Extraction of carcinogenic aromatic amines from aqueous solution using calix[*n*]arene derivatives as carrier

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ARTICLE INFO

ABSTRACT

The extraction abilities of *p-tert*-butylcalix[*n*]arenes (*n* = 6, 8) and their carboxylic acid and methyl ester derivatives upon some carcinogenic aromatic amines have been investigated. The separation and quantification of aromatic amines were performed by high-performance liquid chromatography with Ace 5 C_{18} column and diode array detection. The optimum pH values for aromatic amines sorption were observed at pH 4.0, 7.0 and 8.5 for all calixarene derivatives. In batch sorption experiments of selected carcinogenic aromatic amines, the experimental results show that octacarboxylic acid derivative of *p-tert*-butylcalix[8]arene exhibited a better affinity than other compounds towards all aromatic amines species at almost all pHs. The sorption of aromatic amines by carboxylic acid derivatives of *p-tert*-butylcalix[*n*]arene indicates that carboxyl groups play the major role for the formation of hydrogen bonds and electrostatic interactions between sorbent and aromatic amine.

1. Introduction

Aromatic amines and their *N*-nitroso derivatives are potential carcinogenic agents [1–4]. Aromatic amines are widely used as raw material or as intermediates in the manufacturing of industrial chemicals such as pesticides, drugs, dyestuffs, polymers, surfactants, cosmetics, and corrosion inhibitors [5,6], especially in dyestuff plants. As these amines are discharged into the atmosphere and water, they constitute an important class of environmental pollutants. This attracted an increased attention for the development of reliable, sensitive and rapid analytical methods. Several analytical methods have been reported for the determination of aromatic amines. Among them, GC methods are most commonly employed [7–11]. However, it is difficult to analyze aromatic amines by GC due to their polar nature. To overcome these difficulties, it is usually necessary to derivatize them before GC. Flow injection coupled with voltammetry has been employed with diazotization [12] or bromination [13] reactions. These methods involve tedious and time-consuming sample preparation. Capillary electrophoresis (CE) has also emerged as a fast and efficient tool for chemical analysis, and a few methods for the analysis of aromatic amines using CE are reported in the literature [14–16]. Nevertheless, liquid chromatography (LC) is known as the most convenient technique for aromatic amines. Variety of separation and

detection methods for the analysis of anilines has been reported [17–22].

The increasing number of recent publications on adsorption of toxic compounds shows that there is widespread interest in the synthesis of adsorbent resins able to totally eliminate organic pollutants. Various chemical and physical processes are currently in use. Solid phase extraction (SPE) using sorbents is one of the most efficient and well-established procedures in the field of separation science, which finds application in various fields like environmental, food, clinical, pharmaceutical, and industrial chemistry. SPE is usually performed using a small column or cartridge containing an appropriate sorbent. The sorbents may be of mineral or organic origin. Among these, modified silicas (C_8 and C_{18}), ion exchangers [23], graphitized carbon black [24], various polymeric sorbents polystyrene-divinyl benzene, (PS-DVB) [25], immunosorbents [26], molecularly imprinted polymers [27], conductive polymers [28], porous polymers [29], polysaccharides such as chitin [30,31], starch [32,33] and chitosan [34,35] etc. are reported. 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. This was achieved with the development of macrocyclic molecules such as synthetic crown ethers, cryptands, spherands [36], natural cyclodextrins [37,38], and calixarenes [39–44].

Calixarenes (Fig. 1) have generated considerable interest as useful building blocks for the synthesis of hosts for cations, anions, and neutral molecules. During the last two decades, they have attracted

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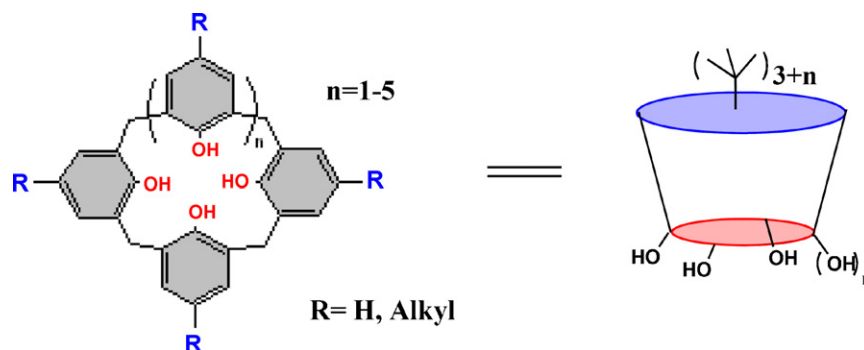*E-mail address:* myilmaz42@yahoo.com (M. Yilmaz).

Fig. 1. The general molecular structures of calix[*n*]arenas.

much attention as receptors in supramolecular chemistry. The increasing interest in these compounds is stimulated by the simple large-scale synthesis of calixarenes, and the different ways in which they can be selectively functionalized at the narrow (phenolic groups) or at the wide rim (aromatic nuclei) [45–47]. 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 or inorganic compounds the calixarenes have received increasing attention during the last two decades [48,49,38,50–52]. Previously, we have reported [53] the synthesis and inclusion abilities of calix[4]arene derivatives for selected water-soluble azo dyes. In another study, it was calculated interaction of mettallocalix[4]arenes and substituted dibenzothiphene known as oil-based fuels pollutants [54].

Previously, we have reported [55] the synthesis and inclusion abilities of calix[4]arene derivatives for selected aromatic amines. However, the results showed that calix[4]arene derivatives were poor sorbents for the aromatic amines. One possible explanation is the small size of the calixarene cavity for the formation of an inclusion host-guest complex. In this work, a series of wide-size cavity calix[*n*]arene (*n* = 6, 8) methyl ester and carboxyl acid derivatives (see Scheme 1) was synthesized and their ligating behavior by means of solid–liquid phase sorption of three carcinogenic aromatic amines from aqueous solution was investigated.

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 and employed without further purification. 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. 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 an 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 900 °C at heating rate of 10 °C/min in argon atmosphere with a gas flow rate of 20 mL/min.

2.3. Reagents

Scheme 1 shows the structures of the extractants used in this study. The extractants the *p-tert*-butylcalix[6]arene (**1**) and *p-tert*-butylcalix[8]arene (**2**) were synthesized using the procedures described by Gutsche [56,57]. The *p-tert*-butylcalix[6]arene hexamethyl ester derivative (**3**) (*t*Bu[6]CH$_2$COOCH$_3$) and the *p-tert*-butylcalix[8]arene octamethyl ester derivative (**4**) (*t*Bu[8]CH$_2$COOCH$_3$) were synthesized referring to the literature [58] by the reaction of *p-tert*-butylcalix[6,8]arenes with methyl bromoacetate in dry acetone in the presence of anhydrous potassium carbonate. Hydrolysis of the compounds **3** and **4** by KOH in ethanol give the *p-tert*-butylcalix[6]arene hexacarboxylic acid derivative (**5**) (*t*Bu[6]CH$_2$COOH) and the *p-tert*-butylcalix[8]arene octacarboxylic acid derivative (*t*Bu[8]CH$_2$COOCH$_3$) (**6**) [59].

2.4. Analytical procedure for sorption

An aqueous solution (10 mL) containing aromatic amine (see Fig. 2 for the structure formula) was pipetted into a vial at a concentration of 1×10^{-4} 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 HPLC. The sorption capacity was then calculated and expressed in percentage uptake.

3. Results and discussion

3.1. Sorption studies of aromatic amines by calix[n]arene derivatives

In order to evaluate the aromatic amines removal efficiency of calixarene derivatives, Firstly, *p-tert*-butylcalix[*n*]arenes (*n* = 6, 8) and their carboxylic acid and methyl ester derivatives were synthe-
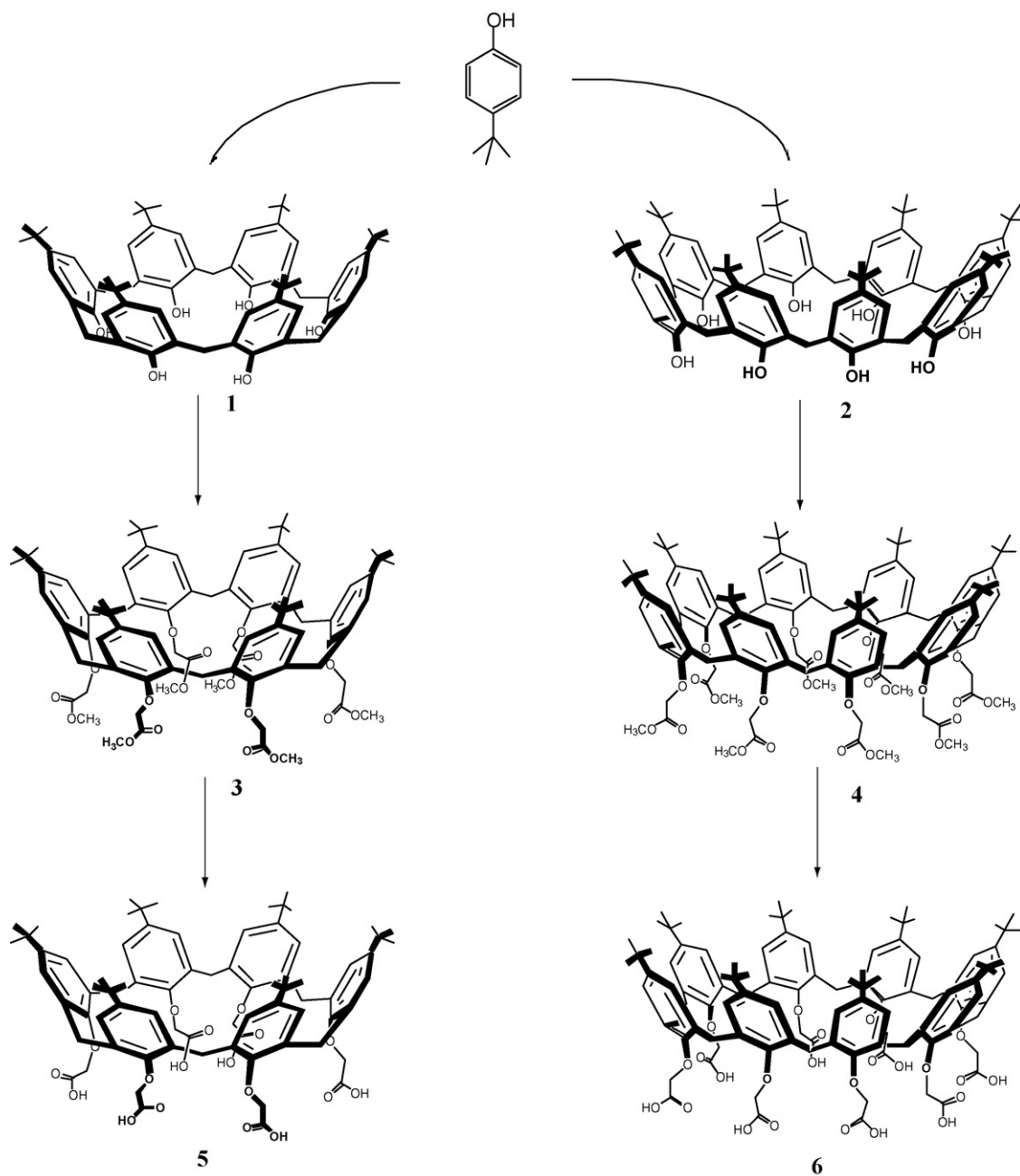
Scheme 1. Molecular structures of the carriers used in this study.

sized and then the solid–liquid phase sorption experiments were conducted. Batch sorption experiments were carried out at different pHs (4.0, 7.0, and 8.5). The aromatic amines removal was analyzed by means of HPLC using acetonitrile-water as mobile phase at 280 nm (Fig. 3). The results of the sorption studies are summarized in Table 1.

These results indicate that the parent calix[n]arenes (**1**) and (**2**) showed less sorption capacities for all three aromatic amines.
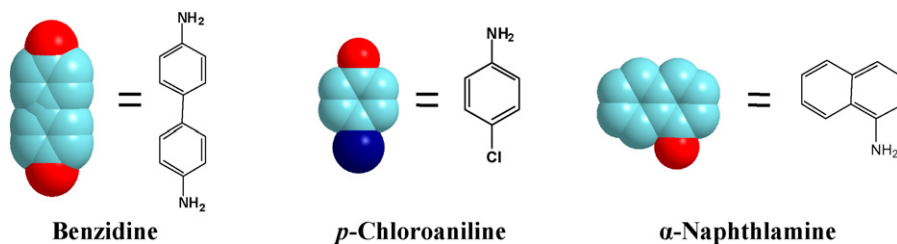

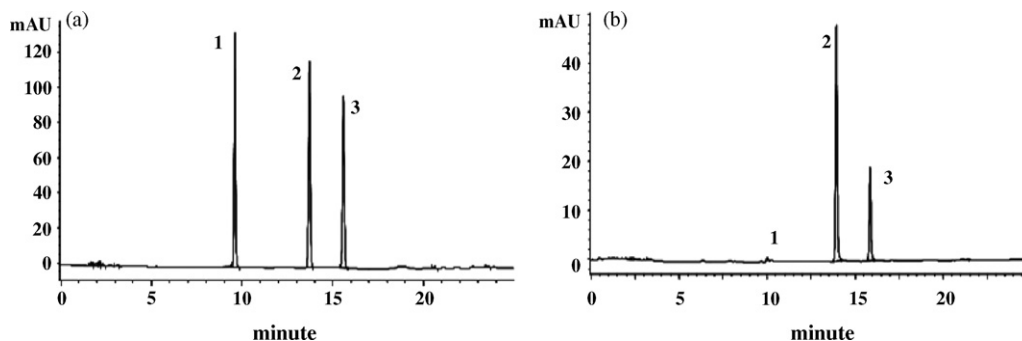**Fig. 2.** The chemical structures of aromatic amines used in experiments.

Fig. 3. Representative HPLC chromatograms of standard aromatic amines solution (a) and aromatic amines which were treated with the tBut[8]CH$_2$COOH (b), in double distilled water samples. (**1**) Benzidine, (**2**) p-chloroaniline, (**3**) α-napthylamine. Conditions: mobile phase: acetonitrile (A) and water (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 at 280 nm, pH 7.
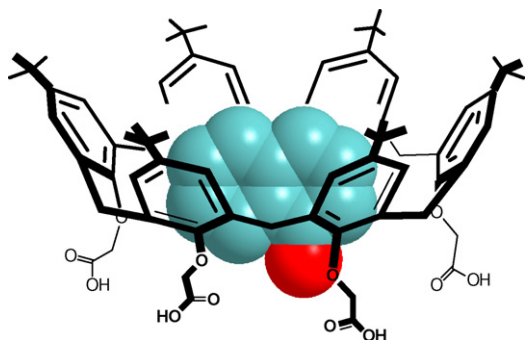

Fig. 4. Complexation model between tBut[6]CH$_2$COOH and α-Naphthalamine.

After the compounds (**1**) and (**2**) were converted to their corresponding carboxylic acid derivatives (**5**) and (**6**), however, these compounds (**5** and **6**) showed high sorption ability towards all aromatic amines. It was suggested that a Coulomb interaction exist between the carboxylic acid groups of calix[n]arenes and the amine groups of aromatic amines (see Fig. 4). Carboxyl groups of calix[n]arenes (**5**) and (**6**) form intermolecular hydrogen bonds to these amino groups. In addition, the compound **5** and **6** might form sandwich and inclusion type interaction with benzidine because

it has two the amine groups (Fig. 5). It is seen from the Table 1 that p-$tert$-butylcalix[8]arene carboxylic acid derivative (6) forms a stable complex than p-$tert$-butylcalix[6]arene carboxylic acid derivative (**5**) with a guest molecule by entrapping it into the cavity. Previously, we have reported [60] the synthesis and inclusion abilities of calix[4] and calix[8]arene derivatives for selected azo dyes. The results showed 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. Hence, the cyclic structure, the cavity size, and the functional groups of the calix[n]arene derivatives were found to be the decisive factors for the sorption of aromatic amines.

In literature, a beta-cyclodextrin-polyurethane (beta-CDPU) polymer was synthesized by reacting beta-cyclodextrin (CD) with hexamethylenediisocyanate (HMDI) and the polymer has been evaluated for the extraction of aromatic amines from water samples pH 4.0, 7.0 and 8.5. The capability of this sorbent to extract aromatic amines has been compared with those of some of the commercially materials (C18, Isolute and Extrelut NT) [20]. When the results of this work compared with our present study, the calix[n]arene derivatives showed higher affinity towards aromatic amines than
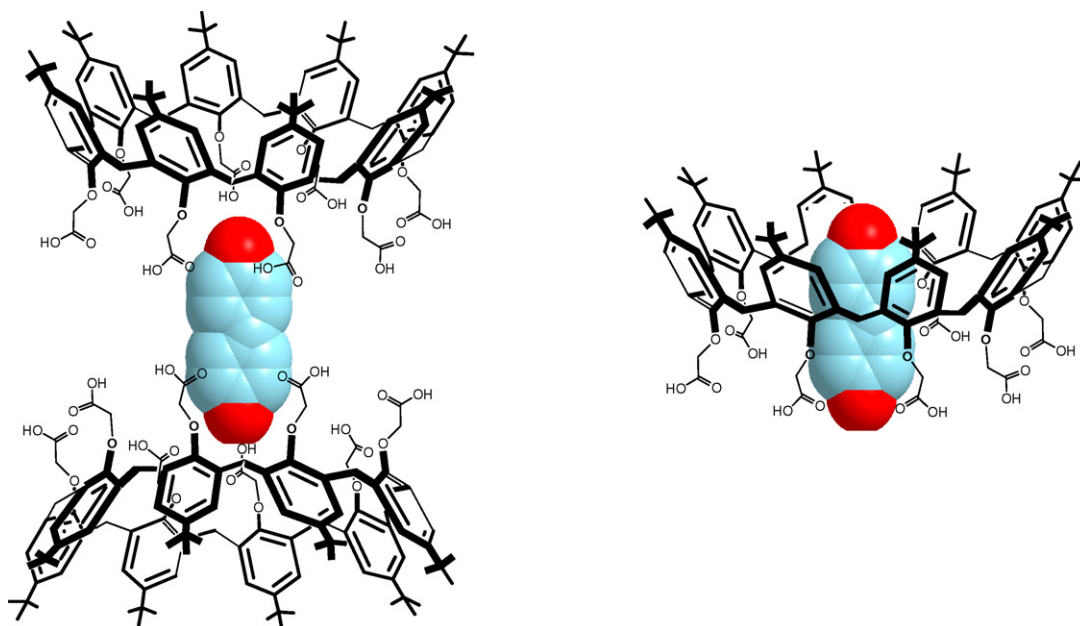

Fig. 5. Proposed complexation models between tBut[8]CH$_2$COOH and benzidine.

Table 1
Comparison of the aromatic amines extractabilities for *p-tert-butylcalix*[6,8]arene extractants (%)[a].

Extraction of aromatic amines (%)									
Calixarene derivatives	Benzidine			*p*-Chloroaniline			α-Naphthalamine		
	pH 4.0	pH 7.0	pH 8.5	pH 4.0	pH 7.0	pH 8.5	pH 4.0	pH 7.0	pH 8.5
1	2.0	12.0	7.5	3.0	3.0	4.3	3.0	9.0	5.5
2	2.0	15.0	9.8	4.0	6.0	9.7	7.0	18.0	15.5
5	84.0	58.0	53.0	59.0	58.0	62.0	67.0	67.0	64.0
6	99.0	98.0	95.0	78.0	58.0	59.0	86.0	84.0	80.0
5[b]	6.19	4.27	3.90	3.01	2.96	3.16	3.84	3.84	3.67
6[b]	7.30	7.22	7.01	3.98	2.96	3.01	4.93	4.81	4.58

[a] Solid phase, adsorbent: 25 mg of calix[6,8]arene derivatives; aqueous phase, aromatic amines (Benzidine, *p*-chloroaniline, α-naphthalamine) 1.0×10^{-4} M, pH 4.0, 7.0 and 8.5, 1 h.

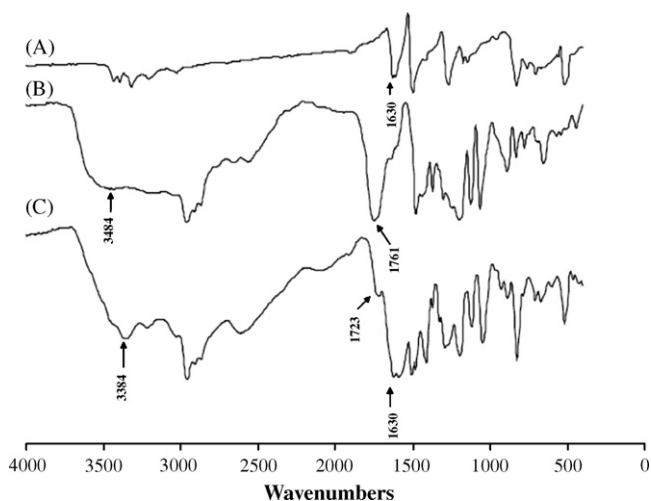[b] Loading pollution (mg-pollution/g-sorbent).

Fig. 6. The FT-IR spectra of (A) benzidine, (B) pure calixarene derivative (**6**), and (C) calixarene derivative **6** treated with benzidine.

the others. These results suggest that the macrocyclic structure and the cavity size of calix[*n*]arenes are the key factors in ensuring their high extraction abilities.

The IR spectra of (**6**) and their benzidine complexes are similar to each other (see Fig. 6). Fig. 6a shows the FT-IR spectrum of benzidine, Fig. 6b shows the FT-IR spectrum of pure compound (**6**). Fig. 6c shows the FT-IR spectrum of compound (**6**) after adsorption of benzidine. The most significant difference between the IR spectra of (**6**) and its benzidine complexes is an absorption band at 1630 cm^{-1} which can be attributed to the bending vibration of —NH$_2$ groups of benzidine. Beside this, the bands of the stretching vibration of O—H (COOH) and N—H overlapped and shifted to a lower wave number (3384 cm^{-1}) compared with that of **6**, and the intensity of the band increases. This shows strong intermolecular hydrogen bonding occurs between **6** and benzidine.

The thermal stability of the compound **6** and its benzidine complex was evaluated by thermal gravimetric analysis (TGA). It was found that **6** undergoes a three-step thermal degradation (Fig. 7). The first step (40–125 °C) is due to the loss of moisture, while the second (270–450 °C) could be attributed to the loss of the functional groups of **6**, and the third step (475–625 °C) is due to the cleavage of the calixarene backbone. The TGA result of the **6** showed the weight loss peak temperatures of 340 and 492 °C shifted to 384 and
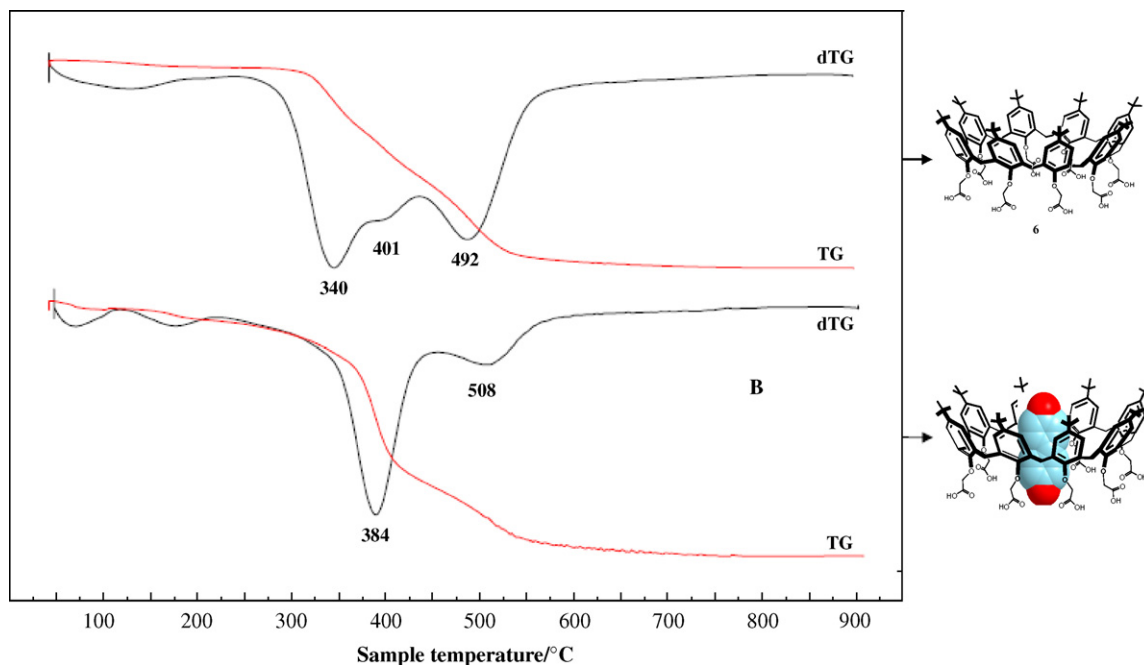

Fig. 7. TG and their 1st derivatives (dTG) of pure calixarene derivative (**6**) and calixarene derivative **6** treated with benzidine.

508 °C in the benzidine complex of **6** (Fig. 7). The results indicated a remarkable electrostatic interaction between the calix[8]arene carboxyl groups and the benzidine ($COO^-{-}^+NH_4$).

In order to evaluate the influence of pH on the affinity of the aromatic amines to the compounds **5** and **6** and to clarify the role of different factors which take place in the sorption mechanism, tests were carried out with benzidine, *p*-chloroaniline and α-naphthalamine at pH 4.0, 7.0, and 8.5 with a contact time of 1 h. The results obtained at pH 7.0 and 8.5 are close to each other but different from those obtained at pH 4.0 which show significantly stronger interactions (see Fig. 5). Furthermore, it was observed that the percentage of benzidine removal was 53–58% for the compound **5** and 95–98% for **6** when the pH of the benzidine solution was 7.0–8.5. However, benzidine removal attained a maximum to 84% for **5** and 99% for **6** when the amine solution pH increased to 4.0. A similar trend was observed for the adsorption of azo dyes and carboxylic acid derivative of calix[6,8]arene [61].

An important issue is the long term stability and reproducibility of the sorption properties of the sorbents. The carboxylic acid derivatives of calix[*n*]arenes (**5**) and (**6**) were easily regenerated by washing with 2 M HCl. The sorption capacities were not changed after this treatment. This is evidence for the chemical stability of the calix[*n*]arene derivatives **5** and **6** and the reproducibility of the results. The desorption of aromatic amines in acidic media is an advantage for the calix[*n*]arene derivatives.

4. Conclusion

This study was carried out to synthesize water insoluble calix[*n*]arene derivatives **5** and **6**. These substances have been evaluated for the extraction of toxic and carcinogenic aromatic amines from aqueous solution. It was observed that the sorption capacities of carboxylic acid derivative of calix[*n*]arenes (**5**) and (**6**) were higher than that of parent calix[*n*]arenes (**1**) and (**2**). Carboxylic acid sites of compounds (**5**) and (**6**) are the main reactive groups for amines. Amine groups of aromatic amines may also contribute to the sorption by hydrogen bonds and Coulomb interactions. It was observed that the highest sorption levels were obtained in a pH range of 4.0–8.5. It was concluded that the sorption of aromatic amines by calix[*n*]arene derivatives **5** and **6** indicate that amino groups are responsible for the formation of hydrogen bonds and electrostatic interactions. The proper calixarene derivatives are recommended for the determination of these aromatic amines in natural water, since a simple calibration curve method can be used. This method for aromatic amines is very simple and practicable in routine analysis. Moreover, the long term stability and reproducibility of the sorption properties of the sorbents are economically very important.

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