Removal of an Azo Textile Dye from Wastewater by Cyclodextrin-Epichlorohydrin Polymers

Paola Semeraro, José Antonio Gabaldón, Paola Fini, Estrella Núñez, José Antonio Pellicer, Vito Rizzi and Pinalysa Cosma

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Abstract

Native cyclodextrins (CDs), α-, β- and γ-CDs, were employed to synthetise three different cyclodextrin-based polymers using epichlorohydrin (EPI) as a cross-linker. These polymers were applied as adsorbent material to remove an azo textile dye, Direct Blue 78 (DB78), from water. The formation of inclusion complexes between the alone CDs and DB78 molecules were first studied in aqueous solutions. Then, adsorption experiments of the dye were performed by means of cyclodextrin/epichlorohydrin (CD/EPI) polymers. The effects of various parameters, such as contact time, adsorbent dosage, initial dye concentration, pH and temperature, were examined to determine the better adsorption conditions. The equilibrium isotherms and the adsorption kinetics were also analysed using opportune mathematic models. The chemical-physical characteristics and the morphology of the adsorbent polymers were, respectively, observed by differential scanning calorimetry and field emission scanning electron microscope. The CD/EPI polymers showed a very good ability in the removal of DB78 from aqueous solution; indeed, the maximum efficiencies in the dye removal were found to be about 99% for β-CD/EPI polymer and about 97% for γ-CD/EPI polymer, at pH 6 and 25°C conditions. It is possible to assume that the good adsorbent aptitude of CD/EPI polymers is due to their double peculiarity to include the dye in the inner cavity of CDs and to adsorb the dye on their porous surfaces by physical interaction.

Keywords: inclusion complexes, electrochemical measurements, adsorption process, textile dye removal, cyclodextrin/epichlorohydrin polymers, thermal analysis
1. Introduction

1.1. Textile dyes

Textile and clothing industries generate a remarkable pollution in natural water due to the discharge of large amounts of dye chemicals in the effluents [1]. These dyes give an undesirable colour to the water body, reducing the sunlight penetration and influencing the photochemical and biological activities of aquatic life [2]. Dye molecules present several chemical structures and, depending on functional groups of their chromophore, are classified as azo, anthraquinone, styryl, acridine, nitro, nitroso, benzodifuranone, diphenylmethane, triphenylmethane, azine, xanthene, cyanine, phthalocyanine, hemicyanine, triarylmethane, stilbene, or oxazine dyes [2]. However, the azo compound class accounts for about 65–70% of all classes of dyes [3], and the azo dyes are the most common synthetic molecules released into the environment. It is now recognised that some azo dyes, under certain conditions, produce aromatic amines which are toxic, allergenic, carcinogenic, and mutagenic [4, 5].

Due to the hazard of reduction products arising from the use of azo dyes, the European Union (EU) AZO Colourants Directive 2002/61/EC already came into force in September 2003, and replaced by REACH regulation, regulated the restrictions on the marketing and use of certain dangerous azo dyes. In addition, these contaminants are highly soluble in water and are very difficult to degrade being stable to light irradiation, heat, and oxidation agents. Therefore, the conventional wastewater treatment systems are not able to remove them [6], and it is necessary to treat the industrial effluents before releasing it into the environment. Hence, in recent years, numerous treatments on the removal of azo dyes from the effluents have been studied. There are different methods for the treatment of wastewaters including chemical, physical, and biological technologies [7]. All these methods present both advantages and disadvantages, which are shown in detail in Table 1 [1, 8–10].

Among all techniques described in Table 1, the adsorption is one of the most efficient and popular methods for the removal of textile dyes from industrial effluents [11] and activated carbon is the most common material used for dye removal by adsorption. This material due to its ability to adsorb cationic, acid dyes, and mordant, and, to a slightly lesser extent, dispersed, direct, and reactive dyes [9]. However, commercially available activated carbons are very expensive, and so it is opportune to use low-cost carbons that are able to absorb pollutants from wastewater. In the last years, the research is pointing towards the use of more efficient and inexpensive adsorbent materials for the treatment of coloured effluents. A wide variety of low-cost materials, such as biosorbents and by-products of industry and agriculture [12–15], are being evaluated as viable substitutes for activated carbon to remove dyes. Industrial and agricultural wastes are indeed very interesting adsorbent materials with good adsorption capacity, high selectivity, low cost, easy regeneration, and free availability. A recent paper [15] reported that oil mill solid waste, previously treated, is able to reduce significantly the amount of an azo direct dye in industrial textile wastewater. In particular experimental conditions, this material can adsorb the 100% of the dye in solution with the possibility to recycle both the dye and the adsorbent [15]. Also, natural and biodegradable polymers showed good biocompatibility and high efficiency in dyes adsorption. Indeed, it was demonstrated that
## Table 1. Advantages and disadvantages of dye removal methods.

| Methods                        | Advantages                                                                 | Disadvantages                                                                 |
|--------------------------------|-----------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| Chemical treatments            |                                                                             |                                                                               |
| Oxidative process             | Simplicity of application                                                   | Oxidising agent, usually hydrogen peroxide ($H_2O_2$), needs to be activated by some means such as ultra violet light |
| $H_2O_2 + Fe(II)$ salts (Fenton’s reagent) | Fenton’s reagent is a suitable chemical means for treatment of wastewaters | Generation of sludge containing concentrated impurities                       |
| Ozonation                      | Ozone, a very good oxidising agent, can be applied in its gaseous state and does not increase the volume of wastewater | Continuous ozonation is required due to its short half-life (20min) with cost increase |
| Photochemical                  | No production of sludge and great reduction of foul odours                  | Formation of by-products                                                       |
| Sodium hypochlorite (NaOCl)    | Attack at the amino group of dye molecules with azo-bond cleavage            | Release of aromatic amines                                                     |
| Electrochemical destruction    | No consumption of chemicals, non-hazardous production of breakdown compounds and no accumulation of sludge | High cost of electricity                                                     |
| Biological treatments          |                                                                             |                                                                               |
| Decolourisation by white-rot fungi | Degradation of dyes by white-rot fungi using enzymes                       | Unreliable enzyme production due to the unfamiliar environment of liquid fermentations |
| Other microbial cultures (mixed bacterial) | Decolourisation of dye mixtures in 24–30 h by anaerobic bacteria and decolourisation of diazo dyes in 15 days by mixed bacterial cultures | Under aerobic conditions, azo dyes are not readily metabolised |
| Adsorption by living/dead microbial biomass | Great affinity for binding between microbial species and several molecules such as anthraquinone, phthalocyanine, and azo dyes | Not effective for all dyes                                                      |
| Anaerobic textile-dye bioremediation systems | Decolourisation of solutions containing azo and other water-soluble dyes | Production of methane and hydrogen sulphide by anaerobic breakdown |
| Physical treatments            |                                                                             |                                                                               |
| Adsorption                     | Removal of wide variety of dyes                                             | Same adsorbent materials are very expensive                                   |
| Membrane filtration            | Removes all dye types                                                       | Production of concentrated sludge                                             |
| Ion exchange                   | No loss of adsorbent on regeneration and recycling of solvent after use     | Not effective for all dyes and high cost                                       |
| Irradiation                    | Effective break down of some dyes and phenolic molecules by radiation       | Request of great quantities of dissolved $O_2$ which affect the cost. Applicability only at a laboratory scale |
| Electrokinetic coagulation     | Economically feasible method for excellent removal of direct dyes           | Not effective for acid dyes removal and production of large amounts of sludge |

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chitosan films [16], chitosan/polyamide nanofibres [17], and alginate-chitosan beads [18] are used as efficient and economic adsorbents for the removal of direct and anionic textile dyes. Numerous experiments are, moreover, conducted to evaluate the possibility to use some polysaccharides, in particular, starch and starch derivatives, as adsorbents for wastewater treatment [19, 20]. Since it was established that the good adsorption properties of polymers derived from starch towards dyes, in this study, cyclodextrin-based polymers were used to remove an azo textile dye, Direct Blue 78 (DB78), from wastewater. In Figure 1 is shown the chemical structure of DB78, a tri-azo compound characterised by the presence of three azo bonds (—N=N—) with four sulphonate groups.

1.2. Cyclodextrins

Cyclodextrins (CDs) are natural cyclic oligosaccharides, derived from starch, that present a truncated cone structure with an inner relatively apolar cavity and an external hydrophilic face [21]. Due to this characteristic conformation, CDs are host molecules able to include in their cavity, a high range of guest molecules, with appropriate dimensions, through the formation of host-guest inclusion complexes [22]. The native CDs, named, α-, β-, and γ-CDs, are respectively constituted by 6, 7 and 8 glucopyranose, connected by α(1,4)-linkages. CDs can be employed both in their native form and in functionalised form, after opportune chemical modifications. Attributable to their numerous and specific properties, CDs are widely employed in several areas such as pharmaceutical, biomedical, biotechnological, and industrial sectors [22, 23]. Several studies also reported that CDs and CD-based materials are used in removal of dyes [18, 19], organic pollutants, and heavy metals from water, soil, and atmosphere [23, 24]. Moreover, in a previous study [25], the interaction between some azo textile dyes and some commercial cyclodextrins was already demonstrated. Therefore, in this chapter, the study on the removal of DB78 dye from wastewater, by using cyclodextrins, is described in detail. However, since the most of CDs are highly soluble in water, insoluble CD-based materials were employed as dye adsorbent. Indeed, after the adsorption process, these materials can be easily removed from treated solutions obtaining clean water.

1.3. Cyclodextrin-based polymers

Among the numerous preparation methods of water insoluble CD-based materials, cross-linked polymers, obtained by copolymerisation of CDs and coupling agents, have received great attention. The most employed cross-linking agent is epichlorohydrin (1-chloro-2,3-epoxypropane)
This cross-linker, shortly named EPI, is a bi-functional coupling agent, which contains two reactive functional groups, an epoxide group and a chloroalkyl moiety. EPI form bonds with polysaccharide molecules in cross-linking step and/or with itself in polymerisation step and the hydroxyl groups of native CDs, at the 2-, 3- and 6-positions of glucose units that are available and reactive to form linkages. The -OH groups in 6-positions are more reactive than those in 3-positions; however, their reactivity depends on the reaction conditions, such as temperature and alkalinity, to allow complete alkoxide formation [26]. Indeed, the secondary hydroxyl groups, which have pKa values of around 12.2 (at 298 K), can be deprotonated with hydroxide or hydride to form alcoholate sites. Consequently, typical methods used to synthesise CDs-based polymers require the addition of NaOH, NaH or NaBH₄ [27]. Despite its toxicity for humans, animals, algae, and bacteria and its potential pollutant characteristics for the environment, EPI is widely used to synthetise CD/EPI polymers [28] due to simplicity and low cost of the synthesis. On the other hand, a careful purification of these polymers allows to eliminate free EPI and other residual solvents making them good and non-toxic drug delivery systems for pharmacological formulations [29]. Furthermore, the CD/EPI polymers present high adsorption properties, high efficiency in pollutant removal and are recyclable and easily recoverable [26–30]. Despite the β-CDs are the most common cyclodextrins used to produce CD-based polymers, in this study, α-, β- and γ-CDs were employed, and their respective polymers were synthetised.

2. Experimental section

2.1. Preparation of DB78/CD solutions

To verify the formation of inclusion complexes between dye and CDs, aqueous solutions of α-, β- and γ-CDs were respectively added to DB78 solution, at different molar ratio. Stock solutions of DB78 and α-, β- and γ-CD were already prepared in distilled water and the desired volumes of these solutions were mixed and diluted to the chosen final volume to obtain the DB78/CD solutions. They were maintained under stirring for 10 min, at room temperature, to ensure the inclusion complex formation, and then studied by electrochemical measurements.

2.2. Preparation of CD/EPI polymers

The α-CD/EPI, β-CD/EPI, and γ-CD/EPI polymers were prepared dissolving opportune amounts of the respective CDs in water, in presence of sodium borohydride. The mixtures were vigorously stirred at 50°C until the reactants were dissolved. Then, NaOH (40% w/w) solution was added and an excess of epichlorohydrin was slowly added dropwise. The mixtures were vigorously stirred and heated gently at 50°C. About after 5 hours, the solutions started to be viscous, and gelatinous solids were obtained. Then acetone was added, and the systems were maintained under stirring and heating for 10 min. After cooling, the insoluble polymers obtained were poured into water, filtered and the resulting solid was purified by several Soxhlet extractions. Next, the CD/EPI polymers were dried in oven, at 50°C for 12 h, crushed and utilised as adsorbent materials to remove DB78 from aqueous solution. Figure 2 shows the scheme of CD/EPI polymer synthesis.
2.3. Instruments

Electrochemical measurements were performed in a standard three-electrode cell using hanging mercury drop electrode (HDME) as working electrode. An Ag/AgCl, KCl sat electrode and a Pt rod were used as reference and counter electrodes, respectively. A LiClO₄ 0.1 M solution was used as supporting electrolyte. Voltammograms were recorded by means of the AUTOLAB PGSTAT10 potentiostat interfaced with a personal computer. Absorption spectra were recorded from 200 to 600 nm using a Shimadzu UV-1601 spectrophotometer. Calorimetric measurements were performed using an LKB 2277 Thermal Activity Monitor Isothermal Microcalorimeter equipped with an LKB 2277–204 flow mixing cell. The photographs of samples were collected by using a field emission scanning electron microscope (Merlin Compact/VP, Carl Zeiss Microscopy, Germany) with a secondary electron detector using an acceleration voltage of 2 KV and an aperture size of 30 μm.

2.4. Batch adsorption experiments

Batch mode experiments were carried out to study the dye adsorption processes by CD/EPI polymers. The required amounts of adsorbent were added to fixed volume of dye solution, at opportune concentration, under constant condition of agitation rate (170 rpm), pH and temperature. At predetermined time intervals, the dye concentration in solution was evaluated by UV–Vis absorption measurements. Different variables, such as contact time, adsorbent dosage, initial dye concentration, pH and temperature, were analysed to recognise the optimum adsorption states. These experiments were performed by varying the parameter under evaluation and maintaining the other parameters constant. Values of dye removal (%) and amount of dye adsorbed onto adsorbent \( q_t \) (mg/g) at time \( t \) were respectively calculated using the following expressions:

\[
\% = \left( \frac{C_i - C_t}{C_i} \right) \times 100
\]

(1)

\[
q_t = \frac{(C_i - C_t) V}{m}
\]

(2)

where \( C_i \) and \( C_t \) (mg/L) are the dye concentration in solution at initial and at \( t \) adsorption time, respectively. \( V \) (L) is the initial volume of dye solution and \( m \) (g) is the mass of adsorbent. All tests were achieved in triplicate and the mean values were reported.
2.5. Adsorption equilibrium isotherms

Adsorption isotherms, by means of accurate mathematical models, allow to evaluate the adsorption behaviour and to describe how the adsorbate interacts with the adsorbent [31]. Among all isotherm models developed, the more common models, Langmuir and Freundlich models were used in this study. The Langmuir adsorption isotherm model presumes that the adsorption occurs on homogeneous sites of adsorbent surface forming a saturated monolayer of adsorbate on the outer surface of adsorbent and that the adsorption of each molecule onto the surface has equal adsorption activation energy [32, 33]. The Freundlich adsorption isotherm is an empirical equation which describes heterogeneous systems having unequal available sites on adsorbent surface with different adsorption energies [31, 32]. The adsorption isotherms were evaluated adding different amounts of CD/EPI polymers to dye solutions and maintaining the systems at constant temperature of 25°C under continuous stirring until the equilibrium was achieved. Values of dye concentration were measured before and after the adsorption processes and the obtained experimental data were fitted with Langmuir and Freundlich models. The values of the linear regression correlation coefficient R² give information about the best-fit model.

The linearised form of Langmuir is represented by Eq. (3):

\[
\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b q_m C_e} \tag{3}
\]

where \( q_e \) (mg/g) is the amount of the dye adsorbed on polymer at equilibrium, \( q_m \) (mg/g) is the maximum monolayer amount of DB78 adsorbed per unit mass of adsorbent, \( C_e \) (mg/L) is the concentration of dye in solution at equilibrium and \( b \) is the constant related to the affinity of the binding sites (L/mg). From the intercept and slope of the plot \( 1/q_e \) versus \( 1/C_e \), it is possible to obtain the values of \( q_m \) and \( b \), respectively. Moreover, the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, \( R_L \), that is defined by the following equation:

\[
R_L = \frac{1}{(1 + b C_0)} \tag{4}
\]

where \( C_0 \) is the initial concentration of adsorbate (mg/L) and \( b \) (L/mg) is Langmuir constant. The value of \( R_L \) indicates the trend of the adsorption process, indeed, the isotherm can be either favourable (0 < \( R_L \) < 1), unfavourable (\( R_L \) > 1), linear (\( R_L \) = 1) or irreversible (\( R_L \) = 0). The Langmuir values, \( q_m \), \( b \), and \( R_L \) are presented in Table 2.

The linear form of Freundlich equation is:

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}
\]

where \( q_e \) (mg/g) is the amount of DB78 adsorbed at equilibrium, \( C_e \) (mg/L) is the concentration of the dye in solution at equilibrium, \( K_F \) (L/g) is the Freundlich constant related to the maximum adsorption capacity of adsorbent and \( n \) (dimensionless) is the heterogeneity factor. The values of \( K_F \) and \( n \), reported in Table 2, were calculated respectively by the intercept and slope of the linear plot \( \ln q_e \) versus \( \ln C_e \). The magnitude of \( n \) gives an indication of the favourability of adsorption process: when \( n = 1 \), the adsorption is linear, when \( n > 1 \), the adsorption is a favourable adsorption condition [31, 33].
2.6. Thermodynamic analysis

Thermodynamic parameters, such as Gibb’s free energy change (ΔG°) (J mol⁻¹), enthalpy change (ΔH°) (J mol⁻¹) and entropy change (ΔS°) (J mol⁻¹ K⁻¹), allow to comprehend the nature of adsorption process and the effect of temperature on adsorption. These parameters can be calculated using the following relations [34]:

\[ \Delta G^\circ = -RT \ln K_c \]  
(6)

where R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), T is the solution temperature (K) and \( K_c \) is defined as:

\[ K_c = \frac{C_i}{C_r} \]  
(7)

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]  
(8)

Therefore, Eqs. (6) and (8) can be rewritten as:

\[ \ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \]  
(9)

ΔH° and ΔS° were obtained by plot of Eq. (9), while the ΔG° values were determined from Eq. (8).

3. Results and discussion

3.1. Electrochemical measurements

Before testing the ability of azo dye removal by CD/EPI polymers, the interactions between DB78 and α-, β- and γ-CDs were investigated in solution by electrochemical measurements. Generally, electrochemical studies of different azo dyes show that the electroreduction of the
N=N double bond occurs at the hydrazo stage (HN-NH), via the consumption of 2e⁻/2H⁺, or at the amine stage (—NH₂), via the consumption of 4e⁻/4H⁺, in one or two steps depending on the chemical structure of the investigated azo compound, the nature of adjacent substituents and the pH of the medium [35]. Furthermore, the electrochemical reduction of azo compounds is an irreversible process complicated by preceding and following chemical reactions leading to the cleavage of the azo bond and resulting in various degradation products [36].

In Figure 3, the cyclic voltammetry measurements of DB78 are reported. It presented three cathodic peaks, located in the range from −0.2 to −1.0 V. The first two weak waves (I and II) were positioned at −0.15 and −0.70 V respectively, while the more intense wave (III), were located at about −0.80 V. Ep, I and Ep, II are both attributable to the azo moieties electroreduction [37, 38]. The different potential for the azo group reduction is due to the different substituents present in ortho position respect to it. The first peak can be attributed to the electroreduction of the azo group with the ortho-OH group that facilitate the electroreduction due to its electron-donating effect.

The electrochemical behaviour of DB78 in presence of increasing CDs concentration was then analysed. Although the addition of α-CD did not greatly influence the cyclic voltammograms of DB78 (data not showed), it is not possible to affirm that there is no interaction between dye and α-CD, but that this technique did not allow to obtain detailed information. On the contrary, the addition of β-CD and γ-CD, at increasing molar ratio, showed regular changes in the cyclic voltammograms of DB78. Indeed, in Figure 4a and b, it is possible to observe a strong increment of current intensity values at the increasing of the CD amount, particularly in the case of γ-CD, while no shifts of the potential peaks were detected. These regular variations indicate that the dye was reduced with more difficulty because its involvement in the inclusion complex. The inclusion of the azo groups of dye inside the cavity of the CDs prevents the interaction with the electrode and reduces the diffusion coefficient of the molecule determining the reduction of the peak current intensity. Consequently, the electrochemical measurements confirmed the formation of inclusion complexes between DB78 and β-CD and between DB78 and γ-CD.
3.2. Dye adsorption efficiency by different CD/EPI polymers

To evaluate the more appropriate material able to adsorb DB78, three different types of adsorbents, α-CD/EPI, β-CD/EPI, and γ-CD/EPI polymers, were used. Ten milliliters of dye (11.00 mg/L) at pH 6 and 25°C were analysed using 1.00 g of polymers as adsorbent. Figure 5a shows that β-CD/EPI polymer presented a better ability to remove DB78 from solution than the other polymers. The dye removal efficiency was 98.90% with β-CD/EPI polymer, in contrast to 97.25% and only 92.70% when γ-CD/EPI and α-CD/EPI polymers were respectively used. Consequently, all adsorption experiments were carried out on β-CD/EPI and γ-CD/EPI polymers. It is possible to suppose that the adsorption is based not only on physical adsorption process in the polymers networks but also on inclusion complex formation [39]. Therefore, β- and γ-CD, which are characterised by a wider cavity, can form more host-guest supramolecular interaction with dye than α-CD. However, β-CD/EPI, despite the intermediate size of β-CD between α- and γ-CD, showed the better efficiency in the removal of dye. This behaviour is due to the highest complexing ability and stability with cross-linking agents of β-CD [40].
3.3. Effect of contact time

To determine the effect of contact time on adsorption processes, 10 mL of DB 78 (11.00 mg/L) was maintained for 24 h under continuous stirring with 1.00 g of β- and γ-CD/EPI polymers at pH 6 and 25°C. The concentrations of dye in solution were measured at several times. Figure 5b shows that both polymers presented the maximum dye removal after 2 h of adsorption process and no further changes were observed after 24 h. Therefore, it is possible to affirm that the time required to achieve the equilibrium was about 2 h. During this time, the complete saturation of active sites of polymers was reached.

3.4. Effect of adsorbent dosage

The amount of the adsorbent used in these experiments is another important parameter that affects the uptake of dye. Indeed, a quantitative removal cannot be achieved when the polymer is less than the optimum amount. To optimise the smallest quantity of polymer able to adsorb the greater amount of DB78, increasing dosage of adsorbents, from 0.05 to 1.25 g, was added into 10 mL of dye solution (11.00 mg/L). The systems, maintained at pH 6 and 25°C, were stirred, until equilibrium achievement, and the remaining amount of dye in solutions were measured. In Figure 6a and b are presented the effect of adsorbent dosage on β-CD/EPI and γ-CD/EPI polymers, respectively. It is possible to observe that both polymers have the same behaviour: the percentage of dye removal increased with the increase in dosage of polymers, due to the major availability of adsorbent surface sites [18]. In presence of β-CD/EPI polymer (Figure 6a), the removal of dye from the initial solutions increased from 41.20 to 98.90% as the adsorbent dosage increased from 0.05 to 1.00 g. When γ-CD/EPI polymer (Figure 6b) was used as an adsorbent, the removal of DB78 increased from 52.01 to 97.25% as the adsorbent dosage increased from 0.05 to 1.00 g. A further increase in dosage of polymers (1.25 g) did not improve the removal of both dye since the systems were achieved the maximum adsorption efficiency. Therefore, 1.00 g of polymers was used for further measurements.

Figure 6. Effect of adsorbent dosage using 10 mL of DB78 (11.00 mg/L) and increasing dosage of polymers, from 0.05 to 1.25 g, at pH 6 and 25°C. (a) Adsorption measurements with β-CD/EPI polymer and (b) adsorption measurements with γ-CD/EPI polymer.
3.5. Effect of initial dye concentration

To study the effect of initial dye concentration on adsorption mechanism onto CD-based polymers, increasing the concentrations of DB78 solutions were used. The experiments were performed at pH 6 and 25°C, using a constant volume of dye solution (10 mL) and a constant dosage (1.00 g) of β-CD/EPI polymer and of γ-CD/EPI polymer. Experimental results show that the amount of dye adsorbed onto adsorbent, \( q_t \) (mg/g), increased with the increase in initial concentration of dye. This behaviour was more evident in the case of β-CD/EPI polymer (Figure 7a), where the amount of dye adsorbed onto polymer at equilibrium, \( q_e \), improved from 0.32 to 1.99 mg/g as the initial concentration of DB78 increased from 11.00 to 70.00 mg/L. In the case of γ-CD/EPI polymer (Figure 7b), \( q_e \) increased from 0.24 to 1.28 mg/g when the initial concentration of dye was incremented from 11.00 to 70.00 mg/L. This occurs because the increase in the initial concentrations of dye induces the optimisation of favourable interaction raising the driving force, able to overcome the resistance to the mass transfer of dye between the aqueous and the solid phase [41]. Furthermore, these measurements demonstrate again the better adsorption ability of β-CD/EPI polymer than γ-CD/EPI polymer.

3.6. Effect of initial pH

To study the influence of pH on the adsorption of azo dye onto the two polymers, experiments were carried out at pH 2, 6 and 11 with a contact time of 2 h. In Figure 8a and b are reported the results respectively obtained with β-CD/EPI and γ-CD/EPI polymers. Generally, the initial pH of solution plays a significant role in the chemistry of adsorbent and dye, however, in this case, no significant changes in the adsorption process were observed at different pH conditions. Indeed, for both polymers, when acid and basic conditions were used, no important variations in the adsorption efficiency were observed. However, the highest percentage of dye removal was obtained at pH 6. It is possible to suppose that at alkaline pH, the presence of excess ─OH ions compete with the anionic dye for the adsorption sites. Indeed, as the pH of...
The system increases, the number of negatively charged sites increases as well, and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent does not support the adsorption of anionic dye due to electrostatic repulsion [42]. On the other hand, at low values of pH, the sulphonate groups of dye are protonated and the number of positively charged sites increases, inducing again electrostatic repulsion. Therefore, all experiments were performed at pH 6 that is the natural pH of DB78 aqueous solution.

3.7. Adsorption equilibrium isotherms

The adsorption isotherms of DB78 onto CD/EPI polymers were determined at pH 6 maintaining the systems at constant temperature of 25, 50 and 80°C. Various quantities of adsorbent, from 0.05 to 1.00 g, were added to 10 mL of dye (80.00 mg/L) and the adsorption process was maintained until the reaching of equilibrium state. The Langmuir and Freundlich values are listed in Table 2, respectively and the value of the linear regression correlation coefficient $R^2$ is used to determine the best-fit model. Based on $R^2$, the results show that the adsorption process with both polymers was better represented by Langmuir isotherm model than the Freundlich equation. The applicability of Langmuir isotherm describes a monolayer and homogeneous adsorption of the dye onto the surface of polymers, where the adsorption of each molecule onto the surface has equal adsorption activation energy [31]. These results agree with a study, reported in the literature [42], where some azo dyes have been removed by β-cyclodextrin-based polymers. Furthermore, these measurements show that increasing the temperature from 25 to 80°C induced a higher maximum adsorption capacity. Since the $R^L$ values were between 0 and 1, it possible to underline that β-CD/EPI and γ-CD/EPI polymers are good and favourable adsorbent for DB78 removal.

3.8. Thermodynamic analysis

The thermodynamic parameters for the adsorption of DB78 dye wastewater on β-CD/EPI and γ-CD/EPI polymers are summarised in Table 3. The negative values of $\Delta G^\circ$ indicated that the dye adsorption by these polymers is a spontaneous and a favourable process. Since the
obtained values of free energy change were in the range of $-9.85$ to $-12.01$ kJ mol$^{-1}$, for the β-CD/EPI polymer, and in range of $-11.26$ to $-14.25$ kJ mol$^{-1}$, for the γ-CD/EPI polymer, it is possible to affirm that the adsorption was principally physical. Indeed, some studies reported that the adsorption is classified as physical adsorption when the $\Delta G^\circ$ values range between $-20$ and $0$ kJ mol$^{-1}$, and as chemical adsorption when $\Delta G^\circ$ values range from $-80$ to $-400$ kJ mol$^{-1}$ [34]. The positive values of $\Delta S^\circ$, for both polymers, showed that the disorder of the systems increased at the solid solution interface during the adsorption of DB78 on polymers. Also, the $\Delta H^\circ$ values for β-CD/EPI and γ-CD/EPI polymers were $4.94$ and $1.86$ kJ mol$^{-1}$, respectively. These positive values indicate that the adsorption followed an endothermic process as in agreement with results derived from the isotherm measurements.

### 3.9. Thermal analysis

The thermal analysis of β-CD/EPI polymer, γ-CD/EPI polymer, and their respective polymers loaded with DB78 was performed with differential scanning calorimetry (DSC) under N$_2$ atmosphere with heating rate of 20°C/min. As shown in Figure 9a, the DSC thermograms of β-CD/EPI polymer exhibited an endothermic peak at about 280°C [43]. After the interaction of this polymer with DB78, the thermogram presented a double endothermic peak at about 250 and 280°C. Since the first signal corresponds to the decomposition temperature of the only dye, it is possible to affirm that DB78 exhibits a thermal instability even after adsorption. This result allows to hypothesise that the interaction between DB78 and the polymers did not occur only in the internal cavities of cyclodextrins but also in the pores present on the external surface of polymer. In Figure 9b, the DSC thermograms of γ-CD/EPI polymer loaded with DB78 were no longer exhibit the typical thermal decomposition phenomena, shown in the thermograms of DB78 and γ-CD/EPI polymer. It confirms the interaction between DB78 and γ-CD/EPI: the inclusion of the dye into the γ-CD by weak forces stabilises both the adsorbent and the adsorbate.

### 3.10. Morphologic study

CD-based polymers were observed by field emission scanning electron microscope (FESEM) to examine their morphology. In Figure 10a and c, FESEM images of unloaded β-CD/EPI and

| Polymers   | T (K) | $\Delta G^\circ$ (kJ mol$^{-1}$) | $\Delta S^\circ$ (J mol$^{-1}$ K$^{-1}$) | $\Delta H^\circ$ (kJ mol$^{-1}$) |
|------------|------|-------------------------------|----------------------------------------|----------------------------------|
| β-CD/EPI   | 298  | $-11.263$                     | 54.352                                 | 4.942                            |
|            | 323  | $-12.622$                     |                                        |                                  |
|            | 353  | $-14.252$                     |                                        |                                  |
| γ-CD/EPI   | 298  | $-9.847$                      | 39.266                                 | 1.860                            |
|            | 323  | $-10.907$                     |                                        |                                  |
|            | 353  | $-12.006$                     |                                        |                                  |

Table 3. Thermodynamic parameters.
**Figure 9.** Thermograms obtained by DSC analysis. (a) Thermograms of DB78, β-CD/EPI polymer and DB78 loaded β-CD/EPI polymer and (b) thermograms of DB78, γ-CD/EPI polymer and DB78 loaded γ-CD/EPI polymer.

**Figure 10.** Scanning electron microscopy images of polymers. (a) Unloaded β-CD/EPI polymer, (b) DB78 loaded β-CD/EPI polymer, (c) unloaded γ-CD/EPI polymer and (d) DB78 loaded γ-CD/EPI polymer.
γ-CD/EPI polymers are respectively showed. It is possible to observe that these materials presented a very porous, rough and irregular structure which cavities are able to adsorb the DB78 molecules. Moreover, the presence of loaded dye molecules on polymers did not affect significantly the morphology of the samples, as reported in Figure 10b and d, confirming the weak and physical interaction of adsorption process.

4. Conclusion

Results of adsorption show that β- and γ-CD/EPI polymers exhibited good adsorption properties towards azo dye Direct Blue 78 (Figure 11a) and the maximum efficiencies in dye removal, performed at pH 6, 25°C, with an initial dye concentration equal to 11.00 mg/L and using 1.00 g of adsorbents, were found to be about 99% for β-CD/EPI polymer and about 97% for γ-CD/EPI polymer, respectively. The proposed adsorption mechanism involved several kinds of interactions such as physical adsorption in the polymer network, hydrogen bonding and formation of inclusion complex due to the presence of CD molecules through host-guest interactions. As illustrated in Figure 11b, this adsorption method allows, after 2 h of treatment with polymers, to obtain clean water that could be reused in further industrial processes of fabric dyeing. Furthermore, these polymers could be promising adsorbents for industrial application due to their low cost of production and their possible recycling in different adsorption cycles.

Figure 11. Adsorption of DB78 (11.00 mg/L) onto β-CD/EPI polymer at pH 6 and at constant temperature of 25°C before and after 2 h of treatment. (a) Image of β-CD/EPI polymer before and after the adsorption process and (b) image of DB78 solution in presence of β-CD/EPI polymer before and after the adsorption process.

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Author details

Paola Semeraro¹, José Antonio Gabaldón², Paola Fini³, Estrella Núñez², José Antonio Pellicer², Vito Rizzi¹ and Pinalysa Cosma¹²*  
*Address all correspondence to: pinalysa.cosma@uniba.it

1 Department of Chemistry, University of Bari Aldo Moro, Bari, Italy  
2 Department of Food Technology and Nutrition, Catholic University San Antonio of Murcia, Murcia, Spain  
3 Department of Chemistry, National Research Council CNR-IPCF, UOS Bari, Bari, Italy

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