the triblock copolymer template.

2.4. Amino-functionalized SBA-15 nanorods

The amino-functionalized SBA-15 samples were prepared through a typical reaction involving addition of 0.1 g of SBA-15 nanorods to 20 mL of anhydrous ethanol, and the solution was heated to 80°C. 1 mL of aminosilanes (APS, AAPS and AEPS) was added to this solution dropwise within 2 min under stirring. The mixture was stirred under reflux condition for 6 h. The solid product was centrifuged, washed with ethanol and left to dry under ambient conditions. This modified SBA-15 was further post-grafted with APS, AAPS and AEPS and the samples were referred to as S-N1, S-N2 and S-N3, respectively.

2.5. Carboxylic group-grafted SBA-15 nanorods

The –COOH functionalization of SBA-15 nanorods was carried out as follows [33]:

0.1 g of amino-functionalized SBA-15 nanorods was dispersed in 25 mL ethanol containing 5 mmol bromoacetic acid. The mixture was allowed to react at 80°C for 4 h. The precipitate was collected by centrifugation, washed with ethanol and dried at room temperature. The obtained modified SBA-15 nanorods, which were subjected to the S-N1, S-N2 and S-N3 were designated as the S-C1, S-C2 and S-C3, respectively. The schematics of the reaction are shown in Fig. 2.

2.6. Removal of RB5

The adsorption experiments were performed in batch mode using the carboxylic group-functionalized SBA-15 to remove RB5 from water samples, by adding 0.005 g of the sorbent to 10 mL of a 20 mg L^{-1} RB5 (pH = 5). Each experiment was conducted three times. The mixtures were gently stirred for 5 min under ambient conditions, and then the supernatant was separated through centrifugation at 3,800 rpm for 5 min, and its RB5 content was determined through spectrophotometer at 598 nm.

The data on the adsorption of RB5 were used to determine the removal efficiency of the sorbent using the expression below:

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

where C_o and C_t are symbols for initial and final concentrations of RB5 (mg L^{-1}), respectively.

The adsorption of dyes onto an adsorbent is known to be a function the qualities of the sorbent including surface area, porosity, active site and operational conditions such as the pH and temperature of the solution, contact time, concentration of the dye and amount of the adsorbent [34]. To evaluate these parameters, experiments were conducted at ambient temperature to evaluate the effects of pH, amount of the adsorbent, contact time and concentration of the adsorbent. The kinetics of the reaction phenomena was evaluated through determining the adsorption capacity of the adsorbent at different intervals and using different solutions with RB5 concentrations in the range of 50–1,000 mg L^{-1} the adsorption isotherms were acquired. To evaluate the effect of temperature, adsorption isotherms were determined at 288, 298 and 313 K.

The amounts of the adsorbed dyes (q_e) were calculated using the following equation:

$$q_e = \frac{C_o - C_e}{m} \times V \tag{2}$$

in which C_o and C_e represent the initial and equilibrium concentrations of RB5 (mg L^{-1}), m stands for the mass of adsorbent (g), and V is the solution volume (L).

2.7. Standard addition calibration

Given the potential of a standard addition procedure for the analysis of complex samples with strong matrix effects, this approach was used for obtaining the result. The typical

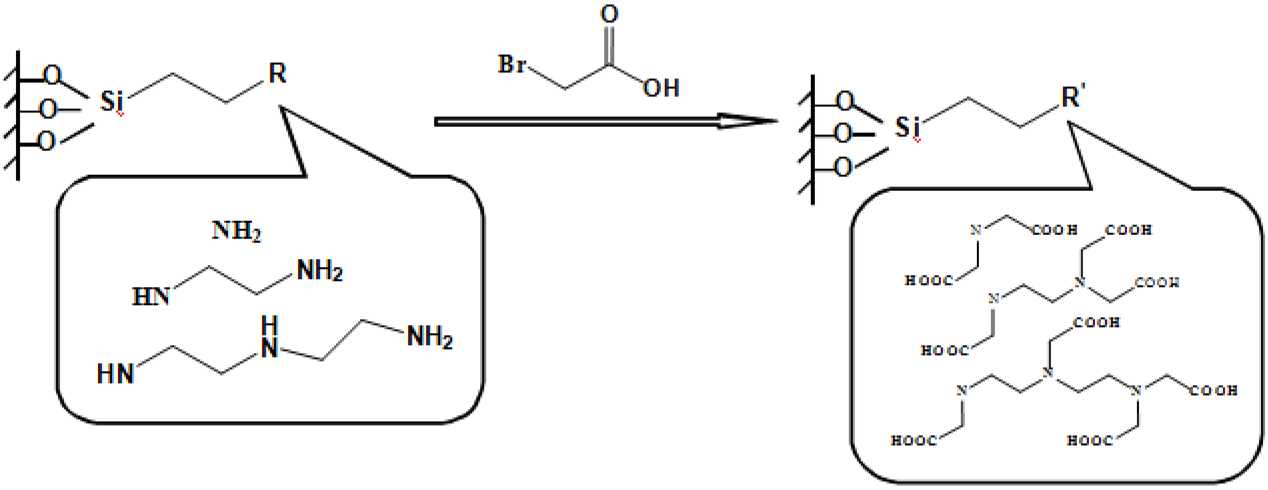

Fig. 2. Schematic illustration of the modification of amino-functionalized SBA-15 with carboxylic acid groups.

method involved preparing several identical RB5 solutions and adding different amounts of the standard to them. Specifically, to 50 mL volumetric flasks were charged, 10 mL of textile wastewater samples, and then the standards (0, 2.5, 5, 7.5 and 10 mL of 100 mg L^{-1}) were added to the flasks and the solutions were diluted to the mark and adequately mixed. The RB5 concentrations were then determined through spectrophotometry and absorption/standard concentration plots were drawn. Then a simple linear least square analysis was performed using the slope and intercept functions of Microsoft Excel. To determine the concentration of RB5 in the samples, the value of X at $y = 0$ was calculated from the $y = mX + b$ equation.

3. Results and discussion

3.1. The structural qualities of the adsorbent

The small angle X-ray (SAXS) patterns obtained for unmodified and carboxylic acid-functionalized SBA-15 samples are presented in Fig. 3. The patterns indicate well-resolved peaks due to the (100), (110) and (200) reflexes of the hexagonal structure [35]. With the functionalized samples, three main diffraction peaks were observed in the patterns indicating that the grafting of the functional groups did not influence the mesoporous structure SBA-15 nanorods. Yet the peaks are less intense, due to the contrast matching between the functional groups and SBA-15.

SEM micrograph of the inorganic matrix (Fig. 4) indicates that it has a rod-like morphology, composed of 100 nm × 1 μm structures.

Measurements of the N_2 adsorption/desorption the unmodified and modified SBA-15 showed typical irreversible type IV nitrogen adsorption isotherms with an H1 hysteresis loop (Fig. 5(a)) [36]. The form and location of the loop (at p/p_0 from 0.60 to 0.85) reflected the sample as having cylindrical mesopores with a narrow pore size distribution. Since the organic groups were grafted into the channels of the nanorods, the location of the hysteresis loop shifted toward lower relative pressures, and a mild decrease in the total nitrogen adsorption volume of the modified nanorods was observed.

Pore size distribution was determined from the desorption branch of the isotherms through the BJH method (Fig. 5(b)). The mesopores were found to have similar uniformity in both samples, indicating the integrity inorganic wall structure in the unmodified SBA-15 is kept after the grafting. According to the data in Table 1, the specific surface area (S_{BET}), pore volume (V_p) and pore diameter (D_p) are decreased in the modified samples.

The IR spectra of the unmodified and modified SBA-15 samples are given in Fig. 6. In all cases, typical vibrational bands of siliceous materials (i.e., the stretching vibration of the silanol groups at 3,400 cm^{-1} and the asymmetric and symmetric stretchings of Si–O–Si at about 1,100 and 800 cm^{-1}) can be seen [33].

The band at about 1,555 cm^{-1} can be attributed to the –COOH groups present in the grafted samples [36]. The modified samples also revealed bands at 2,850 and 2,930 cm^{-1} due to the stretching vibrations of the C–H bonds of the methylene groups.

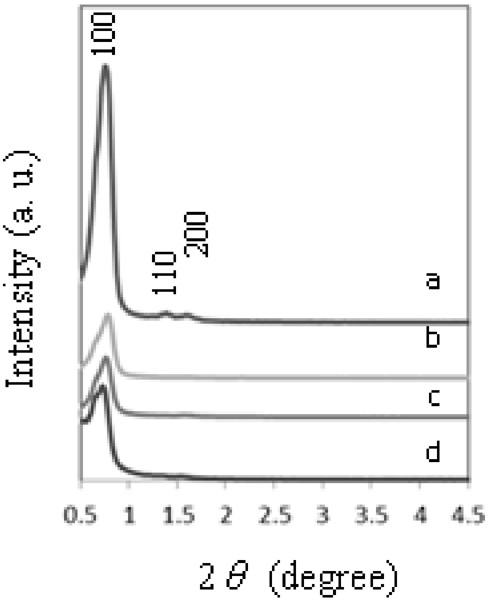

Fig. 3. SAXS patterns of (a) SBA-15 nanorods, (b) S-C1, (c) S-C2 and (d) S-C3.

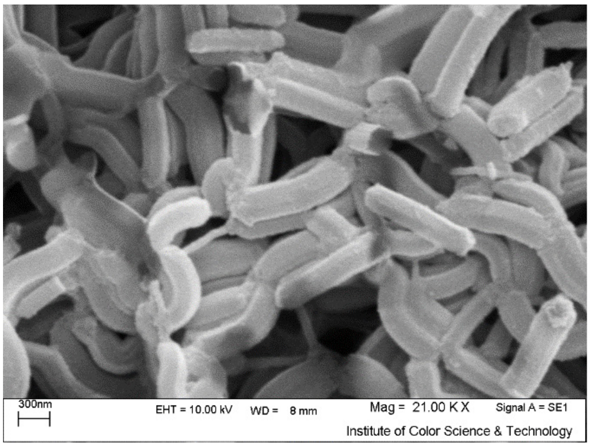

Fig. 4. SEM image of SBA-15 nanorods.

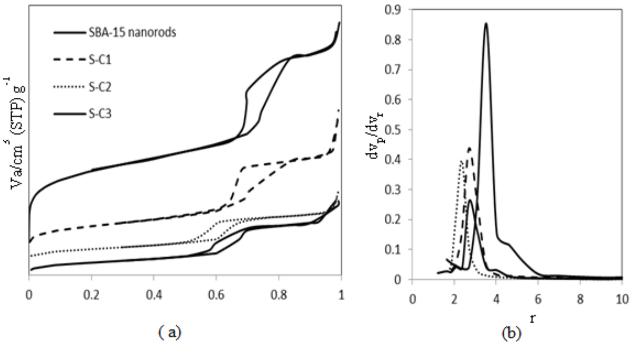

Fig. 5. (a) N_2 adsorption/desorption isotherms and (b) pore size distributions of the non-modified and carboxylic acid-functionalized SBA-15 nanorods.

3.2. Effect of pH on the adsorption efficiency

The results of experiments on the effect of pH on the adsorption of RB5 in the range of 2.0–9.0 are illustrated in Fig. 7. During the experiments, the pH of the test solutions was altered by adding concentrated HCl and NaOH solutions to avoid considerable volume and concentration changes, and the values were monitored using a digital pH meter. It can be noticed that the maximal adsorption efficiency was reached at pH values less than 7 for all three adsorbents (S-C1, S-C2 and S-C3). This is due to the fact that pH may affect the chemistry and surface binding sites of the adsorbent.

RB5 is also considered an anionic dye since it commonly exists in sulfonate form. These $-SO_3-$ groups present in the RB5 easily dissociate and create negative charges in the solution. At acidic pH, the majority of the surface groups (i.e., N and OH) are protonated and hence acquire positive charges, which electrostatically attracts the anionic sulfonic groups. The dye and the carboxyl-grafted SBA-15 can also form hydrogen bonds, which further boosts the adsorption phenomenon. The higher the pH goes, the less becomes the number of the positively charged sites, while the number of negatively charged sites created due to deprotonation increase in parallel. Consequently electrostatic repulsion builds up between the surface of the modified SBA-15 and RB5 molecules.

Table 1
Textural properties of the non-modified and carboxylic acid-functionalized SBA-15 nanorods

Sample	Specific surface area (S_{BET}) (m^2 g^{-1})	Pore volume (V_p) (cm^3 g^{-1})	Pore diameter (D_p) (nm)
SBA-15 nanorods	1,010	1.270	7.06
S-C1	169	0.405	5.40
S-C2	141	0.318	4.20
S-C3	127	0.115	4.20

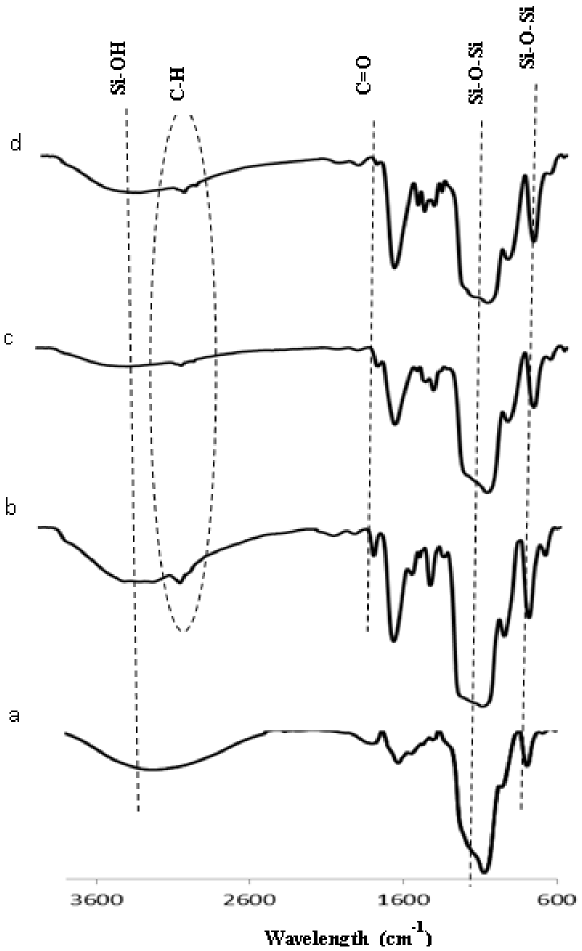

Fig. 6. FTIR spectra of (a) SBA-15 nanorods, (b) S-C1, (c) S-C2 and (d) S-C3.

3.3. Amount of the adsorbent

The influence of the amount of the grafted SBA-15 on removing RB5 was determined at ambient temperature and at pH 5.0. The tests involved varying the amount of the adsorbent from 0.002 to 0.015 g used for removing RB5 from 10 mL of a 20 mg L^{-1} dye solution. Based on the results (Table 2), increasing the amount of the sorbent enhanced the removal efficiency of RB5. 0.002 g of di- and tricarboxyl-functionalized SBA-15 led to a high removal efficiency of 98%, but in the case of tetracarboxyl-functionalized SBA-15, the removal efficiency of 0.002 g of the sorbent was 97%, and reached 98% at 0.005 g.

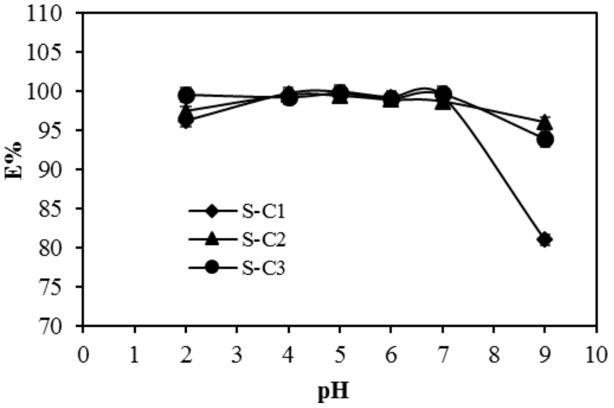

Fig. 7. Effect of pH on the adsorption of RB5 on carboxylic acid-functionalized SBA-15.

Table 2
Effect of the amount of adsorbent on removal efficiency

Adsorbent amounts (mg)	Extraction %		
	S-C1	S-C2	S-C3
2	98.0 (1.3)[a]	98.0 (1.5)	97.1 (0.9)
5	98.3 (0.9)	98.5 (0.8)	98.0 (1.3)
10	98.4 (1.0)	99.0 (1.1)	98.1 (0.9)
15	99.4 (1.6)	99.1 (1.4)	99.2 (1.2)

[a] %RSD based on three replicate analysis.

3.4. Effect of contact time

To investigate the effect of contact time on the adsorption of RB5, a 20 mg L^{-1} solution of the dye (pH = 5.0) was tested at room temperature. The RB5 concentration was then measured at 2, 5, 10, 15 and 20 min, in the presence of the optimal amount of the adsorbent, and the results are illustrated in Table 3. It is easy to note that the adsorption rapidly increases during the initial stage, but this trend lessens over time. Based on the data after around 2 and 5 min for S-C1, and for both S-C2 and S-C3, respectively, about 98% of the total RB5 content is adsorbed. In this light, 5 min was chosen as the optimal contact time for further evaluations.

3.5. Adsorption isotherms

Having the equilibrium adsorption isotherms is a critical point in the design and evaluation of adsorption systems. To obtain this information, the adsorption capacities of the adsorbent for RB5 were measured using solutions with pH = 5.0. One evident fact is that the adsorption capacity of the grafted nanorods is a function of RB5 concentration, which can be attributed to the fact that driving force of concentration gradients the increases with dye concentration. So, as long as enough adsorption sites are available, the adsorption will increase with RB5 concentration.

The equilibrium RB5 concentration (C_e, mg/L) and adsorption (q_e, mg/g) data were fitted to the linear Langmuir adsorption model. The model is based on the basic assumption that the adsorption phenomena occur at specific homogeneous sites within the adsorbent and its linear form is expressed as [37]:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{3}$$

q_m and b being the maximum adsorption capacity (complete coverage of the adsorbent sites with a monolayer of the pollutant) and the equilibrium constant (L/mg), respectively. The data were found to fit well for all three adsorbents (i.e., S-C1, S-C2 and S-C3) with respective correlation coefficients (R^2) of 0.9988, 0.9981 and 0.9998 (Table 4).

Further, Freundlich isotherm is obtained under the assumption of a heterogeneous surface with a non-uniform distribution of heat of adsorption, and its linearized form is as below [38]:

$$\log q_e = \log k_f + \frac{1}{n_f} \log C_e \tag{4}$$

Table 3
Effect of contact time on removal yield

Contact time (min)	Extraction %		
	S-C1	S-C2	S-C3
2	98.9 (1.0)[a]	96.0 (1.8)	96.9 (1.0)
5	99.2 (1.5)	98.0 (0.9)	98.1 (0.8)
10	99.0 (0.8)	98.9 (1.2)	98.0 (0.9)
15	98.6 (0.6)	98.7 (1.9)	97.8 (1.5)
20	98.9 (1.2)	98.4 (0.7)	97.2 (0.8)

[a] %RSD based on three replicate analysis.

In this equation k_f is a rough indicator of the adsorption capacity, and $1/n_f$ is a measure of adsorption intensity or surface heterogeneity, and varies between 0 and 1 as the heterogeneity increases. The constants determined through linear regression analysis are presented in Table 3, which clearly shows that the Freundlich model is not suitable for the process under study (Fig. 8) and the corresponding data fits well in the Langmuir isotherm (Fig. 9) as reflected by the high R^2 values.

Based on the results, the maximum adsorption capacities obtained for S-C1, S-C2 and S-C3 under the experimental conditions reaches 200.0, 312.5 and 256.4 mg/g, respectively. This clearly indicates that the maximum capacity of the tricarboxyl-grafted SBA-15 exceeds that of the di- and tetracarboxyl-functionalized SBA-15 in the case of RB5. This is due to the fact that tricarboxylic acid groups increases the number of sites available as opposed to S-C1. In the case of tetracarboxylic acid grafted SBA-15, the capacity is higher than that of S-C1 and yet less than S-C2. This is due to the fact that although S-C3 has the highest number of surface sites, many of them are not accessible due to steric hindrance caused by the large number of the groups in the relatively small pores of SBA-15.

3.6. Thermodynamics of adsorption

Changes in the Gibbs free energy ($\Delta G°$, kJ mol^{-1}), enthalpy ($\Delta H°$, kJ mol^{-1}) and entropy ($\Delta S°$, J mol^{-1} K^{-1}) act as actual indicators. The thermodynamics of the adsorption phenomenon was evaluated at 288, 298 and 313 K, and the corresponding K_d (distribution coefficient) values were calculated using the Van't Hoff equation [39], as below, to calculate the thermodynamic parameters:

Table 4
Isotherm parameters for adsorption of RB5 on carboxylic acid-functionalized SBA-15

Dye	Langmuir			Freundlich		
	q_m (mg g^{-1})	b (L mg^{-1})	R^2	k_f (mg g^{-1})	$1/n_f$	R^2
Di	200.0	0.296	0.998	137.8	0.078	0.572
Tri	312.5	0.106	0.998	155.1	0.095	0.802
Tetra	256.4	0.619	0.999	142.1	0.093	0.806

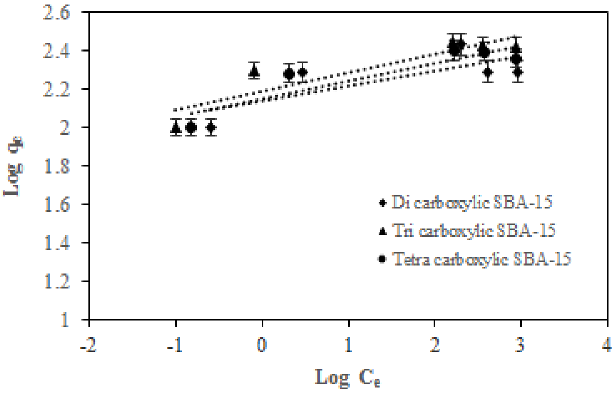

Fig. 8. The Freundlich adsorption isotherm of RB5 on carboxylic acid-functionalized SBA-15.

$$\Delta G^\circ = -RT \ln K_d \tag{5}$$

$$K_d = \frac{q_e}{C_e} \tag{6}$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{7}$$

In the above equations T is the temperature (K), R is the gas constant (8.3145 J mol^{-1} K^{-1}), C_e and q_e represent the equilibrium concentrations in the aqueous phase (mg L^{-1}), and the amount of RB5 per the mass of the adsorbent (mg g^{-1}).

The results are summarized in Table 5. The ΔG° values are negative, indicating the adsorption phenomenon as being spontaneous, and the positive enthalpy changes confirm the fact that the nature of the adsorption process is endothermic. Further the positive ΔS° values indicate increased randomness at the solid–solution interface during the process.

3.7. Effect of modification

To evaluate the effect of modification of the sorbent, 5 mg of the unmodified SBA-15 and tricarboxylic acid-functionalized SBA-15 were added to 10 mL of a 20 mg L^{-1} RB5 solution under gentle stirring at ambient temperature, and kept under these conditions for 5 min. The results of analyzing the treated RB5 solutions showed 99% and 35% removals in the case of the modified and unmodified SBA-15 indicating the great enhancement in the adsorption properties of SBA-15 as a result of the modification.

3.8. Recycling of the sorbent

To evaluate the recyclability of the adsorbent, 5.0 mg samples of the used adsorbents were regenerated using 5.0 mL of a 1.0 M sodium hydroxide solution in a beaker, and the concentration of the desorbed RB5 was determined through spectrophotometry. The obtained results indicated good desorption efficiencies, after a very short time of about 5 min. Once the degeneration was over the adsorbent samples were washed with water and dried in vacuum at room temperature. The experiments proved that the adsorbents could be used at least three times without considerable losses in their adsorption capacity.

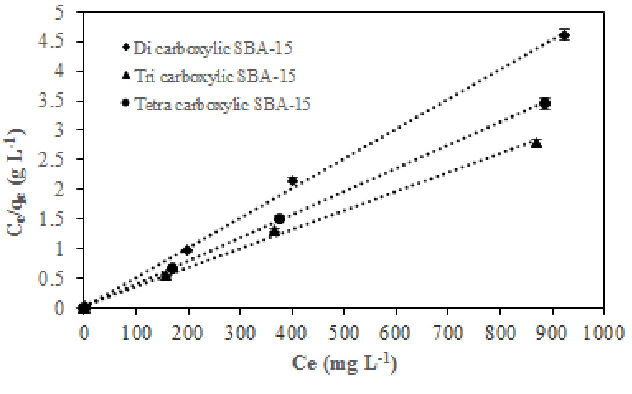

Fig. 9. The Langmuir adsorption isotherm of RB5 on carboxylic acid-functionalized SBA-15.

3.9. Removing RB5 from wastewater samples

Dyeing wastewaters of textile plant were treated using the optimal adsorbent under optimal conditions. To eliminate the matrix effects, the initial and final RB5 concentrations (before and after treatment) were determined through standard addition. The results (Table 6) indicate that the adsorbent can be effectively used for removing RB5 from textile wastewater samples.

3.10. Industrial application of the adsorbents

Treating wastewaters, which are known to contain various dyes, is an important issue. Among the different classes of dyes, reactive dyes are compounds that are widely used due to color fastness, bright colors and ease of application. Concentrations of RB5 in range of 10–1,000 mg/L were reported [40]. At high concentrations, textile dyes may be toxic and more difficult to remove. As a result, a range of sorbent grafted with organic small molecules have been prepared and used for adsorbing dye pollutants from aqueous media. The cost and feasibility of the treatment process depends on the adsorption capacity of the adsorbent, the kinetics of the process and the cost and efficiency of the regeneration process [40]. The SBA was modified with carboxylic acid groups, and the resulting adsorbents were found to be very effective for removing RB5. The adsorption phenomenon was found to be very fast and reach equilibrium in less than 5 min, which in addition to the high adsorption capacities of the adsorbents (which makes all adsorbent suitable for the effective removal of RB5) makes them ideal candidates for large-scale removal of the dyes from various water samples. Although, further studies are needed on cost effectiveness of using this adsorbent to remove dye from industrial effluents, it is clear that high capacity of this adsorbent can be accommodated the cost. Also, the wide range of pH which can be used in this

Table 5
Values of thermodynamic parameters of adsorption of RB5 on carboxylic acid-functionalized SBA-15

Adsorbents	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	$-\Delta G^\circ$ (kJ mol^{-1})		
			288 K	298 K	313 K
Di	85.45	324.8	7.8	11.1	15.9
Tri	55.41	224.0	9.1	11.34	14.7
Tetra	25.11	113.0	7.4	8.5	10.2

Table 6
Removal of RB5 with carboxylic functionalized SBA-15 in real sample

Adsorbent	Initial concentration (ppm)	Final concentration (ppm)	% Removal
S-C1	8.26 (1.21)[a]	0.78 (1.06)	90.56 (1.01)
S-C2	8.26 (1.64)	0.46 (1.37)	94.43 (0.95)
S-C3	8.26 (1.19)	0.33 (1.50)	96.00 (1.08)

[a] %RSD based on three replicate analysis.

Table 7
Comparison of various adsorbents used for removal of RB5 dye

Adsorbent	Adsorption capacities (mg/g)	Ref.
Chitosan/epichlorohydrin/ 3-amino-1,2,4-triazole-5-thiol	487.9	[40]
Chitosan/epichlorohydrin/ melamine	327.3	[40]
Chitosan/gluteraldehyde/ 3-amino-1,2,4-triazole-5-thiol	616.9	[40]
Chitosan/gluteraldehyde/ melamine	692.3	[40]
Yeasts	88.5	[43]
Sepiolite	120.5	[44]
Zeolite	60.5	[44]
Activated carbon	14.08	[45]
Glycidyl methacrylate resin modified with tetraethelenepentamine	62.5	[46]
Multi-walled carbon nanotube	36.2	[47]
Polyaniline nanofibers	312	[48]
Bentonite clay	34.0	[49]
Chitosan/polyamide nanofibers	456.9	[50]
Di-, tri- and tetracarboxylic acid-functionalized SBA-15	200.0; 312.5; 256.4	This work

process is an important advantage for this adsorbent in comparison with the low-cost adsorbent reported in the literature [40–42]. At alkaline pH (usual pH of most of the effluent from textile industry) pre-adjustment for the initial pH to acidic medium is required.

3.11. Comparison of other adsorbents

The dye adsorption capacity data on the application of previously developed adsorbent for removing RB5 [40,43–50] were summarized (Table 7) and compared with those of the di-, tri- and tetracarboxylic acid grafted SBA-15. It can be seen that the adsorption capacities of all modified adsorbent exceed those of most of previously reported samples. It is noteworthy that adsorbent has also less adsorption capacities in comparison with some previous reports. Yet, in terms of the optimal contact time they excel the best previously reported adsorbents (i.e., chitosan/polyamide nanofibers) which require 4 h, to reach the best results.

4. Conclusions

The study focused on developing a simple method for removing RB5 from water and wastewater samples, through the use of surface-modified SBA-15 nanorods. The modification was performed through grafting the sorbent with carboxylic acid groups, and the resulting adsorbents were found to be very effective for removing RB5. The adsorption phenomenon was found to be very fast and the results fitted very well to the Langmuir adsorption model, reaching adsorption capacities of 200.0, 312.5 and 256.4 mg/g for S-C1, S-C2 and S-C3. The highest adsorption capacity was observed with S-C2. S-C1 had a lower capacity due to its lower number of active groups, and S-C3 samples also did not lead to optimal results due to the steric hindrance of the over-abundant functional groups present after grafting with tetracarboxylic acid groups. The adsorbents were successfully used for removing of RB5 from textile wastewater samples.

The adsorption phenomenon was found to be very fast and reach equilibrium in less than 5 min, which in addition to the high adsorption capacities of the adsorbents (which makes all adsorbents suitable for the effective removal of RB5), makes them ideal candidates for large-scale removal of the dyes from various water samples. Although, further studies are needed on cost effectiveness of using this adsorbent to remove dye from industrial effluents, it is clear that high capacity of this adsorbent can be accommodated the cost.

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