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Calixarenes: A Versatile Source for the Recovery of Reactive Blue-19 Dye from Industrial Wastewater

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Abstract

The present work demonstrates the comparative extraction efficiency of *p-tert*-butylcalix[4]arene (**1**) and its derivatives (**2-4**) toward a series of some selected reactive dyes such as Reactive Black-5 (RB-5), Reactive Blue-19 (RB-19) and Reactive Red-45 (RR-45). The study elaborates effectiveness of different anchoring groups present on the periphery of calix[4]arene platform and highlights the importance of preorganization concerning the application of supramolecular chemistry in separation science and technology. It has been observed that compound **4** shows good extraction efficiency toward RB-19 among the selected reactive dyes. Enhanced extraction efficiency was observed with the addition of NaCl at pH 7. The proposed extraction mechanism through inclusion complexation was confirmed by log-log plot analysis, which shows 1:1 complexation between **4** and RB-19. The solvatochromic response of **4** in various solvents of different polarities showed good response in methanol. The log K of complex was found as 5.2. The complex formation between **4** and RB-19 has also been confirmed by FT-IR spectroscopy. The recovery of **4** and RB-19 dye was achieved at pH 8 that signifies the reusability of **4** again and again.

***Keywords*:** Calixarenes; Complexation; Extraction; Reactive blue-19 dye; Recognition.

Introduction

Reactive dyes are water soluble and anionic in nature, which are extensively used in textile industries due to their favorable characteristics of water-fast, bright color, simple and low energy consumption and their ability to bind with cellulosic fiber by covalent bonding [1]. Most of them are synthetic in nature, made up of two key components: the chromophore, responsible for the color, and the auxochrome, that not only supplement the chromophore but also render the solubility of molecule in water and give enhanced affinity to attach the fiber [2]. However, they are an important class of pollutants that enter into the environment through various sources such as textile dyeing, shoe polish, plastic, lather, paper printing, wool, polyamide [3], and food coloring etc [1]. The process of dyeing in the textile industries is main source that produces large amount of colored wastewater, which is drained out into the streams without its proper treatment [4], which is harmful not only for visual nature but also retards the proper transmission of sunlight to the aquatic life [5]. They are toxic, mutagenic and carcinogenic. Once they enter into the aquatic system their biodegradation is very difficult due to their complex aromatic molecular structure, which makes them more stable. For example, Reactive Blue-19 (RB-19) also known as Remazol brilliant blue is an anthraquinone based vinylsulphone dye, which is very resistant to chemical oxidation due to its anthraquinone structure being stabilized by resonance [6]. RB-19 has relatively low fixation ability (75-80 %) due to the competition between the formation of vinylsulphone and the hydrolysis

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reactions, *i.e.* formation of 2-hydroxysulphone, which does not attach to the fiber as a result that dye remains stable into the wastewater for a long period of time, *i.e.* half life of RB-19 is 46 years at pH 7 and 25 ^{o}C that renders the oxygen transfer to aquatic life [1, 6]. Therefore, the strategy to remove the color and to decrease its impact onto the wastewater of textile environment has found to be of significant importance.

Various physical, chemical and biological methods have been employed such as oxidation-ozonation, microbial degradation, biological reductive decolorization, membrane process, sorption, biosorption, decolorization under methanogenic conditions, electro-coagulation, physico-chemical process [1, 7, 8] and adsorption/aggregation [9] including use of rice husk ash [10], lentil straw [11], agricultural waste [12], chitosan [13], activated carbon [14] etc. Nevertheless, the performance of all these processes is slow and not very effective or some of them are efficient only at low concentrations. However, adsorption play a vital role at higher concentrations but regeneration of most of the adsorbents is difficult except for activated carbon, but adsorption through activated carbon is expensive [15]; Furthermore, biological methods are not effective due to the low biodegradability of dyes. Therefore, much attention has been paid during current decades, to the synthesis and design of artificial molecules that not only act as efficient receptors for neutral or ionic species but also prove to be economical, regenerable, environment friendly and conveniently accessible materials. In this regard, the macromolecular synthetic compounds such as calixarenes (Fig. 1) have received considerable importance in supramolecular chemistry because of their ability to selectively interact with anions, cations or neutral molecules and can be used as host-guest type receptors. Previously, calix[4]arenes based resins have also been used for the removal of various dyes [16-19] which concludes only the sorption efficiencies of synthetic resins to different dyes. But the need here is the application to real water samples along with regeneration of costly dyes for industrial reuse. However, no such a finding is referred by previously reported methods. Hence, herein we explore the inclusion mechanism of calix-dye complexation phenomenon and liquid phase extraction (LPE) method as a strategic alternative to all these techniques that may help in organizing the dye removal processes. This process may prove to be useful not only for transfer from one phase to another but also become advantageous for economical purpose and provides a cheaper source for the recovery of costly dyes from effluent mixtures that could be reused.

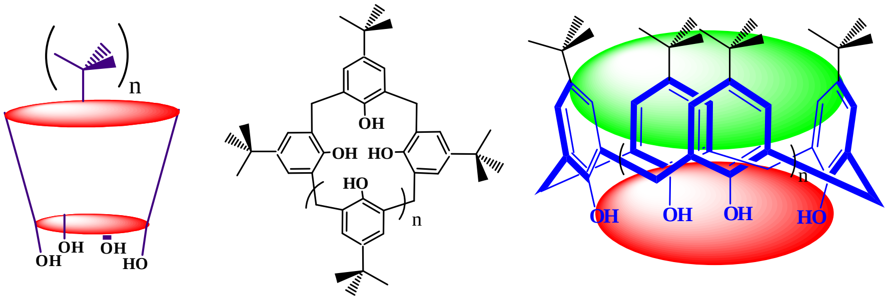


***Figure 1*. The chemical structures of calix[n]arene.**

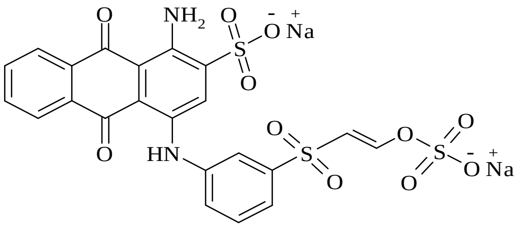
Material and Methods

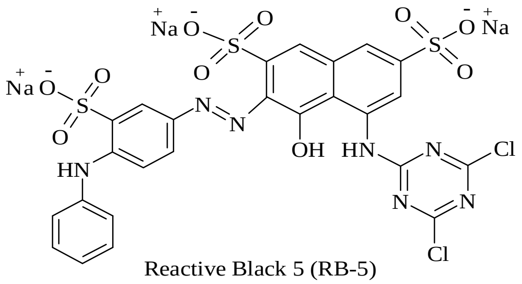
Instrumentation

Melting points were determined on a Gallenkamp apparatus in a sealed capillary. FT-IR spectra were recorded on a Thermo Nicollet AVATAR 5700 FT-IR spectrometer using KBr pellets (spectral range from 4000 to 400 cm^{-1}). Elemental analyses were performed using a CHNS instrument model Flash EA 1112 elemental analyzer (20090; Rodano, Milan, Italy). A Gallenkamp thermostat automatic mechanical shaker model BKS 305-101, UK was used for liquid-liquid extraction. The pH measurements were made with pH meter (781-pH/Ion meter, Metrohm, Herisau, Switzerland) with glass electrode and internal reference electrode. UV–vis spectra were recorded on a Perkin Elmer (Shelton, CT 06484, USA) Lambda 35 through UV–vis spectrophotometer.

Reagents

All reagents used for the preparation of solutions were of analytical grade. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system (Elga model classic UVF, UK). For pH (2 to 12) adjustment NaOH and HCl (0.1 M) solutions were used. Reactive dyes (Fig. 2) such as Reactive Black-5 (RB-5), Reactive Blue-19 (RB-19) and Reactive Red-45 (RR-45) used in this study were procured from commercially available source. The *p-tert*-butylcalix[4]arene (Fig. 3) and its derivatives (**1-4**) were synthesized according to previously reported methods [20, 21, 22].


Reactive Blue 19 (RB-19)


Reactive Black 5 (RB-5)

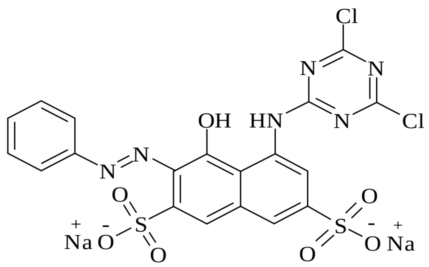
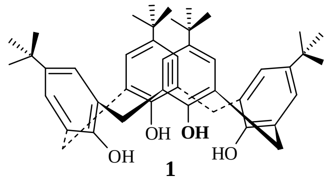

Reactive Red 45 (RR-45)

***Figure 2*. The chemical structures of some reactive dyes used in experiments.**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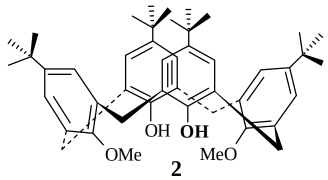
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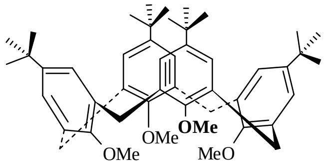
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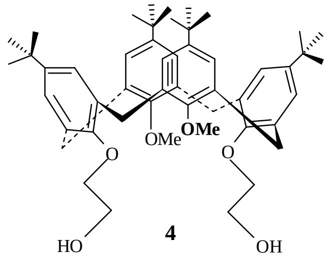

4

***Figure 3*. The chemical structures of *p-tert*-butylcalix[4]arene (1) and its derivatives (2-4).**

Analytical Procedures

Liquid–liquid Extraction Study

Pederson's procedure was used for simple liquid-liquid extraction studies [23]. 10 mL of a $2.5x10^{-5}$ M aqueous solution of reactive dye with 0.1 g of NaCl and 10 mL of $1.0x10^{-3}$ M of *p-tert*-butylcalix[4]arene or its derivative in $CHCl_3$ were vigorously agitated in 25 mL stoppered flask with a mechanical shaker for 1 hour and finally left standing for additionally 15 min to settle down the two phases. The upper aqueous layer was taken and examined spectrophotometrically to determine the remaining concentration of reactive dye in that phase. The percent extraction (E %) has been calculated by Eq. (1);

$$E\% = \left[\frac{(C_o - C)}{C_o}\right] \times 100 \qquad (1)$$

where C_o and C are the initial and final concentrations of reactive dyes in aqueous solution before and after extraction, respectively.

Log-Log Plot Analysis

The obsession of distribution coefficient D of selective dye between two phases upon the calixarene concentration and its extraction ability was examined by using Log-log plot analysis.

The general extraction equilibrium is assumed to be Eq. 2 with '*G*' be the neutral guest, '*H*' be the Host in the organic phase, the overall extraction equilibrium constant is given by Eq. (3). When introduce the distribution coefficient *D*, as given in Eq. (4), and taking log of both sides, we obtain Eq. (5);

$$nG_{(aq)} + xH_{(org)} \leftrightarrow [(G)_n(H)_x]_{org} \qquad (2)$$

Extraction equilibrium constant is expressed as Eq. (3);

$$K = \frac{[(G)_n(H)_x]}{[G]^n[H]^x} \qquad (3)$$

Whereas, the distribution ratio *D* can be defined by the Eq. 4;

$$D = \frac{[(G)_n(H)_x]}{[G]^n} \qquad (4)$$

One obtains Eq. 5, by introducing Eq. 4 it into Eq. 3 and taking log of both sides.

$$\log D = \log K + x\log[H] \qquad (5)$$

Accordingly, the plot of log *D* versus log [*H*] shows a straight line with a slope that is responsible for the stoichiometry of the extracted dye species at various concentrations, where as [*H*] is defined as the analytical concentration of host in the organic phase.

Job's Plot Analysis

To examine the stoichiometric ratio between **4** and RB-19 dye for their inclusion complexation, Job's plot (method of continuous variation) has been used. The solutions were prepared by mixing the different ratios (1:9-9:1) of equimolar concentrations ($2.5 \text{ x } 10^{-7}$ M) of **4** and RB-19 in methanol. Then the absorbance was measured at 206 nm.

Calculation of the Complex Formation Constant

The complex formation constant can be calculated by Benesi-Hildebrand method [24] by using Eq. 6.

$$\frac{[G][H]}{A} = \frac{1}{K_f\varepsilon} + \frac{[g]}{\varepsilon} \qquad (6)$$

Eq. 6 is a modified Hildebrand and Benesi equation that is valid only for 1:1 complex under the conditions when concentration of host is much smaller than the concentration of guest, i.e. [*H*]<<[*G*].

Where [*G*] denotes the total concentration of guest, [*H*] refers to the total concentration of host, ε is the molar extinction coefficient of *HG* complex at λ, K_f indicates the equilibrium constant of *HG* complex formation and *A* is the absorbance of *HG* complex at wavelength λ. The plot of $\frac{[G][H]}{A}$ *versus* [*G*] yields a straight line, which further proves 1:1 molar ratio of reactants in the complex. The values of K_f and ε can be calculated from the slope and intercept, whereas the value of Gibbs free energy (ΔG) can be calculated from the Eq. 7.

$$\Delta G = -RT \ln K_f \qquad (7)$$

FT-IR Study of Inclusion Complex

For FT-IR spectral measurements, saturated solutions of **4** and RB-19 dye were prepared by dissolving their stoichiometric (1:1) amounts in methanol. Both contents were mixed up and stirred at room temperature for 24 hrs. Finally, poured on a Petri dish, evaporated the entire solvent and the resultant crystals were vacuum dried.

Regeneration of RB-19 dye and 4

For regeneration study 10 mL of RB-19 dye extracted solution of host in chloroform was vigorously agitated with a little amount of deionized water samples (*ca.* 2.5 mL) of varying pH (pH of the water was adjusted from 2-12) for 1 hour. The regeneration of compound **4** was made by separating upper aqueous layer that was examined spectrophotometrically to calculate the percent recovery of RB-19 dye as stated previously by using Eq. 1. Finally, water containing regenerated dye was exposed to open air for evaporation to obtain the pure RB-19 dye.

Results and Discussion

Synthesis

The *p-tert*-butylcalix[4]arene (**1**) and its derivatives (**2-4**) were synthesized according to the methods reported elsewhere [20-22]. The condensation of *p-tert*-butyl phenol with formaldehyde in the presence of NaOH produces **1** in good yield (65%) [20]. Dimethoxy (**2**) and tetramethoxy (**3**) derivatives were synthesized by the treatment of **1** with methyl iodide in the presence of K_2CO_3 in dry acetone according to the method described elsewhere [21]. The compound **4** was prepared through a multistep pathway by the reduction of tetraestercalix[4]arene as described in the literature [22]. All the synthesized compounds were characterized and confirmed by available techniques such as TLC, melting point, FT-IR and NMR, which was also matched with the literature, reported previously [20-22].

Solvent Extraction Study

Preliminarily, two phase solvent extraction experiments were carried out in $CHCl_3$ without calixarenes to optimize and diminish the effect of solvent for the transfer of reactive dye from aqueous phase to organic phase at different pH of the solution (i.e. pH 3, 7, and 11). These results are summarized in (Fig. 4). It can be estimated from the results that the acidic or basic media is slightly favorable, i.e. less than 10% for the transfer of dyes between two phases, so the neutral pH was selected for further study in order to evaluate the actual reactive dye extraction efficiency of *p-tert*-butylcalix[4]arene (**1**) and its derivatives (**2-4**).

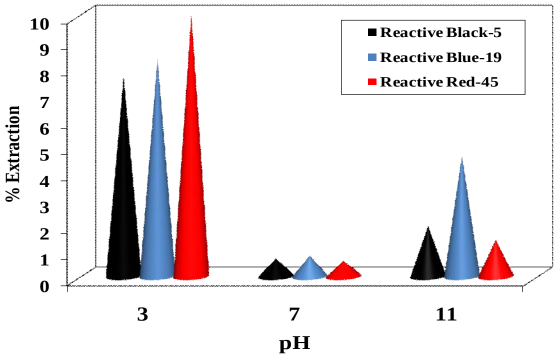


Figure 4. **Effect of pH on the extraction of RB-19 by *p-tert*-butylcalix[4]arene derivative (4).**

Some experiments were performed without NaCl. The results obtained are given in the Fig. 5, which reveal that a very small amount of dye could be transported from one phase to another in the absence of electrolyte (as justified by cylindrical shaped bars), this situation discloses the importance of electrolyte in the solution. Because of the fact that the ionic balance and transport efficiency of the two phases is balanced by NaCl. In addition, NaCl reduces the solubility of dyes through common ion effect, resulting in an enhanced and facilitated transport to the organic phase [25].

Results of extraction experiments at neutral pH with compounds **1-4** are compiled in (Fig. 5), cone shaped bars reveal that compound **4** shows much greater extraction efficiency for the transfer of dyes spatially for RB-19 as compared to the compounds **1-3**.

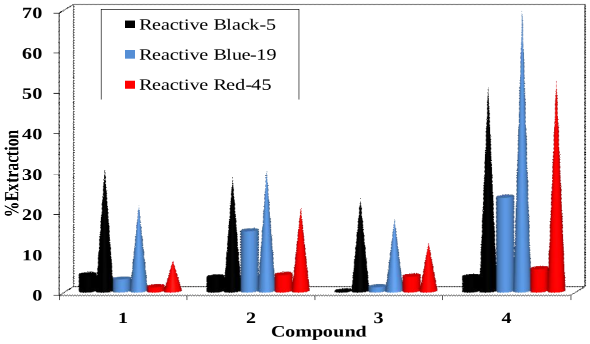


***Figure 5*. Percentage extraction of reactive dyes without NaCl (Cylindrical shaped bars) and with *p-tert*-butylcalix[4]arene and its derivatives (Cone shaped bars).**

Influence of NaCl on Extraction

Furthermore, to estimate the role of pH on the extraction ability and recognition mechanism of compound **4** for RB-19 dye, experiments were performed at different pH (6, 7 and 8) with the same concentration of RB-19 at shaking time of 1 h (Fig. 6).

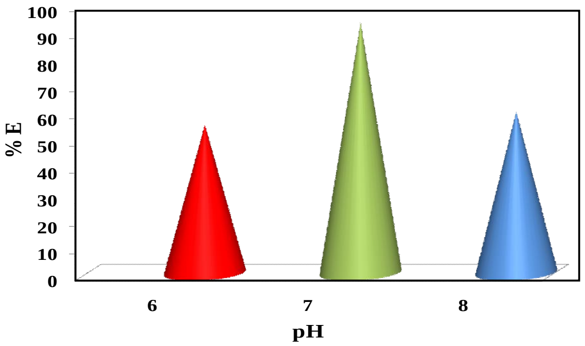
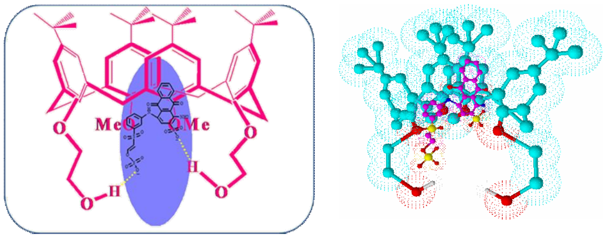


***Figure 6*. Effect of pH on the extraction of RB-19 by *p-tert*-butylcalix[4]arene derivative (4).**

The results show that extraction efficiency of **4** at pH 6 and 8 is almost same but is greater at pH 7, which reveals that the strong interactions between RB-19 and **4** occur at pH 7 may be due to the ionization of dye at this pH that ultimately forms strong inclusion complex through hydrogen bonding between oxoanions of dye and hydrogens of the binding sites of **4** (Fig. 7a-b). Whereas, at acidic conditions the dye get protonated, which ultimately reduce the interaction between the host and guest. Similarly, at basic conditions partial deprotonation of the binding sites of **4** may be the main reason of little affinity. The greater affinity between RB-19 and **4** as compared to other dyes may due to the compatibility of both host and guest, *i.e.* molecular size of dye and cavity size of **4**.



(a) (b)

***Figure 7*. Proposed interaction of RB-19 with 4 at neutral pH. (a) Structural model (b) Ball and stick model.**

Fig. 8 shows a plot of log *D* versus log [*H*] for the extraction of RB-19 by **4**. A linear relationship between log *D* and log [*H*] with the slope of lines of RB-19 is equal to 0.8 suggesting that host **4** forms 1:1 complex with RB-19 dye.

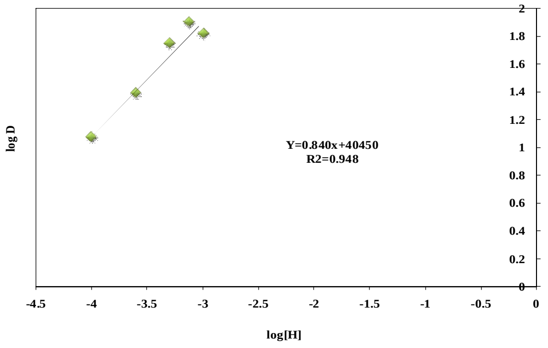


***Figure 8*. Log D versus log [H] for the extraction of RB-19 by 4 from an aqueous to organic phase, i.e. Chloroform at 25 °C.**

Molecular Recognition Study

Solvatochromic Study

Study of solvatochromic effect helps in selecting the solvent for a particular ligand that could not show similar spectra in various solvents [26]. Its general perception is that with increasing solvent polarity, the ground state molecule is better stabilized by solvation than the molecule in the excited state, *negative* solvatochromic (blue shift) will result. Better stabilization of the molecule in first excited state relative to the ground state with increasing solvent polarity will lead to *positive* solvatochromism (red shift) [27]. Consequently, variations in the position, intensity, and shape of the absorption spectra can directly measure the specific interactions between the solute and solvent molecules. Moreover, it has been found that solvent plays an important role in complexation phenomena involving ionic and neutral species including macrocyclic ligands in general and calixarenes in particular [28,29]. Therefore, the attemps were made to evaluate the behaviour of **4** in different solvents such as ethanol, methanol and dimethylsulfoxide (DMSO). The UV-vis spectra of **4** in various solvents are shown in (Fig. 9).

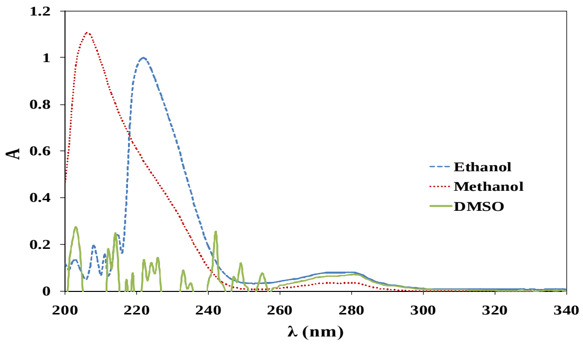


Figure 9. **Absorption spectra of 4 (2.5×10^{-5} M) in different solvent systems.**

It is clear from the (Fig. 9) that absorption spectra of **4** show significant changes in solvents of different polarities, indicating sensitivity of **4** in solvents environment. (Fig. 9) reveals that **4** exhibits red shift in its absorption maxima (~ 16 nm range) in ethanol, i.e. 222 nm with respect to methanol (206 nm), which indicates that **4** exhibits negative solvatochromism, i.e. absorption bands shift towards longer wavelength with decreasing solvent polarities. And accordingly, the absorption coefficient (ε) of **4** also changes from 43900 to 39972 L $mol^{-1}cm^{-1}$ in methanol and ethanol solvents, respectively. Consequently, red shift can be attributed to the π-π* and n-π* transitions arising from different solvent polarities. Whereas, in DMSO **4** shows aggregation and too much noise even at low concentrations thus, methanol was selected as a suitable solvent for recognition studies.

Stability of 4 in Selected Solvent

After the selectivity of a suitable solvent it is necessary to determine the stability of compound for a long time in that solvent. Therfore, U.V-visible spectra of **4** in methanol were immediately obtained after continous U.V irradiations at different time intervals, i.e. 0, 30, 60, 90, 120, 150, 180 and 210 minutes. It was confirmed from the results (Fig. 10) that compound **4** is stable in methanol as there was no change appearing in the spectra with the passage of time.

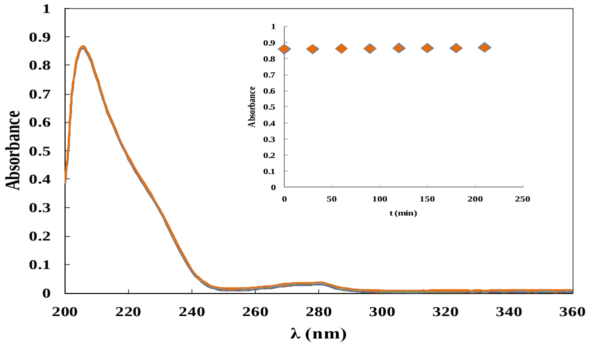


Figure 10. **Time dependent U.V-visible absorption spectra of 4 in methanol (2.5×10^{-5} M) upon irradiation of U.V light.**

Complexation Study

In order to confirm the complexation efficiency of **4** with RB-19, U.V-visible study was carried out. The attemps were made to evaluate the behavior of **4** in different solvents such as ethanol, methanol and DMSO. Because of the best response of **4** in methanol, solubility of dyes, the appearence of bands in the absorption limits and well-defined spectral properties, it was selected as a solvent media for complexation studies. However the shifts in the bands of complexes to the shorter or longer wavelengths or the high intensity of bands than that of the free ligand are the general indications of the complex formation. Primarily, the complexation behavior of **4** in methanol (2.5×10^{-5} M) with selected dye (RB-19) was checked. The U.V-visible spectra of free ligand **4** shows a strong band at 206 nm, which is attributed to the π→π* and another band at 267-284 nm due to n→π* transition. Consequently, addition of guest (RB-19) in host (**4**) causes enhancement in the previous bands and appearance of new bands as well (Fig. 11).

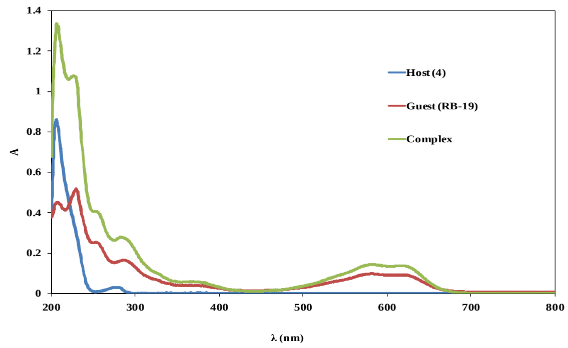


Figure 11. **UV-visible responce of 4 (2.5 x 10^{-5} M) before and after the addition of guest (RB-19).**

In an effort to have further insight into the chromogenic behavior of **4**, the absorption profile as a function of dye concentration was obtained followed by increase in the intensity of absorbance with respect to increased dye concentration (Fig. 12). This profile also confers the complexation of dye through the binding sites in two lobes of calixarene moiety. Since the bands at 227-300 and 600 nm are significantly affected due to the interaction of dye with alcoholic binding sites through hydrogen bonding (Fig. 7). While the band at 206 nm, belongs to the aromatic core of the calixarene moiety that has considerably affected confirming endo-complexation.

Complex stability constant was also determined by plotting $A_{206/227}$ *versus* 1/[RB-19], as shown in (Fig. 13). The stability constant was calculated from the intercept/slope ratio [30]. The value of log K was calculated as 5.2 for **4**-RB-19 complex.

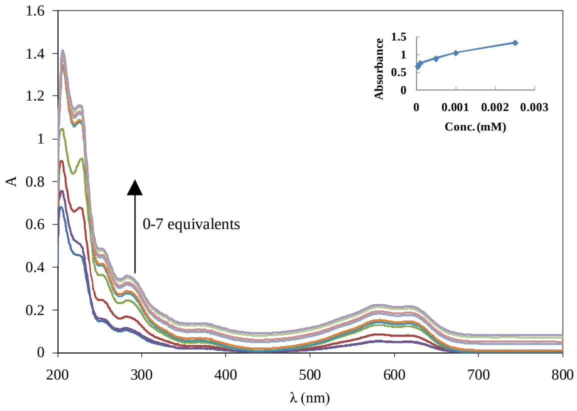


Figure 12. **UV-visible responce of 4 (2.5 x 10^{-5} M) upon addition of various equivalents of RB-19.**

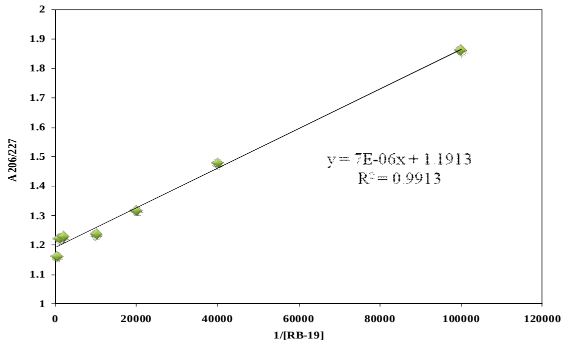


Figure 13. **Caliberation plot of 4-RB-19 complex with various concentrations of RB-19.**

Again Job's plot (method of continuous variation) was used to confirm the stoichiometric ratio between host (**4**) and guest (RB-19) molecules by varying their concentrations (Fig. 14). For **4**-RB-19 complex the maximum mole fraction value was found to be 0.5, which justifies the 1:1 ratio of host-guest complex as calculated by log-log plot analysis.

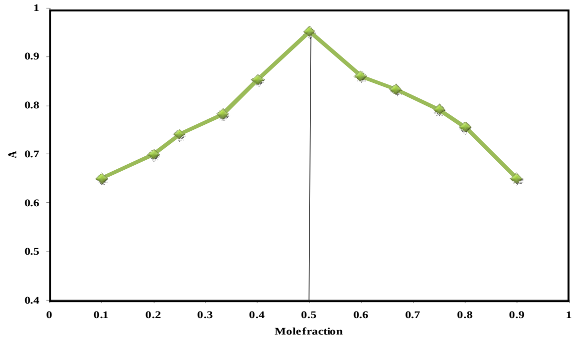


Figure 14. **Job's plot of 4 and RB-19. The concentrations of host and guest were fixed (2.5 x 10^{-5}). The absorbance was measured at 206nm.**

Furthermore, the assumption of 1:1 host-guest complexation between RB-19 (G) and **4** (H) has also been confirmed by Hildebrand and Benesi plot (Fig. 15), where the calculated values of $\frac{[G][H]}{A}$ and $[G]$ provide the excellent linear relationship with coefficient of determination R^2=0.997 having a slope of 2×10^{-5} and intercept 6×10^{-10}. The value of formation constant (K_f = 3.3×10^4 mol·dm^{-3}) of **4**-RB-19 complex was calculated from slope/intercept, while ε, the molar extinction coefficient of complex can also be determined by 1/slope that was found to be 5×10^4 L mol^{-1} cm^{-1} and the free energy change ($-\Delta G$) was calculated as 11.0 KJ mol^{-1}. The term ($-\Delta G$) refers to the negative value of (ΔG) and reveals the feasibility of a particular reaction.

A typical Benesi-Hildebrand plot is shown in (Fig. 15) and yields $\log K_f$ =4.5 and $\log \varepsilon = 4.69$. The higher value of K_f may show the high stability of the complex in methanol solution. However, the high value of free energy indicates the selectivity/recognition ability of **4** for RB-19 dye. Furthermore, the value of formation constant was close to the value of stability constant calculated above, which further confirms the host-guest ratio of 1:1 in the complex.

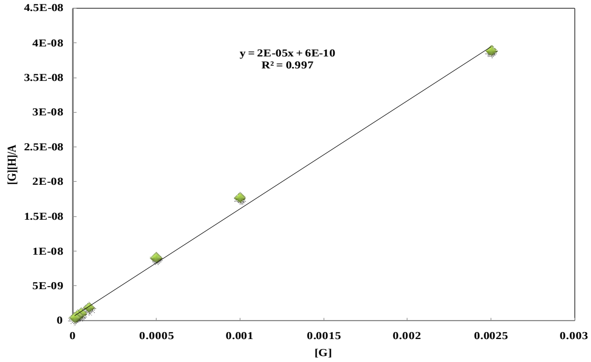


Figure 15. **The Benesi-Hildebrand plot of 4-RB-19 complex.**

Stability and Time Response of Complex in Selected Solvent

The determination of stability of complex with respect to time in selected solvent is a very important area of study. Therefore, it was suggested to explore the stability and response time of **4**-RB-19 complex. (Fig. 16) shows that **4** responds very immediately when titrated with RB-19, so that a significant enhancement in the band at 206 nm and appearance of new band at 227 nm occurs very rapidly and remains constant for a long time even up to one week.

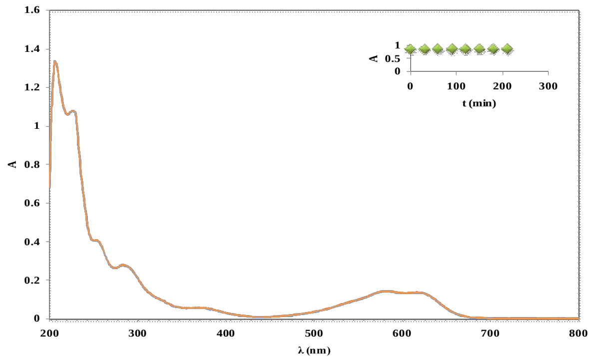


Figure 16. **Time dependent U.V-visible absorption spectra of 4-RB-19 dye complex (2.5 x 10^{-5} M) in methanol upon irradiation of U.V light; (inset) graph shows the stability of 4-RB-19 dye complex with respect to time.**

FT-IR Study

The FTIR spectra shown in (Fig. 17 a-b) clearly indicate that the complexation has been occurred between **4** and RB-19 dye, which is evident from shifting of band at 3469 cm^{-1} to 3453 cm^{-1} with a shoulder that highlights hydrogen bonding type interaction between OH functionalities of calixarene and sulphonate anions of the dye.

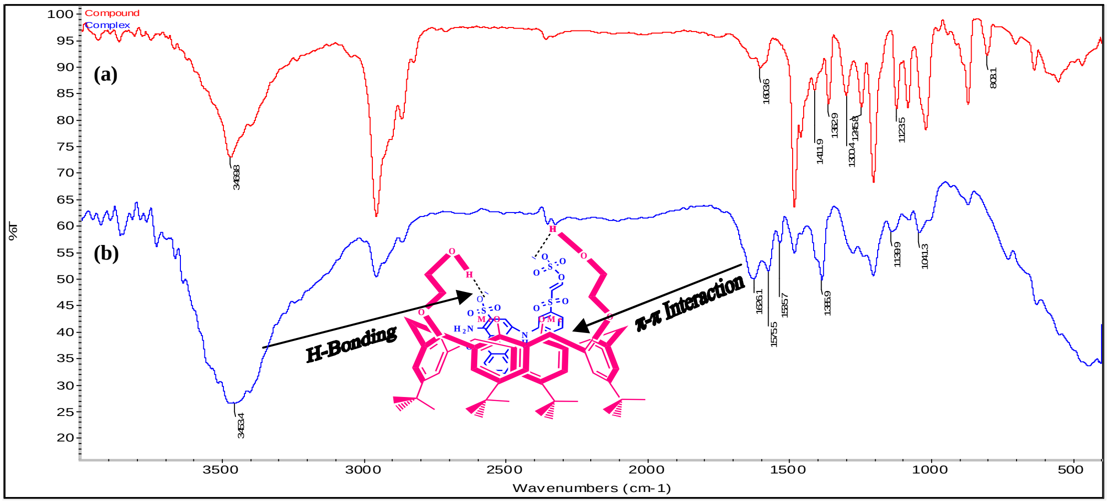


Figure 17. **FT-IR spectra (a) 4 (b) 4/RB-19 complex.**

Moreover, shifting of an aromatic C=C band at 1603 cm^{-1} to 1626 cm^{-1} also reflects the information about an endo complex formation indicating π-π interaction between RB-19 and **4** (Fig. 7). Consequently, the disappearance of older and appearance of other new bands in FT-IR spectra are clear indications of complexation between host and guest.

Regeneration Study

It has been aimed to regenerate compound **4** and recover RB-19 dye from organic phase. Thus, experiments were carried out at varying pH and observed that about 95 % recovery of RB-19 dye could be achieved at pH 8 (Fig. 18), Supporting Information) in a minimum amount of water. After the evaporation of water RB-19 dye could be reused industrially. Simultaneously, compound **4** in chloroform that is free of RB-19 dye could be reused for extraction of RB-19 dye from contaminated water that is produced from textile industries (Fig. 19). Shows the cyclic process of use and reuse of compound **4** as well as RB-19 dye.

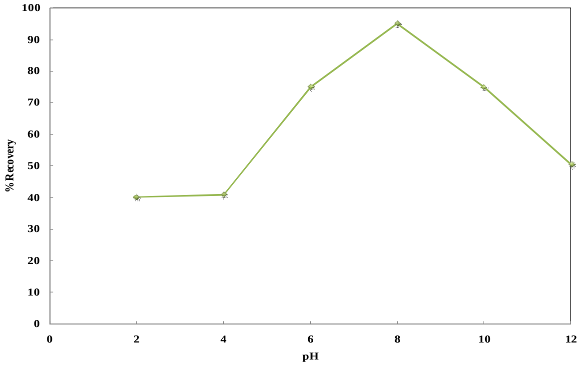


***Figure 18*. Effect of pH on % Recovery of RB-19 Dye.**

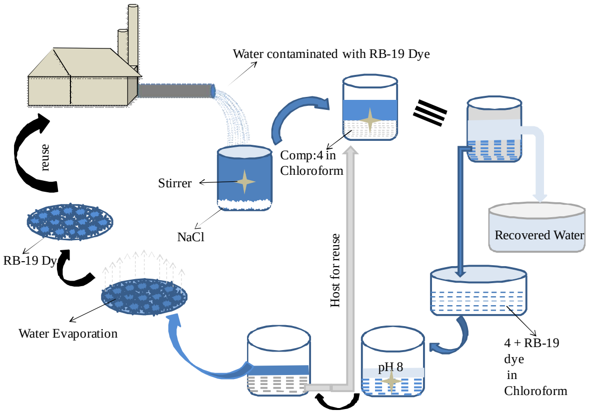


***Figure 19*. Cyclic process of use and reuse of compound 4 as well as RB-19 dye.**

Application to Real Wastewater Samples.

The extraction affinity of **4** for RB-19 dye was also studied on real water samples. Thus for this study, real wastewater samples were collected from the vicinity of Jamshoro industrial area. The samples were diluted and analyzed by U.V-visible spectroscopy to check their absorbance then RB-19 dye was extracted in chloroform with **4**. The absorbance was checked after extraction and % extraction was calculated. It has been noticed that greater than 80 % RB-19 dye was extracted with **4** at the same conditions as stated above.

Conclusion

The comparative extraction / recognition behavior of *p*-*tert*-butylcalix[4]arene (**1**) and its derivatives (**2-4**) as host molecules reveals the effectiveness of **4** for RB-19 among the series of reactive dyes. The work also demonstrates the role of pH and influence of electrolyte for the transfer of RB-19 from organic to aqueous phase. U.V-visible and FT-IR spectroscopy confirms 1:1 complexation between **4** and RB-19. The study proves the efficiency of preorganization concerning the modification of calixarene platform for neutral molecule's recognition and to provide the basis for the large scale demonstration and application of the calixarene based dye removal method. The work may support the efforts being made for site reclamation polluted by RB-19 dye and its recovery as well as the regeneration of **4** for reuse.

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