

Evaluation of the performance of calix[8]arene derivatives as liquid phase extraction material for the removal of azo dyes

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Abstract

This paper presents a study on the removal of azo dyes (Reactive Black 5, Trapaeolin 000, Methyl Orange and Direct Violet 51) with calix[*n*]arene derivatives from aqueous solution into the organic phase in order to explore the potential use of calixarenes as low-cost efficient extractants for wastewater dye removal. The carboxylic acid derivative of calix[8]arene shows highest affinity towards the azo dyes.

The influence of NaCl (present in the solution) on extraction process was also studied. The extent of the dye removal increased with the addition of NaCl. The proposed extraction mechanism involves several kinds of interactions: electrostatic repulsion between carboxylic acid groups of calix[8]arenes and sulfonate groups of azo dyes, hydrogen bonding and formation of an inclusion complex due to three dimensional cavity type calix[*n*]arene molecules through host–guest interactions.

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1. Introduction

Azo compounds have been the most widely used class of organic dyes, because of their versatile application in various fields; such as textile and fibers, pulp and paper, dyeing, paint, laser, liquid crystalline displays, ink-jet printer, and electro-optical devices, etc. [1,2]. Many industries including plastic, paper, textile and cosmetics use dyes in order to color their products. These molecules are common water pollutants and they may be frequently found in trace quantities in industrial wastewater. Their presence in water, even at very low concentrations, is highly visible and undesirable. In addition, many dyes are difficult to degrade due to their complex aromatic structure and thus tend to persist in the environment, creating serious water quality and public health problems [3–5]. Therefore, it would be advantageous to develop technologies to eliminate them.

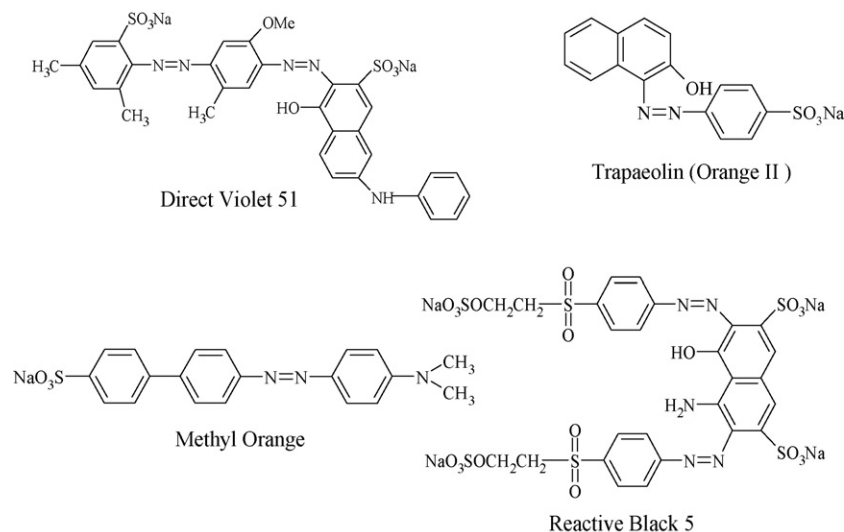
In recent years, many studies of dye wastewater treatment have been reported. Gregorio Crini [6] made solid and liquid

extraction of colors by using beta-cyclodextrin (β -CD) polymer. He explored adsorption mechanism and found that β -CD polymer has got high sorption capacity. A study was conducted by Banerjee and Dastidar [7] to examine the potential of jute processing waste for the treatment of wastewater contaminated with dye and other organics generated from various activities associated with jute cultivation and fiber production. Lee et al. [8] has systematically evaluated physiochemical processes of adsorption for the removal of reactive dyes. Uzun [9] has reported the kinetics of the adsorption of reactive dyes by chitosan. Besides this, many chemical, physical and biological methods, such as membrane filtration, oxidation–ozonation, adsorption, fungal decolorization, coagulation, flocculation, etc. are used for the removal of dyes from an effluent [10–14]. Among them, the most common procedure involves the use of activated carbons as adsorbents [15–17]. However, their use is limited to its high cost [18]. For this reason, several workers have attempted to use low cost materials, such as waste orange peel [19], peat [20], corncob and barley husk [21], wheat straw [22], starch-enriched flour [23] and clay material [24].

The existing adsorption processes for removal of color from wastewater are slow and performance is limited. Liquid phase

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Scheme 1. The chemical structures of some selected azo dyes used in experiments.

extraction (LPE) process may be an attractive alternative in this regard. In fact, LPE process is gradually emerging as a technically significant process in the treatment of wastewater. This process not only provides the separation but reuse of the costly dyes from the effluent mixtures can be an added advantage. Therefore, during recent decades, much interest has been focused on the design and synthesis of artificial receptors and related compounds. Molecules possessing ability for selective interactions with defined ions or neutral molecules are of great importance in supramolecular chemistry, where they can be used for the construction of host–guest type receptors [25–27]. Calix[*n*]arenes (Fig. 1) are the third major class of supramolecular host systems along with the crown ethers and the cyclodextrins [28–32].

Their ease of production and relative simplicity of chemical modification have produced increased interest in the host–guest chemistry over the last few years. The complexation properties of these molecules appear to be highly dependent upon the nature, number of donor groups and the conformation of the calix[*n*]arene moiety [33–36].

However, the objectives of the present work were to study the liquid–liquid extraction process of azo dyes with calixarene derivatives and evaluate the efficiency of these supramolecules. Furthermore, the sequence of experiments was performed to optimize the pH of the solution in the absence of calixarene derivatives and the overall efficiencies of the compounds were

compared with the results when sodium chloride was present in the system.

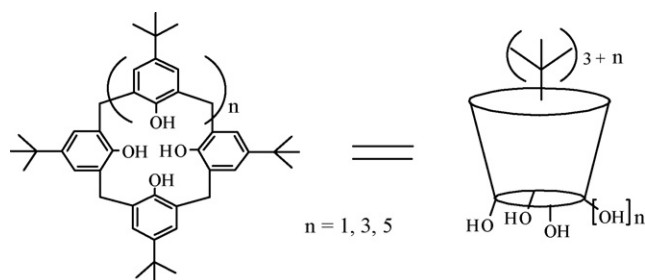
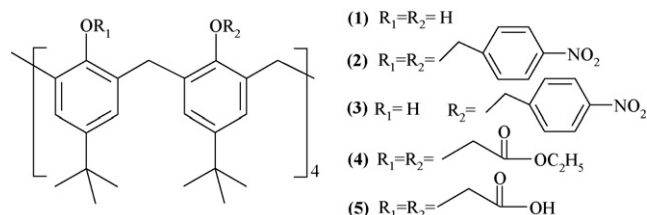
2. Experimental

2.1. Instrumentation

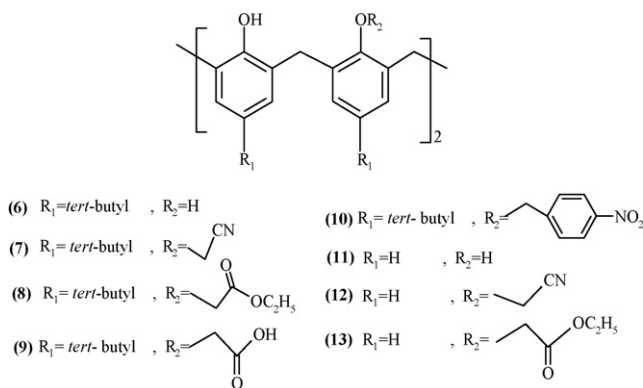
UV–vis spectra were obtained on a Shimadzu 106A UV–vis recording spectrophotometer.

2.2. Reagents

Analytical TLC was performed on precoated silica gel plates (SiO₂, Merck PF₂₅₄), while silica gel 60 (Merck, particle size 0.040–0.063 mm, 230–240 mesh) was used for preparative column chromatography. Generally, solvents were dried by storing them over molecular sieves (Aldrich, 4 Å, 8–12 mesh). Acetone and dichloromethane were distilled from CaSO₄ and CaCl₂ respectively. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system. Azo dyes such as Reactive Black 5, Trapaeolin 000, Methyl Orange and Direct Violet 51 (Scheme 1) used in this study were purchased from Aldrich. The structures of the extractants developed for this purpose are shown in Schemes 2 and 3. The *p*-*tert*-butylcalix[*n*]arenes (1 and 6) and their derivatives (2–5 and 7–13) were synthesized according to the literature procedures [37–45].

Fig. 1. Structures of calix[*n*]arenes.

Scheme 2. Calix[8]arene derivatives.



Scheme 3. Calix[4]arene derivatives.

2.3. Analytical procedure

The liquid–liquid extraction studies were performed following Pedersen's procedure [46]. A 10 ml of a 2.0×10^{-5} M aqueous solution of azo dye with 0.1 g NaCl and 1.0×10^{-3} M solution of calixarene derivative in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min. Then magnetically stirred in a thermostated water-bath at 25°C for 1 h, and finally left standing for an additional 30 min. The concentration of azo dye (Direct violet 51: $\lambda_{\text{max}} = 549$ nm, Reactive black 5: $\lambda_{\text{max}} = 612$ nm,

Trapaeolin 000: $\lambda_{\text{max}} = 484$ nm, Methyl Orange: $\lambda_{\text{max}} = 463$ nm) remaining in the aqueous phase was then determined spectrophotometrically. The percent extraction ($E\%$) has been calculated as:

$$E\% = \left[\frac{(C_0 - C)}{C_0} \right] \times 100$$

where C_0 and C are initial and final concentrations of the azo dyes before and after the extraction, respectively.

3. Results and discussion

3.1. Synthesis

In terms of this work we synthesized a series of calix[n]arene ($n=4, 8$) derivatives bearing different functional groups and investigated their ligating behavior by means of solvent extraction from a basic media (pH 8, 9 and 11). The calixarene acts as a cavity type molecular backbone to which the functional groups are anchored in vicinity to each other. The purpose of the functional groups is to provide binding sites through non-covalent binding forces. The position and the number of functional groups per molecule, as well as the size and flexibility of the calixarene vary among the ligands in order to systematically study the influence of the molecular structure. In addition, all the substituents were attached to the so-called "lower rim" of the calixarene.

The synthesis of *p*-*tert*-butylcalix[8]arene **1**, *p*-*tert*-butylcalix[4]arene **6**, and calix[4]arene **11** was conducted using the described Gutsche procedures [37–39]. The compounds **2–5** were prepared according to the published procedures [40–43]. Usually, reactions involving the hydroxyl groups at the lower

Table 1

Percentage extraction of azo dyes without ligand^a

Dye	pH	
	7	11
Direct Violet 51	1.8	<1.0
Reactive Black 5	<1.0	<1.0
Trapaeolin	2.9	<1.0
Methyl Orange	<1.0	<1.0

^a Aqueous phase [azo dye] = 2.0×10^{-5} M, 0.1 g NaCl; organic phase, dichloromethane; at 25°C , for 1 h.

rim are carried out with a large excess of strong reagents. In the case of calix[8]arenes it has been demonstrated [42] that alkylation in the presence of weak bases is mainly driven by the preferential formation of monoanions stabilized by two flanking hydrogen bonds leading to 1,3,5,7-tetraalkyl derivatives. The use of strong bases that should originate polyanions usually leads to exhaustive substitution or, with limiting amounts of electrophile to complex mixtures. Thus, arylmethylation of **1** has been achieved using BaO/BaOH and CsF separately with the commercially available *p*-nitrobenzyl bromide as an electrophile for the formation of octasubstituted derivative **2** and tetrasubstituted derivative **3** respectively [43].

The earlier synthesis procedures of our group [44] for compound **10** and Collins et al. [45] for compounds **7–9**, **12**, **13** gave the corresponding dialkyl derivatives of **6** and **11**.

3.2. Solvent extraction

In this study, to evaluate the azo dye removal efficiency of calixarene derivatives; two-phase solvent extraction experiments were carried out. Firstly, to optimize the pH of the solution for the maximum removal of azo dyes with calixarenes from the aqueous phase into the organic phase (dichloromethane), experiments were performed without calixarene derivatives at different pH (i.e. 7, 8, 9 and 11). The results of the extraction studies are summarized in Table 1. As it can be estimated from the results that, neutral (pH 7) condition is slightly favorable for the transportation of some of the azo-dyes to organic phase without the ligand (Table 1) therefore, basic condition was selected for the extraction of azo dyes with calixarene ligands.

Table 2 shows that the extraction data of compounds **1**, **2** and **3** are very close to each other. On the other hand, compound **4**

Table 2

Percentage extraction of Azo Dyes with calix[8]arene derivatives*

Compound	Direct Violet 51 (DV51)	Reactive Black 5 (RB5)	Trapaeolin (TP)	Methyl Orange (MO)
1	13.0	10.4	<1.0	3.0
2	11.9	4.0	<1.0	<1.0
3	11.7	8.2	<1.0	<1.0
4	13.2	6.4	80.0	70.7
5	77.0	40.0	80.0	46.8

* Aqueous phase [Azo dyes] = 2.0×10^{-5} M, 0.1 g NaCl; at pH 11; at 25°C , organic phase, dichloromethane [Ligand] = 1.0×10^{-3} M; at 25°C , for 1 h.

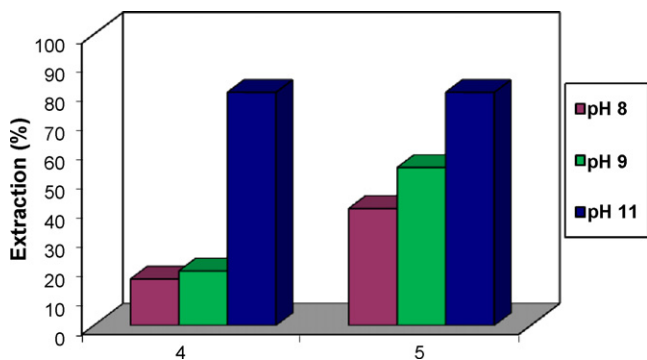


Fig. 2. pH effect on the extraction of TP by calix[8]arene derivatives(4,5).

seems to be very effective in transportation of species, especially trapaeolin 000 and methyl orange, to organic phase. Furthermore, compound **5** seems to be better extractant of azo dyes with a high efficiency than **4**.

To evaluate the influence of pH on the affinity of the azo dyes for compound **4**, **5** and to clarify the role of different factors which take place in the extraction mechanism, experiments were carried out at different pH (i.e. 8, 9 and 11). The influence of pH on the extraction capacity of the calix[8]arene derivatives **4** and **5** versus starting concentration of the TP and DV51 using a contact time of 1 h was studied (Fig. 2 and Fig. 3). The results obtained at pH 8 and 9 are close to each other but different from those obtained at pH 11. It has been observed that the percentage extraction of TP and DV51 with ligand **5** increases from 45% to 80% and 44% to 77% respectively when pH of the solution increases from 8 to 11. These results significantly show very strong interactions between ligand and dye molecule at high pH.

As the pH of the system increases, the number of negatively charged sites increases as well and the number of positively charged sites decreases. DV51 is a relatively large molecule and negatively charged at pH range >5. In the aqueous solution, the acid dye is first dissolved and the sulfonate groups of the acid dye (Dye-SO₃Na) are dissociated and converted to dye anions. As the dyes are negatively charged and the calixarene derivative may also be negatively charged, in this case; the dyes are extracted through hydrophobic interaction and metal ion coordination. The electrostatic repulsions may suppress the dye extraction but metal cation coordinated by negative sites of ligand and dye may eventually enhance the extraction percentage.

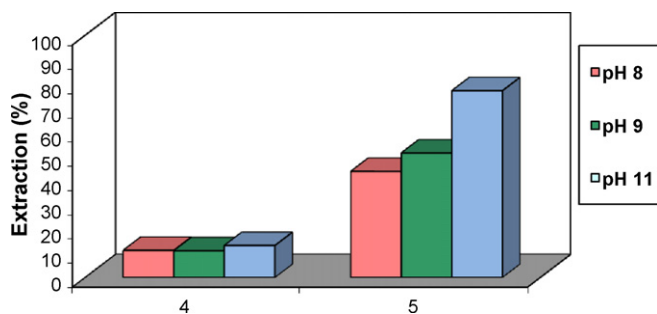


Fig. 3. pH effect on the extraction of DV51 by calix[8]arene derivatives(4,5).

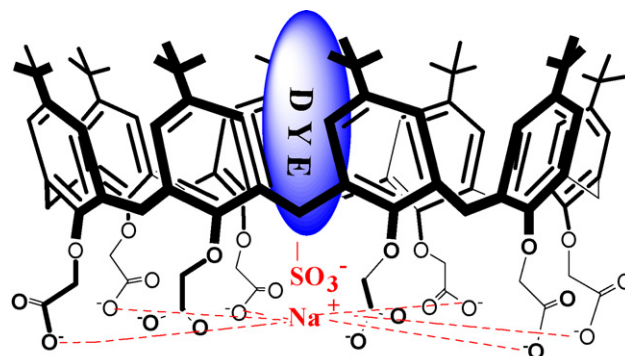


Fig. 4. Model of inclusion of azo dye into host **5**.

The much higher levels of azo dye removal by calix[*n*]arene carboxyl derivative **5** than the other calix[*n*]arene ligands suggest that an electrostatic repulsion between carboxylic acid groups of calix[*n*]arenes and sulfonate groups of azo dyes may play an important role. Here, it should be pointed out that the carboxyl groups of *p*-*tert*-butylcalix[*n*]arenes show binding abilities toward sodium cations [47,48]. The pronounced Na⁺ binding suggests an ion-pair extraction mechanism in which Na⁺ coordinates with the carboxyl groups binding site, while the azo dye anion inserts into the hydrophobic calixarene cavity (Fig. 4).

Thus, the important factors for azo dye extraction were found to be cyclic structure, cavity size, and the functional groups of the calixarene derivatives. The size, structure, hydrophobicity and the ionic property of guest molecules also affect the extraction efficiency. Calix[8]arene forms a stable complex with a guest molecule by entrapping it into the cavity.

It is, however, seen from the Table 3 that calix[4]arene and its derivatives have no influence on the extraction of azo dyes. Comparing to calix[8]arene derivatives, the molecular size of calix[4]arene derivatives is smaller and has higher steric hindrance. For this reason, it will be very difficult for azo dye molecules to enter into the cavity of calix[4]arene, resulting in no complex formation.

Table 3
Percentage extraction of azo dyes with calix[4]arene derivatives^a

Compound	Direct Violet 51	Reactive Black 5	Trapaeolin	Methyl Orange
6	13.8	11.4	<1.0	9.1
7	1.2	<1.0	<1.0	<1.0
8	15.0	5.0	6.5	21.4
9	28.0	2.8	4.6	<1.0
10	24.2	11.8	5.0	4.3
11	11.2	5.0	<1.0	1.2
12	11.1	<1.0	1.6	<1.0
13	18.2	8.3	5.6	2.8

^aAqueous phase [Azo dyes] = 2.0 × 10⁻⁵ M, 0.1 g NaCl; at pH 11; at 25 °C. Organic phase, Dichloromethane [Ligand] = 1.0 × 10⁻³ M; at 25 °C, for 1 h.

Table 4
Percentage extraction of azo dyes without NaCl^a

Compound	Direct Violet 51	Reactive Black 5	Trapaeolin	Methyl Orange
1	<1.0	<1.0	<1.0	<1.0
2	1.1	<1.0	<1.0	<1.0
3	<1.0	<1.0	<1.0	<1.0
4	1.1	<1.0	<1.0	4.4
5	6.3	<1.0	<1.0	<1.0
6	<1.0	<1.0	<1.0	<1.0
7	<1.0	<1.0	<1.0	<1.0
8	<1.0	<1.0	<1.0	<1.0
9	1.1	<1.0	<1.0	<1.0
10	<1.0	<1.0	<1.0	<1.0
11	1.7	<1.0	<1.0	<1.0
12	3.2	<1.0	<1.0	<1.0
13	3.8	3.4	<1.0	<1.0

^a Aqueous phase [azo dyes] = 2.0×10^{-5} M, at pH 11; at 25 °C organic phase, dichloromethane [Ligand] = 1.0×10^{-3} M; at 25 °C, for 1 h.

3.3. Influence of the NaCl on extraction

In order to investigate effect of NaCl content on extraction yield, some experiments were carried out without any NaCl addition to the medium. The obtained results are given in Table 4 showing almost no any transport to the organic phase. This situation reveals the importance of NaCl content within the solution, because NaCl provides an ionic balance between the two phases and affects the transport efficiency. Furthermore, NaCl would diminish the solubility of azo-dyes through the common ion effect, resulting in an increased and facilitated transport to the organic phase [14].

4. Conclusions

Inclusion phenomena of azo dyes by calixarene derivatives were investigated in a liquid–liquid extraction system. The carboxylic derivative of calix[8]arene was found to be one of the best host compound currently available for the recognition of azo dyes. The high affinity being created by the fit between the cavity of the cyclic ligand and the guest molecule. Extraction of azo dyes by the calix[8]arene **5** indicates that Na⁺ enhances an ion-pair complexation with the negatively charged azo dyes. The calix[8]arene carboxylic acid derivative is expected to be a novel tool for recognition of various molecules.

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