Removal efficiency of a calix[4]arene-based polymer for water-soluble carcinogenic direct azo dyes and aromatic amines

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ABSTRACT

A Mannich base derivative of 5,11,17,23-tetrakis-[(1,4-dioxa-8-azaspiro-[4.5]decanyl)methyl]-25,26,27,28-tetrahydroxy calix[4]arene **3** was synthesized by the treatment of calix[4]arene with a cyclic secondary amine (1,4-dioxa-8-azaspiro-[4.5]decane) and formaldehyde. The compound **3** was treated with dibromoxylene to obtain a calix[4]arene-based copolymer **4**. In batch sorption experiments of selected carcinogenic azo dyes and aromatic amines, the compounds **3** and **4** were found to be a better sorbent for azo dyes than for the aromatic amines. It was observed that the percentage of azo dye removal was 95–99% for compound **3** and 83–97% for **4** when the pH of the dye solution was in the range of 2.0–8.0. The sorption of azo dyes and aromatic amines by calix[4]arenes-based compounds indicates that amino groups play the major role for the formation of hydrogen bonds and electrostatic interactions.

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1. Introduction

Azo dyes are synthetic organic colorants commonly prepared by coupling of a diazonium compound with a phenol or an aromatic amine. They are widely used as colorants in a variety of consumer goods, for example leather, textiles, and foodstuff. Some of these dyes can be reduced in vivo through cleavage of the azo groups (N=N), forming mutagenic and carcinogenic aromatic amines [1,2]. With the increased awareness of the potential risk for consumers, the European Parliament recently accepted the 19th amendment of the Council Directive 76/769/EEC and issued the European Directive 2002/61/EC [3]. This directive particularly restricts the marketing and use of azo dyes, which may form any of 22 listed harmful aromatic amines in textile and leather articles after reductive cleavage, and may come into direct and prolonged contact with human skin or oral cavity.

The total dye consumption of the textile industry worldwide is more than 10^7 kg/year, and is estimated 90% of ending up on fabrics. Dye producers and consumers are interested in stability and fastness and consequently, are producing dyestuffs which are more difficult to degrade after use [4,5]. In the textile industry, it is estimated that 10–15% of the dye is lost during the dyeing process and released with the effluent [6]. The release

of those colored wastewaters in the environment is a considerable source of non-aesthetic pollution since the presence of small amounts of dyes (below 1 ppm) is clearly visible. Dyes wastes can also generate eutrophication and dangerous by-products through oxidation, hydrolysis or other chemical reactions taking place in the wastewater-phase [7,8]. Due to the large degree of aromatics present in dye molecules and the stability of modern dyes, biological treatment is ineffective for their degradation [6,9,10]. Azo compounds are resistant to aerobic degradation and under anaerobic conditions, the azo linkage is reduced to generate aromatic amines that are colorless but can also be toxic and potentially carcinogenic [11]. There are many processes available for the removal of dye by conventional treatment technologies including biological and chemical oxidation, chemical coagulation, foam flotation, electrolysis, biodegradation, advanced oxidation, photocatalysis and adsorption processes [12–14]. Among all the treatments proposed, adsorption using sorbents is one of the most applied methods for the removal of pollutants from the wastewater [15,16]. Various chemical and physical processes are currently in use. However, it is well known that solid-phase extraction (SPE) using sorbents is one of the most efficient and popular methods for the removal of organic compounds from wastewater [17,18]. The sorbents may be of mineral or organic origin. Silica beads, activated carbon, zeolites, polyamines and organic and inorganic gels [19–21] are just few examples. Many studies have been undertaken for the development of cheaper and more effective adsorbents containing natural polymers. Among these, polysaccharides such as chitin [22,23] and

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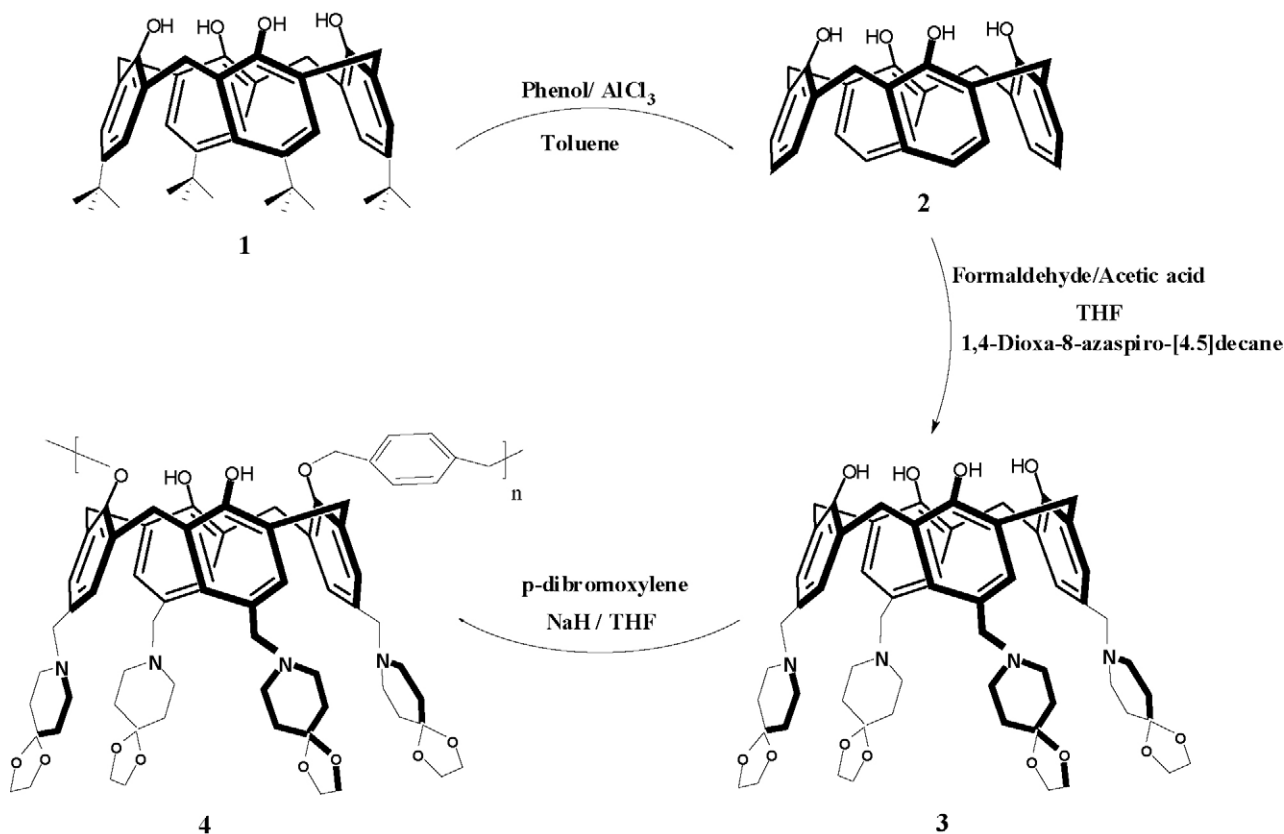E-mail address: myilmaz42@yahoo.com (M. Yılmaz).

Fig. 1. Schematic representation of the synthesis of calix[4]arene derivative **3** and its corresponding polymeric derivative **4**.

starch [24,25] as well as their derivatives chitosan [26,27] have received particular attention. 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, spherands [28], natural cyclodextrins [29,30] and calixarenes [31–36].

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. 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 [28,37,38]. Previously, we have reported [39,40] the synthesis and inclusion abilities of calix[4]arene derivatives for selected water-soluble azo dyes.

We now synthesized a calix[4]arene polymer and its monomeric precursors (Fig. 1) and investigated their ligating behavior by means of solid–liquid-phase sorption of three carcinogenic reactive azo dyes (Fig. 2) and aromatic amines (Fig. 3) from aqueous solution.

2. Experimental

2.1. Materials

Analytical TLC was performed on precoated silica gel plates (SiO$_2$, Merck PF$_{254}$), 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 storage over molecular sieves (Aldrich; 4 Å, 8–12 mesh). Dichloromethane was distilled from CaCl$_2$. MeOH was distilled from Mg and stored over molecular sieves. All chemicals were purchased from Merck and Fluka. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

2.2. Apparatus

Melting points were determined on a Gallenkamp apparatus in a sealed capillary and are uncorrected. ^{1}H NMR spectra were recorded with a Bruker 400-MHz spectrometer in CDCl$_3$ with TMS as internal standard. IR spectra were recorded with a PerkinElmer 1605 FTIR spectrometer as KBr pellets. UV–vis spectra were obtained with a Shimadzu 160 A UV–vis recording spectrophotometer. High-performance liquid chromatography (HPLC) Agilent 1200 Series were carried out using a 1200 model quaternary pump, a G1315B model Diode Array and Multiple Wavelength UV–vis detector, a 1200 model Standard and preparative autosampler, a G1316A model thermostated column compartment, a 1200 model vacuum degasser, and an Agilent Chemstation B.02.01-SR2 Tatch data processor. The amines were separated on a Ace 5 C$_{18}$ column (25 cm, 4.6 mm). The mobile-phase consisted of acetonitrile (eluent A) and water (eluent B), flow rate: 1 mL/min, at 25 °C, injection volume 20 μL, gradient elution: 0 min 20% A and 80% B; 25 min 80% A and 20% B. Detection was performed at 280 nm. Thermal gravimetric analysis (TGA) was carried out with Seteram thermogravimetric analyzer. The sample weight was 15–17 mg. Analysis was performed from room temperature to 1000 °C at heat-

Evans Blue (EB)

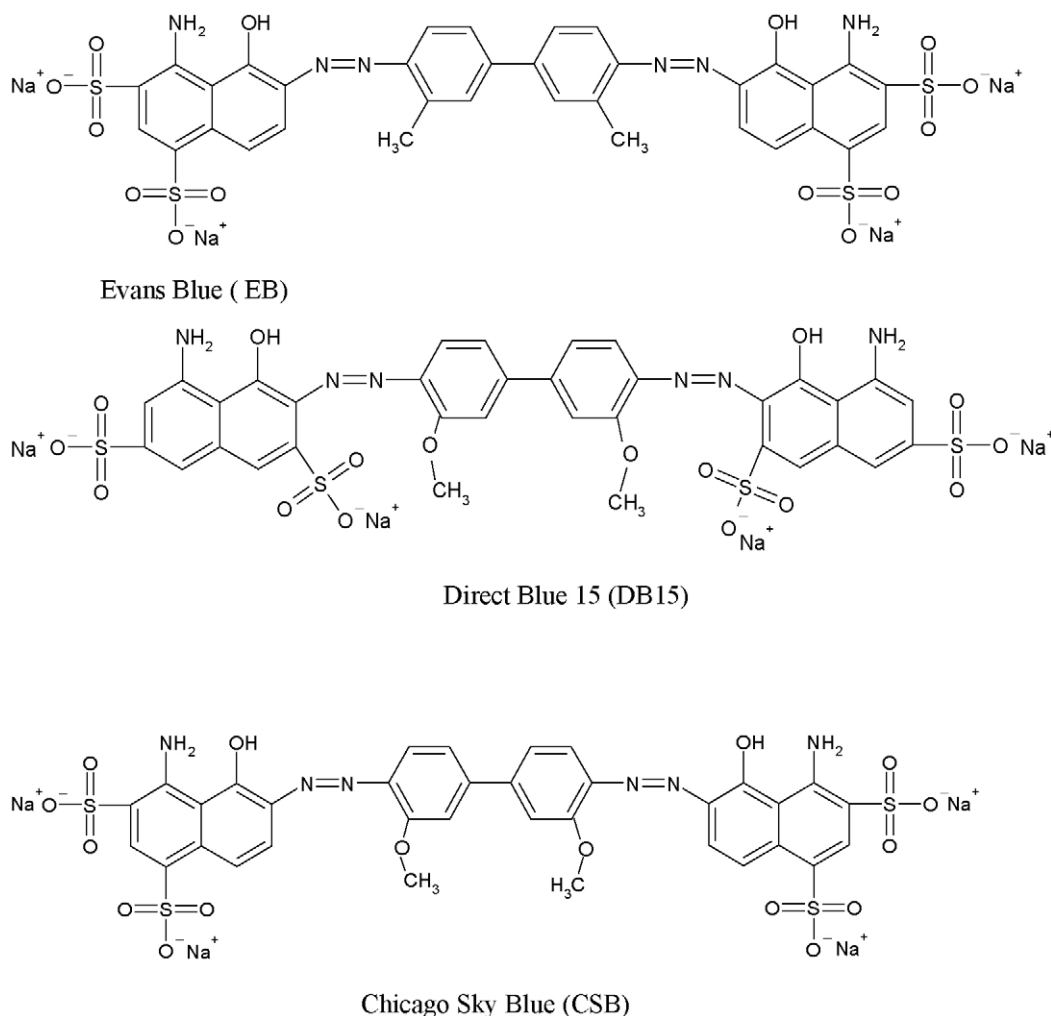Direct Blue 15 (DB15)

Chicago Sky Blue (CSB)

Fig. 2. The chemical structures of some selected azo dyes used in experiments.

ing rate of 5 °C/min in argon atmosphere with a gas flow rate of 20 mL/min.

2.3. 5,11,17,23-Tetrakis-[(1,4-dioxa-8-azaspiro-[4.5]decanyl)methyl]-25,26,27,28-tetrahydroxy calix[4]arene (3)

To a solution of calix[4]arene (2) (10 mmol) in 90 mL of THF were added 11 mL of acetic acid, the secondary amine 1,4-dioxa-8-azaspiro-[4.5]decane (50 mmol), and 37% aqueous formaldehyde (50 mmol) and the reaction mixture was stirred for 24 h at room temperature. The solvent was removed in vacuo and the residue was dissolved in 75 mL of water. The aqueous solution was extracted twice with 50 mL of diethyl ether and then neutralized with 10% aqueous K_2CO_3 solution. The precipitate that formed was removed by suction filtration. The product was dried in vacuo and recrystallized from chloroform. 75% yield—m.p.: 165 °C (dec). ^{1}H NMR (CHCl$_3$): δ = 6.98 (s, 8H, Ar–H), 4.21 and 3.50 (pair of d, Ar–CH$_2$–Ar), 3.94 (s, 16H OCH$_2$), 3.28 (s, 8H, N–CH$_2$–Ar), 2.45 (br s, 16H, NCH$_2$), 1.73 (t, 16H, CH$_2$C); ^{13}C NMR (CHCl$_3$): δ = 147.8, 132.2, 129.6 and 128.0 (Ar). 107.4 (OCO), 64.2, 62.1 and 51.3 (OCH$_2$, NCH$_2$ and NCH$_2$Ar), 34.8 and 31.8 (ArCH$_2$Ar and CH$_2$C); Anal. Calcd for C$_{60}$H$_{76}$N$_4$O$_{12}$: C, 68.97; H, 7.28; N, 5.36; Found: C, 68.29; H, 7.26; N, 4.71.

2.4. Oligomer 4 from 5,11,17,23-tetrakis-[(1,4-dioxa-8-azaspiro-[4.5]decanyl)methyl]-25,26,27,28-tetrahydroxy calix[4]arene (3) and p-dibromoxylene

A mixture of 3 (3.63 g, 5 mmol) and sodium hydride (1 g, 25 mmol of 60% suspension in oil) in 50 mL of THF was vigorously stirred under a nitrogen atmosphere at room temperature for about 30 min (2.64 g, 10 mmol), p-dibromoxylene was added to the reaction mixture. The mixture was then stirred under a nitrogen atmosphere at room temperature and refluxed for 24 h. The solvent was removed under reduced pressure and the precipitate was filtered, rinsed with water, and 1N HCl, and then repeatedly washed with CHCl$_3$ and MeOH to ensure removal of any unreacted Mannich base. Finally, product was dried in a vacuum oven. The oligomer 4 was obtained in 70% yield.

2.5. Sorption studies of azo dyes

The first approach was a batch method. 25 mg of the sorbent was mixed with 10 mL of NaCl (0.2 mol L^{-1}) and an aqueous solution of the pollutant (2 × 10^{-5} mol L^{-1}) in a stopped flask at 25 °C that was stirred on a horizontal shaker operating at a constant agitation speed of 170 rpm until equilibrium for 1 h. The residual concentration of the organic solute in water was determined by means spectrophotometry. All solutions were centrifuged before measure-
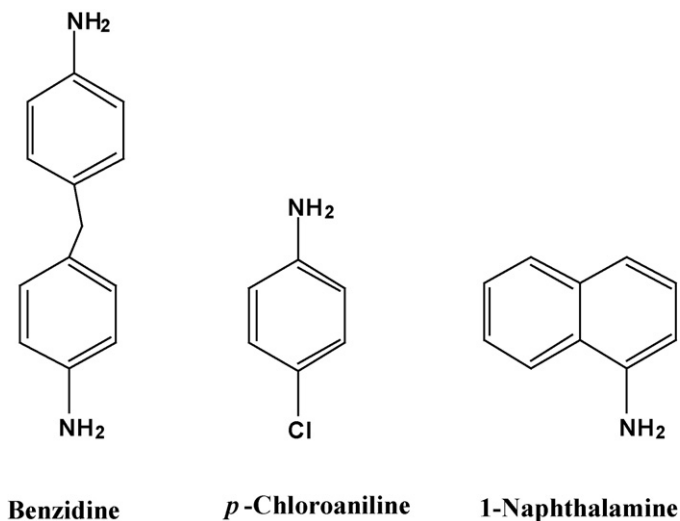
Fig. 3. The chemical structures of aromatic amines used in experiments.

ments. Absorbance values were recorded at λ_{max} for each solution: at 620 nm for Chicago Sky Blue (CSB), 590 nm for Direct Blue 15 (DB15) and 596 nm for Evans Blue (EB) (see Fig. 2 for the structure formula). The sorption capacity was then calculated and expressed in percentage uptake (%) which represents the ratio between the amount of adsorbed dye and the starting amount of dye [37–41].

2.6. Sorption studies of aromatic amines

An aqueous solution (10 mL) containing aromatic amine (see Fig. 3 for the structure formula) was pipetted into a vial at a concentration of 1×10^{-3} M, a few drops of 0.01 M KOH/HCl solution in order to obtain the desired pH at equilibrium and maintain the ionic strength, and 25 mg of the sorbent were added. The mixture was stirred at 25 °C on a horizontal shaker at 170 rpm until equilibrium for 1 h. After the sorbent was removed by centrifugation the residual concentration of the organic moiety was determined by means of an HPLC. The sorption capacity was then calculated and expressed in percentage uptake (%, see above).

3. Results and discussion

3.1. Synthesis

The main focus of this work was the design of new calixarene-based ionophores that are easily accessible, has an effective binding characteristics for a particular set of cations/anions and molecules, and could be useful for multiple applications such as laboratory, clinical, environmental, and industrial process analyses. To achieve the desired goal, *p-tert*-butylcalix[4]arene (**1**) has been chosen as the precursor. A syntheses strategy has been developed to enable its derivatization. Such a syntheses route is depicted in Fig. 1. The syntheses for compounds **1** and **2** are based on the previously published procedures [42–44]. The substitution of calix[4]arene (**2**) at its upper rim (Mannich Reaction) [45,46] was conducted in the presence of AcOH in THF with a cyclic secondary amine (1,4-dioxa-8-azaspiro-[4.5]decane) and formaldehyde to afford the cone conformer **3** at high yields (75%). The ^{1}H NMR spectra of **3** has a typical AB pattern for the methylene bridge protons (ArCH$_2$Ar) of the calixarene moiety at 3.55 and 4.38 ppm ($J = 14$ Hz) which demonstrates that the compound exist in the cone conformation [35]. The compound 5,11,17,23-tetrakis-[(1,4-dioxa-8-azaspiro-[4.5]decanyl)methyl]-25,26,27,28-tetrahydroxy calix[4]arene has

been converted to **4** by copolymerization with *p*-dibromoxylene in the presence of NaH in THF. After purification and reprecipitation from a chloroform–methanol system, polymer has been obtained in 70% yield and this compound was insoluble in most of the organic solvents.

The thermal stability of calix[4]arene-based polymer was evaluated by thermal gravimetric analysis (TGA). It was found that the polymer undergoes a three-step thermal degradation (Fig. 4). The first step (40–125 °C) is due to the loss of moisture, while the second (189–394 °C) could be attributed to the loss of the functional group of calix[4]arene, and the third step (395–532 °C) is due to the breakage of the polymer backbone.

3.2. Sorption studies of selected azo dyes

In order to evaluate the azo dye removal efficiency of calixarene derivatives, solid–liquid-phase sorption experiments were conducted. Batch sorption studies were carried out to examine the influence of parameters such as the initial concentrations of the dyes and the effect of pH on their removal from aqueous solutions. The results of the sorption studies are summarized in Table 1. These results indicate that the parent calix[4]arene showed less sorption capacities for all three azo dyes. The conversion of compounds **2** into its corresponding Mannich base derivative of calix[4]arene (**3**) resulted in a remarkable increase of its sorption capacity towards all azo dyes. The conversion of **3** into copolymeric structure **4** does not alter its azo dye extraction capacity (Table 1). The higher level of dye
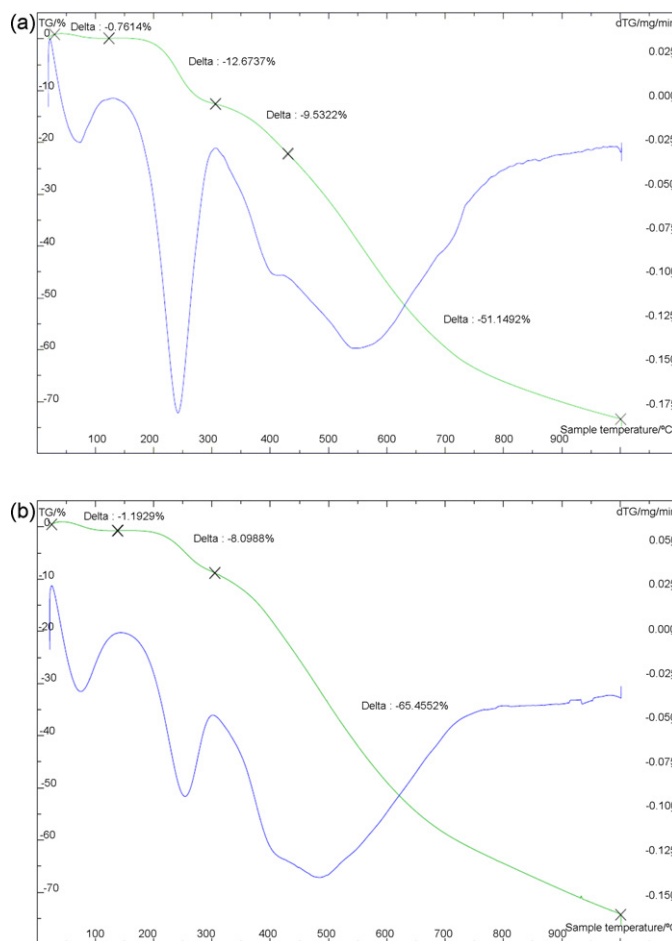

Fig. 4. (a) TG and DTG curves of the compound **4**; (b) TG and DTG curves of compound **4** treated with CSB.

Table 1
Percent sorption of azo dyes by calix[4]arenes and copolymer **4** (%)[a]

Compound	Evans Blue			Direct Blue 15			Chicago Sky Blue		
	pH 2.0	pH 5.2	pH 8.0	pH 2.0	pH 5.2	pH 8.0	pH 2.0	pH 5.2	pH 8.0
Removal of azo dyes (%)									
2	14	7	9	8	<1.0	7	17	9	11
3	97	95	98	95	98	96	97	99	98
4	96	89	87	97	95	88	94	92	83

[a] Solid-phase, adsorbent: 25 mg of calixarene derivatives; aqueous-phase, azo dyes: 2.0×10^{-5} M, pH 2.0, 5.2 and 8.0, at 25 °C, 1 h.

Table 2
FTIR spectral properties of **4** before and after treated with CSB

IR band	Before	After	Difference	Assignments
FT-IR absorption bands (cm^{-1})				
1	2922	2914	−8	Aliphatic C–H groups
2	1602	1598	−4	Aromatic C=C stretching
3	1479	1470	−9	Aromatic C=C stretching
4	1223	1209	−14	Etheric C–O stretching

removal by compound **3** compared with the parent calix[4]arene sorbent (**2**) suggest that a Coulomb interaction exist between the amino groups of calix[4]arene and the sulfonate groups of azo dyes (see Fig. 5). In our previous publication [47] we concluded that the sorption levels of dyes on the sorbent were dependent on the sulfonate groups in the molecule. Alkylamino groups of calix[4]arenes (**3** and **4**) form intermolecular hydrogen bonds to these sulfonate groups. Hence, the cyclic structure, the cavity size, and the functional groups of the calixarene derivatives were found to be the important factors for the sorption of azo dyes. The IR spectra of **4** and its CSB complex is similar to each other (see Fig. 6). Fig. 6(a–c) shows the FT-IR spectrum of CSB, compound **4**, and compound **4** after adsorption of CSB, respectively.

The most significant difference between the IR spectra of **4** and its CSB complex is the absorption bands of CSB complex which shifted to a lower wavenumber (4–14 cm^{-1}) (Table 2). The TGA result of the polymer **4** showed the weight loss peak temperature of 532 °C (51.5%) shifted to 485 °C (65.7%) in the CSB complex of **4** (Fig. 4). The results indicated a remarkable interaction between the calixarene and the azo dye.

In order to evaluate the influence of pH on the affinity of the azo dyes to compounds **2**–**4** and to clarify the role of different factors which take place in the sorption mechanism, experiments were carried out with selected azo dyes at pH 2.0, 5.2, and 8.0 with a contact time of 1 h. Furthermore, it was observed that the percentage of azo dye removal was 95–99% for compound **3** and 83–97%
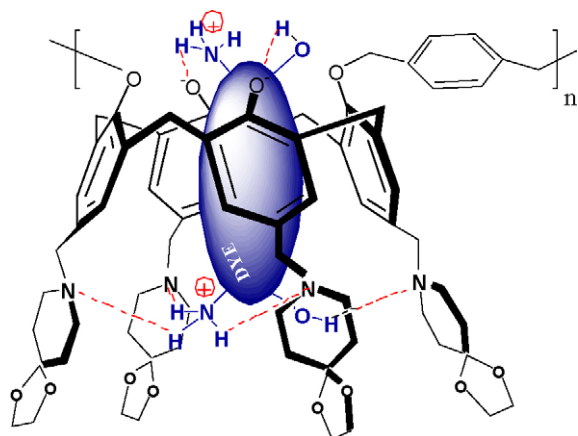
for compound **4** when the pH of the dye solution was 2.0–8.0 (Table 1).

3.3. Sorption studies of selected aromatic amines

Azo dyes are readily decolorized by splitting the azo bond(s) in anaerobic environment. Azo dye reduction leads to the formation of aromatic amines. Aromatic amines are generally not degraded and accumulate under anaerobic conditions [48] with the exception of a few compounds characterized by the presence of hydroxyl and/or carboxyl groups [49]. Aromatic amines are expected to form inclusion complexes with insoluble calix[4]arene derivative **3** and polymer **4**. Solid–liquid batch sorption experiments were used to assess their ability to remove the water-soluble aromatic amines from aqueous solution. Sorption capacity of calix[4]arene derivative **3** was compared with the calix[4]arene-based polymer **4**.

Batch sorption experiments were carried out by agitating 1×10^{-3} M, 10 mL of aromatic amines (benzidine, p-chloroaniline, α-naphthalamine) solutions with 25 mg of adsorbent in glass bottles at different pH (2.5, 7.0, and 8.5), 200 rpm, and room temperature (25 °C) using an incubator with a contact time of 1 h. The amine solutions were separated from the adsorbent by centrifugation at 2200 rpm for 5 min. The aromatic amines removal was analyzed by means of HPLC. From the data given in Table 3, it was observed that parent calix[4]arenes **1** and **2** did not show a significant extraction efficiency towards none of the amines used in the extraction studies. A small change in extraction ability towards amines has been observed by the introduction of 1,4-dioxa-8-
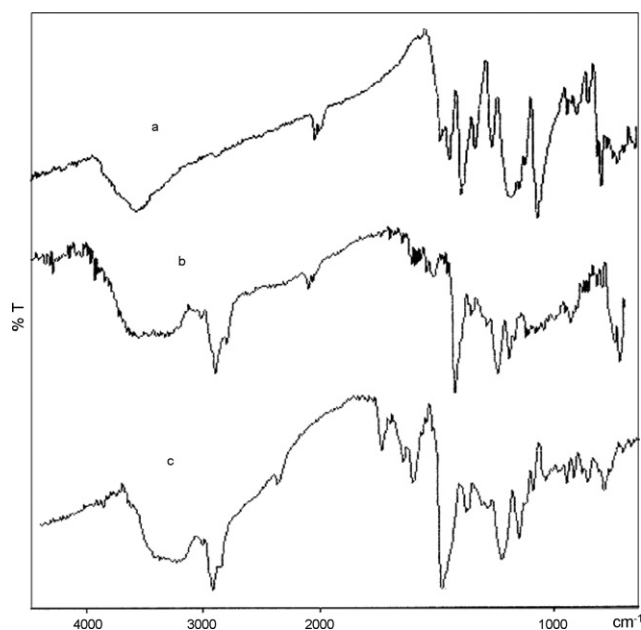

Fig. 5. Proposed interactions of the compound **4** with azo dyes.

Fig. 6. The FT-IR spectra of (a) CSB, (b) compound **4** treated with CSB and (c) compound **4**.

Table 3
Percent sorption of aromatic amines by calix[4]arenes and polymer **4** (%)[a]

Compound	Benzidine			p-Chloroaniline			α-Naphthalamine		
	pH 2.5	pH 7.0	pH 8.5	pH 2.5	pH 7.0	pH 8.5	pH 2.5	pH 7.0	pH 8.5
Extraction of aromatic amines (%)									
1	<1.0	2.0	4.0	<1.0	2.2	4.3	<1.0	1.5	4.7
2	1.9	2.5	4.7	<1.0	3.2	4.8	<1.0	3.1	4.8
3	<1.0	3.5	15.3	13.2	14.8	17.7	8.0	14.0	24.0
4	9.4	33.9	42.0	25.9	41.5	42.0	34.6	59.0	59.6

[a] Solid-phase, adsorbent: 25 mg of calixarene derivatives; aqueous-phase, aromatic amines (benzidine, p-chloroaniline, α-naphthalamine) 1.0×10^{-3} M; pH 2.5, 7.0 and 8.5, 1 h.

azaspiro-[4.5]decanyl groups to the upper (wide) rim of compound **3**. But when it was converted to a rigid structure by anchoring it in a polymeric backbone it showed remarkable extraction ability. The polymer **4** showed higher affinity of the guest compounds than compound **3**.

In our previous publication [50,51] we have prepared Schiff base derivatives of calix[4]arenes and studied inclusion complexation of various amines. Thereby, weak intermolecular forces such as ion–dipole, dipole–dipole, dipole-induced dipole, van der Waals, electrostatic interaction, hydrogen bonding, and hydrophobic interaction are known to cooperatively contribute to the inclusion complexation of guest molecules with calixarenes. In the present study, hydrogen bonding was considered to determine the complex stability to a large extent.

In order to evaluate the influence of pH on the affinity of the aromatic amines to the compounds **3** and **4** and to clarify the role of different factors which take place in the sorption mechanism, experiments were carried out with selected amines at pH 2.5, 7.0, and 8.5 with a contact time of 1 h (see Table 3). From the extraction data given in Table 3, it is clear that the compound **4** is more effective for the sorption of the aromatic amines at pH 7.0 and 8.5 but this compound shows less affinity towards these amines at pH 2.5. This is not a surprising result because a positively charged surface site on the adsorbent does not favor the adsorption of protonated aromatic amines due to electrostatic repulsion (Fig. 7). The conversion of calix[4]arene derivative **3** into its polymeric form **4** significantly increases the aromatic amine sorption ability. This can be explained by the fact that the calixarene derivative in the polymeric matrix may have gained a more rigid and appropriate structure, which assists the sorption of amine in SPE system. It is possible that the polymer plays a role in which it folds into conformations that place functional groups from multiple calix[4]arene moieties in the polymer into a pre-ferred conformation where they can associate with the aromatic amines.

4. Conclusion

According to Mannich reaction procedure an alkylamine derivative of calix[4]arene was prepared with a cyclic secondary amine (1,4-dioxa-8-azaspiro-[4.5]decane) and formaldehyde to afford the cone conformer **3**. This compound was converted to its polymer **4** with p-dibromoxylene. They were utilized to extract selected toxic and carcinogenic water-soluble azo dyes and aromatic amines from aqueous solution. It was observed that calix[4]arene derivative **3** and its polymer **4** show high affinity towards azo dyes but show less affinity toward aromatic amines. The sorption of azo dyes and aromatic amines by calix[4]arenes derivative (**3**) and polymer **4** indicates that amino groups are responsible for the formation of hydrogen bonds and electrostatic interactions.

Fig. 7. Proposed interactions of compound **4** with benzidine.

References

[1] K. Golka, S. Kopps, Z.W. Myslak, Carcinogenicity of azo colorants: influence of solubility and bioavailability, Toxicol. Lett. 151 (2004) 203–210.

[2] K.T. Chung, Mutagenicity and carcinogenicity of aromatic amines metabolically produced from azo dyes, Environ. Carcinogen. Ecotoxicol. Rev. C 18 (2000) 51–71.

[3] European Commission, Off. J. Eur. Commun. (2002), L243, 15.

[4] F. Rafii, J.D. Hall, C.E. Cerniglia, Mutagenicity of azo dyes used in foods, drugs and cosmetics before and after reduction by clostridium species from the human intestinal tract, Food Chem. Toxicol. 35 (1997) 897–901.

[5] I.M. Bassat, P. Nigam, D. Singh, R. Marchant, Microbial decolorization of textile–dye-containing effluents: a review, Bioresour. Technol. 58 (1996) 217–227.

[6] J. Weber, V.C. Stickney, Hydrolysis kinetics of reactive blue 19-vinyl sulfone, Water Res. 27 (1993) 63–67.

[7] H. Zollinger, Color Chemistry: Synthesis Properties and Applications of Organic Dyes and Pigments, 2nd revised ed., VCH, New York, 1991, p.150–250.

[8] W.Z. Tang, Z. Zhang, H. An, M.O. Quintana, D.F. Torres, TiO$_2$/UV photodegradation of azo dyes in aqueous solutions, Environ. Technol. 18 (1997) 1–12.

[9] S. Dai, W. Song, Y. Zhuang, H. Yan, Biotechnical treatment of wastewater containing azo dyes, in: Proceedings of the Fourth Mainland—Taiwan Environmental Technology, Seminar 1, 1996, pp. 407–411.

[10] S. Dai, Y. Zhuang, Y. Chen, L. Chen, Study on the relationship between structure of synthetic organic chemicals and their biodegradability, Environ. Chem. 14 (1995) 354–367.

[11] K.T. Chung, G.E. Fulk, A.W. Andres, Mutagenicity testing of some commonly used dyes, Appl. Environ. Microbiol. 42 (1981) 641–648.

[12] E. Forgacs, T. Cserhati, G. Oros, Removal of synthetic dyes from wastewaters: a review, Environ. Int. 30 (2004) 953–971.

[13] S. Papic, N. Koprivanac, A.L. Bozic, A. Metes, Removal of some reactive dyes from synthetic wastewater by combined Al(III) coagulation/carbon adsorption process, Dyes Pigments 62 (2004) 293–300.
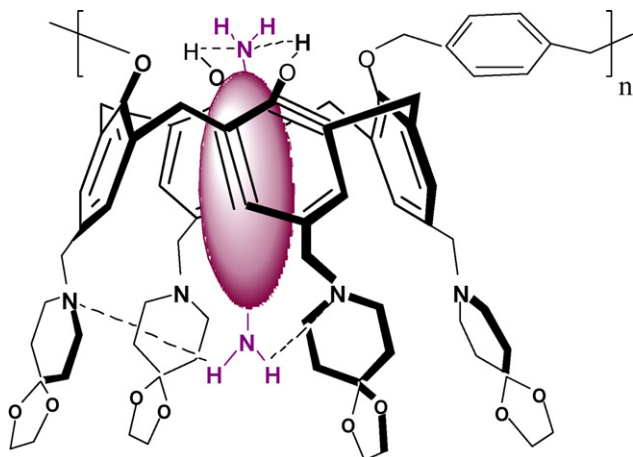
[14] P.C. Vandevivere, R. Bianchi, W. Verstrete, Treatment and reuse of wastewater from wet-processing industry: review of emerging technologies, J. Chem. Technol. Biotechnol. 72 (1998) 289–302.

[15] M. Otero, F. Rozada, L.F. Calvo, A.I. Garcia, A. Moran, Kinetic and equilibrium modeling of the methylene blue removal from solution by adsorbent materials produced from sewage sludges, Biochem. Eng. J. 15 (2003) 59–68.

[16] R.S. Blackburn, Natural polysaccharides and their interactions with dye molecules: applications in effluent treatment, Environ. Sci. Technol. 38 (2004) 4905–4909.

[17] A.A. Vaidya, K.V. Datye, Environmental pollution during chemical processing of synthetic fibers, Colourage 14 (1982) 3–10.

[18] S.T. Ambrosio, G.M. Campos-Takaki, Decolorization of reactive azo dyes by Cunninghamella elegans UCP 542 under co-metabolic conditions, Bioresour. Technol. 91 (2004) 69–75.

[19] V. Bekiari, P. Lianos, Ureasil gels as highly efficient adsorbent for water purification, Chem. Mater. 18 (2006) 4142–4146.

[20] V. Bekiari, P. Lianos, Use of Ureasil gels to extract ions from aqueous solutions, J. Hazard. Mater. 147 (2007) 184–187.

[21] V. Bekiari, M. Sotiropoulou, G. Bokias, P. Lianos, Use of poly(N,N-dimethylacrylamide-co-sodium acrylate) hydrogel to extract cationic dyes and metals from water, Colloids Surf. A: Physicochem. Eng. Aspects 312 (2008) 214–218.

[22] J. Synowiecki, N.A. Al-Khateeb, Production, properties and some new applications of chitin and its derivatives, Crit. Rev. Food Sci. Nutr. 43 (2003) 145–171.

[23] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low costs sorbents for heavy metals, Water Res. 33 (1999) 2469–2479.

[24] V.P. Yuryev, A. Cesaro, W.J. Bergthaller (Eds.), Starch and Starch Containing Origins—Structure, Properties and New Technologies Starch, Nova Science Publishers Inc., New York, 2002, pp. 50–150.

[25] P.A. Sandford, J. Baird, In industrial utilization of polysaccharides, in: G.O. Aspinall (Ed.), The Polysaccharides, vol. 2, Academic Press, New York, NY, 1983, pp. 411–490.

[26] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater. 97 (2003) 219–243.

[27] A.J. Varma, S.V. Deshpande, J.F. Kennedy, Metal complexation by chitosan and its derivatives: a review, Carbohydr. Polym. 55 (2004) 77–93.

[28] K.H. Feber, Benzidine and related diaminobiphenyls Encyclopedia of Chemical Technology, vol. 3, 3rd ed., Wiley, New York, 1978, pp. 772.

[29] J.M. Chern, S.N. Huang, Study of nonlinear wave propagation theory. 1. Dye adsorption by activated carbon, Ind. Eng. Chem. Res. 37 (1998) 253–254.

[30] G. Crini, M. Morcellet, Synthesis and applications of adsorbents containing cyclodextrins, J. Sep. Sci. 25 (2002) 789–813.

[31] S. Memon, M. Tabakci, D.M. Roundhill, M. Yilmaz, A useful approach toward the synthesis and metal extractions with polymer appended thioalkyl calix[4]arenes, Polymer 46 (2005) 1553–1560.

[32] S. Memon, M. Tabakci, D.M. Roundhill, M. Yilmaz, Synthesis and evaluation of the Cr(VI) extraction ability of amino/nitrile calix[4]arenes immobilized onto a polymeric backbone, React. Funct. Polym. 66 (2006) 1342–1349.

[33] A. Yilmaz, S. Memon, M. Yilmaz, Synthesis and study of allosteric effects on extraction behavior of novel calixarene-based dichromate anion receptors, Tetrahedron 58 (2002) 7735–7740.

[34] M. Tabakci, S. Memon, M. Yilmaz, D.M. Roundhill, Synthesis and extraction studies of a versatile calix[4]arene-based proton-switchable extractant for toxic metals and dichromate anions, J. Inclus. Phenom. Macrocycl. Chem. 45 (2003) 265–270.

[35] M. Yilmaz, S. Memon, M. Tabakci, R.A. Bartsch, in: R.K. Bregg (Ed.), New Frontiers in Polymer Research, Nova Science Publishers, Hauppauge, NY, 2006, pp. 125–171.

[36] S. Memon, E. Akceylan, B. Sap, M. Tabakci, D.M. Roundhill, M. Yilmaz, Polymer supported calix[4]arene derivatives for the extraction of metals and dichromate anions, J. Polym. Environ. 11 (2003) 67–74.

[37] F. Delval, G. Crini, N. Morin, J. Vebrel, S. Bertini, G. Torri, The sorption of several types of dye on crosslinked polysaccharides derivatives, Dyes Pigments 53 (2002) 79–92.

[38] L. Janus, G. Crini, V. El-Rezzi, M. Morcellet, A. Cambiaghi, G. Torri, A. Naggi, C. Vecchi, New sorbents containing beta-cyclodextrin. Synthesis, characterization, and sorption properties, React. Funct. Polym. 42 (1999) 173–180.

[39] E. Ozmen Yilmaz, A. Sirit, M. Yilmaz, A calix[4]arene oligomer and two beta-cyclodextrin polymers: synthesis and sorption studies of azo dyes, J. Macromol. Sci. A: Pure Appl. Chem. 44 (2007) 167–173.

[40] A. Yilmaz, E. Yilmaz, M. Yilmaz, R.A. Bartsch, Removal of azo dyes from aqueous solutions using calix[4]arene and β-cyclodextrin, Dyes Pigments 74 (2007) 54–59.

[41] G. Crini, Studies on adsorption of dyes on beta-cyclodextrin polymer, Bioresour. Technol. 90 (2003) 193–198.

[42] C.D. Gutsche, M. Iqbal, D. Stewart, Calixarenes. 18. Synthesis procedures for p-tert-butylcalix[4]arene, J. Org. Chem. 51 (1986) 742–745.

[43] C.D. Gutsche, L.-G. Lin, The synthesis of functionalized, Calixarenes Tetrahedron 42 (1986) 1633–1640.

[44] C.D. Gutsche, Calixarenes Revisited, The Royal Society of Chemistry, Cambridge, 1998, p.25–150.

[45] C.D. Gutsche, K.C. Nam, Calixarenes. 22. Synthesis, properties and metal complexation of aminocalixarenes, J. Am. Chem. Soc. 110 (1988) 6153–6162.

[46] E. Akceylan, M. Yilmaz, R.A. Bartsch, Immobilization of cyclic alkylamine calix[4]arene derivatives on merrifield resin: evaluation of extraction ability toward dichromate, J. Macromol. Sci. Pure Appl. Chem. 43 (2006) 477–486.

[47] E. Ozmen Yilmaz, S. Erdemir, M. Bahadir, M. Yilmaz, Removal of carcinogenic direct azo dyes from aqueous solutions using calix[n]arene derivatives, Clean Soil Air Water 35 (2007) 612–616.

[48] C.O. Neill, A. Lopez, S. Esteves, F.R. Hawkes, D.L. Hawke, S. Wilcox, Azo dye degredation in an anaerobic–aerobic treatment system operating on simulated textile effluent, J. Appl. Microbiol. Biotechnol. 53 (2000) 249–254.

[49] E. Razo-Flores, M. Luijten, B.A. Donlon, G. Lettinga, J.A. Field, Complete biodegradation azo dye azodisalicylate under anaerobic conditions, Environ. Sci. Technol. 31 (1997) 2098–2103.

[50] M. Durmaz, S. Alpaydin, A. Sirit, M. Yilmaz, Chiral Schiff base derivatives of calix[4]arene: synthesis and complexation studies with chiral and achiral amines, Tetrahedron Asymm. 17 (2006) 2322–2327.

[51] S. Erdemir, M. Tabakci, M. Yilmaz, Synthesis and chiral recognition abilities of new calix[6]arenes bearing amino alcohol moieties, Tetrahedron Asymm. 17 (2006) 1258–1263.