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A Calix[4]arene Oligomer and Two Beta-cyclodextrin Polymers: Synthesis and Sorption Studies of Azo Dyes

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Two insoluble β-cyclodextrin polymers were synthesized by reacting β-cyclodextrin with hexamethylene diisocyanate (HMDI) or 4,4′methylene bis phenyldiisocyanate (MPDI) as a crosslinking agent and a calix[4]arene-based oligomer was prepared by the condensation of p-tert-butylcalix[4]arene with HMDI and utilized to remove selected water-soluble azo dyes from aqueous solution. Oligomer **2** was found to be a poor sorbent for the azo dyes. The influence of several parameters (pH, contact time, and NaCl concentration) on the sorption capacity was evaluated using the batch and recycling column methods. The proposed sorption mechanism involved several kinds of interactions: physical adsorption, hydrogen bonding and formation of an inclusion complex due to the β-CD molecules through host-guest interactions.

Keywords: β-cyclodextrin; calix[4]arene oligomer; azo dye; hexamethylene diisocyanate

1 Introduction

Dyes and dyestuffs are widely used in many industries such as textiles, papers, leathers, gasoline, additives, foodstuffs and cosmetics. Over 100,000 commercially available dyes exist and more than 7×10^5 tons of dyestuff are produced annually (1, 2). Due to their good solubility, industrial effluents often contain residual dyes which significantly affect water quality. Usually 30–70% of reactive azo dyes are hydrolyzed and eliminated into wastewater for dyeing processes (3–7). In addition, inappropriate disposal of dyes in wastewater can cause a threat to public health, as certain azo dyes or their metabolites (e.g., aromatic amines or amino-azo compounds) are highly toxic and potentially carcinogenic (8). Basically, cytotoxicity of typical azo dyes may be relatively low, but the toxicity of related aromatic amine intermediates is very likely it is still significantly high due to their carcinogenicity or mutagenicity (3). Therefore, the corresponding wastewaters should be treated before discharge (9). Many dyes are difficult to remove due to its synthetic origin and mainly complex aromatic molecular structure, designed to resist fading on exposure to sweat, soap, water, light or oxidizing agents, making it very stable and not readily biodegradable (10) and conventional biological wastewater treatment methods are ineffective for decolorization and degradation.

Dye wastewater is usually treated by physical, chemical, and biological treatment processes, such as flocculation, membrane-filtration, ozonation, coagulation, precipitation, adsorption, and fungal decolorization. Among these techniques, adsorption is a procedure of choice for the removal of dissolved organic compounds from wastewater (11) and also has a specific advantage of removing the complete dye molecule, unlike certain removal techniques, which destroy only the dye chromophore leaving the harmful residual moieties (like metals) in the effluent.

Many studies have been undertaken for the development of cheaper and more effective adsorbents containing natural polymers. Among these, polysaccharides such as chitin (12–14) and starch (15–17), and their derivatives chitosan (18, 19), cyclodextrin (20–22) have received particular attention. These natural polymers represent an interesting and attractive alternative as adsorbents because of their particular structure, physico-chemical characteristics, chemical stability, high reactivity and excellent selectivity towards aromatic compounds and metals, resulting from the presence of hydroxyl, acetamido or amino functional groups in polymer chains. These biopolymers are renewable, easily available and, biodegradable resources have a capacity to associate by physical and chemical interactions with a wide variety of molecules (23, 24). Thus, adsorption on polysaccharide derivatives can be a low-cost procedure of choice in water decontamination for extraction and separation

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of compounds, and a useful tool for protecting the environment. Furthermore, the increasing number of publications on adsorption of toxic compounds by these natural polymers shows that there is a recent interest in the synthesis of new adsorbent materials containing polysaccharides.

Because of their ability to link covalently or noncovalently specifically to other cyclodextrins, they can be used as building blocks for the construction of supramolecular complexes. Cyclodextrins (CDs) are torus-shaped cyclic oligosaccharides containing six to twelve glucose units. The most characteristic feature of CDs is the ability to form inclusion complexes with various aromatic molecules, including dyes. CDs possess a hydrophobic cavity in which a pollutant can be trapped. Like other polysaccharides, cyclodextrins can be crosslinked by a reaction between the hydroxyl groups of the chains with a coupling agent to form a water-insoluble crosslinked resin which exhibits specific adsorption base on inclusion complex formation (25–29). Therefore, cyclodextrins can play a major role in environmental science in terms of solubilization of organic contaminants, enrichment and removal of organic pollutants and heavy metals from soil, water and atmosphere (30). CDs are also applied in water treatment to increase the stabilizing action, encapsulation and adsorption of contaminants (31). Using cyclodextrins, highly toxic substances can be removed from industrial effluent by inclusion complex formation.

Previously, we have reported (32) the synthesis and inclusion abilities of calix[4]arene oligomers and a β-cyclodextrin-based polymer for selected water-soluble azo dyes. We now report the synthesis and efficiency of calix[4]arene oligomer and β-cyclodextrin polymers as solid phase and column materials for the removal of selected azo dyes from aqueous solutions.

2 Experimental

2.1 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 Perkin–Elmer 1605 FTIR spectrometer as KBr pellets. UV-Vis spectra were obtained with a Shimadzu 160A UV-Vis recording spectrophotometer. Elemental analyses were performed with a Leco CHNS-932 analyzer, and TGA was carried out with Perkin-Elmer Pyris 1 thermogravimetric analyzer. The sample weight was 13–15 mg. Analysis was performed at room temperature to 800°C at a heating rate of 20°C/min in a nitrogen atmosphere with a gas flow rate of 40 mL/min.

2.2 Reagents

Analytical TLC was performed on pre-coated 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.

2.3 Synthesis

2.3.1 Preparation of Calix[4]arene Oligomer (2)

Simultaneously, a solution of **1** (1.00 g, 1.377 mmol) in dry DMF (10 mL) and a solution of hexamethylene diisocyanate (HMDI) (0.34 g, 2.055 mmol) in dry DMF (20 mL) were added to a stirred, 100-mL, three-necked flask via two dropping funnels at 70°C under nitrogen, and the stirring was continued for 4 h. The solvent was removed *in vacuo* to give a semi-solid, which was stirred with ice-cold water to furnish a precipitate. This precipitate was stirred with hexane, then with MeOH. It was filtered and dried under vacuum for 12 h. Yield: 65%, m.p. 265°C. IR (KBr) 3350 cm^{-1} (N-H, O-H) and 1652 cm^{-1} (NC=O), ^{1}H-NMR (DMSO) δ (ppm) 0.85–1.82 (m, 72H), 1.18–2.20 (m, 12H), 2.85 (s, 4H), 3.00–4.5 (m, 32H), 6.50–7.30 (m, 20H), 8.00–8.20 (bs, 4H).

2.3.2 Preparation of β-CD Polymers

β-CD (2.00 g, 1.76 mmol) was dissolved in 10 mL of dry DMF in a 100 mL round bottom flask at room temperature. Then, 6.55 mmol of hexamethylene diisocyanate (HMDI) for polymer **1** or 6.55 mmol of 4,4′methylene bis phenyldiisocyanate (MPDI) for polymer **2** in dry DMF (10 mL) was added dropwise. The mixture of polymer **1** or **2** was stirred at 70°C for 4 h. At the end of this period, polymer **1** or **2** was precipitated by the addition of ethanol and acetone, respectively, then the precipitate was filtered and washed with acetone and water several times. The product was *dried in vacuo* for 24 h. The yield was 85% for polymer **1** and 75% for polymer **2**. IR (KBr) 3350 cm^{-1} (N-H, O-H), 1715 cm^{-1} (OC=O) for polymer **1**; 3350 cm^{-1} (N-H, O-H), 1664 cm^{-1}(NC=O) for polymer **2**.

2.4 Sorption Studies

2.4.1 Batch Experiments

The first is the batch method 25 mg of the sorbent was mixed with 10 mL of a NaCl 0.2 mol L^{-1} and an aqueous solution of the pollutant compound (concentration 2.10^{-5} mol L^{-1}) 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 was reached. The residual concentration of the organic solute was determined by spectrophotometer and the sorption capacity calculated. All solutions were centrifuged before measurements. Absorbance values were recorded at λ_{max} for each solution: at 484 nm for tropaeolin 000 (TP), 549 nm for direct violent 51 (DV-51), 463 nm for methyl orange (MO), and 407 nm for titanium yellow (TY) (see Figure 1 for the structural formulae). 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 (28–33).

2.5 Column Studies

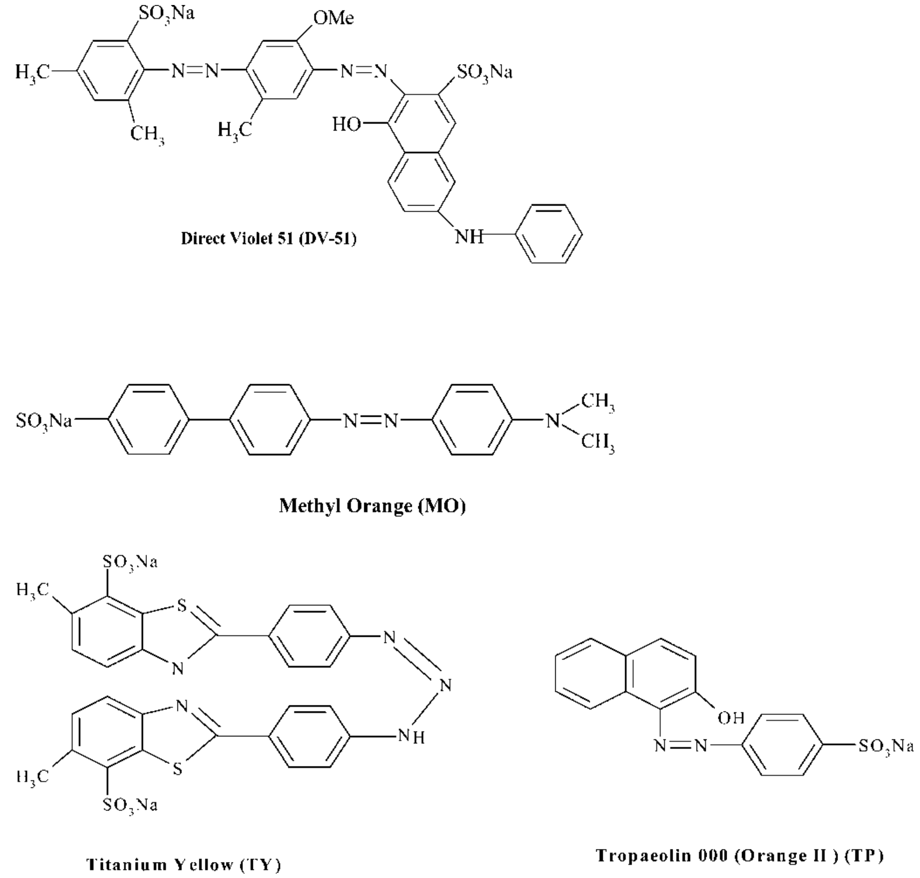
The second technique involved the use of recycling columns. We used the following equipment: a tank, a peristaltic pump; a two-way collector, 1-mL column; and a fraction collector. The column was filled with 50 mg of polymer **1** or **2**. The column was eluted using only water until the flow rate became constant. For the recycling system column, the experimental conditions are as follows: concentration of 2.10^{-5} mol L^{-1} in water for azo dyes, flow rate of 1.5 mL/min; and a column filled with the insoluble polymer with respect to organic 50 mg of polymer **1** or **2**. A fixed volume (20 mL) of the solution was eluted through the column many times over a period of about 210 min. The sorption capacity of the polymers in these two types of experiments were obtained by UV analysis of the eluted solutions at fixed times.

3 Result and Discussion

3.1 Characterization of Sorbents

Structures of calix[4]arene monomer **1** and oligomer **2** and β-cylcodextrin polymers (polymer **1** and **2**) are shown in Scheme 1. The syntheses of **1** are based on the reported procedure (34). Oligomerization of **1** with hexamethylene diisocyanate (HMDI) in a minimum amount of DMF gave oligomer **2** in 65% yield. The molecular weight (Mw) of oligomer **2**, as determined by GPC in THF against polystyrene standards, was 1590 g/mol. This indicates the presence of two calixarene units in the oligomeric skeleton. Oligomer **2** was also characterized by FTIR and ^{1}H-NMR spectroscopy. The IR spectra of **2** showed a characteristic amid band about 1652 cm^{-1} and the disappearance of isocyanate band at 2275 cm^{-1} and a band at 3350 cm^{-1} for the amino end groups (-NH_2). The resonance signals of -NH_2 appeared at 1.80–1.20 ppm in the ^{1}H-NMR spectra of oligomer **2**. Therefore, it was not possible to discern the conformation of the calixarene moieties in the oligomeric skeleton.

To allow for comparison of the sorption results obtained using the calixarene-based oligomers with those for two β-cyclodextrin (β-CD) polymers, crosslinked β-CD polymer **1** and **2** were prepared by the reaction of β-CD with HMDI



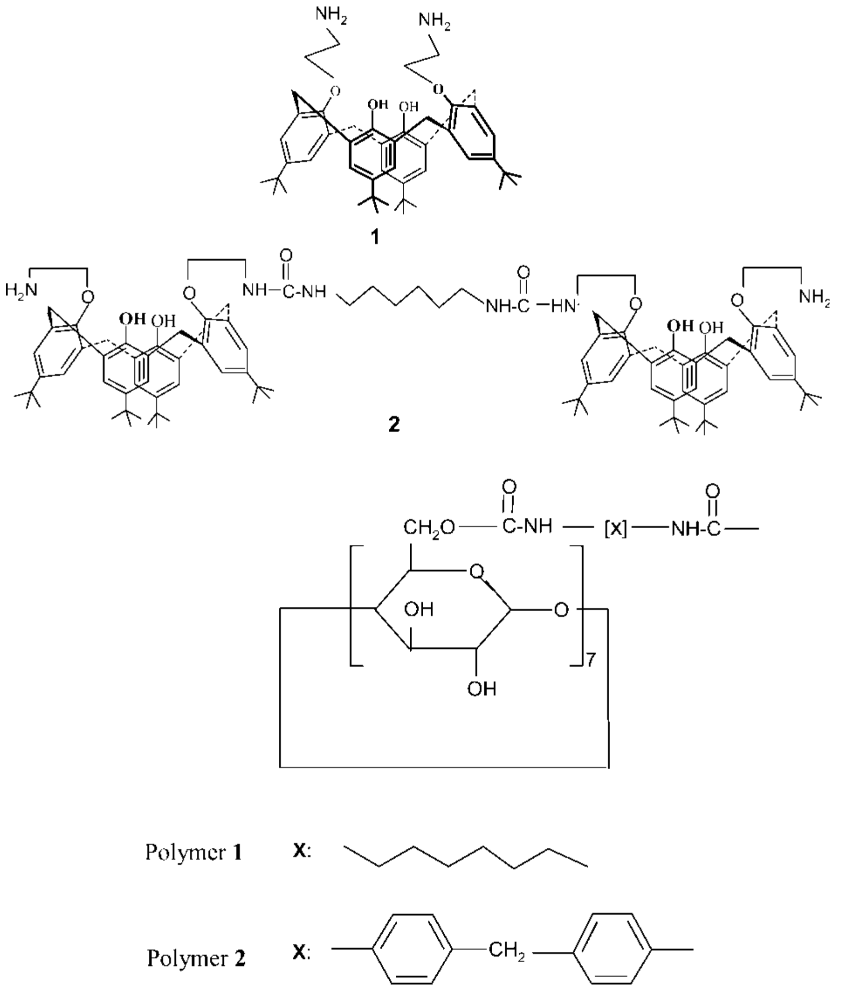
Direct Violet 51 (DV-51)

Methyl Orange (MO)

Titanium Yellow (TY)

Tropaeolin 000 (Orange II) (TP)

Fig. 1. Structure of azo dyes.



Sch. 1. Chemical structure of sorbents.

or MPDI. The crosslinked polymers were insoluble in water, as most of the organic solvents. Consumption of the isocyanate reactant was followed by observing the decrease in absorbance of the -N=C=O anti-symmetric stretching band at 2275 cm^{-1} for polymer **1** and **2**. A band at 3310 cm^{-1} for polymer **1** and at 3319 cm^{-1} for polymer **2** due to the free NH and OH stretching absorption for the hydroxyl and urethane groups developed as the polymerization progressed. Upon completion of the reactant mixing, urethane groups were present, as seen from an absorption at 1715 cm^{-1} N-C=O for polymer **1** and at 1664 cm^{-1} for polymer **2**.

The thermal stability of β-CD polymer **1** and **2** was evaluated by thermal gravimetric analysis (TGA) and compared with its β-CD precursor. It was found that the polymer undergoes a two-step thermal degradation. The first step arises from decomposition of β-CD, while the second is due to the polymer. According to the literature (35), CD starts to decompose at temperatures ranging from 290 to 300°C. The onsets of degradation for CD polymers were found to occur at 325°C for polymer **1** and for polymer **2** at 35°C. This is quite high compared to conventional polyurethanes, which generally begin to decompose around 200–220°C. The enhanced thermal stability of β-CD polymers are attributed to their cross-linked nature, since it is well-known that crosslinking leads to increased thermal stability. Since polymer **2** contains aromatic bridges, it showed more thermal stability than polymer **1**. A weight loss maximum of 44–45% for polymer **1** and 30–32% polymer **2** during the first stage of thermal decomposition results from cleavage of the urethane linkage and volatilization of the resultant decomposition products. The absence of a glass transition is due to the highly cross-linked nature of the polymer. A previously reported β-CD polymer exhibited no thermal transition before decomposition with an endothermic peak at around 272°C (35).

3.2 Sorption Studies

3.2.1 Batch Studies

Batch sorption studies were carried out to examine the influence of various parameters such as a type of azo dye, initial concentration of dye, time of sorption and effect of pH on the removal of azo dye from a synthetic azo dye solution.

Azo dyes are expected to form inclusion complexes with insoluble calix[4]arene-based oligomer and β-CD polymers. Solid-liquid batch sorption was utilized to assess their ability to remove the water-soluble azo dyes from an aqueous solution. Sorption capacity of oligomeric calix[4]arene was compared with the β-CD based polymers (Figure 2).

To allow for comparison of solid-liquid batch sorption results for the calixarene-loaded oligomer **2**, sorption experiments were performed with the β-CD-polymers. The results shown in Table 1 and Figure 2 clearly establish that β-CD-polymers are better sorbents for azo dyes than the calix[4]arene-based oligomer **2**. The results presented are in agreement with our previous work where we used a calix[4]-arene ester oligomer. The cavity size of calix[4]arene unit is smaller than the β-CD, and in this case, the oligomer does not form inclusion complexes with azo dyes.

Other researchers have found that alkylated β-CD exhibited stronger binding ability for an azo dye than the parent β-CD (36). The sorption capacity of polymer **2** is higher than polymer **1**. The polymer **2** which contains rigid aromatic bridge showed higher affinity of the guest compounds than polymer **1** which contains flexible hexamethylene bridges.

Figure 3 indicates the effect of contact time on percentage of sorption. The percentage of color removed was observed to increase with increasing contact time. During 15 min of contact time, 25 mg of polymer **1** removed the color to 33% for initial dye concentration of 2×10^{-5} mol L^{-1} and at 25°C, the same solution polymer **2** removed as high as 47% of color. Further contact time (i.e., 30 min) only reduced up to 52% removal in the case of polymer **1**, but in the case of polymer **2** it is 78%. Therefore, it can be said that both polymers require the same contact time to remove the maximum percentage of color. The kinetics of sorption was fast and the maximum capacity was obtained after nearly 1 h and this confirms the strong interactions between dye, β-CD molecules and the polymers network.

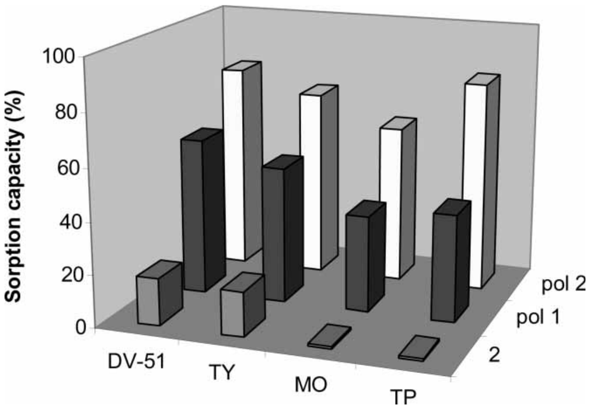


Fig. 2. Sorption percentages of the azo dyes with 2, and polymer 1, 2. (polymer dose 25 mg, contact time 1 h, concentration 2×10^{-5} mol L^{-1}, pH:11).

Table 1. Percent sorption of azo dyes by sorbents (%)^{a}

Compound	DV-51	TY	TP	MO
Polymer **1**	60	52	41	37
Polymer **2**	78	72	81	61
2	18	17	<1.0	<1.0

^{a}Aqueous phase, [azo dye] = 2×10^{-5} mol L^{-1}, at pH 11; at 25°C for 1 h.

This stronger inclusion ability was attributed to enlargement of the larger opening of the β-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 β-CD cavity. We propose that incorporation of β-CD units into cross-linked polymer **1** and polymer **2** similarly serves to enhance their azo dye inclusion properties.

The sorption mechanisms of polysaccharide-based materials are different from those of other conventional adsorbents. These mechanisms are, in general, complicated because they may involve several different interactions (37, 38). Some of the reported interactions include: ion-exchange, complexation, coordination/chelation, electrostatic interactions, acid–base interactions, hydrogen bonding, hydrophobic interactions, and physical adsorption.

3.2.2 *Influence of the pH on the Sorption Capacity*

To evaluate the influence of the pH affinity of the azo dyes for polymer **1** and **2** and to clarify the role of different factors which take place in the sorption mechanism, tests were carried out at different pH 7, 8.5 and 11. The influence of the pH on the sorption capacity of polymer **1** and polymer **2** vs. starting concentration of the DV-51 using a contact time of 1 h was studied (Figure 4). The results obtained at pH 7 and 8.5 are very similar but are different from those obtained at pH 11, which show significantly stronger interactions. Further, it was observed that the percentage of color removed was 55% for polymer **1** and 65% for polymer **2** when the pH of DV-51 solution was 7.0 and they attained a maximum of 60% for polymer **1** and 78% for polymer **2** when the pH of dye solution increased to 11.

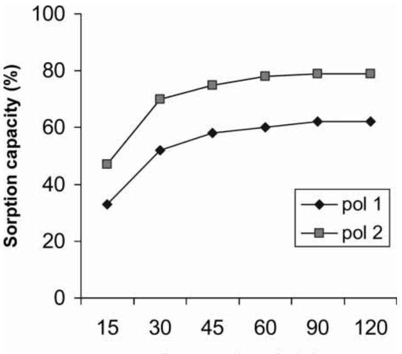


Fig. 3. Effect of contact time on per cent adsorption of direct violet-51 by polymers (dye concentration 2×10^{-5} mol L^{-1} pH: 11).

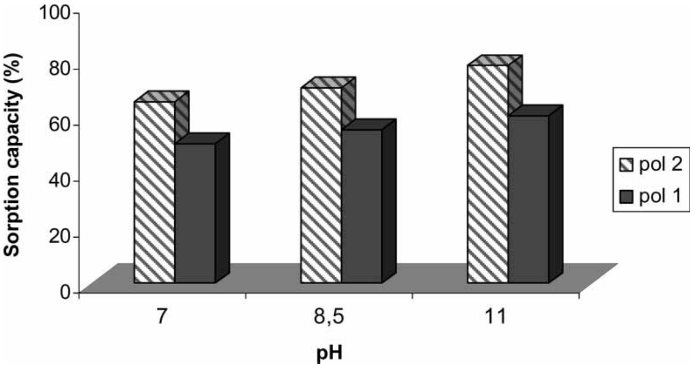


Fig. 4. pH effect on sorption percentage (contact time 1 h; concentration 2×10^{-5} mol L^{-1}, dye direct violet-51).

This reflects the fact that the inclusion complexes with β-CD polymers are more stable in basic conditions.

3.3 *Column Studies*

In a kind of experiment, we used a recycling column and tried to saturate the polymer using a significant amount of solution containing the azo dye. The aim was to confirm the roles played in the sorption, by β-CD and also the polymer network introduced by hexamethylene or 4,4′-methylenebisphenyl bridging groups. In this work, as described above, DV-51 exhibits the best interaction with these sorbents (polymer **1** and polymer **2**). Figure 5 shows the amount of DV-51 adsorbed for 50 mg of sorbent. The sorption capacity of the polymer was found to be independent of the flow rate used in the range between 1 and 2.5 mL/min. This experiment is analogous to that which was made batchwise, where the amount of the guest adsorbed increases as a function of the increase of the guest concentration. Figure 5 shows that the amount of DV-51 sorbed for polymer **1** and **2** in the recycling column experiment was higher than the batchwise technique. Similar trends were obtained for the MO dye solution (Figure 6).

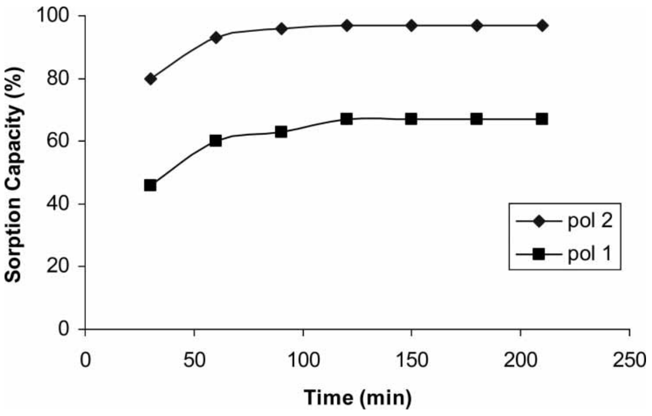


Fig. 5. Evaluation of sorption capacity by polymers using a recycling column (dye: DV-51, concentration 2×10^{-5} mol L^{-1}, pH:11, sorbent: 50 mg.).

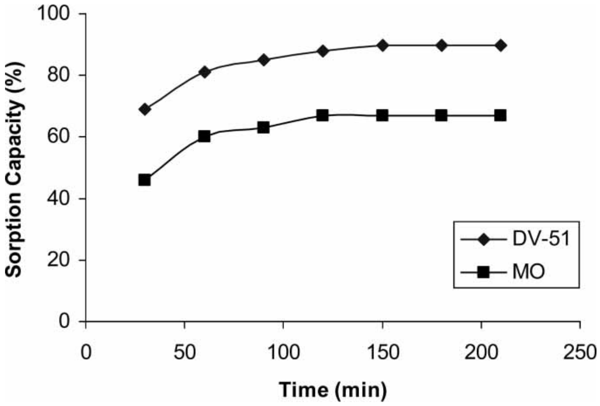


Fig. 6. Influence of the β-CD polymers dose on per cent adsorption of dye (dye concentration 2×10^{-5} mol L^{-1}, pH:11).

Due to anionic azo dyes used in this work, the addition of sodium chloride to aqueous solutions produced an increase in the performance of the β-CD polymers (Figure 7).

NaCl minimizes electrical charge on the surface of the polymer **2** and increases the adsorption. Similar results have been published by Shao et al. and Crini (30, 38). The long term stability and reproducibility of the sorption properties of the polymers is important. Organic solvents could be used for the regeneration of the adsorbents, because the interaction between the dye and the polymer were driven mainly by inclusion complexes. After saturation, the polymers were easily regenerated (75–85%) using ethanol as washing solvent by soxhlet extraction. It was observed that the sorption capacity was not changed after this treatment. This showed the chemical stability of the polymers and reproducibility of the values.

4 Conclusions

A calix[4]arene-based oligomer **2** and two β-CD-based polymers were synthesized and utilized to remove selected

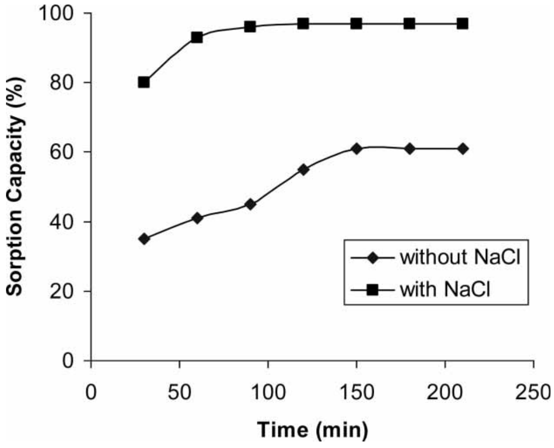


Fig. 7. Effect of NaCl concentration on per cent adsorption (polymer **2**; Dye Direct Violet-51; concentration 2×10^{-5} mol L^{-1}, pH: 11).

water-soluble azo dyes from an aqueous solution. Oligomer **2** was found to be a poor sorbent for the azo dyes. β-CD polymers were prepared by the reaction of β-CD with HMDI or MPDI and the polymers have been evaluated for the extraction of azo dyes from an aqueous solution. It was observed that the sorption capacity of polymer **2** was higher than polymer **1**. The polymer **2**, which contained a rigid aromatic bridge showed higher affinity of the guest compounds than polymer **1**, which contained flexible hexamethylene bridges. The most important parameters which affect the efficiency of a sorbent were studied and include pH, contact time, and NaCl concentration. The separation mechanism of the polymers is also different from those of other adsorbents. Physical adsorption plays little role in the interaction between β-CD polymers and azo dyes because β-CD polymer has a very small surface area (28). The proposed sorption mechanism involved several kinds of interactions: hydrogen bonding and formation of an inclusion complex due to the β-CD molecules through host-guest interactions.

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