



Synthesis and application of *p*-*tert*-butylcalix[8]arene immobilized material for the removal of azo dyes

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ABSTRACT

The present study describes synthesis of a new resin through immobilization of *p*-*tert*-butylcalix[8]arene onto silica and its application for the removal of azo dyes from aqueous media as well as from textile effluents. The newly synthesized material **4** is characterized by FT-IR spectroscopy, scanning electron microscope (SEM) and thermogravimetric analysis (TGA). Reactive Black-5 (RB-5) and Reactive Red-45 (RR-45) azo dyes were used as sorbate. Batch wise sorption experiments were conducted to optimize various experimental parameters such as the effect of sorbent dosage, electrolyte, pH, dye concentration, and contact time. The optimized pH for the effective removal of RB-5 and RR-45 dyes was 9 and 3, respectively. The increase in material **4** dosage increased the percent sorption. Both Langmuir and Freundlich isotherm models were applied to experimental data and Langmuir isotherm model found to be best fit. The results revealed that material **4** was potentially more effective sorbent for the sorption of selected azo dyes as compared to pure silica and *p*-*tert*-butylcalix[8]arene. The field studies also supported the effectiveness of material **4**, which could be useful for the removal of both the dyes and also for the normalization of pH, TDS, conductivity and salinity near to the drinking water.

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1. Introduction

In recent decades with the rapid development of human society as well as science and technology, no doubt the world is reaching to new sky scraping horizon; but at the same time the cost, which the world is paying or will pay in near future in the form of extensive global contamination is certainly very high [1]. Azo dyes pollution is one of the biggest problems in the world that troubles physically and economically [2,3]. The per annum worldwide production and consumption of approximately 10,000 different dyes have been exceeded 7×10^5 tons, furthermore; the dye user industries such as cosmetics, printing, paper, plastics, as well as textiles industries have been recognized as the major environmental polluters [4,5]. Textile and dyestuff manufacturing industries are the two main source of dye waste into the environment; according to the recent estimation about 280,000 tons of the textile dyes per year are discharged in the form of industrial effluents which pose serious threat to natural environment [6]. From an environmental point of view, disposal of colored contaminated waste waters into aquatic systems is of great concern because it can be mixed in surface water and ground water systems, then they may also be transferred to drinking water and bring a chief threat to human health

[7,8]. Although these dye molecules are biologically inactive, but when the soluble azo dyes incorporate into body the liver enzymes and intestinal micro flora split them into corresponding aromatic amines, most of them are toxic, mutagenic and even carcinogenic. Toxicity of these dye intermediates, i.e. aromatic amines have been extensively reviewed [9–12]. Dyes at very low concentrations (less than 1 mg L^{-1}) in the effluent are highly visible and can be toxic to creature in water, but an average concentration 300 mg L^{-1} has been reported in effluents from textile manufacturing process [13,14]. Hence, removal of these dyes from aqueous system has significant importance to the environment and still a technological challenge [15]. Many researchers have paid strenuous attention to dye removal studies and a number of technologies, such as coagulation–flocculation, membrane process, oxidation–ozonation and biological treatment have been used for the removal of the dye contaminants from waste water [16]. However, their low removal efficiency or high operational costs as well as disposal problems often limit their application and thus, there still remains a need for searching economical, reprocess able and environmental friendly techniques [17]. Sorption technique has proven to be an effective and attractive process for the decontamination of the dye-containing effluents. An extensive list of natural as well as synthetic sorbent for dye removal has been accumulates recently by Liu et al. [18]. The close analysis of the literature revealed that by virtue of relatively low sorption efficiency and problems with regeneration their use is limited [19]. Therefore, some innovative, regenerable

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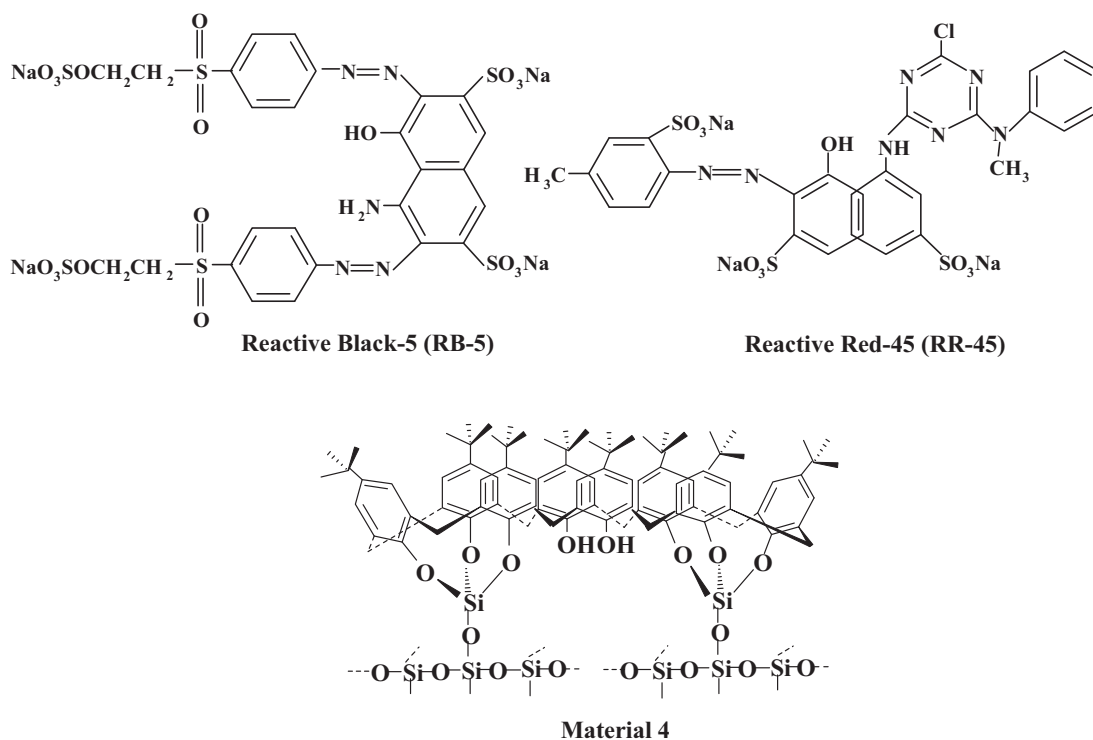


Fig. 1. The chemical structures of sorbate (RB-5 and RR-45 dyes) and sorbent (material 4) used in experiments.

and highly efficient sorbents are still under investigation. In this respect, promising synthetic materials such as calixarenes have got much interest because these are the most important platforms for the preparation of new macrocyclic hosts for the recognition of harmful and toxic species [20–23]. Consequently, the chemical immobilization of calix[*n*]arene framework onto the surface of silica not only enhances its reusability but at the same time can lead to materials with important applications in separation science. The silica-based resins could provide excellent chemical, physical and thermal stability under various experimental conditions. Moreover, silica deserves particular attention due to the hydrophilic surface and presence of silanol groups which are weakly acidic and are very reactive and by virtue of hydrophilic character, the silica surface physically sorbs water molecules. Such property indicates that on modification with calixarene moieties, silica surface permits interaction with various organic dyes [24–28].

The main focus of this study was to enhance the sorption property of the pure silica (1) by immobilizing *p*-tert-butylcalix[8]arene (3) onto its surface. Furthermore, the influence of dosage, contact time, initial dye concentration, pH and temperature on the sorption capacity of material 4 is also investigated in detail.

2. Materials and method

2.1. Reagents

Two commercial textile dyes Reactive Black-5 (FW: 991.82, λ_{\max} : 597 nm) and Reactive Red-45 (FW: 801.7, λ_{\max} : 540 nm) were obtained from commercially available source and used in all experiments as a sorbate without any further purification. The chemical structures of both dyes are shown in Fig. 1. The waste water samples were collected from textile and dyeing manufacturing industries. The pH of the solution was adjusted by mixing appropriate amount of (0.1 N) HCl and/or NaOH. All chemicals used were of analytical grade. Toluene and triethylamine were freshly distilled from CaH₂ under nitrogen prior to use. Silica gel (230–400 mesh) was procured

from Fluka (Germany). Analytical TLC was performed on precoated silica gel plates (SiO₂, Merck PF₂₅₄). Deionized water that had been passed through a Milli-Q system (Elga Model Classic UVF, UK) was used for the preparation of solutions.

2.2. Apparatus

Elemental analyses were performed using a CHNS elemental analyzer (model Flash EA 1112, 20090-Rodano, Milan, Italy). Melting points were determined on a Gallenkamp apparatus model (MFB. 595. 010 M, England). IR spectra were recorded on a Thermo Nicolet 5700 FT-IR spectrometer (WI. 53711, USA) as KBr pellets. Scanning Electron Microscopic (SEM) studies were performed using JSM-6380 instrument. UV–vis spectra were obtained with Perkin Elmer (Shelton, CT06484, USA) Lambda 35 UV–vis spectrophotometer. The pH measurements were made with pH meter (781-pH/Ion meter, Metrohm, Herisau Switzerland) with glass electrode and internal reference electrode. A Gallenkamp thermostat automatic mechanical shaker (model BKS 305-101, UK) was used for batch study.

2.3. Synthesis

p-tert-Butylcalix[8]arene (3) as illustrated in Fig. 2 was synthesized according to the previously published method [29].

2.3.1. Immobilization of *p*-tert-butylcalix[8]arene (3) onto the silica

10 g of silica (230–400 mesh) washed with deionized water and dehydrated at 300 °C in 250 mL round bottom flask in vacuum oven for 5 h. After the silica was cooled to room temperature, a solution of SiCl₄ in dichloromethane (1 M, 50 mL) was added followed by the addition of triethylamine (4.6 g, 6.36 mL). On addition milky fumes were observed. The resulting cloudy solution was stirred at room temperature for 24 h. Then the solvent was evaporated through rotary evaporator.

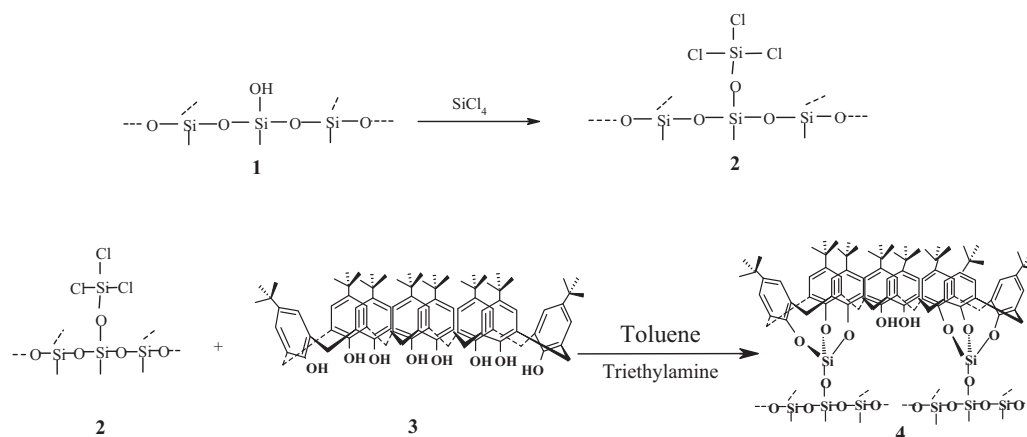


Fig. 2. The synthesis of *p-tert*-butylcalix[8]arene immobilized material (4).

A solution of *p-tert*-butylcalix[8]arene (3.96 g, 3.06 mmol) in chloroform (100 mL) was added to the white powder of modified silica **2**. Again triethylamine (15 g, 20.7 mL) was added (Once again milky fumes were observed) and the reaction mixture was refluxed for a period of 50 h. The immobilization was monitored by FT-IR spectroscopy. The resulting grayish resin was filtered off, washed with hot chloroform (300 mL), methanol (200 mL), water (200 mL), methanol (200 mL) and finally with chloroform (100 mL). The resulting resin was dried at 100 °C under vacuum. The immobilization was confirmed by evaluating the FT-IR spectrum, SEM analysis and Thermogravimetric analysis (TGA) of material **4**, which are discussed below.

2.4. Batch method

The sorption capacity of the material **4** for RB-5 and RR-45 azo dyes was determined by batch wise tests. Various parameters such as amount of dosage, pH, contact time, dye concentration and effect of electrolyte were optimized. The experiments were conducted in 25 mL Erlenmeyer flasks with glass cap which contain particular amount of the sorbents as well as particular concentration of sorbets solution. To obtain sorption equilibrium, the Erlenmeyer flasks were stirred on a horizontal shaker operating at a constant speed (170 rpm) at 25 °C for 30 min. The resin was filtered and the sorbed dye was analyzed by the UV–vis. spectrophotometer. The % sorption of RB-5 and RR-45 azo dyes was calculated (Eq. (1)) as follows:

$$\% \text{ Sorption} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i (mol L^{-1}) is the initial concentration of solution before sorption and C_f (mol L^{-1}) is the final concentration after the sorption of azo dye.

3. Results and discussion

3.1. Characterization

3.1.1. FT-IR spectra

The material **4** shows some additional bands at 2961, 2863, 1482 and 1384 cm^{-1} for $-\text{C}-\text{H}_3$, $-\text{C}-\text{H}_2$, $\text{C}=\text{C}$ and $\text{C}-\text{O}$ groups of calixarene moiety (Fig. 3B) in FT-IR spectrum, which confirms the immobilization of *p-tert*-butylcalix[8]arene onto the silica.

3.1.2. Scanning electron microscope

Since, the sorption is a surface phenomenon, the rate and degree of sorption is highly dependent on the surface functional groups, pore size and surface area of the sorbent. Therefore, SEM is known

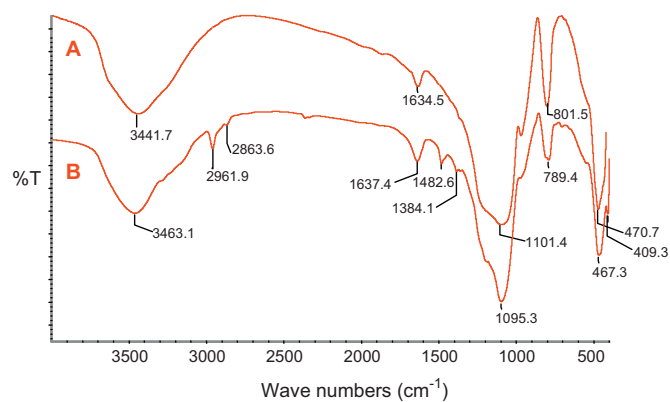


Fig. 3. FT-IR spectra (A) pure silica **1** (B) material **4**.

as one of the most widely used surface diagnostic tools [30], for that reason SEM micrographs were obtained (by applying 05 kV electron acceleration voltage) to observe the surface morphology of pure silica (**1**) and material **4**. The SEM micrograph of pure silica (**1**) (Fig. 4A) shows a very smooth morphology while after the immobilization of *p-tert*-butylcalix[8]arene onto the surface of pure silica (Fig. 4B); it shows an irregular morphology covered by foreign material, i.e. *p-tert*-butylcalix[8]arene.

The presence of attached particles i.e., *p-tert*-butylcalix[8]arene onto the surface of silica confirms the immobilization.

3.1.3. Thermogravimetric analysis

Thermal degradation of *p-tert*-butylcalix[8]arene immobilized material (**4**) in inert atmosphere was analyzed, the result is shown in Fig. 5. The thermal degradation of material **4** occurs in two stages. The first stage, from 30 °C to 130 °C, is a quick weight loss region corresponding to the removal of physically adsorbed water. The slow weight loss from 130 °C to 750 °C is a result of the dehydration between silanol groups, while the maximum rate of weight loss is observed at 450 °C as a result of calixarene combustion.

3.2. Sorption study of selected azo dyes

3.2.1. Effect of sorbent dosage

To study the effect of sorbent dosage (**1** and **4**) on the % sorption of RB-5 and RR-45 azo dyes, the experiments were carried out at 25 ± 1 °C by using different amounts of sorbent (i.e. 25, 50, 75, 100, 125 and 150 mg of **1** and **4**) at fixed dyes concentration (2×10^{-5} M) as represented in Fig. 6. The % sorption of RB-5 and RR-45 increased with increasing dosage of sorbents. This is most probably due to

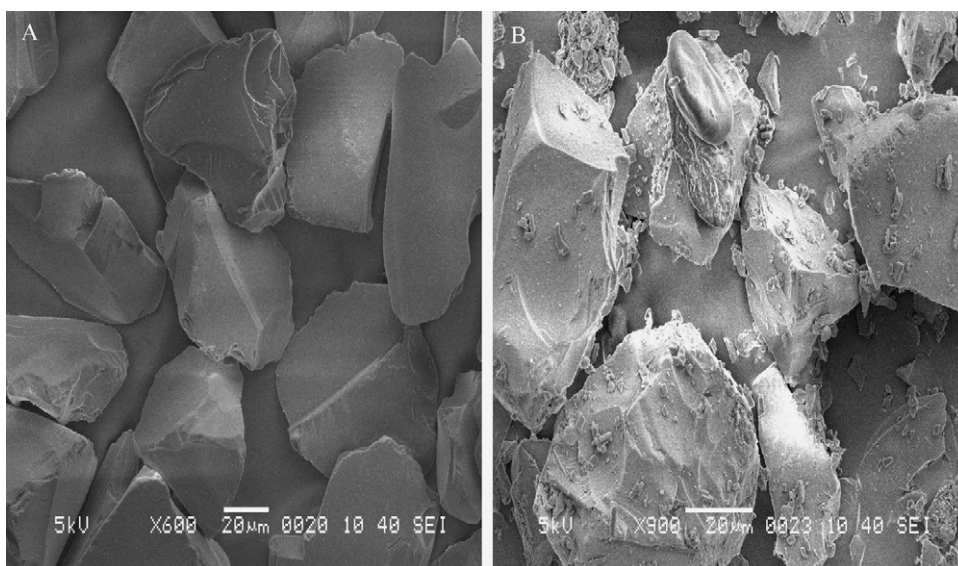


Fig. 4. SEM images of (A) pure silica **1** (B) material **4**.

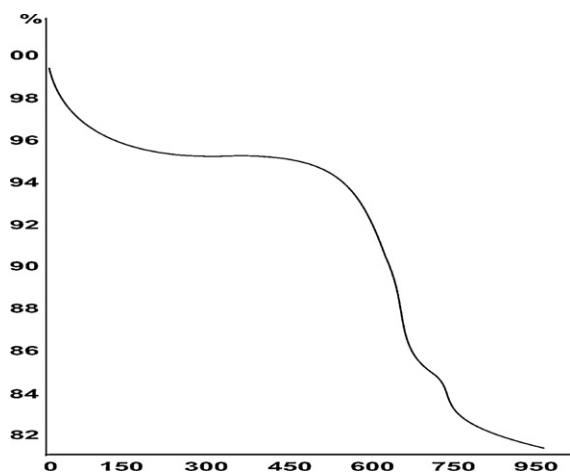


Fig. 5. TGA curve of material **4**.

the fact that sorption sites increases with increasing dosage of sorbents. However, the maximum dye removal efficiency has been achieved at 100 mg of the sorbents, after which an increase in sorbents dosage does not further improve the dye removal efficiency.

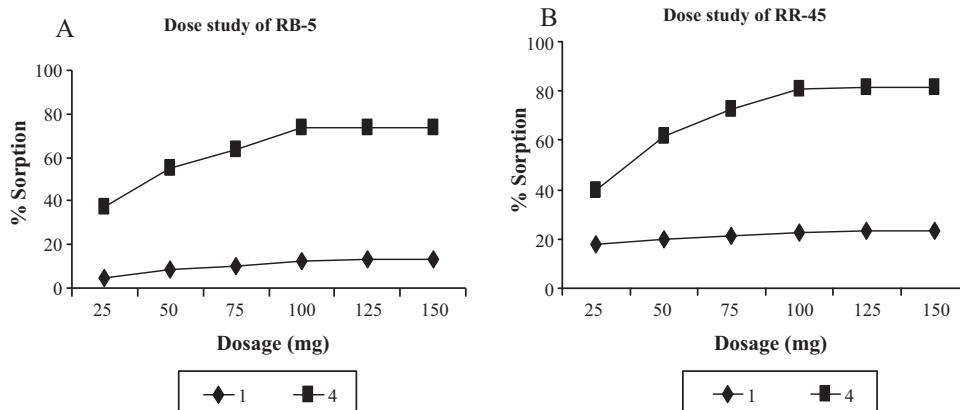


Fig. 6. Effect of sorbent dosage (**1** and/or **4**) on the percent sorption of: (A) RB-5 and (B) RR-45. (Contact time 30 min, NaCl 0.2 M and dye concentration 2×10^{-5} M).

Thus, all the experiments were carried out with a fixed amount of sorbents, i.e. 100 mg.

3.2.2. pH effect on the sorption of azo dyes

The extent of sorption depends upon various factors, pH is also one of them most important parameter, because the solution pH affects surface charge of the sorbents as well as the degree of ionization of the materials present in the solution. As in this study, the influence of pH (i.e. 3, 5, 7, 9 and 11) on the sorption of azo dyes was investigated with different sorbents, i.e. pure silica (**1**), *p*-*tert*-butylcalix[8]arene (**3**) and material **4** as represented in Fig. 7. The results obtained indicate that the pH affects the RB-5 dye sorption onto material **4**. The amount of sorbed RB-5 dye was higher (93%) at pH 9.0 as represented in Fig. 7 A. This may be due to the fact that the change of pH affects the adsorptive process through dissociation of functional groups on the active sites of the sorbent. RB-5 dye is comparatively a large molecule and contains sulfonate groups and upon dissolution in aqueous media these groups can easily dissociate and thus, the dye molecule becomes negatively charged at higher pH. On the other hand at higher pH the deprotonation of the phenolic hydroxyl groups of *p*-*tert*-butylcalix[8]arene moiety in the material **4** converts them into negative charged phenoxide ions. The deprotonation not only suppress the electrostatic repulsion between the dye and sorbent but also at the same time, it provides a favor-

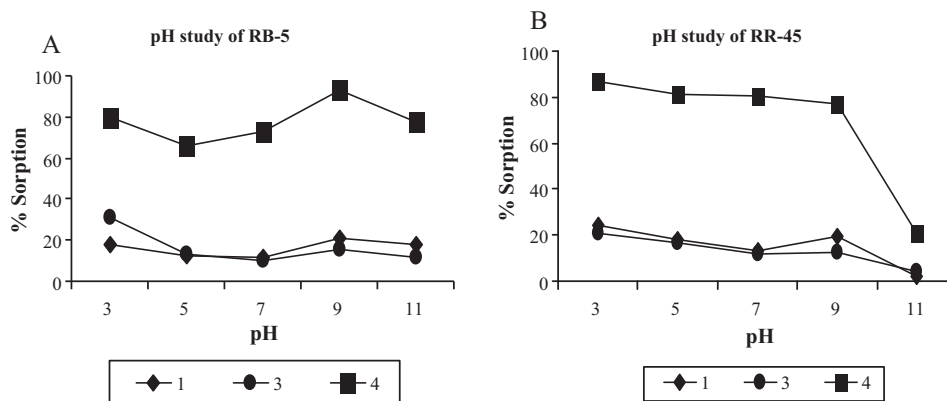


Fig. 7. pH effect on the percent sorption of: (A) RB-5 and (B) RR-45. (Sorbent dose 100 mg, Contact time 30 min, NaCl 0.2 M and dye concentration 2×10^{-5} M).

able environment in which due to the electrostatic interactions through metal ion coordination the dyes are extracted. The phenoxide ions of *p-tert*-butylcalix[8]arene show binding abilities toward sodium cations which suggests an ion-pair extraction mechanism in which Na^+ coordinates with the phenoxide ions along with the azo dye anions, while the rest of the azo dye molecule inserts into the hydrophobic calixarene cavity. On contrary, the lower sorption above the pH 9 may be due to the abundance of OH^- ions, which compete with the outer surface of the sorbent [31–33].

The influence of pH plays a key role on separation sciences thus, to recognize the pH effect on sorption of RR-45 onto different sorbents (i.e. **1**, **3** and **4**) experiments was carried out at different pH (Fig. 7B). The results obtained show that by decreasing the pH, % sorption increases and it attains maximum value (86%) at pH 3. Here in this case, the main mechanism is surface complexation by means of surface association between the acidic phenolic hydroxyl ($^+\text{OH}_2$) groups of *p-tert*-butylcalix[8]arenes moiety in the material **4** and the dye anion [19]. In contrast, the dye removal efficiency decreases at higher pH, may be due to the deprotonation.

The sorption efficiency of material **4** over all has been found greater than the **1** and **3** (Fig. 7A and B); may be due to the greater surface area and appropriate projection of binding sites of calixarene moiety in material **4**.

3.2.3. Influence of the NaCl concentration on the sorption of azo dyes

Dye sorption depends strongly on electrostatic parameter such as ionic strength. The electrostatic interactions can be screened by the addition of electrolyte, as in this study influence of NaCl concentration on the sorption of RB-5 and RR-45 dyes onto material **4** as represented in Fig. 8 clearly indicates that electrostatic interactions might be the important driving force in azo dyes sorption.

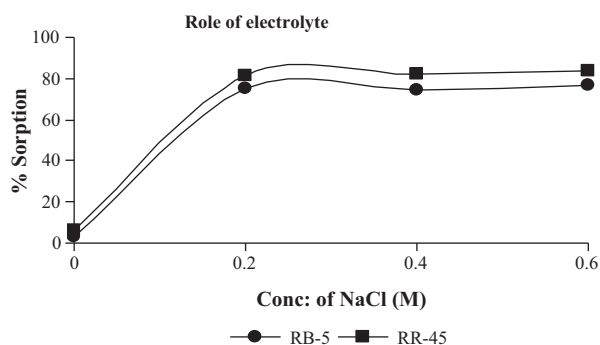


Fig. 8. Effect of NaCl concentration on percent sorption of RB-5 and RR-45 (Sorbent dose 100 mg, Contact time 30 min, dye concentration 2×10^{-5} M).

The general trend observed that the color removal efficiency increased with increase of NaCl concentration up to 0.2 mol L^{-1} , above which there was no additional effect.

This is due to the fact that NaCl provides an ionic balance between the two phases and affect the transport efficiency. Furthermore, NaCl increases solubility of azo dyes through the common ion effect, resulting in an increased and facilitated transport to the organic phase [34,35].

3.2.4. Effect of contact time

Sorption of RB-5 and RR-45 dyes as a function of shaking time was studied onto material **4** at 25°C . The color removal percentage increases with the increase of contact time and remains constant after a particular time as shown in Fig. 9. The obtained results show that % sorption of dyes increases rapidly in the beginning and then equilibrium was established within 10 min but slowly it increases up to 30 min.

3.2.5. Sorption isotherm

Sorption isotherm is fundamental concept in separation science and it may be constructed by measuring the concentration of the sorbate in the medium before and after sorption, at constant temperature. Several sorption equilibrium models have been broadly accepted for the study of liquid/solid phase sorption behavior and by applying these sorption models some very useful information such as sorption capacity, structure of the sorbed layer and the interaction between sorbate and sorbent can be predicted [36].

In this work the experimental data was fitted into two most important isotherms, Langmuir and Freundlich models at optimized parameters to investigate the sorption capacity of material **4** toward the selected azo dyes. The Langmuir isotherm model assumes monolayer coverage of sorbate on a homogeneous sur-

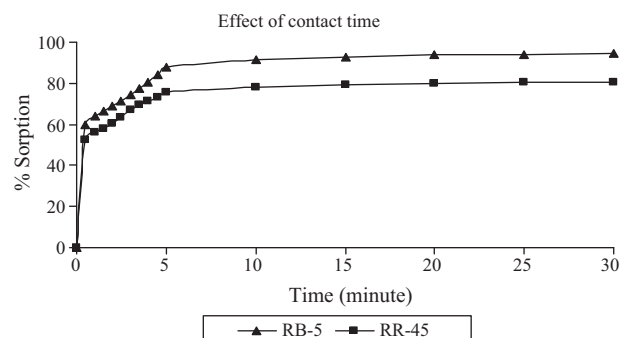


Fig. 9. Effect of contact time on percent sorption of RB-5 and RR-45 (Sorbent dosage 100 mg and dye concentration 2×10^{-5} M).

Table 1
Freundlich and Langmuir constants for azo dyes sorbed onto material **4**.

Azo dye	Langmuir			Freundlich					
	$Q_{\text{mmol g}^{-1}}$	$b \times 10^4 \text{ L mol}^{-1}$	R_L	R^2	$A \text{ mol g}^{-1}$	n	$1/n$	R^2	
RB-5	318.2	31 .4	0.137	0.030	0.998	1069.5	2.491	0.401	0.948
RR-45	230.88	7 .21	0.409	0.121	0.988	12.85	2.360	0.424	0.981

face of sorbent; where as Freundlich isotherm model suggest the heterogeneity of the sorbent surface and multilayer formation. The details of the isotherms are also available elsewhere in literature [2,37,38].

The experimental data have been analyzed by using the linearized forms of Langmuir and Freundlich isotherm models [39,40] in the following way;

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

$$\ln C_{\text{ads}} = \ln A + \left(\frac{1}{n}\right) \ln C_e \quad (3)$$

where C_{ads} is the amount of sorbate (mol g^{-1}) at the sorbent surface and C_e is the amount of sorbate in the liquid phase at equilibrium (mol L^{-1}).

The initial concentration of sorbate is in the range of 2×10^{-5} to $1 \times 10^{-4} \text{ mol dm}^{-3}$ using 100 mg of sorbent per 10 mL of sorbate and 30 min of shaking time at 25°C . These equations were used to correlate the amount of azo dyes sorbed per unit amount of the sorbent. The constants for both models (Q and b for Langmuir isotherm, A and n for Freundlich isotherm) were experimentally calculated and are summarized in Table 1.

The values of Q and the Langmuir constant b are calculated from the slope and intercept of the plot of C_e/C_{ads} vs C_e , as shown in Fig. 10.

The characteristic of the Langmuir isotherm can be expressed by the dimensionless constant called equilibrium parameter, R_L , which is calculated as;

$$R_L = \frac{1}{(1 + bC_i)} \quad (4)$$

where b is the Langmuir constant and C_i is the initial concentration of adsorbate (mol L^{-1}), the R_L values indicate favorability ($0 < R_L < 1$) of isotherm.

In the same way the values of A and $1/n$ are calculated from the intercept and slope of plot $\ln C_{\text{ads}}$ against $\ln C_e$ as shown in Fig. 11.

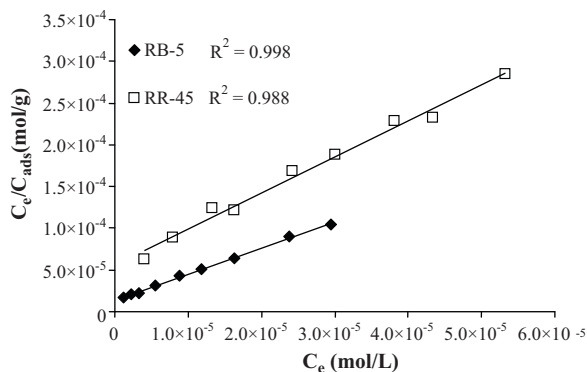


Fig. 10. Langmuir sorption isotherms of the RB-5 and RR-45 azo dyes onto material **4**.

The n values demonstrate the favorability the Freundlich isotherm model [41,42].

The calculated values of the Langmuir and Freundlich equations parameters are given in Table 1. The comparison of correlation coefficients (R^2) of RB-5 and RR-45 azo dyes indicates that sorption of both azo dyes onto material **4** can be better demonstrate by the Langmuir isotherm equation compared to the Freundlich isotherm equation. The applicability of the Langmuir sorption model suggests the monolayer coverage of RB-5 and RR-45 dyes on the surface of material **4**.

3.3. Comparison of RB-5 azo dye sorption with other sorbents

The maximum sorption capacity (Q_m) of material **4** for RB-5 dye has been calculated as $318.2 \text{ mmol g}^{-1}$ at pH 9. A comparison of maximum RB-5 azo dye sorption capacity of material **4** with other sorbents reported in the literature [44–46] is given in Table 2. The data show that the sorption capacity of material **4** is relatively high when compared with other sorbent materials. It may be due to the greater surface area and appropriate projection of binding sites of calixarene moiety in material **4**.

3.4. Field application of material **4**

The field studies for real waste water samples have been conducted. The samples were collected from the dyes manufacturing as well as textile industries of Karachi. The batch study have been performed to evaluate practical applicability of material **4** by using 200 mg sorbent and 20 mL of dye waste water sample that has been stirred for 30 min, at ambient temperature in 50 mL Erlenmeyer flasks. The concentrations of RB-5 and RR-45 dyes were investigated before and after the treatment of waste water with material **4**. From the results, it has been noted that the material **4** reduces the concentrations of both azo dyes (i.e. RB-5 and RR-45) as for RB-5 8.29×10^{-5} , 3.30×10^{-5} , 3.33×10^{-5} from 1.02×10^{-4} , 7.13×10^{-5} and 7.94×10^{-5} for the samples 1–3, respectively. For RR-45, 7.29×10^{-5} , 4.57×10^{-5} , 4.47×10^{-5} from 8.49×10^{-5} , 7.38×10^{-5} , 8.37×10^{-5} for the samples 1–3, respec-

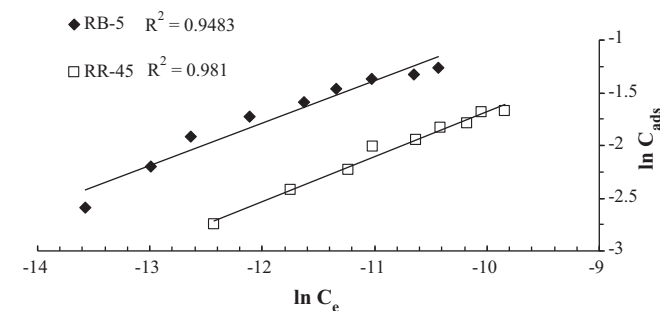


Fig. 11. Freundlich sorption isotherms of the RB-5 and RR-45 azo dyes onto material **4**.

Table 2
Comparison of sorption performance of material **4** for the RB-5 dye with others.

Name of sorbent	pH	Temp.	Q_m	Reference
Thermophilic cyanobacterium <i>Phormidium</i> sp	2	25 °C	24.3 mg g ⁻¹	[43]
Activated carbons, SPS-200 (sawdust-based)	10.7	25 °C	415.4 mg g ⁻¹	[44]
Activated carbons, SPC-100 (coal-based)	10.7	25 °C	180.8 mg g ⁻¹	[44]
<i>Aspergillus foetidus</i>	2.3	50 °C	106.4 mg g ⁻¹	[45]
BTM (Basic oxygen furnace (BOF) slag treated by milling)	2	25 °C	74.4 mg g ⁻¹	[46]
BTA (Basic oxygen furnace (BOF) slag treated by acid)	2	25 °C	109.5 mg g ⁻¹	[46]
Material 4	9	25 °C	318.2 mmol g ⁻¹	In current study

Q_m stands for Langmuir sorption capacity of sorbent.

Table 3
Comparison of pH, TDS, conductivity and salinity of waste water samples by using material **4**.

S. no.	Before treatment				After treatment			
	pH	TDS mg L ⁻¹	Conductivity μ S cm ⁻¹	Salinity	pH	TDS mg L ⁻¹	Conductivity μ S cm ⁻¹	Salinity
01	10.5	391	792	0.2	8.80	301	612	0.0
02	7.49	237	482	0.0	7.4	233	471	0.0
03	6.90	250	507	0.0	7.83	223	455	0.0

tively. The material **4** is also effective for the normalization of pH, TDS, conductivity and salinity near to the drinking water (Table 3).

4. Conclusions

FT-IR spectroscopy, scanning electron microscopy and thermogravimetric analysis techniques confirmed the synthesis of material **4**. The different parameters, i.e. dosage of sorbent, pH, dye concentration and electrolyte were optimized through batch sorption experiments and results revealed that sorption is highly pH dependent. The sorption trend was found to follow Langmuir isotherm model as compared to the Freundlich isotherm. The field studies also support the effectiveness of material **4** not only for the removal of both the dyes but also for the normalization of pH, TDS, conductivity and salinity near to the drinking water. The results of the present study indicated that material **4** has high capacity to adsorb RB-5 and RR-45 azo dyes from the contaminated waste water.

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