



# Removal of direct azo dyes and aromatic amines from aqueous solutions using two $\beta$ -cyclodextrin-based polymers

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## ABSTRACT

Two  $\beta$ -cyclodextrin ( $\beta$ -CD)-based polymers were synthesized using 4,4'-methylene-bis-phenyldiisocyanate (MDI) or hexamethylenediisocyanate (HMDI) as a cross linking agent in dimethylformamide and used as sorbents for the removal of azo dyes (Evans Blue and Chicago Sky Blue), as well as aromatic amines (benzidine, *p*-chloroaniline and  $\alpha$ -naphthalamine) from aqueous solutions. The sorption experiments were carried out by using batch-wise procedure involving the determination of pH effect, sorbate concentration and contact time. Moreover, from the equation isotherms such as Langmuir and Freundlich were successfully applied to model the experimental data. From the results polymer **2** was found to be a better sorbent for both azo dyes and the aromatic amines as compared to polymer **1** as proved by Langmuir isotherm model. The proposed sorption mechanism involved several kinds of interactions: physical adsorption, hydrogen bonding and formation of an inclusion complex due to the  $\beta$ -CD molecules through host–guest interactions.

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## 1. Introduction

Synthetic dyes are common water pollutants and due to their good solubility they may frequently be found in trace quantities in industrial wastewater. Many of these dyes are also toxic and even carcinogenic and these pose a serious hazard to aquatic living organisms. The formation of a carcinogenic amine from a dye by human skin bacteria and the antifungal activities of diazobenzene dyes have been reported [1–3].

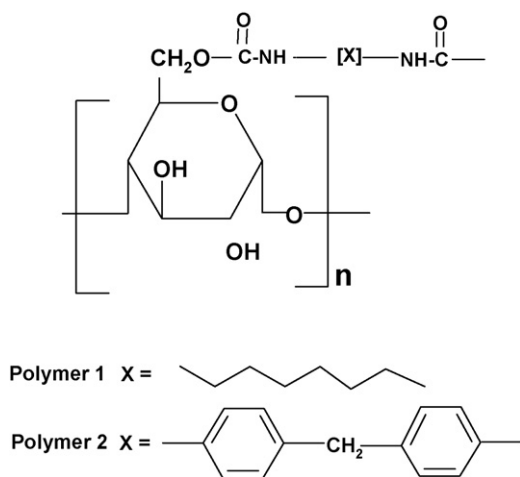
In the textile industry, it is estimated that 10–15% of the dyestuffs are lost during the dyeing process and released with the effluent, which are more difficult to degrade [4–6]. The release of those colored wastewaters in the environment is a considerable source of non-aesthetic pollution since the 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]. Moreover, 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 poten-

tially carcinogenic [11]. Various chemical and physical processes are currently in use for the removal of dyes by conventional treatment technologies including biological and chemical oxidation, chemical coagulation, foam flotation, electrolysis, biodegradation, advanced oxidation, photocatalysis and adsorption processes as discussed in the present reports [12–14]. However, among all the techniques solid-phase extraction (SPE) using sorbents is one of the most efficient and popular methods for the removal of organic compounds from wastewater. The sorbents may be of mineral or organic origin; silica beads, activated carbon, zeolites, polyamines beads, polyurethanes resins, gels, calixarenes, chitosan and  $\beta$ -cyclodextrin are significant examples [15–19].

$\beta$ -Cyclodextrin ( $\beta$ -CD) is a torus-shaped cyclic oligosaccharide made up of seven  $\alpha$ -1,4-linked D-glucopyranose units with an internal hydrophobic cavity. It is well known that this structure gives rise to a remarkable capacity to form inclusion complexes in solution or in the solid state with organic molecules, especially aromatics, through host–guest interactions. Generally, cyclodextrins are water-soluble in their native form, which are often modified to prepare new insoluble derivatives. These materials which form water insoluble cross-linked polymers are obtained using some polyfunctional crosslinking agents such as aldehydes, ketones, isocyanates or epoxides. There have been considerable studies of the preparation, properties and applications of insoluble polymers and copolymers containing  $\beta$ -CD [20–22]. The utility of these  $\beta$ -CD-containing polymers has been recognized in many applications such as; these polymers have been used for synthetic purposes,

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Scheme 1. Chemical structure of sorbents.

in chromatography, in the pharmaceutical and food industries, and in the clean-up of industrial waste effluents [23–25].

Previously, we have reported [26–30] the synthesis and inclusion abilities of  $\beta$ -CD-based polymers (**1** and **2**) for selected aromatic azo dyes and the polymers showed high affinity towards them. In this work, we proposed the use of those polymers as a heterogeneous system to sorb two carcinogenic reactive azo dyes (Evans Blue and Chicago Sky Blue), as well as aromatic amines (benzidine, *p*-chloroaniline and  $\alpha$ -naphthalamine) from aqueous solutions.

## 2. Experimental

### 2.1. Apparatus

IR spectra were recorded with a Perkin Elmer 1605 FTIR spectrometer as KBr pellets. UV–vis spectra were obtained with a Shimadzu 160A 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<sub>18</sub> column (25 cm, 4.6 mm). The mobile phase consisted of acetonitrile (eluent A) and water (eluent B), flow rate: 1 mL min<sup>-1</sup>, at 25 °C, injection volume 20  $\mu$ L, gradient elution: 0 min 20% A and 80% B; 25 min 80% A and 20% B. Detection was performed at 280 nm. Confirmation of the product was made with the chromatogram and the corresponding UV spectra of the standard amines [18].

### 2.2. Materials and methods

$\beta$ -Cyclodextrin ( $\beta$ -CD), 4,4'-methylene-bis-phenyldiisocyanate and hexamethylene diisocyanate were purchased from Fluka and used without further purification. Evans Blue (EB), Chicago Sky Blue (CSB), benzidine, *p*-chloroaniline and  $\alpha$ -naphthalamine and other chemicals were obtained from Sigma. Solvents were dried by storage over molecular sieves (Aldrich; 4 Å, 8–12 mesh). Commercial grade solvents such as chloroform, methanol, acetonitrile, toluene, ethyl acetate and hexane were distilled and stored over 4 Å molecular sieves. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system. The polymers **1** and **2** shown in Scheme 1 were prepared according to the reported procedures [26–29]. Standard solutions 1000 mg/L from each individual compound were prepared in HPLC grade methanol and stored at 4 °C when not in use. A mixture of these compounds were prepared by diluting the standard solutions with methanol and more diluted working solutions were prepared prior to use by diluting the standard solutions with double distilled water.

### 2.3. Sorption methods

#### 2.3.1. Sorption method for azo dyes

The first approach was a batch method in which sorbent (25 mg) was mixed with 0.2 M NaCl (10 mL) and an aqueous solution of the pollutant ( $2 \times 10^{-5}$  M) in a stoppered 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 of spectrophotometry. All solutions were centrifuged before measurements. Absorbance values were recorded at different  $\lambda_{\max}$  for each solution, i.e. at 620 nm for Chicago Sky Blue (CSB) and 596 nm

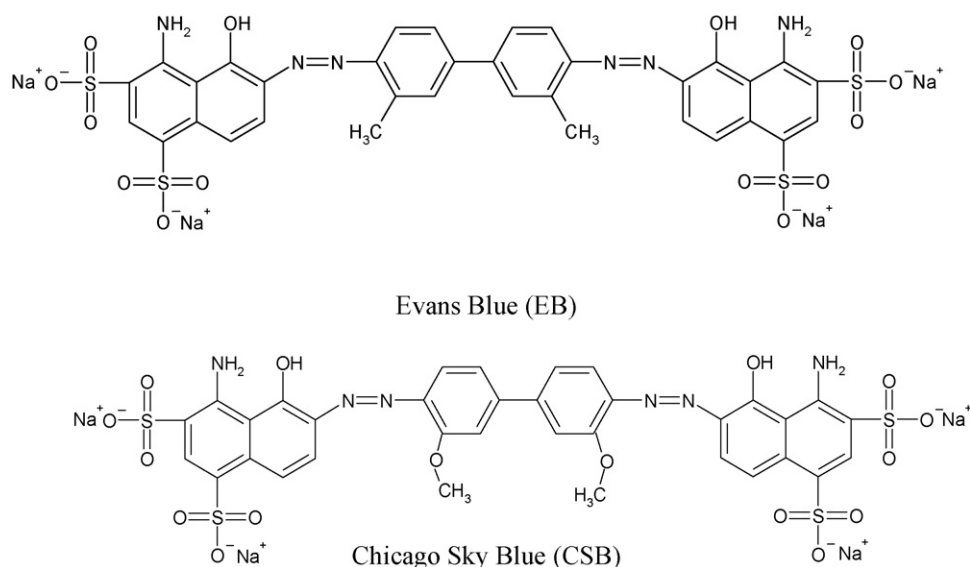


Fig. 1. The chemical structures of selected azo dyes used in experiments.

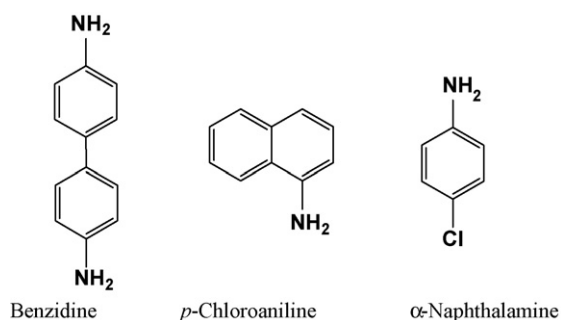


Fig. 2. The chemical structures of aromatic amines used in experiments.

for Evans Blue (EB) (see Fig. 1 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 [26–33].

### 2.3.2. Sorption method for aromatic amines

An aqueous solution (10 mL) containing aromatic amine (see Fig. 2 for the structure formula) was pipetted into a vial at a concentration of  $1 \times 10^{-3}$  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. Effect of shaking time

The effect of shaking time on the sorption of dyes as well as aromatic amines onto  $\beta$ -CD polymers (**1** and **2**) has been carried out. It was observed that the % sorption increases by increasing the contact time. The % sorption increases significantly up to 30 minutes, and thereafter gradual increase in % sorption by increasing shaking time till 60 min. On the basis of this observation, a 1 h shaking time were found suitable for the maximum sorption and further study carried out at 1 h shaking time for azo dye and aromatic amines.

### 3.2. pH effect on the sorption of selected azo dyes/aromatic amines

The influence of pH plays a significant role in the chemistry of sorbent and sorbate. As in this study the influence of pH on the sorption of the azo dyes to polymers **1** and **2**, experiments were carried out with selected azo dyes at 2–8 pH with a contact time of 1 h. However, it has been observed that the polymer **2** exhibits significant dye sorption affinity as compared to the polymer **1**. The maximum percentage of azo dyes removal for polymers **1** and **2** were observed at pH 2.0 (Fig. 3a and b). The lower sorption rates at alkaline pH are due to the presence of excess  $\text{HO}^-$  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 sorbent does not favor the adsorption of dye anions due to electrostatic repulsion.

However, the batch sorption experiments for aromatic amines (benzidine, *p*-chloroaniline,  $\alpha$ -naphthylamine) were also carried out by agitating their 10 mL ( $1 \times 10^{-3}$  M) solution with 25 mg of adsorbent in glass bottles at different pH (7.0, and 9.0). The process

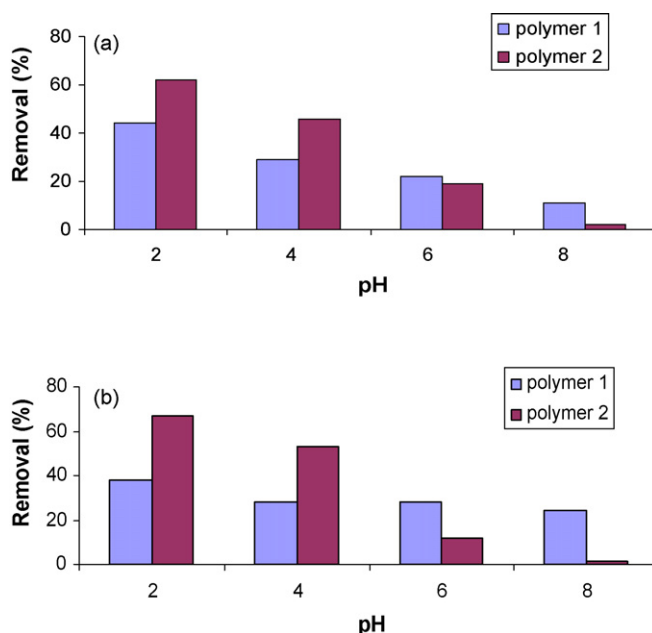


Fig. 3. pH effect on the sorption of (a) Evans Blue; (b) Chicago Sky Blue (CSB) by  $\beta$ -cyclodextrin-based polymers (**1** and **2**).

was carried out with 200 rpm at 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. Thereafter, aromatic amines were analyzed by means of HPLC. The % sorption results of selected aromatic amines are given in Table 1.

### 3.3. Adsorption isotherms

In order to evaluate the sorption capacity of  $\beta$ -CD polymers (**1** and **2**), the equilibrium study has been performed by analyzing the experimental data and applying the most common isotherm models, i.e. Langmuir and Freundlich at optimized parameters. These models demonstrate the interaction of solute and sorbate matrix. The basic assumption of the Langmuir theory is the sorption takes place at homogeneous sites within the sorbent [34]. By the comparison to Langmuir isotherm, the Freundlich model is generally found to be better suited for characterization of multilayer sorption process [35]. The linearized forms of Langmuir and Freundlich isotherm models were tested in the following form:

$$\left(\frac{C_e}{C_{\text{ads}}}\right) = \left(\frac{1}{Qb}\right) + \left(\frac{C_e}{Q}\right) \quad (1)$$

$$\log C_{\text{ads}} = \log A + \left(\frac{1}{n}\right) \log C_e \quad (2)$$

where  $C_{\text{ads}}$  is the amount of sorbate (mol/g) at sorbent surface and  $C_e$  is the amount of sorbate in liquid phase at equilibrium (mol/L),  $Q$ ,  $b$ ,  $A$  and  $1/n$  are the constant (Table 2) related to Langmuir and Freundlich equations, respectively. These equation were applied to correlate the amount of the azo dyes sorbed per unit amount of the

Table 1  
Percent sorption of aromatic amines by cyclodextrin-based polymers **1** and **2**.<sup>a</sup>

	Benzidine		<i>p</i> -Chloroaniline		$\alpha$ -Naphthalamine	
	pH 7.0	pH 9.0	pH 7.0	pH 9.0	pH 7.0	pH 9.0
Polymer <b>1</b> (HMDI)	28.7	<1	16.3	<1	31.1	<1
Polymer <b>2</b> (MDI)	97.2	55.0	87.1	25.7	96.3	43.0

<sup>a</sup> Solid-phase, adsorbent: 25 mg of cyclodextrin-based polymer; aqueous-phase, aromatic amines (benzidine, *p*-chloroaniline,  $\alpha$ -naphthylamine)  $1.0 \times 10^{-3}$  M; pH 7.0 and 9.0, 1 h.

**Table 2**Langmuir and Freundlich characteristic constants for azo dyes sorption onto polymers (**1** and **2**).

Polymers/azo dyes	Langmuir				Freundlich			
	Q (mmol/g)	b ( $\times 10^4$ mol/L)	$R_L$	$R^2$	A (mol/g)	1/n	n	$R^2$
Polymer 1/EB	9.58	5.22	0.21–0.49	0.99	0.57	0.44	2.27	0.98
Polymer 2/EB	10.59	10.49	0.12–0.32	0.99	0.20	0.31	3.18	0.99
Polymer 1/CSB	7.63	5.95	0.19–0.46	0.99	0.33	0.41	2.46	0.93
Polymer 2/CSB	12.09	13.78	0.09–0.27	0.99	0.27	0.32	3.11	0.95

sorbents and can be calculated from slope and intercept, the initial concentration of sorbate is in the range of  $2.00 \times 10^{-5}$  to  $7.00 \times 10^{-5}$  using 25 mg sorbent per 10 mL of sorbate and 1 h shaking time at 25 °C.

In Fig. 4 plot of  $C_e/C_{ads}$  mol/g versus  $C_e$  mol/L shows straight line which demonstrates that sorption data follows the Langmuir sorption equation very well. The value of sorption capacity Q and Langmuir constant b with respect to polymer (**1** and **2**) for both azo dyes (i.e. EB and CSB) are given in Table 2. The characteristic of the Langmuir isotherm can be expressed by the dimensionless constant called equilibrium parameter,  $R_L$ , calculated as:

$$R_L = \frac{1}{1 + bC_i} \quad (3)$$

where  $b$  is the Langmuir constant and  $C_i$  is the initial concentration of sorbate (mol/L), the  $R_L$  values indicate favorability ( $0 < R_L < 1$ ) of isotherm [36].

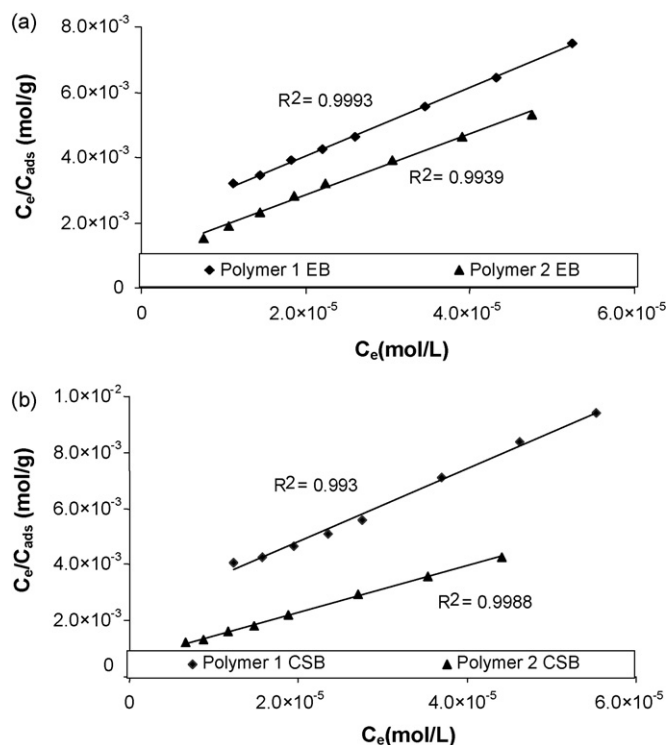
In Fig. 5 plot of  $\log C_{ads}$  mol/g versus  $\log C_e$  mol/L shows straight line which demonstrates the applicability of sorption data that follows the Freundlich sorption equation. The values of  $1/n$  and  $A$  were calculated and are given in Table 2. The  $n$  values demonstrate the favorability of Freundlich isotherm model.

Moreover, on the basis of correlation coefficient ( $R^2$ ) shown in Table 2, the sorption process with polymer (**1** and **2**) can be better demonstrated by Langmuir isotherm equation and also it has been observed that the Langmuir equation concedes a better fit of the

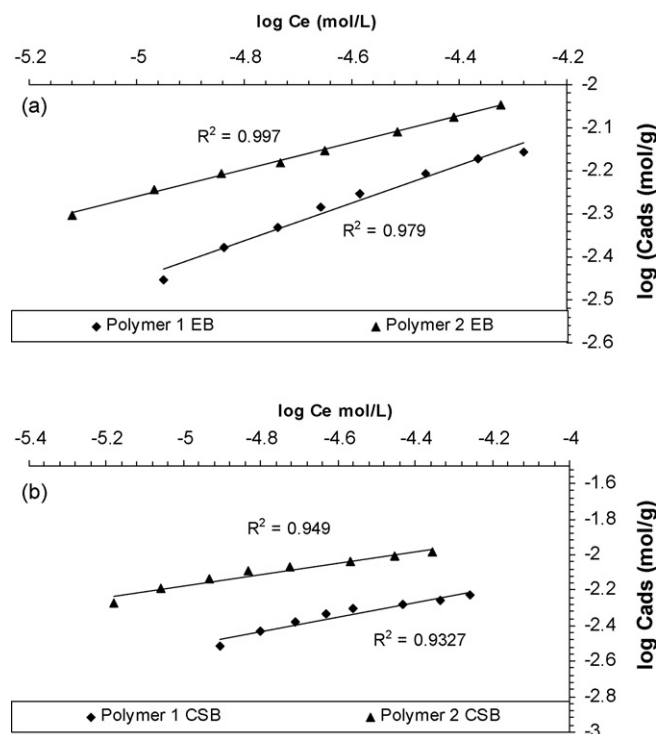
experimental data then the Freundlich equation (Figs. 4 and 5). The applicability of Langmuir isotherm describes monolayer coverage of the selected azo dyes on the surface of polymer (**1** and **2**).

### 3.4. Sorption studies of selected aromatic amines

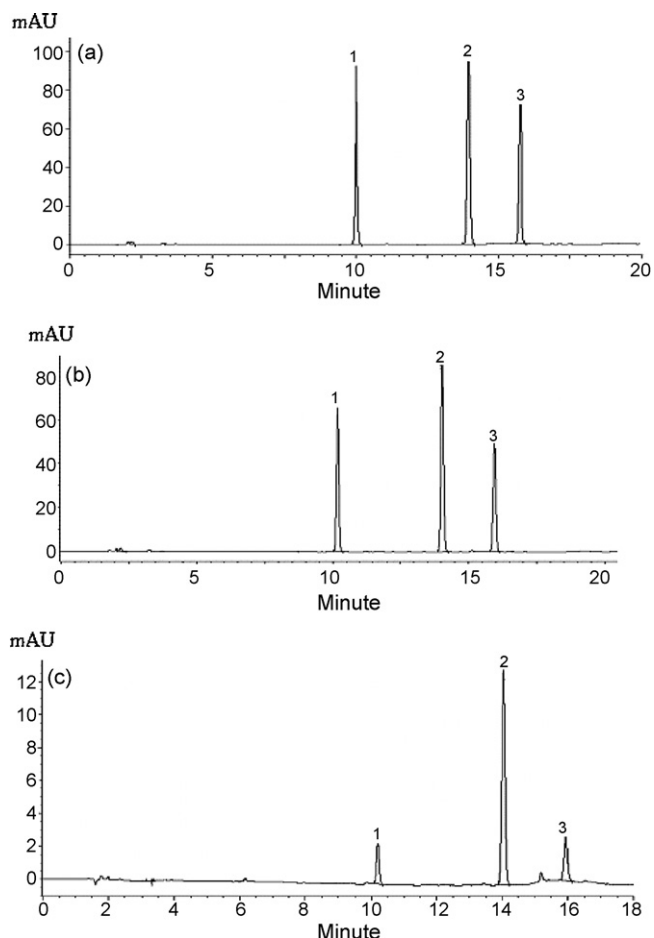
Azo dyes are readily decolorized by splitting the azo bond(s) in anaerobic environment. Azo dye reduction leads to the formation of aromatic amines. Aromatic amines are generally not degraded and accumulate under anaerobic conditions [37] with the exception of a few compounds characterized by the presence of hydroxyl and/or carboxyl groups [38]. Aromatic amines are expected to form inclusion complexes with insoluble  $\beta$ -CD polymer **1** and **2**. Solid-liquid batch sorption experiments were used to assess their ability to remove the water-soluble aromatic amines from aqueous solution. Sorption capacity of  $\beta$ -CD polymer **1** was compared with the polymer **2**. In our previous work [39,40], we have prepared Schiff base derivatives of calix[4]arenes and studied their inclusion complexation ability toward 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  $\beta$ -CDs. In the present study, hydrophobic interaction was considered to determine the complex stability to a large extent.



**Fig. 4.** Langmuir sorption isotherm: (a) polymer (**1** and **2**) for EB; (b) polymer (**1** and **2**) for CSB.



**Fig. 5.** Freundlich sorption isotherm: (a) polymer (**1** and **2**) for EB; (b) polymer (**1** and **2**) for CSB.



**Fig. 6.** Representative HPLC chromatograms of standard aromatic amines solution: (1) benzidine, (2) *p*-chloroaniline, (3)  $\alpha$ -naphthylamine: (a) aromatic amines which were treated with polymer **1** (b), treated with polymer **2** (c), in double distilled water samples. Conditions: mobile phase: acetonitrile (A) and water (B), flow rate: 1 mL/min, at 25 °C, injection volume 20  $\mu$ L, gradient elution: 0 min 20% A and 80% B; 25 min 80% A and 20% B. Detection at 280 nm, pH 7.

In order to evaluate the influence of pH on the affinity of the aromatic amines to the polymers **1** and **2** to clarify the role of different factors which take place in the sorption mechanism, experiments were carried out with selected amines at pH 7.0, and 9.0 with a contact time of 1 h (see Table 1). Thereafter, aromatic amines were analyzed with the help of HPLC (Fig. 6). From the extraction data given in Table 1, it is clear that the polymer **2** is more effective for the sorption of the aromatic amines at pH 7 but this compound shows less affinity towards these amines at pH 9.0. The conversion of  $\beta$ -CD into its polymeric form **2** significantly increases the aromatic amine sorption ability. This can be explained by the fact that the  $\beta$ -CD in the polymeric matrix may have gained a more rigid and appropriate structure, which assists the sorption of amine in SPE system.

This stronger inclusion ability was attributed to enlargement of the larger opening of the  $\beta$ -CD cavity and contraction of the smaller opening by the aromatic groups, which destroys the strong hydrogen-bond network and makes it easier for a guest molecule to gain access to the  $\beta$ -CD cavity. We propose that incorporation of  $\beta$ -CD units were cross-linked with MDI in the polymer **2** does serve to enlargement of the larger opening of the  $\beta$ -CD cavity. It contributes to the inclusion complexation of guest molecules with the  $\beta$ -CD cavity.

#### 4. Conclusions

Adsorbents made from insoluble two  $\beta$ -CD polymers possess specific inclusion recognition capabilities with aromatic compounds. The results indicate that these materials are high-capacity sorbents for the recovery of organic pollutants. The inclusion complex formation resulting from the presence of  $\beta$ -CD introduced into the polymer network by the MDI/HMDI have contributed in the sorption mechanism. In addition, hydrogen bonding, hydrophobic interactions (pollutant–polymer and pollutant–pollutant interactions), complexation and acid–base interactions between the sorbent and the pollutant as well as the physical sorption due to the polymer network are all involved.

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