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Removal of basic dyes from aqueous solutions using calix[4]resorcinarene carboxylic acid derivatives

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Abstract

Water-insoluble calix[4]resorcinarenes derivative 1 and 2 were synthesized and used as sorbents to extract selected basic dyes rhodamine B (RB), methylen blue (MB) and methyl violet (MV). The isolated complex: calix[4]resorcinarene 1-dye were characterized by Fourier transform infrared spectroscopy, Fluorescence spectroscopy, PDRX and Differential scanning calorimetric analysis. The dye adsorption experiments were carried out from an aqueous solution in a batch reactor. The effect of several parameters has been determined to obtain the best experimental conditions. The equilibrium adsorption data were interpreted using Langmuir and Freundlich isotherms models (best correlation: $R^2 > 0.997$). The calculated maximum adsorption capacity (q_{max}) for the RB at 25 °C were 29.49 mg/g at pH=8.3. The mechanism of adsorption onto the calix[4]resorcinarene is considered to be due to a host-guest interaction between the dye and azo-calix[4]resorcinarene molecular cavity. The results showed that calix[4]resorcinarene (1) can be considered as potential adsorbents for basic dye from dilute aqueous solution**.**

Keywords: Calix[4]resorcinarene, Basic dye, Sorption isotherm, Sorption capacity, inclusion, Host-Guest

Introduction

Several industries, such as textile, ceramic, paper, printing, and plastic use dyes in order to colour their products. The release of coloured wastewater from these industries may present eco-toxic hazard and may eventually affect human through food chain if accumulated. In the colouring process, these industries also consume substantial volumes of water, and as a result, large amount of coloured wastewater are generated [1, 2]. Some of these dyes are toxic in nature; their removal from the industrial effluents is a major environmental problem. Furthermore, wastewater containing dyes is very difficult to be treated, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion and stable to light, heat and oxidizing agents [3, 4]. Many methods of treatment have been adopted to remove dyes from wastewater, which can be divided into physical, chemical and biological methods. Generally, physical methods which include adsorption [5, 6], Photocatalytic degradation [7], ion exchange [8], and membrane filtration is effective for removing reactive dyes without producing unwanted by-product [9]. Therefore, during recent decades, much interest has been focused on the design and the synthesis of artificial receptors and the related compounds. Molecules possessing ability for selective interactions with defined ions or neutral molecules has great importance in supramolecular chemistry, where they can be used for the construction of host-guest type receptors. This was achieved with the development of macrocyclic receptors, such as crown ethers [10, 11], cyclodextrins [12, 13] and calix[n]arene [14-17].

Calixarenes are the third major class of supramolecular host of phenolic units. One of the important properties of calixarene is its ability to recognize cationic and anionic species, as well as neutral molecules. These receptors have the possibility to form interesting complexes both with metal cations and biological compounds by exhibiting extractability and selectivity. Many studies that have been published were dedicated to calixarenes, particularly in the molecular inclusion of biological substrates, such as amino acids [18]. Various applications of calixarenes also refer to purification, chromatography, catalysis, enzyme mimics, ion selective electrodes, phase transfer, transport across membranes, ion channels, and self-assembling monolayers [19, 22]. In this work, we report the use of the carboxylic derivatives of calix[4]resorcinarene, as a sorbent, in aqueous solutions for the removal abilities of basic dyes such as Methylene Blue (MB), Methyl Violet 2B (MV), and Rhodamine B (RB) with a model system of aqueous dyes solutions. The effects of contact time, initial dye concentration, ionic strength, agitation rate, sorbent content, and pH on the sorption capacity are investigated.

2. Materials and methods

2.1. Apparatus

IR spectra were recorded with a Shimadzu FTIR-8300 spectrometer as KBr pellets. UV-Vis spectra were obtained with a Shimadzu 160 A UV-Vis recording spectrophotometer. Fluorescence measurements were carried out using JASCO FP-8200 spectrophotometer in quartz cuvette of 1 cm path length. Differential Scanning Calorimetric (DSC) was performed from 0 to 400 °C at a heating rate of 10°C/min under a nitrogen atmosphere with a gas flow rate of 40 ml/min. The analysis was carried out in sealed aluminum pans and the amount of the sample was 8-10 mg. Powder X-ray diffraction patterns (PDRX) of all samples were determined using Philips model X-Pert X-ray diffractometer, with a CuK α anode at 40 kV and 30 mA and at a scan rate of 1°/min from 2θ rang 1° to 65°.

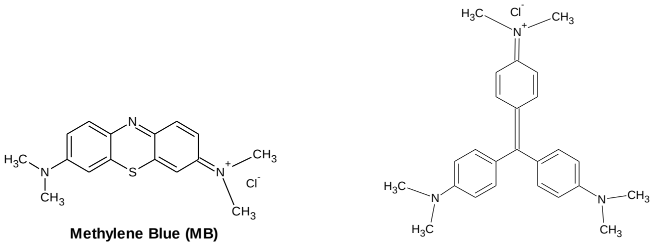
The pH values were measured with HANNA pH Meter 210 and adjusted by the addition of aqueous solutions of HCl or NaOH (1M). The pH meter was standardized.

Standard reference materials obtained from Sigma-Aldrich, as well as blank samples, were included in each batch of analyses for quality assurance and quality control (QA/QC) procedures.

Results were considered satisfactory for UV-vis analysis when within a range of ±10% from certified values. All samples were analyzed in duplicate and results were accepted when the relative standard deviation was within 5%.

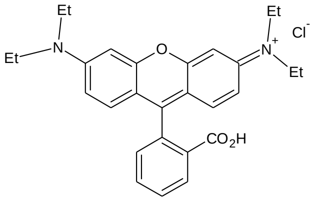
2.2 Reagents

Basic dyes such as Methylene Blue (MB), Methyl Violet 2B (MV), and Rhodamine B (RB) (Scheme 1.) used in this study were purchased from Sigma-Aldrich, with 98% of purity, the purity of the dyes was verified by their absorbance spectra, and they were used without any additional purification.



Methylene Blue (MB)

Methyl Violet 2B (MV)



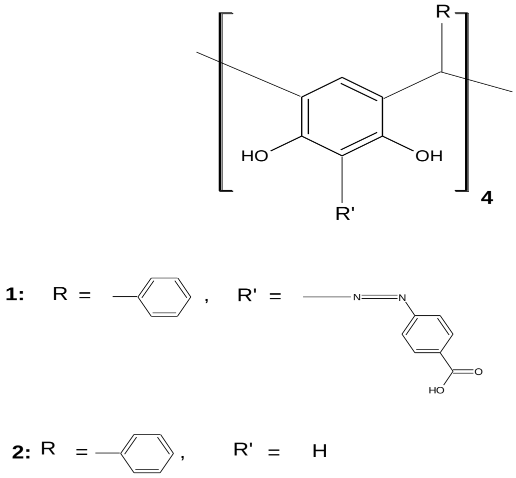
Rhodamine B (RB)

Scheme 1: Structure of basic dyes

The structure of the sorbents developed, for this purpose, is shown in scheme 2. The calix[4]resorcinarenes (1) and (2) were synthesized according to the literature procedures [23]. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q plus water purification system.

2.3 Methods

In each sorption experiment, 10 ml of dye aqueous solution with known concentration and pH ware added to 0.05 g of the macrocycle in a 25 ml glass stoppered flask at room temperature, 25± 1°C, and the mixture was magnetically stirred at 180 rpm. After 3 hours finally left to stand for an additional 30 min, and the solution was centrifuged for 10 min at 5 Krpm to separate the sorbent. The absorbance of supernatant solution was estimated to determine the residual concentration. Residual dye concentration was determined by UV-Vis analyses. Using absorbance values recorded at λ_{max} for each basic dye solutions: at 665 nm for MB, 586 nm for MV, and 553 nm for RB.



Scheme 2: Calix[4]resorcinarene derivatives (1,2)

The percentage of dye removal (%) was calculated from the concentration (C) of the aqueous phases at λ_{max} for each dye according to Eq (1).

Dye Removal (%) = 100 $(C_0 - C)/C_0$ (1)

Where C_0 and C are the initial and the final concentration of basic dyes before and after adsorption, respectively.

The amount of adsorption at equilibrium q_e (mg/g), was calculated by

$$q_e = \frac{C0 - Ce}{m} . V$$

Where V is the volume of the dye solution in ml and m is the mass of the loaded adsorbent (1) C0 is the dye concentration in the aqueous solution before contact with sorbent and Ce dye concentration in the aqueous solution after contact with adsorbent (Table-1).

Table 1: Sorption of basic dyes by examined macrocycles ($m_{1,2}$ = 0.05 g; V_{dye} = 10 mL)

Macrocycles	**RB**	**MB**	**MV**
	C°_{Dye}(mM) Dye Removal (%)	**C°_{Dye}(mM) Dye Removal (%)**	**C°_{Dye}(mM) Dye Removal (%)**
1	0,02 98,33	0,02 **91,41**	0,02 **72,29**
2	0,02 1>	0,02 1>	0,02 1,13

Contact time 3h

Initial pH was controlled by the addition of dilute 0.1 N HCl or 0.1 N NaOH solution, and the concentration of dye solution ($2.5\ 10^{-6} - 2.\ 10^{-5}$M) at different time intervals, as well as by varying the amount of sorbent (0.02-0.09g/10 ml). The experiments were carried out at initial pH values ranging from 2 to10. Each experimental point is the average of three independent runs and all the results were reproducible with ± 6% error limit.

The macrocycles (1,2) taken for the present study have a very limited solubility in water controlled by their UV-Vis spectra in deionized water. The presence of the sorbent in aqueous solutions could be verified by the presence of their characteristics bands in the range of 200-450 nm (fig. 1.).

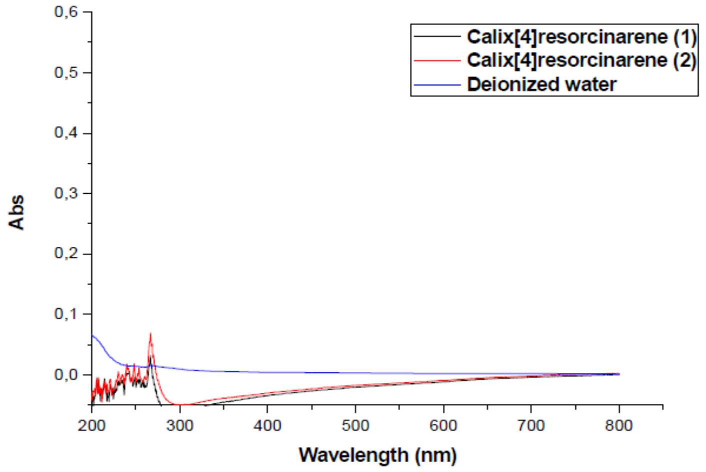


Figure 1: Evaluation of solubility of Calix[4]resorcinarene derivatives (1,2) in deionized water by UV-Vis

3. Results and discussion

Effect of pH and aquatic environment on the calibration curves and λ_{max} (maximum wavelength of the each dye) were studied (Fig. 2.). For single-component dye solutions, the absorbance was measured at λ_{max} of each dye.

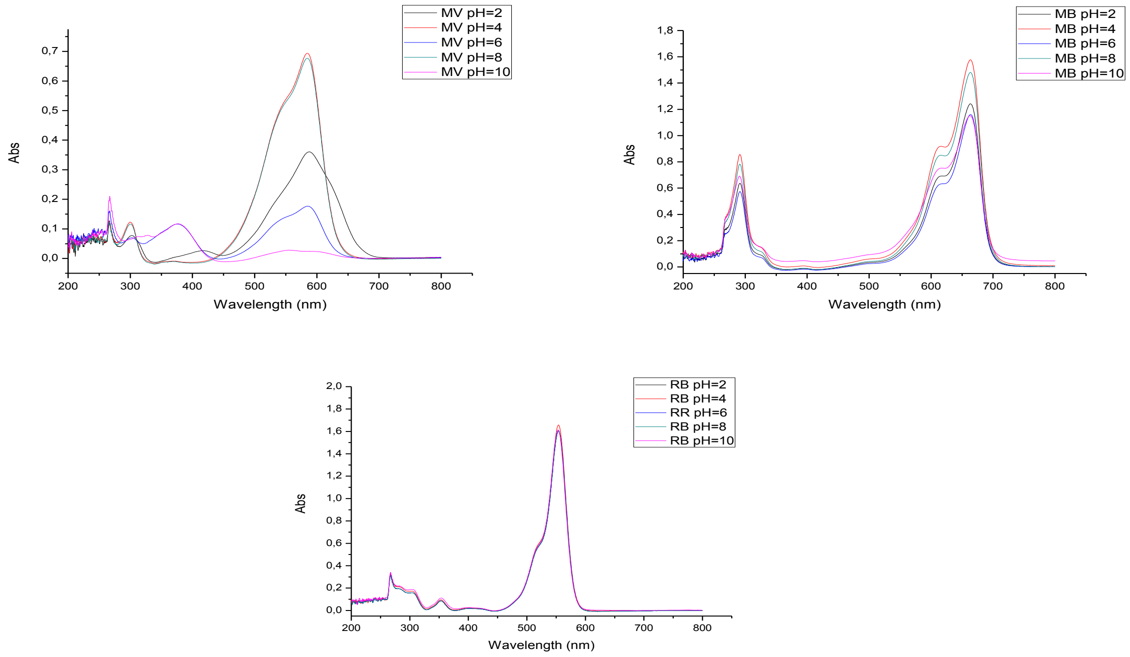


Figure 2: Effect of pH and aquatic environment on dyes absorption of UV-Vis Spectra

We can notice that there were no changes appeared neither in the absorption spectrum or more additional peaks formed for the dye solutions (MB, MV, RB) after being in contact with the sorbent (fig.3), this indicated that there were no break-down products of the dye as well supportes the fact that the dye removal from the solution in this study was through the mechanism of sorption (inclusion) [24].

For insoluble calix[4]resorcinarene derivative solid-liquid batch sorption was realized to assess its ability to remove the basic dyes from aqueous solutions. Compared with calix[4]resorcinarene (1), calix[4]resorcinarene (2) that showed enhanced removal of three basic dyes MB, MV, and RB.

To allow the comparison of solid-liquid batch sorption, sorption was performed with the calix[4]resorcinarene (1,2), the results shown in Table-2 clearly established the fact that the calix[4]resorcinarene (1) is a better sorbent for basic dyes than that the calix[4]resorcinarene (2), this strong inclusion ability was attributed to the presence of polar functional groups (acid function) in upper rim. The sorption mechanisms of calix[4]resorcinarene materials are different from those of other conventional adsorbents. These mechanisms are in general complicated because they may involve several different interactions [25, 26].

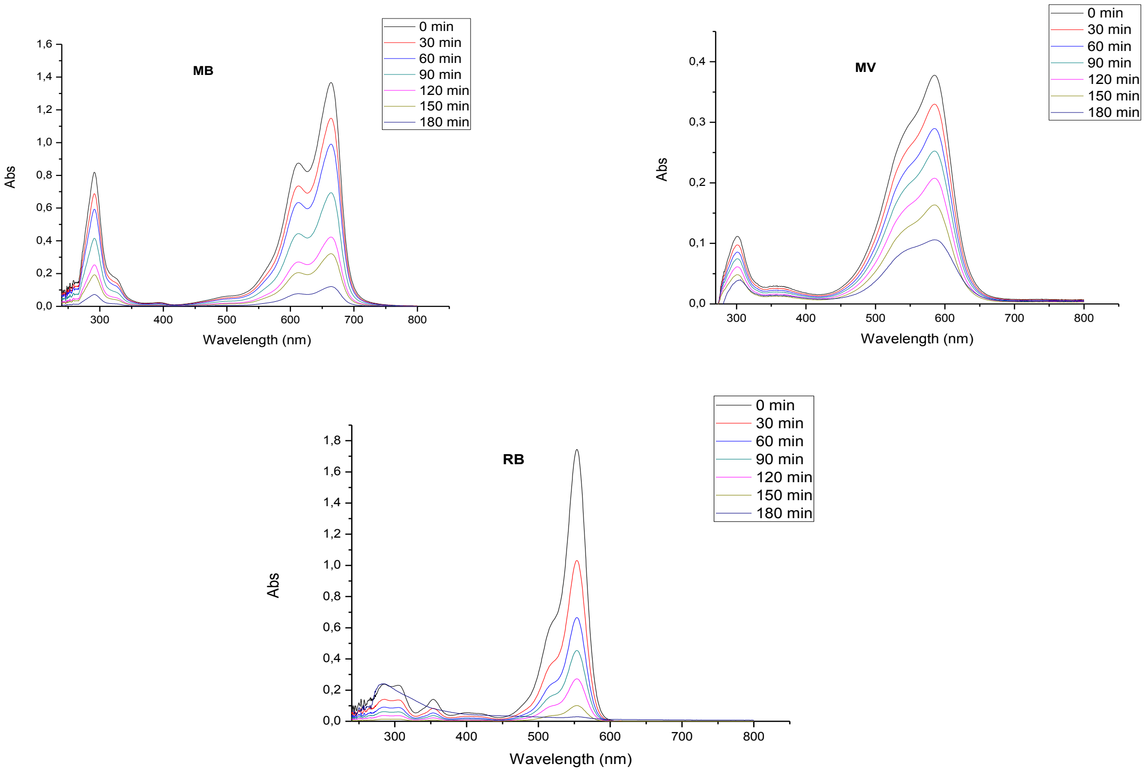


Figure 3: UV–vis spectra of Dyes (0.02 mM) before and after sorption experiment

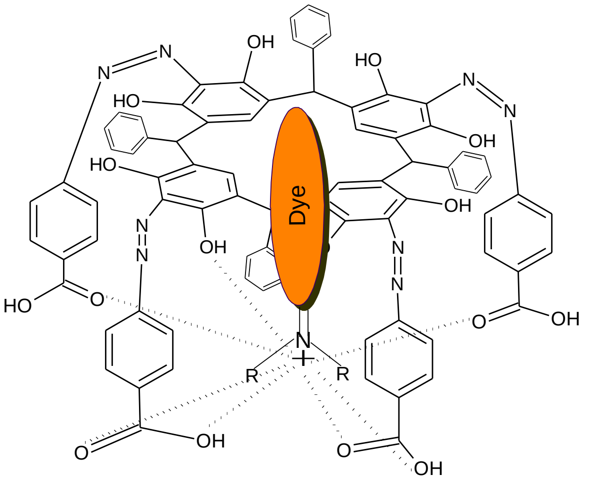
Table 2: Summary of the isotherm constants and the correlation coefficients for the different isotherms

Freundlich isotherm			**Langmuir isotherm**				
K_F (L g^{-1})	***n***	**R^2**	**K_L (Lg^{-1})**	**a_L (Lmg^{-1})**	**R^2**	**q_{max} (mg.g^{-1})**	**R_L**
3,857	**1,75**	**0,997**	**3,303**	**0,112**	**0,956**	**29,49**	**0,501**

Some of the reported interactions include: ion-exchange, complexant, coordination/chelation, electrostatic interaction, acide-base interactions, hydrogen bonding, hydrophobic interactions, and physical adsorption.
Thus, the factors behind the basic dyes sorption were found to be the cyclic structure, the cavity size, and the functional groups (ionic property) of the calix[4]resorcinarene derivatives, that also affect the sorption efficiency. Calix[4]resorcinarene(1) forms a stable complexe with a guest molecule by entrapping it into the cavity. However, it is seen from the table-1 that calix[4]resorcinarene (2) have no influence on the sorption of basic dyes comparing to calix[4]resorcinarene (1) usually having upper rim with polar functional groups that can be involved in acid (Host)-base (guest dyes) interactions. Some proposed interactions of calix[4]resorcinarene (1) and basic dyes (MB, MV, RB) are shown in scheme 3.

3.1 Effect of agitation rate on the sorption capacity of basic dyes

The effect of agitation rate on dyes removal % was observed by mixing 0.05g of sorbent (1) with 10 ml of 2.10^{-5}M basic dyes solutions (single component). The suspensions were shaken for 3 hours at natural pH 8.3 for RB, pH 8.1 for MB, and pH 8.7 for MV in water bath at 25 °C. The rate of agitation was ranged from 60 to 180 rpm. (Fig.4.). the agitation is an important parameter in sorption phenomenon, influencing the distribution of the solute in the bulk solution and the formation of the external boundary film. Generally, the rate of the dye removal is influenced by the rate of agitation and the uptake increased with stirring rate. The rate of agitation reduced the boundary-layer resistance and increased the mobility of the system.



Scheme 3: Proposed interactions of Calix[4]resorcinarene (1) and basic dyes (RB, MB, MV)

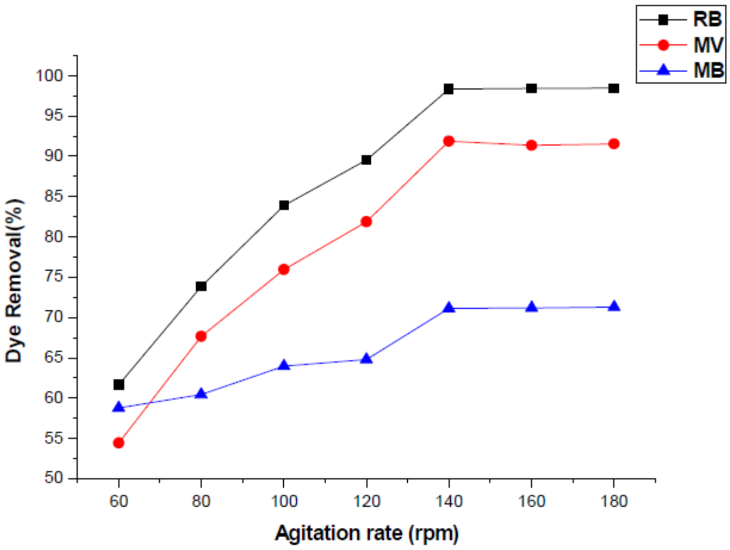


Figure 4: Effect of agitation rate on sorption of RB, MV and MB onto Calix[4]resorcinarene (1), Experimental conditions: initial dye concentration 0.02 mM; mass of Calix[4]resorcinarene (1) 0.05 g; volume of solution 10 mL; temperature 25.0 °C; pH=8.3, RB; pH=8.7 , MV; pH=8.1 ,MB. 60-180 rpm; contact time 3h.

The effect of agitation rate on adsorption is presented in fig. 4. The trend of agitation curve is similar for both dyes studied. When the agitation rate increase a slight in the dye removal occurs. However, over 140 rpm, there is no increase. For low agitation rates (60- 80 rpm), the dyes can hard find the possible actives sites on the calix[4]resorcinarene, with the enhancement of the agitation speed, the sorption increase, reaching a rate-limit over which there is no significant change. So, the optimum agitation rate was found to be 140 rpm [27].

3.2 Effect of initial dye concentration on the sorption capacity of basic dyes

The effect of initial basic dyes concentration in the aqueous solution on the rate of sorption onto sorbent (1) was studied. The experiments were carried out at fixed sorbent (1) dose (0.05g/10ml) in the test solution, temperature (25°C), pH (natural) and at different initial concentration of dyes (2.5 10^{-6}M, 5 10^{-6}M, 10^{-5}M, 2 10^{-5}M) for 3 hours equilibrium time.

At the initial dye concentration of 2.5 10^{-6}M, 96% extraction of RB, 89% removal of MB, and 69% removal of MV were obtained. The results are show in Fig. 5.

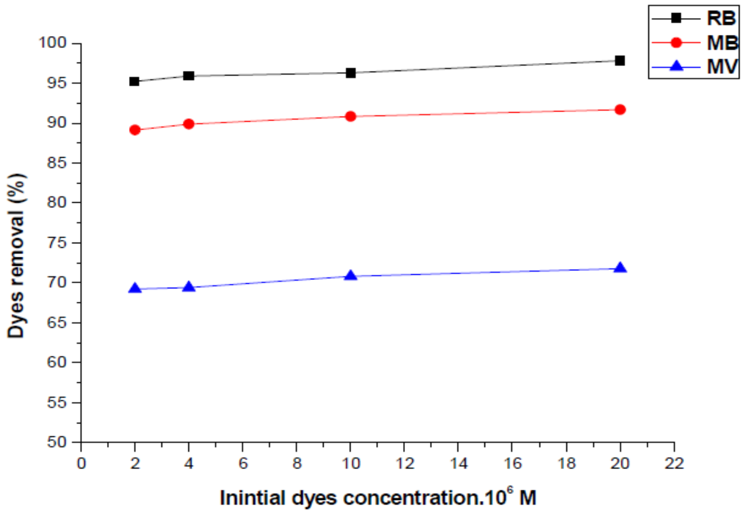


Figure 5: Effect of initial dyes concentration on dyes sorption, Experimental conditions: initial dye concentration (0.002-0.02 mM); mass of Calix[4]resorcinarene (1) 0.05 g; volume of solution 10 mL; temperature 25.0 °C; pH=8.3, RB; pH=8.7 , MV; pH=8.1 ,MB. 140 rpm; contact time 3h.

The sorption capacity increases with the increase of initial basic dyes concentration, the reason could be that any increase in the number of molecules competes for the available binding sites on the surface of sorbent. In addition the increase of basic dye concentration increases the number of collisions between basic dye cationic and acidic sorbent, which enhances the sorption process [28].

3.3 Effect of sorbent content on the sorption capacity of basic dyes

The effect of calix[4]resorcinarene on the sorption capacity of basic dyes from aqueous solutions containing 0.02 mM RB, MV and MB was studied with varying sorbent quantity from 0.02g to 0.09 g. The experimental data for the percentage of sorption versus sorbent content are plotted in fig. 6.

The percentage of sorption of dyes increased linearly from 67 to 97% RB, 53 to 73% MV and from 62 to 92% MB, with the increase in calix[4]resorcinarene content from 0.02g to 0.05 g. The increase in sorption with sorbent dose can be attributed to increased sorbent surface area and availability of more sorption sites [24]. This confirm that calix[4]resorcinarene is effective in sorption cationic dyes. Hence in the succeeding tests the sorbent quantity was fixed at 0.05 g.

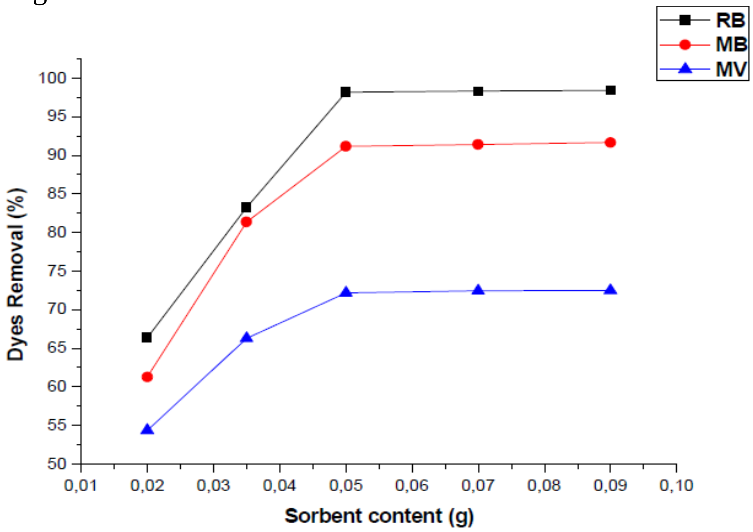


Figure 6: Effect of sorbent content on dyes sorption, Experimental conditions: initial dye concentration 0.02 mM; mass of Calix[4]resorcinarene (1) (0.02-0.09 g); volume of solution 10 mL; temperature 25.0 °C; pH=8.3, RB; pH=8.7 , MV; pH=8.1 ,MB. 140 rpm; contact time 3h.

3.4 Effect of contact time on the sorption capacity of basic dyes

The effect of contact time on sorption capacity of basic dyes by sorbent (1) is shown in fig. 7. Equilibrium was established after 3 hours of contact time for all the dye, but high sorption rates were observed during the first 60 minutes. The plots could be split in three distinct regions: from 0 to 60 min, which indicates the instantaneous sorption of dyes, suggesting rapid external diffusion and surface sorption; from 30 to 180 min, shows a gradual equilibrium, and from 180 to 240 min, indicates the equilibrium state [29].

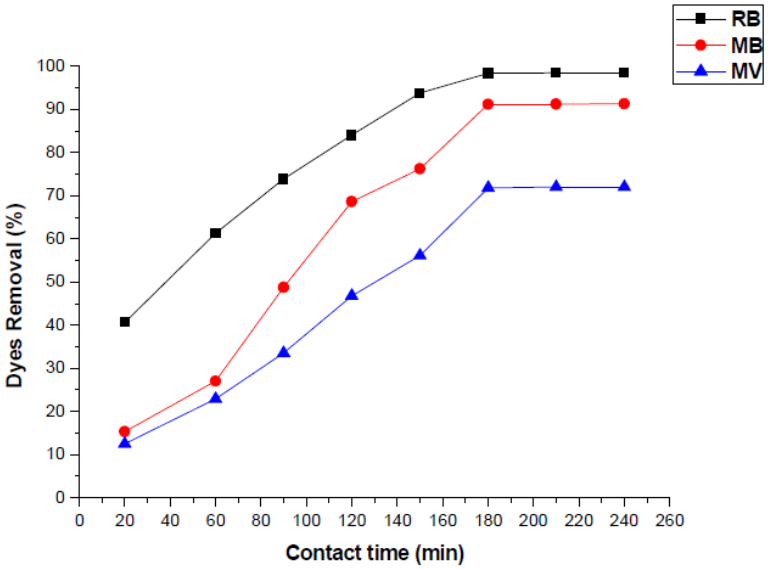


Figure 7: Effect of contact time on dyes sorption on sorbent Calix[4]resorcinarene (1), Experimental conditions: initial dye concentration 0.02 mM; mass of Calix[4]resorcinarene (1) 0.05 g; volume of solution 10 mL; temperature 25.0 °C pH=8.3, RB; pH=8.7, MV; pH=8.1 ,MB. 60-180 rpm; contact time (20-240 min).

It can be seen that the adsorption of both dyes is gradually slowing down until it reaches equilibrium. The fast sorption at the initial stage may be due to the fact that a large number of surface sites are available for sorption. After a lapse of time, the remaining surface sites are difficult to be occupied because of the repulsion between the solute molecules of the solid and bulk phases, that cause make it to long time to reach equilibrium [30]. This phenomenon was more intense for RB. This is mainly attributed to the chemical structure of dye [31]. So, the sorption of RB was direct and fast in equilibrium.

3.5 Effect of ionic strength on sorption of basic dyes

Industrial wastes and natural water often contain dissolved salts like NaCl which compete with basic dye for binding sites on the polar site of sorbent [32].

The ionic strength of the solution is one of the factors that control both electrostatic and non-electrostatic interactions between the sorbet and the sorbent surface [33]. There is the need to ascertain the influence of this factor on sorbent sorption capacity.

To study the influence of ionic strength on removal of basic dyes from the aqueous solutions by sorbent (1), dye concentration with different concentration of NaCl were tested at pH 10. Under these conditions both calix[4]resorcinarene will be charged negatively inducing the attractive forces between the basic dyes molecules and the calix[4]resorcinarene. The results are shown in fig. 8.

Which shows that the sorption efficiency of dyes decrease when NaCl concentration increase in the dye solution. Since the salt screens the electrostatic interaction of opposite changes of the polar groups in the calix[4]resorcinarene and the dye molecules, the sorbed amount should decrease with increase of NaCl concentration which increase in the degree of dissociation of the sorbent molecules by facilitating the deprotonation. This might be due to competitive sorption between dye and Na^+ counter ions with the calix[4]resorcinarene (34), explained by the screening effect of added salt resulting in the reduction of the electrostatic attractive interactions [35] for example percentage of sorption decreased from 98 % to 60% for RB, 91% to 56% for MB, and 71% to 50% for MV.

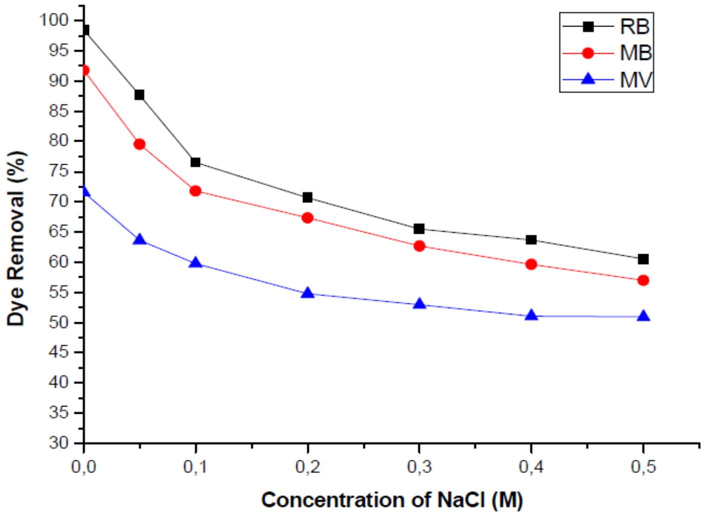


Figure 8: Effect of ionic strength on sorption of basic dyes, Experimental conditions: initial dye concentration 0.02 mM; mass of Calix[4]resorcinarene (1) 0.05 g; volume of solution 10 mL; temperature 25.0 °C; pH= 10. 140 rpm; contact time (3h).

3.5 Effect of pH on the sorption capacity of basic dyes

To evaluate the influence of pH on the affinity of the basic dyes for sorbent (1), and to clarify the role of different factors which take place in the sorption mechanism, experiments were carried out at different pH (i.e. 2, 4, 6, 8, and 10). The influence of pH on the sorption capacity of the calix[4]resorcinarene derivative (1) versus starting concentration of RB, MB, and MV using a contact time of 3 hours was studied (fig. 9).

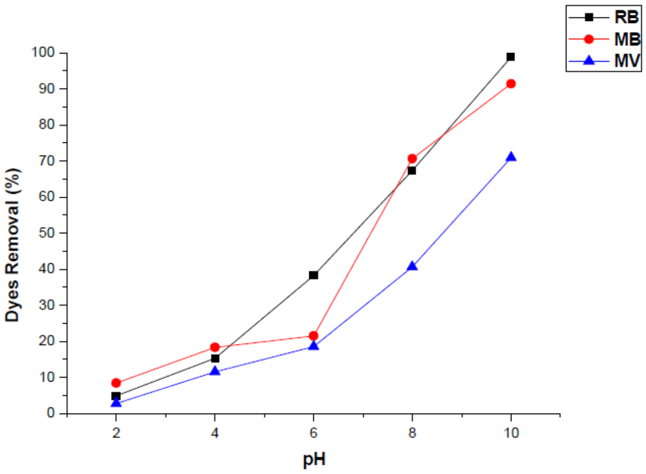
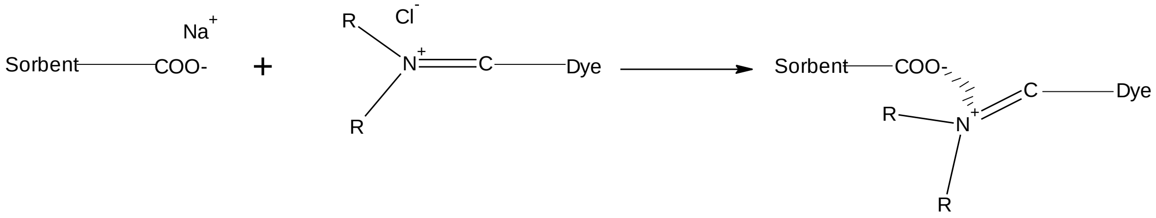


Figure 9: Effect of pH on dyes sorption on sorbent Calix[4]resorcinarene (1), Experimental conditions: initial dye concentration 0.02 mM; mass of Calix[4]resorcinarene (1) 0.05 g; volume of solution 10 mL; temperature 25.0 °C; pH= 2-10, 140 rpm; contact time (3h).

As the pH of the system decrease, the number of positively charged system increases and number of negatively charged surface site decreases. Also, lower adsorption of RB at lower pH<4 is due to the presence of excess protons H^+ competing with the dye cations for the adsorption sites. However, for pH values ranging from 8 to 10, the sorption could be explained taking into account other sorption mechanisms, such as acid-base interaction, hydrogen bonds, and/or π-π stacking interactions. Hence, natural pH of solution dye 8.3 for RB, 8.1 for MB, and 8.7 for MV was chosen while studying the effect of other system variables on sorption process. These suggest that formation of the associate is accompanied by interactions of carboxyl polar functional groups of macrocycle with aromatic amino groups of the basic dyes. The letter is positively charged and carboxyl groups of sorbent (1) are negatively charged indicating the sites for coulomb interactions between the dye and the sorbent. That is apparently responsible for greater dye sorbent capacity of (1) as compared to (2). The much higher levels of basic dyes removal by calix[4]resorcinarene carboxylic acid derivative than other calix[4]resorcinarene (2) suggest that an acid-base interactions, calix[4]resorcinarene carboxylic acid derivative usually contains polar functional groups that can be involved in chemical binding and are responsible for cationic dye sorption, the reaction could be represented :



3.6. Adsorption isotherms

The Freundlich isotherm is the earliest known relationship describing the sorption equation [36]. The application of the Freundlich equation suggests that sorption energy exponentially decreases on completion of the sorptional centers of an adsorbent. This isotherm is an empirical equation employed to describe heterogeneous systems and is expressed by the following equation [36, 37]:

$$q_e = K_F C_e^{\left(\frac{1}{n}\right)} \qquad (2)$$

where q_e is the equilibrium dye concentration on adsorbent (mg.g^{-1}), C_e is the equilibrium dye concentration in solution (mg.L^{-1}), K_F is Freundlich constant (L.g^{-1}), and $1/n$ is the heterogeneity factor. The capacity constant K_F and the affinity constant n are empirical constants dependent on several environmental factors. A linear form of the Freundlich expression can be obtained by taking logarithms of Eq. (3):

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \qquad (3)$$

Therefore, the plot of ln q_e versus lnC_e was employed to generate the intercept value of K_F and the slope of $1/n$. The results are given in Fig. 10a. The fit is well for the adsorption system under the concentration range studied (correlation coefficient, $R^2 > 0.99$). The value of R^2 is higher than the Langmuir isotherm value and the value of n was >1, reflecting the favorable adsorption. Apparently, the plots in Fig. 10a demonstrate that the Freundlich equation provides a reasonable description of the experimental data.

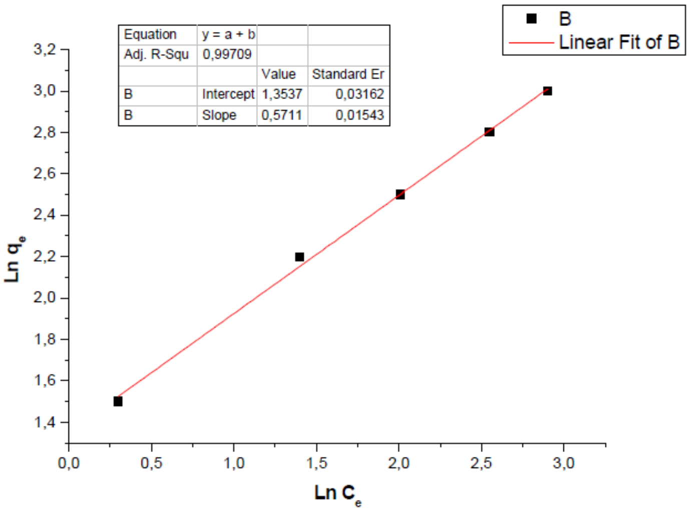


Figure 10a: Freundlich plot of Ln q_e versus Ln C_e for RB dye adsorption

The Langmuir sorption isotherm is the most widely used for the sorption of a pollutant from a liquid solution assuming that the sorption takes place at specific homogeneous sites within the adsorbent [37-39]. The application of the Langmuir model suggests that the sorptional energy is constant and does not depends on the degree of occupation of the active centers of an adsorbent. It also assumes that once a dye occupies a site, no further sorption can take place at that site. All sites are energetically equivalent and there is no interaction between molecules adsorbed on neighboring sites. The linearized equation of Langmuir is represented as follows:

$$\boldsymbol{q_e = \frac{x}{m} = \frac{K_L C_L}{1+a_L C_L}} \qquad (4)$$

where x is the amount of dye adsorbed (mg); m is the amount of adsorbent used (g); C_e (mg L^{-1}) and q_e (mg.g^{-1}) are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium, respectively; K_L (L.g^{-1}) and a_L (L.mg^{-1}) are the Langmuir isotherm constants. The Langmuir isotherm constants, K_L and a_L are evaluated through linearisation of Eq.

$$\boldsymbol{\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e} \qquad (5)$$

Hence by plotting C_e/q_e against C_e (Figure.10b), it is possible to obtain the value of K_L from the intercept which is $1/K_L$ and the value of a_L from the slope, which is a_L/K_L. The theoretical monolayer capacity is q_0 (or q_{max} the maximum adsorption capacity of the adsorbent) and is numerically equal to K_L/a_L.

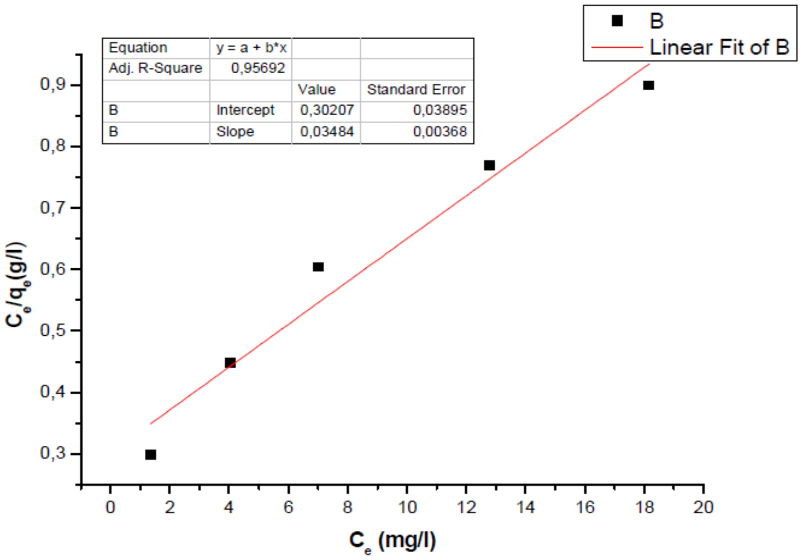


Figure10b: Langmuir plot of Ce/qe versus ce for RB dye adsorption

Experimental conditions: initial dye concentration 0.02 mM; mass of Calix[4]resorcinarene (1) 0.05 g; volume of solution 10 mL; temperature 25.0 °C pH=8.3

The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor for equilibrium parameter, R_L [40] which is defined as given below:

$$\boldsymbol{R_L = \frac{1}{(1+a_L C_0)}}$$

where C_0 is the initial dye concentration (mg/L) and b= a_L is the Langmuir constant (L/mg). The values of R_L for the studied system at different initial concentrations were found to be in between 0 and 1 (Table 2) which indicate favorable adsorption of dye onto the adsorbent.

3.7. Regenerability

The repeated use of the sorbent (regenerability), which is a key factor in improving wastewater process economics, was estimated in four sequential cycles of adsorption–desorption (Fig. 11). Regeneration of sorbent can easily be done by washing the solid material with an acid solution (pH=2). The loss in the adsorption capacity between the first and the last cycle was approximately 10%. This gives evidence that the prepared materials can be used repeatedly without losing significantly their adsorption capacities.

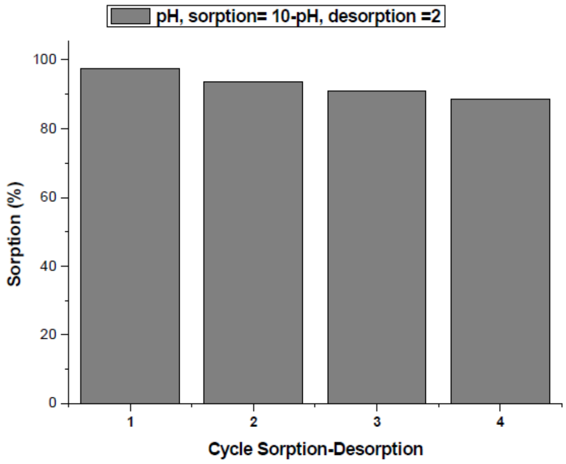


Figure 11: Sorption–desorption cycles for calix(1)-RB**.**

3.8. *Characterizations of adsorbent (Calix[4]resorcinarene(1), adsorbate(RB) and complex : adsorbent- adsorbate*

The FTIR spectra of the complex of inclusion calix-RB after adsorption processes are presented in Fig. 12. The overall analysis of the spectra revealed that after the inclusion of RB into the calix, the vibrational bands became more intense and their shape sharpened compared to sence of the material calix[4]resorcinarene (1) and RB, the vibrational bands in the 3000–2800 cm^{-1} and the 1750–1400 cm^{-1} spectral regions were slightly shifted towards lower wavenumbers. Namely, these changes were the most visible in the case of the vibrational band at 1646, characteristic for the stretching of the C=O of calix, which was strongly increased and insignificantly blue-shifted to the wavenumber 1728 cm^{-1} after inclusion of RB in calix. Since the band at 1690 cm^{-1} associated with C=O stretching of the pure RB (Fig. 3, spectrum b) does not appear in the spectra of complex inclusion (Fig. 12), the existence of such a strong band at 1615 cm^{-1} could be attributed to the mutual vibrations of the C=O groups in the structure of complex. In addition, the vibration of C=N groups of the RB, found at 1702 cm^{-1}, could also produce a slight shift in the band from 1621 to 1616 cm^{-1}.

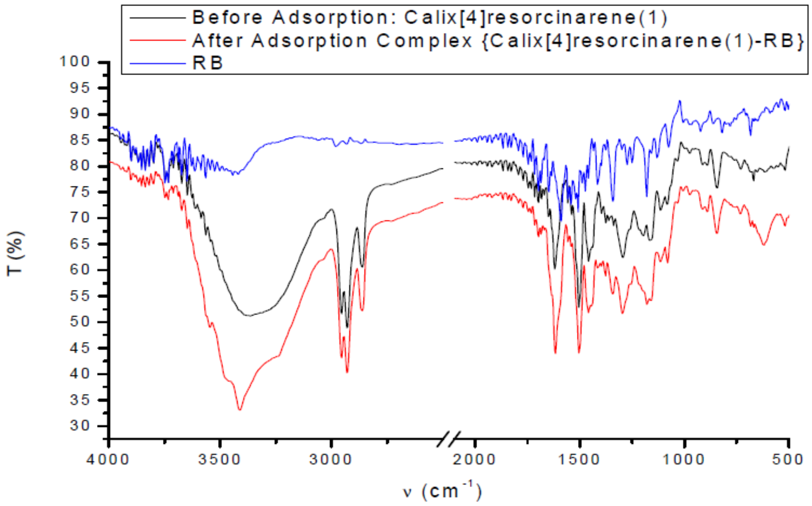


Figure 12: FTIR spectra of samples

Detailed inspection of the FTIR spectra of complex also revealed the existence of new vibrational bands of rather weak intensities, appearing at 1078 and 828 cm^{-1}. While the latter two could be attributed to the C–H vibration of the aromatic ring of RB, the appearance of the band at 1590 cm^{-1}, characteristic for the COO^{-} vibrations, confirms that RB did not react with the functional groups of calix[4]resorcinarene. Although it could be expected to have hydrogen bonding between the hydrogen atom of the OH group present at the cavities of calix and the oxygen atom in the group C=O of RB confirmed by the modification of broad band at 3400 cm^{-1}. By appearance of these peaks, the presence of RB molecules within the calix[4]resorcinarene matrix was confirmed, implying that the RB was not chemically bonded but rather physically embedded within the calix[4]resorcinarene.

Differential scanning calorimetric enables the quantitative detection of all processes in which energy is required or produced (endothermic or exothermic phase transformation).

The thermograms of calix[4]resorcinarene (1) and isolated complex : calix[4]resorcinarene (1)-RB after adsorption are presented in Fig. 13. In the thermogram of calix[4]resorcinarene (1) peak between 90-100 °C was due to loss of water from calix[4]resorcinarene (1) cavity.

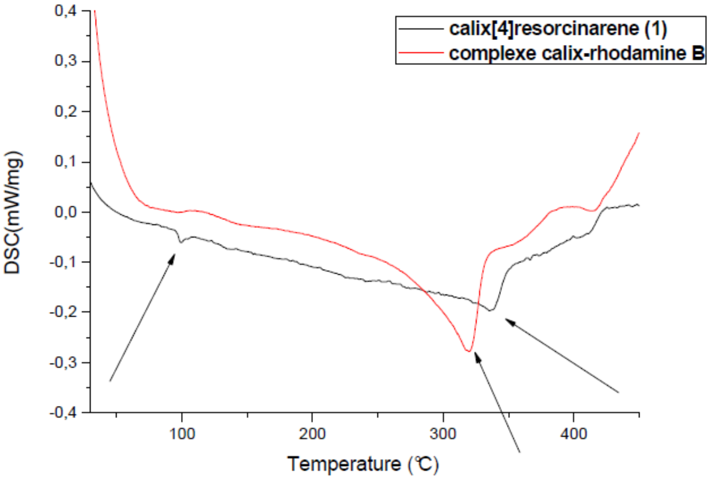


Figure 13: DSC analysis of samples

In the thermogram of complex : calix[4]resorcinarene (1)-RB dye peak between 90-100 °C is almost disappeared this may be due to the substitution of water molecules by RB, indeed the peak at 337 °C were modified, this also confirmed that the inclusion of RB in the calix[4]resorcinarene (1) cavity.

The fluorescence emission spectrum of the materiel before and after adsorption is shown in Fig. 14. The fluorescence peak at 573 nm confirms the presence of RB in material after adsorption. A shift of the fluorescence peak towards higher wavelengths from 569 to 573 nm could be noticed with inclusion of RB in the cavity of calix[4]resorcinarene (1) resulted in a red shift in the fluorescence wavelength as can be seen in Fig. 4, which shows the dependence of the wavelength of maximum emission on the presence of RB in calix[4]resorcinarene.

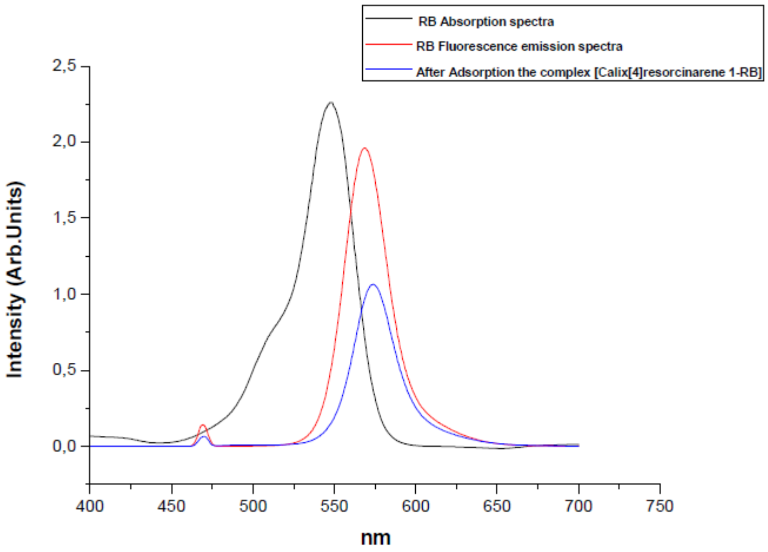


Figure 14: Fluorescence emission spectra

Powder X-ray diffraction spectroscopy (PXRD) has been used to assess the degree of crystallinity of the given sample. The PXRD diffractograms of all the samples are show in Fig. 15. Due to amorphousness of calix[4]resorcinarene (1) and RB dye, no major d_{hkl} peak at 2θ were observed. In the complex calix[4]resorcinarene-RB we have no d_{hkl} peak at 2θ indicating the amorphous phase of the complex and confirming the trapping of RB in the calix[4]resorcinarene cavity.

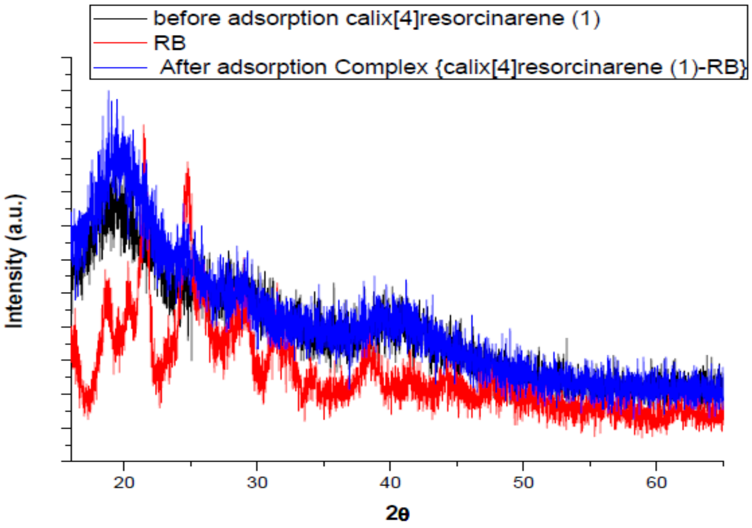


Figure 15: Powder X-ray diffraction (PXRD) analysis

Conclusion

Inclusion phenomena of basic dyes by calix[4]resorcinarene derivatives were investigated in a solid-liquid extraction system. The carboxylic derivative of calix[4]resorcinarene was fond to be one of host compound currently available for the recognition of basic dyes with acid base interaction process. The high affinity being created by the fit between the cavity of the cyclic ligand, and the guest molecule. The sorption of basic dyes was dependent on sorbent dose and basic dyes concentration in wastewater. The pH affects the adsorption capacity and the effective pH range for the sorption was found to be 8-10, lower sorption of RB at pH < 4 is due to the presence of excess of H^+ competing with the dye cations for the adsorption sites. A positively charged site on the adsorbent does not favor the adsorption of the dye cations due to electrostatic repulsion. In addition the separation factor (R_L) was fond to be favorable ($0< R_L< 1$). The isotherm data could be well described by the Freundlich and Langmuir isotherms models. It was concluded that adsorption mechanism mainly electrostatic interactions between adsorbent and adsorbate. Beside, hydrogen bonding, hydrophobic interactions (dye-calix, and dye-dye interactions), complex of inclusion were also occurred. The Azo-calix[4]resorcinarene carboxylic acid derivative is expected to be a novel tool for recognition of various molecules.

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