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# Carcinogenic direct azo dye removal from aqueous solution by amino-functionalized calix[4]arenes

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**Abstract** This study contains a convenient synthesis and azo dye extraction efficiency of amino-functionalized calix[4]arene derivatives. Two calix[4]arene derivatives bearing alkyl amino groups on their upper and lower rim have been successfully synthesized and used as extractant for dye removal in liquid–liquid extraction system. The effect of electrolyte concentration, contact time, and pH on azo dye extraction was also investigated for all calixarene derivatives. From the results, it has been deduced that the amino-functionalized calix[4]arenes showed a better affinity than other parent calix[4]arenes towards the selected azo dyes.

**Keywords** Calix[4]arene · Carcinogens · Azo dye · Liquid–liquid extraction

## Introduction

Environmental problems have become increasingly critical and frequent, due to population growth and increased industrial activity associated with contamination of natural waters which is one of the major problems of modern society [1]. Chemicals such as dyes and pigments are widely used for coloring in various sectors of industry including textile manufacture, leather tanning, paper production, food technology and cosmetics manufacture. The annual production of dyes and pigments is in excess of  $7 \times 10^5$  tones, of which an estimated 2–15 % are lost in the effluent

Ezgi Akceylan eakceylan@gmail.com during the dyeing process [2-5]. In some cases water coloration can be observed in dye concentrations of less than 1 ppm [6, 7]. Many of these dyes are toxic, even carcinogenic, persistent in the environment and non-biodegradable [8, 9]. Consequently the wastewater effluents have become a global issue, because the wastewaters are often heavily contaminated with synthetic dyes which cause discoloration and high chemical oxidation demand (COD) making the water unsuitable for drinking or other applications [10, 11]. Another dangerous problem involving dyes is exemplified with azo compounds that cause carcinogenic and mutagenic effects [12, 13]. In attempting to remove color from effluents, several methods can be applied, such as membrane filtration related to nanofiltration, biological treatment, coagulation/flocculation, reverse osmosis, electro dialysis, ion exchange, sorption techniques [14–18]. Liquid-phase extraction (LPE) due to its high extraction efficiency has been proved as an effective and attractive process for the decontamination of the dye-containing effluents.

In this respect, the supramolecular chemistry has provided a much better solution to search for molecular structures that can serve as building blocks for the production of sophisticated molecules by anchoring functional groups oriented in such a way that they provide a suitable binding site for dyestuff. This was achieved with the development of macrocyclic molecules such as synthetic crown ethers, cryptands, natural cyclodextrins and calixarenes [19–24].

Calix[n]arenes are a class of cyclooligomers formed via a phenol–formaldehyde condensation. They exist in a 'cup' like shape with a defined upper and lower rim and a central annulus. Their rigid conformation enables calixarenes to act as host molecules because of their preformed hydrophobic cavities. Also, they can be easily functionalized

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both at the phenolic OH groups (lower rim) and, after partial removal of *tert*-butyl groups, at the para positions of the phenol rings (upper rim) [23]. A polar lower rim composed of phenolic oxygens was extensively derivatized to bind and transport ionic species. The upper rim is a shallow bowl lined with aromatic rings that can encapsulate small organic molecules or a polar section of larger compounds. Due to this ability to form host–guest type complexes with a variety of organic and inorganic compounds the calixarenes have received increasing attention during the last two decades [25–28].

Previously, we have reported [26, 28] the synthesis and inclusion abilities of mannich base and crown ether derivatives of calix[4]arene for some water-soluble azo dyes. In this paper, we synthesized two calix[4]arene derivatives bearing alkyl amino groups on their upper and lower rim and investigated their extraction efficiency towards the selected azo dyes from aqueous media in liquid– liquid extraction system.

#### Materials and methods

#### General

<sup>1</sup>H NMR spectra were recorded with a Varian 400 MHz spectrometer in CDCl<sub>3</sub>. FT-IR spectra was recorded with a Perkin Elmer spectrum 100. Elemental analyses were performed on a Leco CHNS-932 analyzer. UV-Visible spectra were obtained on a Shimadzu 160A UV-Visible spectrophotometer. Thermal gravimetric analysis (TGA) was carried out with Setaram thermogravimetric analyzer. The sample weight was 15-17 mg. Analysis was performed from room temperature to 900 °C at heating rate of 10 °C/min in argon atmosphere with a gas flow rate of 20 mL/min. All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli Q Plus water purification system. All chemicals used were of analytical grade and purchased from Merck or Aldrich and used without further purification. Two commercial textile dyes Chicago Sky Blue (CSB) ( $\lambda_{max}$ 615 nm) and Tropaeolin 000 (TP) ( $\lambda_{max}$  485 nm) were purchased from (Aldrich; Steinheim, Germany). The pH of the solution was adjusted by mixing appropriate amount of HCl and/or NaOH (0.1 N).

#### Synthesis

The synthesis of compounds, *p-tert*-butylcalix[4]arene (1), 25,27-*bis*(3-bromopropoxy)-26,28-dihydroxycalix[4]arene (2), calix[4]arene (4) and 25,17-*bis*-[(4-benzyl piper-idine)methyl]-25,26,27,28-tetrahydroxy-calix[4]arene (5) and 4-((4-benzylpiperidin-1-yl)methyl)phenol (6) as the

monomer analog of 5 were synthesized according to the reported literature procedure [23, 29, 30] while compound 3 is reported for the first time.

#### Synthesis of compound 3

To a solution of 25.27-bis(3-bromopropoxy)-26.28-dihydroxycalix[4]arene (2) (6.0 mmol) in CH<sub>3</sub>CN (100 mL) were added NaI (12 mmol) and 4-benzylpiperidine, (30 mmol) and the reaction mixture was stirred and heated at reflux. The reaction was monitored by using a TLC. After 72 h, the reaction mixture was filtered and the solvent was removed under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (150 mL) and the organic layer extracted three times with water. The combined organic phases were dried over anhydrous MgSO<sub>4</sub>, the solvent was removed under reduced pressure. Compound 3 was obtained in 72 % yield; m.p. 145 °C. FT-IR (cm<sup>-1</sup>); 2916, 1602, 1583, 1450, 1144 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm): 0.9 (s, 18H, <sup>t</sup>Bu), 1.27 (s, 18H, <sup>t</sup>Bu), 1.7-1.91 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N, NCH<sub>2</sub>CH<sub>2</sub>), 1.99–2.1 (m, 2H, CHCH<sub>2</sub>-Ar), 2.61 (d, 4H, CHCH<sub>2</sub>Ar), 3,32 (d, 4H, ArCH<sub>2</sub>Ar), 4.05-4.2 (m, 8H, ArCH<sub>2</sub>Ar, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 6,97 (s, 4H, ArH), 7,07 (s, 4H, ArH), 7.12–7.3 (m, 10H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ (ppm): 25.5, 31.2, 32.1, 32.4, 32.9, 35.3, 37.1, 44.4, 47.2, 51.5, 77.6, 125.4, 125.7, 126.1, 129.3, 129.6, 133.7, 134, 138.6, 150.1, 151.7. Anal. calcd for: C74H98O4N2: C, 82.33; H, 9.15; N, 2.59 %. Found: C, 82.39; H, 9.20; N, 2.60 %.

# Liquid-liquid extraction

The liquid-liquid extraction studies were carried out to evaluate the efficiency of synthesized calix[4]arenes (1-5) to remove the CSB and TP dyes from aqueous media. Various parameters such as pH, contact time, and effect of electrolyte were also optimized. For liquid-liquid extraction, 10 mL dye solution  $(2 \times 10^{-5} \text{ M})$  and 10 mL of ligand solution  $(1 \times 10^{-3} \text{ M in CH}_2\text{Cl}_2)$  were taken in a 50-mL stoppered erlenmeyer flask and vigorously agitated with a mechanical shaker for 1 h. To obtain extraction equilibrium, the erlenmeyer flasks were stirred on a horizontal shaker operating with a constant speed (170 rpm) at 25 °C. Finally, dyes concentration before the treatment as well residual concentration of dyes in aqueous phase after the treatment was analyzed through UV-Vis spectrophotometer at 615 and 485 nm for CSB and TP dyes, respectively. 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.

#### **Results and discussion**

#### Synthesis

The synthetic route for the preparation of calix[4]arene derivatives is described in Scheme 1. The synthesis of compounds 1, 2, 4 and 5 was realized according to previously published procedures [23, 29]. Otherwise, the diamine derivative of calix[4]arene 3 was synthesized by reacting of the dialkyl bromide derivative of *p*-tert-butyl-calix[4]arene 2 and 4-benzylpiperidine in the presence of NaI in CH<sub>3</sub>CN. Compound 3 was characterized by <sup>1</sup>H NMR <sup>13</sup>C NMR, FT-IR, and elemental analyses. <sup>1</sup>H NMR data showed that compound 3 was in the cone conformation (Fig. 1). A typical AB pattern was observed for the methylene bridge ArCH<sub>2</sub>Ar protons at  $\delta$  3.32 and 4.09 ppm for 3 in <sup>1</sup>H NMR. The high field doublets at  $\delta$  3.32 ppm

was assigned to the equatorial protons of the methylene groups, whereas the low field signals at  $\delta$  4.09 ppm was assigned to the axial protons in the <sup>1</sup>H NMR.

#### Liquid-liquid extraction studies of selected dyes

Since removal of azo dyes from aqueous media is environmentally important, their extraction from aqueous samples was investigated. Azo dyes are expected to form inclusion complexes with amino-substituted-calix[4]arene (**3** and **5**). Liquid–liquid extraction of water soluble azo dyes (CSB and TP) (Fig. 2) by calixarene derivatives was conducted. Also, to avoid the influence of solubility of dyes in  $CH_2Cl_2$ , the blank experiments were performed without calixarene derivatives at different pH. The extraction procedure was schematically depicted in Fig. 3. The results of the extraction studies are summarized in Tables 1 and 2. These data were obtained using a dichloromethane solution of the extractant to remove the azo dye from an aqueous phase. The residual concentration of azo dye in the aqueous phase was then determined spectrophotometrically. Also,



Scheme 1 A schematic representation of the synthesis of calix[4]arene diamine derivatives



Fig. 1 <sup>1</sup>H NMR spectrum of compound 3 in CDCl<sub>3</sub>



Tropaeolin 000 (Orange II)

the influence of various parameters such as electrolyte concentration, contact time, and pH on the removal of selected azo dyes was examined.

#### pH effect on the extraction of azo dyes

The value of pH was known as one of the most important role in separation science because the pH of the solution affects both degree of ionization of the material present in the solution and the dissociation of functional groups on the active sites of the extractant [31]. Therefore, the influence of pH on the percent extraction of CSB and TP dyes was studied and the results were given in Tables 1 and 2. These results indicated that the parent calix[4]arenes (1, 2 and 4) have less sorption capacities for selected azo dyes. The percentage of CSB extracted was reached maximum that 91 % for 3, and 99 % for 5 when the pH of the aqueous solution was 3.0. Also, the monomer analog 4-((4-



Fig. 3 Schematic illustration of removal of azo dye from aqueous solution by compound 3

Table 1 Percent sorption of Chicago Sky Blue (CSB) by calix[4]arenes (%)

pH	3.0	5.0	7.0	9.0	11.0
Calix-ligand-1	5	3	6	8	7
Calix-ligand-2	5	4	3	3	2
Calix-ligand-3	91	43	37	25	19
Calix-ligand-4	5	4	4	4	4
Calix-ligand-5	99	99	98	97	8
Ligand-6	25	16	13	12	4
Blank	2.6	2.1	1.8	<1.0	<1.0

Aqueous phase, azo dye (CSB):  $2.0 \times 10^{-5}$ , organic phase (dichloromethane), ligand:  $1.0 \times 10^{-3}$ , 25 °C, 1 h

**Table 2** Percent sorption of Tropaeolin 000 (TP) by calix[4]arenes (%)

pН	3.0	5.0	7.0	9.0	11.0
Calix-ligand-1	5	5	6	5	3
Calix-ligand-2	4	5	5	6	2
Calix-ligand-3	99	99	99	99	51
Calix-ligand-4	5	5	5	4	2
Calix-ligand-5	99	99	99	99	29
Ligand-6	29	21	19	15	10
Blank	2.8	2.4	2.1	<1.0	<1.0

Aqueous phase, azo dye (TP):  $2.0\times10^{-5},$  organic phase (dichloromethane), ligand:  $1.0\times10^{-3},$  25 °C, 1 h

benzylpiperidin-1-yl)methyl)phenol **6** did not show any extraction ability compared to that of **5**. The results show that the macrocyclic structure of calixarenes is essential for the recognition of an azo dye. The extraction of CSB dye for **3** was decreased when the pH increased from 3.0 to

11.0. The results (Table 1) revealed that the significant extraction of the CSB azo dye for **3** occurs in a pH 3.0. On the other hand, the pH effect on the percent extraction of TP dye was summarized in Table 2. As seen Table 2, the percent extraction attained a maximum value 99 % at pH 3.0–9.0 for compound **3** and **5**. The lower sorption rates at alkaline pH (>9.0) are due to the presence of excess OH<sup>-</sup> ions competing with the dye anions for the sorption sites. As the pH of the system increases, the number of negatively charged sites increases as well, and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent does not favor the adsorption of dye anions due to electrostatic repulsion [32]. In the extraction of CSB, the cavity sizes of hosts (3 and 5) are prominent as well as pH. Since the tert-butyl groups in compound 3 induce a steric hindrance, compound 3 interacts weaker with CSB having a large size compared with that of TP.

The higher level of dye removal by compound **3** and **5** compared with the parent calix[4]arenes (**1**, **2** and **4**) suggest that a Coulomb interaction exist between the amino groups of calix[4]arene and the sulfonate groups of azo dyes (Fig. 4). Alkylamino groups of calix[4]arenes (**3** and **5**) form intermolecular hydrogen bonds to these sulfonate groups. The molecular recognition mechanism between host and guest related to the geometrical shape, size of the guest, the polar, and the cavity size of host, which were important factor of forming host–guest inclusion complexes. The complex interaction was attributed to the weak forces including hydrogen bonding, hydrophobic interaction, electrostatic interaction,  $\pi$ - $\pi$  and dipole–dipole interactions.

The thermal stability of the compound **5** and its Tropaeolin complex was evaluated by TGA. It was found that **5** undergo a three-step thermal degradation (Fig. 5). At the first decomposition step, the functional groups of **5** left from the







main structure at 150–340 °C. The mass loss of within the temperature range 350–620 °C may be attributed to the loss of the calixarene backbone. The TGA result of the **5** showed the weight loss peak temperatures at 243 and 379 °C shifted to 350 °C in the Tropaeolin complex of **5** (Fig. 5). These results indicated that there is a remarkable interaction between the calixarene and the azo dye.

# Influence of the NaCl concentration on the extraction of azo dyes

Dye extraction strongly depends on the ionic strength because the influence of electrolyte plays a key role on

separation sciences. NaCl provides an ionic balance between the two phases. Furthermore, NaCl increases the solubility of azo dyes through the common ion effect, resulting in an increased and facilitated transport to the organic phase [33–35]. The molar concentration of NaCl was varied as 0.1, 0.2 and 0.4 mol L<sup>-1</sup>. Figure 6 obviously demonstrates that dyes' extraction efficiency improved remarkably by increasing the ionic strength up to 0.2 mol L<sup>-1</sup>, beyond which the dyes' extraction efficiency once again tend to decrease. The decrease in percent extraction of CSB and TP dyes beyond the 0.2 mol L<sup>-1</sup> concentration of NaCl is may be due to the commutative ion interferences.



Fig. 6 Effect of NaCl concentration on extraction of CSB (a) and TP (b) dye

#### Effect of contact time

The equilibrium time between the pollutant and the extractant is of significant importance during the extraction process. For an efficient extractant, it is obligatory to show a rapid uptake of the pollutants and reach the equilibrium in a short time. Hence, the effect of shaking time on the extraction of azo dyes by compound **3** and **5** was studied at 25 °C. The results are depicted in Figs. 7 and 8. The obtained results showed that percent extraction of azo dyes increased rapidly in the beginning and rapid equilibrium was established within 15 min, but slowly, it increased up to 30 min.

### Conclusion

In this study we have reported the synthesis and characterization of a novel amino functionalized p-tert-butylcalix[4]arene derivative (3). The prepared calix[4]arene derivatives (3 and 5) were used as the extractants towards the selected azo dyes (CSB and TP) in liquid–liquid extraction. Also, the influence of various parameters such as



Fig. 7 Effect of contact time on percent extraction of CSB and TP by compound 3 (pH 3.0, NaCl: 0.2 mol  $L^{-1}$ )



Fig. 8 Effect of contact time on percent extraction of CSB and TP by compound 5 (pH 3.0, NaCl: 0.2 mol  $L^{-1}$ )

electrolyte concentration, contact time, and pH were investigated in extraction experiments. The results achieved from the present study clearly showed that **3** and **5** are very efficient extractants for the removal of selected dyes as compared to other parent calix[4]arenes. During the extraction process, various kinds of interactions such as dipole–dipole, electrostatic repulsion, hydrogen bonding and  $\pi$ – $\pi$  interaction between the azo dyes and calix[4]arene molecules due to the formation of an inclusion complex by host–guest type interaction and dissociation of azo dyes into anions/cations were monitored and found that extraction is highly dependent on pH and salinity concentration.

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