

## Dyes and Pigments

Volume 149, February 2018, Pages 736-746

### **Removing of Direct Red 83:1 using $\alpha$ - and HP- $\alpha$ -CDs polymerized with epichlorohydrin: Kinetic and equilibrium studies.**

José Antonio Pellicer<sup>a</sup>, María Isabel Rodríguez-López<sup>a</sup>, María Isabel Fortea<sup>a</sup>, José Antonio Gabaldón<sup>a</sup>, Carmen Lucas-Abellán<sup>a</sup>, María Teresa Mercader-Ros<sup>a</sup>, Ana Serrano-Martínez<sup>a</sup>, Estrella Núñez-Delicado<sup>a\*</sup>, Pinalysa Cosma<sup>b</sup>, Paola Fini<sup>c</sup>, Esther Franco<sup>d</sup>, Rocío García<sup>d</sup>, Marcela Ferrándiz<sup>d</sup>, Enrique Pérez<sup>e</sup>, Miguel Ferrándiz<sup>e</sup>.

<sup>a</sup>Dpto. de Ciencias de la Salud. Universidad Católica San Antonio de Murcia (UCAM), Avenida de los Jerónimos s/n, 30107 Guadalupe, Murcia, Spain.

<sup>b</sup>Università degli Studi “Aldo Moro” di Bari, Dip. Chimica, Via Orabona, 4, 70126 Bari, Italy.

<sup>c</sup>Consiglio Nazionale delle Ricerche CNR-IPCF, UOS Bari, Via Orabona, 4, 70126 Bari, Italy.

<sup>d</sup>Biotechnology Department, Textile Industry Research Association (AITEEX), Plaza Emilio Sala, 1, 03801 Alcoy, Spain.

<sup>e</sup>Colorprint Fashion, SL, Avda. Fco. Vitoria Laporta 104, 03830 Muro de Alcoy, Alicante, Spain.

<https://doi.org/10.1016/j.dyepig.2017.11.032>

© <2018>. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

## **Removing of Direct Red 83:1 using $\alpha$ - and HP- $\alpha$ -CDs polymerized with epichlorohydrin: Kinetic and equilibrium studies.**

José Antonio Pellicer<sup>a</sup>, María Isabel Rodríguez-López<sup>a</sup>, María Isabel Fortea<sup>a</sup>, José Antonio Gabaldón<sup>a</sup>, Carmen Lucas-Abellán<sup>a</sup>, María Teresa Mercader-Ros<sup>a</sup>, Ana Serrano-Martínez<sup>a</sup>, Estrella Núñez-Delicado<sup>a\*</sup>, Pinalysa Cosma<sup>b</sup>, Paola Fini<sup>c</sup>, Esther Franco<sup>d</sup>, Rocío García<sup>d</sup>, Marcela Ferrándiz<sup>d</sup>, Enrique Pérez<sup>e</sup>, Miguel Ferrándiz<sup>e</sup>.

<sup>a</sup>Dpto. de Ciencias de la Salud. Universidad Católica San Antonio de Murcia (UCAM), Avenida de los Jerónimos s/n, 30107 Guadalupe, Murcia, Spain.

<sup>b</sup>Università degli Studi “Aldo Moro” di Bari, Dip. Chimica, Via Orabona, 4, 70126 Bari, Italy.

<sup>c</sup>Consiglio Nazionale delle Ricerche CNR-IPCF, UOS Bari, Via Orabona, 4, 70126 Bari, Italy.

<sup>d</sup>Biotechnology Department, Textile Industry Research Association (AITEC), Plaza Emilio Sala, 1, 03801 Alcoy, Spain.

<sup>e</sup>Colorprint Fashion, SL, Avda. Fco. Vitoria Laporta 104, 03830 Muro de Alcoy, Alicante, Spain.

\* Corresponding author:

Phone: +34 968 278 689

E-mail: enunez@ucam.edu

**HIGHLIGHTS**

- The adsorption of Direct Red 83:1 was performed using cyclodextrin polymers
- The adsorption capacity was higher (93%) for  $\alpha$ -CDs polymer
- The adsorption kinetics was controlled by pseudo second order model
- Freundlich isotherm presented the best fit to the experimental data

**ABSTRACT**

The adsorption properties of two cyclodextrin-epichlorohydrin polymers to remove Direct Red 83:1 textile dye from wastewater solutions was evaluated. Adsorption studies were performed in a batch reactor, and the efficiency of the polymers under different parametric values such as contact time, adsorbent dosage, initial dye concentration, pH of initial solution and temperature was followed by spectrophotometry. Both Langmuir and Freundlich equations were used to fit the equilibrium isotherms and the kinetic data were analyzed by the pseudo-first-order and pseudo-second-order models. Adsorption process follows a pseudo-second-order kinetic and was influenced by intra particle diffusion model, dye concentration and contact time, reaching equilibrium within the first 30 minutes. Experimental data were better fitted to Freundlich isotherm model than to Langmuir and Temkin isotherms. Since about 93% of dye removal was achieved under optimized conditions, the  $\alpha$ -cyclodextrin-epichlorohydrin polymer seems to be a useful device for removing Direct Red 83:1 from aqueous solutions and industrial effluents.

**KEYWORDS**

Absorption; Direct Red; Cyclodextrins; Epichlorohydrin; Kinetics; Isotherm

**1. Introduction**

Nowadays, pollution due to industrial wastewater is one of the most important issues that affect the environment. Among the different industries, the textile factories produce high quantities of water polluted with a variety of chemicals, including dyes. According to the literature, the total production of textile dyes is over 10,000 tonnes/year, being 100 tonnes/year the amount of dyes discharged into wastewater [1-2], that provoke serious drawbacks in environmental compartments.

There is a wide variety of dyes used in the textile industry, azo dyes being the most employed. The application of this kind of dyes represents approximately 60% of the total, followed by the anthraquinone group. Azo dyes can be divided into monoazo, disazo or trisazo depending on the number of azo units in their structure, all conjugated with aromatic or heteroaromatic rings [3].

It is well known that many azo dyes are toxic, mutagenic and carcinogenic to wildlife and humans [4]. Therefore, the removal of dyes from industrial effluents is a fundamental issue, and appropriate treatments of wastewater should be done to decrease the environmental impact and its wildlife collateral effects.

Current methodology employed to reduce this problem, deals with a combination of chemical, physical and biological techniques. In this sense, adsorption, membrane-filtration, coagulation, flocculation, flotation, precipitation, oxidation, aerobic and anaerobic microbial degradation processes, have been developed for the removal of dyes from industrial effluents [5]. However, some of these approaches are expensive, have a very low efficiency or seem to be impracticable because of the production of toxic by-products [6]. On the contrary, it has been proved that adsorption is one of the most effective and cheap methods which industries employ to reduce hazardous pollutants presents in the effluent [7]. Indeed, synthesis and design of new adsorbent materials are now being studied. In this context, supramolecular chemistry has provided important

support in the research for innovative material able to removal of azo dyes from aqueous solutions [8].

Considering their excellent adsorbent ability and easily dissociation from guest molecules, cyclodextrins or their derivatives could be used to synthesize supramolecular polymeric cyclodextrins systems, emerging as an interesting material class with attractive properties and a wide range of emerging applications, supporting a viable solution for pollutant removal from wastewater.

There are three native CDs, including  $\alpha$ -CDs, a six-membered sugar ring molecule,  $\beta$ -CDs, a seven-membered sugar ring molecule and  $\gamma$ -CDs, an eight-membered sugar ring molecule [9]. The main characteristic of these compounds is the presence of an inside cavity with hydrophobic properties and a hydrophilic outside. This conformation permits CDs to form non covalent host/guest inclusion complexes with organic and hydrophobic compounds. In addition, CDs have the ability to form polymers by assembling to other CDs monomers leading to a polymeric network structure [10]. Cross-linking of biopolymers such as CDs, offers a simple method to modify the physicochemical properties of these materials (e.g. absorption and hydration properties) because of the alteration of the surface area and surface chemical properties of the polymer [11]. One of the most common cross-linking agents used to obtain insoluble CDs-based polymers is epichlorohydrin (1-chloro-2,3-epoxypropane), designed as EPI [12]. This crosslinker is a bi-functional agent which contain two reactive functional groups, an epoxide group and a chloroalkyl moiety. Therefore, it can form bonds with polysaccharide molecules in a cross-linking step and / or with itself in a polymerization step.

On the other hand, the numerous hydroxyl groups, present at the 2-, 3- and 6-positions in the glucose units of native CDs, are available and reactive to form linkages. The -OH groups in the 6-positions are more reactive than those in 3-positions; however their

reactivity depends on the reaction conditions, such as temperature and alkalinity [13]. Indeed, the secondary hydroxyl groups, which have pKa values of around 12.2 (at 298 °K), can be deprotonated with hydroxide or hydride. Consequently, typical methods used to synthesize CDs-based polymers needs strong alkaline conditions to achieve deprotonation of the –OH groups (cyclodextrin dissolution in water followed by addition of NaOH, NaH, or NaBH<sub>4</sub>) [14]. Generally, this mixture needs either stirring for several hours or elevated temperatures, in order for EPI to react with the alkoxide to form intra or inter linkages [15]. Then the required amounts of cross-linking agent are added dropwise and the system is vigorously stirred.

Despite the  $\beta$ -CDs are the most common cyclodextrins used to produce CDs-based polymers, in this paper  $\alpha$ - and HP- $\alpha$ -CDs were employed and their respective polymers, synthesized by EPI as cross-linker, were utilized as adsorbent material to remove an azo textile dye (Direct Red 83:1), from aqueous solutions. According to this approach, the influence of contact time, adsorbent dosage, initial dye concentration, pH of initial solution and temperature was investigated. Furthermore, the isotherm and kinetic models were evaluated and the thermodynamic data were determined to understand the physicochemical process implicated in the adsorption of this dye. Finally, the structural properties of the polymers were investigated using SEM analysis.

## **2. Materials and methods**

### **2.1. Chemicals**

$\alpha$ - and HP- $\alpha$ -CDs were purchased from AraChem (The Netherlands), sodium borohydride, sodium hydroxide, epichlorohydrin and acetone were from Sigma-Aldrich (Spain). Direct Red 83:1 was kindly provided by AITEX (Asociación de Investigación de la Industria Textil, Alcoy, Spain).

### **2.2. Polymer synthesis**

The ( $\alpha$ - and HP- $\alpha$ )-CD-EPI polymers were prepared following the protocol described by Renard et al. [16], with slight modifications. Briefly, 60 mg of sodium borohydride were mixed with 24 g of each CDs, in 24 mL of water. After stirring for 10 minutes at 50 °C, 26 mL of sodium hydroxide (40%) were added to the solution and this was stirred 5 minutes. After this time, 264 g of EPI were added drop wise, this mixture was stirred for 6 hours at 50 °C until the solution becomes a polymer. The polymer was washed with 100 mL of acetone for 10 minutes. Finally, the polymer was dried in an oven overnight at 50 °C.

### 2.3. Dye solution preparation

To carry out adsorption experiments, various concentrations of Direct Red 83:1 were prepared. Direct Red is an azo dye (CAS 90880-77-6) whose formula is  $C_{33}H_{20}N_6Na_4O_{17}S_4$  (Fig. 1) and its molecular weight is 992.77 (95% purity; Colorprint, Alcoy, Spain). The concentrations of Direct Red 83:1 used to evaluate the absorption capacity of the different polymers were: 25, 50, 75, 100, 150, 200, 250 and 300 mg/L.

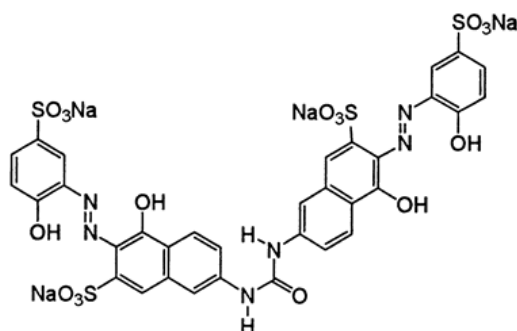


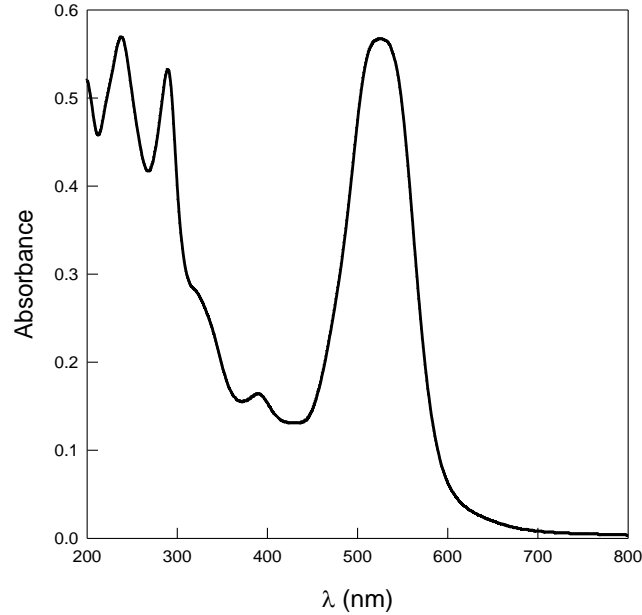
Fig. 1

### 2.4. Analyses and data evaluation

After equilibrium was reached, the supernatant was collected to determine the dye concentration using a spectrophotometer (Shimadzu UV-1603). The absorbance was



measured before (as control), and after the treatment with the polymers at the maximum absorbance of the dye ( $\lambda_{\text{max}} = 526 \text{ nm}$ ;  $\epsilon_{526} = 1065 \text{ M}^{-1}\text{cm}^{-1}$ ) (Fig. 2).



**Fig. 2**

## 2.5. Sorption studies

Sorption tests were carried out at 25 °C using batch equilibrium technique in flasks containing 50 mL of a fixed polymer amount (1 g) and different amounts of dye (from 25 mg/L to 300 mg/L). After stirring at 500 rpm in a thermostatic water-bath until the equilibrium was reached, at a fixed time interval (10 minutes) a sample of each flask was centrifuged (4000 rpm, 5 min), and UV-vis measurements of the supernatant were carried out using a Shimadzu UV-1603 spectrophotometer.

The amount of dye adsorbed on the polymers ( $q_t$ ), in mg/g, was determined by a mass balance relationship [17], following the equation (1):

$$q_e = \frac{V(C_o - C_e)}{m} \quad (1)$$

where  $C_o$  and  $C_e$  are the initial and final solution concentration of dye (mg/L) respectively,  $V$  (L) the volume of dye solution used, and  $m$  (g) is the dry mass of polymer utilized. The experiments were carried out in triplicate.

## 2.6. Adsorption kinetics

For adsorption studies, it is necessary to know the kinetics of the process in order to predict the rate at which a target pollutant is removed from aqueous solutions. To determine the best-fit model for the adsorption of dye onto CDs-EPI polymers, the pseudo first order, pseudo second order and intraparticle diffusion models were evaluated using the experimental data.

The pseudo first order rate of Lagergren [18] is given by the equation (2):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

where  $q_e$  and  $q_t$  are the amounts of dye adsorbed per mass of adsorbent at equilibrium (mg/g) respectively, at a time  $t$  (min) and  $k_1$  ( $\text{min}^{-1}$ ) is the pseudo first order rate constant. Values of  $k_1$  were worked out from the plot of  $\ln(q_e - q_t)$  versus  $t$ .

The adsorption kinetics of the dye was investigated with pseudo second order model [19], which is expressed by the following equation (3):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where  $q_e$  and  $q_t$  represent the amount of dye adsorbed on adsorbent (mg/g) at equilibrium at any time  $t$  (mg/g), respectively, and  $k_2$  is the equilibrium rate constant of pseudo second order adsorption ( $\text{g/mg min}$ ). The initial adsorption rate,  $v_0$  ( $\text{mg/g min}$ ) of the dye was also calculated from the pseudo-second-order model using  $[v_0 = k_2 (q_e)^2]$ .

The slope and intercept of the plot of  $t/q_t$  versus  $t$  were used to calculate  $k_2$  and  $q_e$  (rate parameters).

Finally, the kinetic results were analysed using the intra particle diffusion model to clarify the absorption behaviour of Direct Red on CDs-EPI polymers. This model is significant to know the rate determining step in the liquid adsorption systems. The rate limiting step may be either the boundary layer (film) or the intraparticle diffusion (pore) of solute on the solid surface from bulk of the solution in a batch process. In diffusion studies, the rate is expressed in terms of the square root time. According to the intraparticle diffusion model proposed by Weber and Morris [20], the root time dependence could be expressed by the following equation (4):

$$q_t = k_i \sqrt{t} + C \quad (4)$$

where  $q_t$  is the amount of solute on the surface of the sorbent at time  $t$  (mg/g),  $k_i$  the intraparticle diffusion rate constant (mg/g min<sup>1/2</sup>),  $t$  the time and  $C$  is the intercept (mg/g). The  $k_i$  values are determined from the slopes of  $q_t$  versus  $t^{1/2}$  plots.

## 2.7. Isotherm analysis

The absorption isotherm indicates how the adsorbing molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. In order to optimize the design of an adsorption system to remove Direct Red 83:1 from aqueous solutions, it is essential to determine the most appropriate correlation for the equilibrium studies. Although there are different sorption models, for this study Freundlich, Langmuir and Temkin isotherms were fitted to the experimental data.

The Freundlich adsorption isotherm is an empirical equation which describes heterogeneous systems that have unequal available sites on adsorbent surface with different adsorption energies [21]. The Freundlich model can be represented by the linearised form by the following equation (5):

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \quad (5)$$

where  $q_e$  is the equilibrium dye concentration on adsorbent (mg/g),  $C_e$  the equilibrium dye concentration in solution (mg/L),  $K_F$  the Freundlich constant (L/g) and  $1/n_F$  is the heterogeneity factor. The plot of  $\ln q_e$  versus  $\ln C_e$  was used to determine the intercept value of  $K_F$  and the slope of  $1/n_F$ .

On the other hand, Langmuir isotherm model considers that the adsorption process takes place on homogeneous sites of adsorbent polymer surface forming a saturated monolayer phase of adsorbate dye on the outer surface of adsorbent without interaction between adsorbed molecules [22]. The linearised form of the model is given by the following equation (6):

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (6)$$

where  $C_e$  (mg/L) and  $q_e$  (mg/g) are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium respectively.  $K_L$  (L/g) and  $a_L$  (L/mg) are the Langmuir isotherm constants. Plotting  $C_e/q_e$  versus  $C_e$  is possible to know the value of  $K_L$  from the intercept ( $1/K_L$ ) and the value of  $a_L$  from the slope ( $a_L/K_L$ ).  $q_{max}$  is the maximum adsorption capacity of the polymer and is defined by  $K_L/a_L$ .

The most important characteristics of this isotherm can be described using a dimensionless constant ( $R_L$ ) which is called separation factor and is described by the following equation (7):

$$R_L = \frac{1}{1 + a_L C_o} \quad (7)$$

where  $C_o$  is the initial concentration of dye (mg/L) and  $a_L$  is the Langmuir constant (L/mg). The value of  $R_L$  indicates the form of the adsorption process, being  $R_L > 1$  an unfavourable process, linear for  $R_L = 1$ , favourable for  $R_L$  between 0 and 1 or irreversible for  $R_L = 0$ .

Moreover, Temkin isotherm model considers the interactions between the pollutant and the polymer and assumes that, unlike suggested by Freundlich model, fall in the heat of adsorption is linear rather than logarithmic [23]. The linearized form of the model is given by the following equation (8):

$$q_e = \frac{RT}{b_T} \ln a_T + \frac{RT}{b_T} \ln C_e \quad (8)$$

where  $b_T$  is the Temkin constant, related to the heat of absorption (kJ/mol),  $a_T$  is the constant of Temkin isotherm (L/g),  $R$  the universal gas constant (8.314J/mol K) and  $T$  is the absolute temperature in Kelvin.

## **2.8. Scanning Electron Microscopy (SEM) analysis**

Images of dried powders were recorded by a MERLIN VP COMPACT scanning electron microscope (SEM, Zeiss, Germany), and were used to evaluate the morphology of the obtained polymers. Samples were fixed onto SEM stubs with double sided adhesive carbon tapes, and the surface was coated with a thin layer of gold and examined at 15kV.

## **3. Results and discussion**

### **3.1. Effect of contact time**

The first step was directed to optimise the best experimental conditions to achieve an effective adsorption process. For that, adsorption processes were performed by batch mode experiments adding specific amount of adsorbent to fixed volume of dye solutions in controlling condition of agitation rate, pH and temperature. Every 10 minutes, the residual dye concentration was determined at the maximum absorption wavelength ( $\lambda_{max}$ ) of UV-Vis absorption spectra. Influence of different variables, including contact time, polymer dosage, initial dye concentration, pH and stirring rate were evaluated. These experiments were performed by varying the parameter under evaluation, while all other parameters were maintained constant. The best results to accomplish the effect of

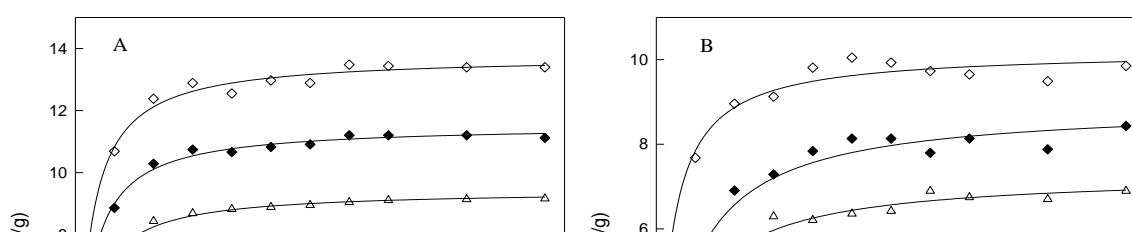
contact time, adsorption kinetics as well as the absorption equilibrium (data not shown), were achieved at pH 7.0, using 1.0 g of polymer and a controlled agitation (500 rpm).

Using optimised conditions, sorption experiments were conducted to compare the effectiveness of both CDs-EPI polymers in the removal of target azo dyes from spiked aqueous solutions at different concentrations (from 25 to 300 mg/L). The absorption percentage for  $\alpha$ -CDs-EPI presented an average of 92.8% when the concentrations of Direct Red 83:1 varied from 25 to 150 mg/L, noting that when the dye concentration increases above 300 mg/L only a loss of 4% of the absorption capacity was observed.

In the case of HP- $\alpha$ -CDs-EPI, although the absorption capacity was significantly lower, a similar behaviour that previously described for  $\alpha$ -CDs-EPI was observed 75.5% (from 25 to 150 mg/L), decreasing its absorption capacity by 7% at high concentrations of dye (67.8% for 300 mg/L), the average was and 67.8% with the highest concentrations. These results indicating that the adsorption capacity of the polymer is inversely proportional to the concentration of dye present in the reaction medium.

The absorption data of  $\alpha$ -CDs-EPI and HP- $\alpha$ -CDs-EPI polymers for the removing of different concentrations of dye Direct Red 83:1 (from 25 to 300 mg/L) versus contact time is shown in Fig. 3.

As can be observed in Fig. 3a and 3b, the absorption capacity increased with concentration until the equilibrium is reached, indicating that the absorption of dye on the polymer stopped. When this point is reached, the amount of absorbed dye inside the polymer is in a dynamic equilibrium with the amount of dye desorbed. The time needed to reach this point is called equilibrium time, and the amount of dye removed by the polymer at this point indicates the maximum absorption capacity of each polymer in these conditions [13].



**Fig. 3**

Different absorption phases may be differentiated in the range of concentrations analyzed (25-300 mg/L). In this sense, the absorption process increased rapidly in the first stages of contact between Direct Red 83:1 and the polymers, due to the fast union between the dye and the polymer surface. The absorption is continuous until the equilibrium is reached, note that after 30 minutes of contact time approximately, the adsorption process evolves asymptotically. In resume, the absorption process could be considered fast due to the largest amount of dye absorbed inside the polymer within the first 30 minutes because of surface mass transfer. It is important to remark that an increase in the initial concentration of dye brings about increased dye removal, confirming the strong interaction between Direct Red and CDs-EPI polymers.

Fig. 3 showed that in the whole range of concentrations analyzed,  $\alpha$ -CDs-EPI polymer presented higher values of  $q_t$  than HP- $\alpha$ -CDs-EPI. The maximum amounts of dye absorbed ranged from 1.1 to 13.4 for  $\alpha$ -CDs-EPI and from 0.9 to 10.0 for HP- $\alpha$ -CDs-EPI (see Table 1).

**Table 1.** Quantity (mg/g) of dye absorbed depending on the polymer.

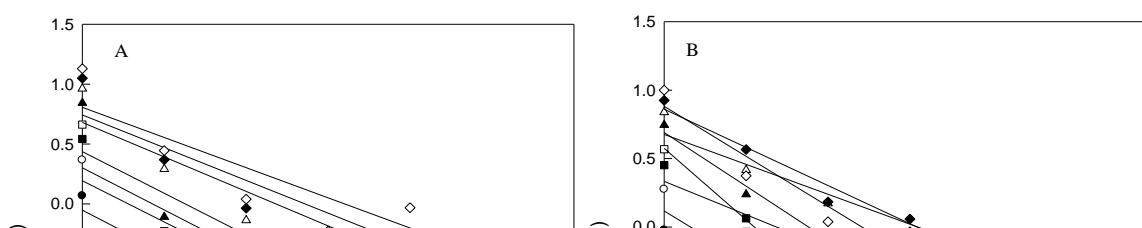
		Direct Red 83:1 concentrations (mg/L)							
Polymer		25	50	75	100	150	200	250	300
qt (mg/g)	$\alpha$ -	1.1	2.3	3.5	4.6	6.9	9.1	11.2	13.4
	HP- $\alpha$ -	0.9	1.9	2.8	3.7	5.5	6.9	8.4	10.0

### 3.2. Adsorption kinetics

The isotherm describes the equilibrium between the concentration of the adsorbate on the solid phase and the concentration in the liquid phase. The equilibrium biosorption data have been analyzed using the Langmuir,

With the objective to determine the different mechanisms implicated in the absorption process of Direct Red and the CDs-EPI polymers, such as absorption surface, mass transfer or intraparticle diffusion, the equilibrium sorption data obtained by optimised conditions have been analyzed using pseudo first order, pseudo second order and the intraparticle diffusion models. Such analysis is important to develop a relation that accurately represents the experimental results and could be used for further design purposes. Fig. 4 showed the fitting of the experimental data to the pseudo first order model with both polymers in contact with Direct Red.

The parameters obtained for this model could be observed in Table 2. The goodness of the adjustment of this model was expressed using the linear regression coefficients ( $R^2$ ); a relatively high value indicates that the data fits properly to the model. The linearity of the model ( $\log (q_e - q_t)$  versus  $t$ ) was plotted in the first 60 minutes of contact. The  $R^2$  values for  $\alpha$ -CDs-EPI ranged from 0.777 to 0.876 and between 0.880 and 0.984 for HP- $\alpha$ -CDs-EPI. Despite the fact that some values were relatively high, the  $q_e$  values calculated with this model were not adequate and reasonable.





**Fig. 4**

This finding suggests that the absorption process was not correctly explained by a pseudo first order model. In addition, this model only fitted to the experimental data in the first minutes of the adsorption process (60 minutes approximately), from this moment the experimental data differ from the theoretical ones, decreasing  $R^2$  values.

This fact indicates that the model is only suitable for the first stages of absorption, since the absorption of dye by the polymer is fast. Thus, a new adjustment was carried out using a pseudo second order model (Fig. 5).

**Table 2.** Kinetics parameters for the pseudo first order model.

Pseudo first order model								
$\alpha$ -CDs-EPI					HP- $\alpha$ -CDs-EPI			
Co (mg/L)	$q_{eexp}$	$q_{ecal}$	$k_l$ ( $\text{min}^{-1}$ )	$R^2$	$q_{eexp}$	$q_{ecal}$	$k_l$ ( $\text{min}^{-1}$ )	$R^2$
25	1.168	0.458	0.076	0.832	0.948	0.676	0.069	0.967
50	2.327	0.887	0.081	0.833	1.885	1.309	0.084	0.976
75	3.485	1.559	0.079	0.876	2.826	2.152	0.056	0.922
100	4.598	1.999	0.080	0.865	3.704	3.749	0.120	0.969
150	6.971	2.728	0.080	0.839	5.561	4.897	0.090	0.938
200	9.165	4.786	0.066	0.875	6.896	4.742	0.050	0.880
250	11.204	5.520	0.062	0.827	8.432	7.244	0.064	0.984
300	13.478	6.397	0.058	0.777	10.05	7.603	0.084	0.942

As could be seen, the plot of  $t/q_t$  versus  $t$  produced straight lines in the whole range of measure.  $R^2$  and  $q_e$  values obtained, confirmed the best-fit of model to the experimental data. In the majority of the cases, the  $R^2$  values were 0.99 or higher. In addition, the experimental  $q_e$  values were close to  $q_e$  data obtained by applying theoretical model.

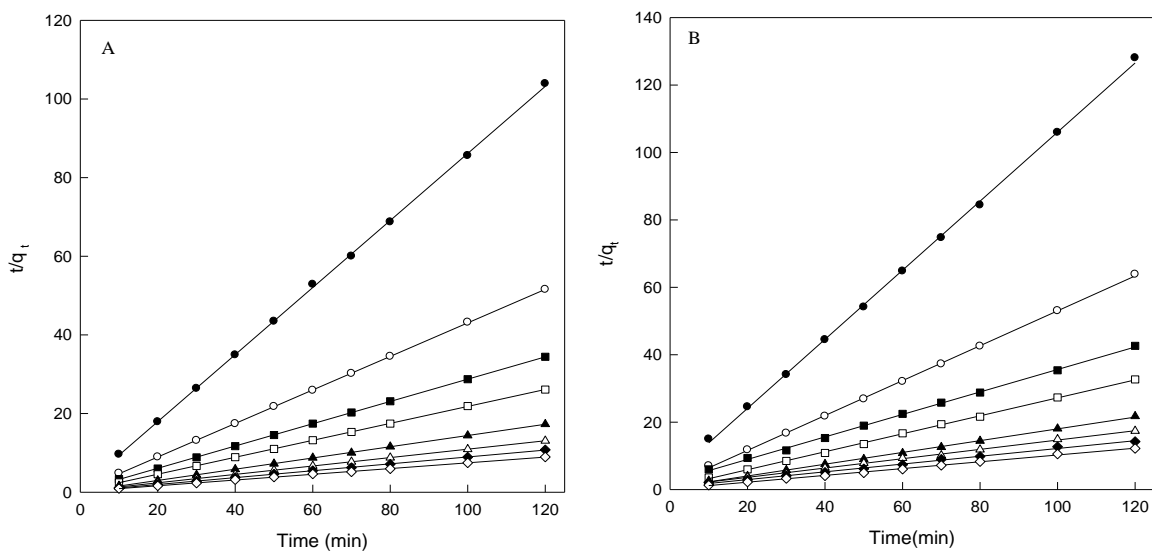


Fig. 5

The initial rapid phase may be due to an increase in the number of available vacant sites. At lower concentrations, dye molecules present in the adsorption medium could interact with the binding sites, hence a higher rate constant was obtained. At higher concentrations, because of the saturation of the adsorption sites, the rate constant of dye absorption onto the CDs-EPI polymer shows a decreasing trend (Table 3).

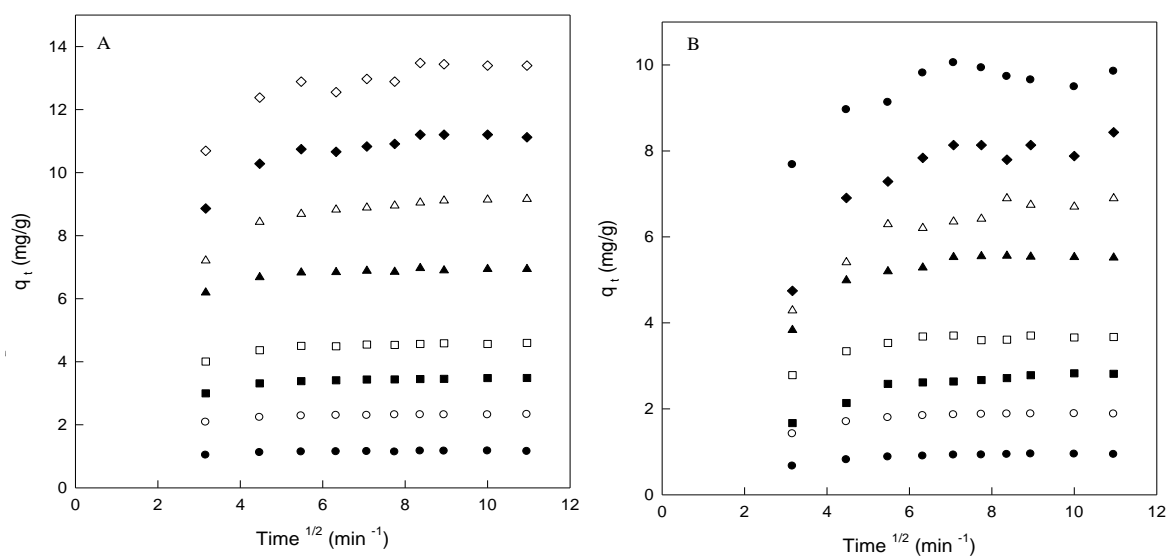
**Table 3.** Kinetics parameters for the pseudo second order model.

Pseudo second order model								
$\alpha$ -CDs-EPI					HP- $\alpha$ -CDs-EPI			
(mg/L)	$q_{eexp}$	$q_{ecal}$	$k_2$ (g/mg min)	$R^2$	$q_{eexp}$	$q_{ecal}$	$k_2$ (g/mg min)	$R^2$
25	1.168	1.173	0.82	0.999	0.948	0.976	0.292	0.999
50	2.327	2.347	0.43	0.999	1.885	1.934	0.209	0.999
75	3.485	3.533	0.19	0.999	2.826	3.0	0.048	0.999
100	4.598	4.651	0.16	0.999	3.704	3.759	0.127	0.999
150	6.971	7.042	0.14	0.999	5.561	5.747	0.057	0.999
200	9.165	9.433	0.041	0.999	6.896	7.246	0.022	0.998
250	11.204	11.494	0.036	0.999	8.432	8.695	0.020	0.995
300	13.478	13.888	0.027	0.999	10.05	9.910	0.064	0.998

These results suggested that the absorption process of Direct Red is controlled by the pseudo second order model and thus supports the main conclusion of this model that the absorption is due to chemisorption. The absorption is carried out by surface exchange reactions, Direct Red molecules diffuse inside the polymer where inclusion complexes, hydrogen bonds or hydrophobic interactions could take place. Similar kinetics were also observed in the absorption of methylene blue on papaya seeds [24], malachite green onto polylactide/spent brewery grains films [25], or Congo red dye on cattail root [26] and *Eichhornia crassipes* roots [27].

The absorption is a multi-step process with different stages implicated; firstly, there is a transport of dye molecules from the aqueous solution to the surface of the polymer, followed by the diffusion of dye molecules onto the polymer.

An intra-particle diffusion model was used to identify the diffusion mechanism. The plots of dye absorbed versus the square root of time (Fig. 6) for both polymers, indicating the existence of two different stages during the sorption process.



**Fig. 6**

The first sharp stage represents the transfer (effect of the boundary layer) of dye from the solution to the outer surface of the  $\alpha$ - and HP- $\alpha$ -CDs-EPI polymer (quick external diffusion); the second gradual stage can be attributed to the penetration of dye into the interlayer of the sorbent where the intra-particle diffusion is rate limiting.

The intra-particle diffusion rate constant ( $k_i$ ), which is the slope of the linear zone, is gathered in Table 4, whereas the intercept of each curve is proportional to the boundary layer thickness.

**Table 4.** Kinetics parameters for the intraparticle diffusion model.

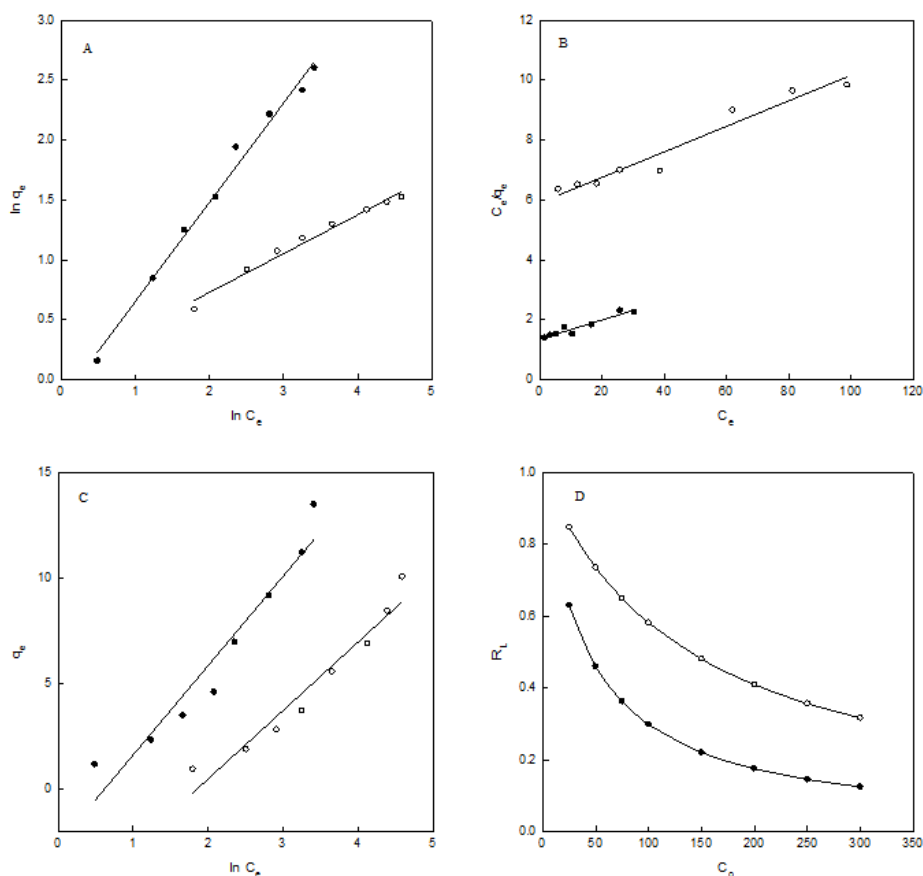
Intraparticle diffusion model								
$\alpha$ -CDs-EPI					HP- $\alpha$ -CDs-EPI			
Co (mg/L)	$q_{eexp}$	$q_{ecal}(C)$	$k_i(\text{mg/g min}^{1/2})$	$R^2$	$q_{eexp}$	$q_{ecal}(C)$	$k_i(\text{mg/g min}^{1/2})$	$R^2$
25	1.168	1.114	0.004	0.447	0.948	0.837	0.010	0.721
50	2.327	2.247	0.007	0.800	1.885	1.749	0.013	0.677
75	3.485	3.301	0.017	0.946	2.826	2.302	0.049	0.943
100	4.598	4.398	0.018	0.812	3.704	3.532	0.013	0.179
150	6.971	6.716	0.021	0.607	5.561	5.026	0.053	0.507
200	9.165	8.259	0.088	0.933	6.896	5.519	0.128	0.734
250	11.204	10.15	0.102	0.705	8.432	6.917	0.127	0.477
300	13.478	11.921	0.148	0.626	10.05	9.412	0.36	0.530

In general,  $k_i$  values increased with increasing concentrations of Direct Red. The  $R^2$  values were very different depending on the concentration and polymer. However, it is important to remark that the results obtained for each curve do not pass through the origin and because of this circumstance, each polymer presented different intercepts, ranging from 1.1 to 11.9 mg/g for  $\alpha$ -CDs-EPI and from 0.8 to 9.4 mg/g for HP- $\alpha$ -CDs-EPI. This result indicated that the intraparticle diffusion plays an important role in the absorption process, but it is not the unique mechanism implicated in the process. The  $C(q_e)$  values obtained gave information about the thickness of the boundary layer; a higher intercept indicates a higher effect of it. This value increased with increasing dye concentrations (see Table 4).

### 3.3. Adsorption equilibrium

The equilibrium isotherms for the adsorption of dye in the CDs-EPI polymers at 25 °C are presented in Fig. 7. The equilibrium data are fitted by Langmuir, Freundlich and

Temkin adsorption isotherm models. As can be seen in the representation of the Freundlich isotherm (plot of  $\ln q_e$  versus  $\ln C_e$ ), both polymers increase in adsorption capacity when increase in equilibrium dye concentration, showing a linear tendency (Fig. 7a).



**Fig. 7**

The parameters  $K_F$ ,  $n_F$  and  $R^2$  were calculated using these straight lines. For  $\alpha$ -CDs-EPI, the value of the Freundlich constant ( $K_F$ ) was 0.838 (L/g), whereas this value was 1.082 (L/g) for HP- $\alpha$ -CDs-EPI (Table 5).

Apart from this parameter, the value of Freundlich exponent ( $n_F$ ) was determined, obtaining 1.207 for  $\alpha$ -CDs-EPI and 3.086 for HP- $\alpha$ -CDs-EPI (Table 5). When the value of  $n_F$  is in the range between 1-10 indicates a favourable absorption process, a fact that

was confirmed by the experimental data obtained for both polymers. Finally, the values of  $R^2$  were 0.989 for  $\alpha$ -CDs-EPI and 0.980 for HP- $\alpha$ -CDs-EPI (Table 5).

**Table 5.** Absorption isotherm constants.

<b>Isotherm</b>	<b>Parameters</b>	<b><math>\alpha</math>-CDs-EPI</b>	<b>HP-<math>\alpha</math>-CDs-EPI</b>
<b>Freundlich</b>	$K_F$	0.838	1.082
	$n_F$	1.207	3.086
	$R^2$	0.989	0.980
<b>Langmuir</b>	$q_{max}$	31.5	23.41
	$K_L$	0.74	0.169
	$a_L$	0.0235	0.00721
	$\Delta G$	0.746	4.40
	$R^2$	0.913	0.950
	$R_L$	0.629-0.124	0.847-0.316
<b>Temkin</b>	$a_T$	0.540	0.157
	$b_T$	0.586	0.765
	$R^2$	0.931	0.944

The experimental data obtained were also fitted to the Langmuir isotherm. The plot of  $C_e/q_e$  versus  $C_e$  gave a straight line for both polymers (Fig. 7b). The slope is  $a_L/K_L$ , the intercept  $1/K_L$  and the parameter  $q_{max}$  is  $K_L/a_L$  which is the maximum absorption capacity of each polymer (mg/g). The different parameters obtained for this isotherm may be observed in Table 5, being  $q_{max}$  one of the most interesting parameters of this model. The value obtained for  $\alpha$ -CDs-EPI was 31.50 mg/g and 23.41 for HP- $\alpha$ -CDs-EPI. This result indicated that  $\alpha$ -CDs-EPI presented better absorption capacity of Direct Red than its modified cyclodextrin. Finally, the adsorption isotherm data are better fitted to the Freundlich isotherm model ( $R^2 \geq 0.98$ , for both sorbents) compared to the Langmuir model since  $R^2$  values were significantly lower, 0.913 for  $\alpha$ -CDs-EPI and 0.950 for HP- $\alpha$ -CDs-EPI (see Table 5).

**Table 6.** Comparison of the adsorption properties of different cyclodextrin polymers.  
**GNS:** graphene, **AH:** anhydride, **CA:** citric acid, **EPI-CMC:** epichlorohydrin-carboxymethylcellulose,

Dye	Polymer	$q_{\max}$ (mg/g)	Reference
Phenolphthalein	$\beta$ -CDs-GNS	468	[28]
Methylene Blue Rhodamine B	$\beta$ -CDs-AH	333 250	[29]
Methylene Blue	$\beta$ -CDs-CA	105	[30]
Malachite Green	$\beta$ -CDs-EPI-CMC	91.9	[31]
Methylene Blue	$\beta$ -CDs-CA-WF	86.2	[32]
Methyl Orange	GO-IPDI-CDs	83.4	[33]
Basic Fuchsin	$\beta$ -CDs-CMC-GO	58.6	[34]
Basic Blue 9	$\beta$ -CDs-EPI-CMC	56.5	[35]
Methyl Blue	$\beta$ -CDs/g-C <sub>3</sub> N <sub>4</sub>	47.6	[36]
Congo Red	$\beta$ -CDs-HMDI	36.2	[37]
Reactive dyes	CDs-MIPs	35	[38]
Direct Red 83:1	$\alpha$ -CDs-EPI	31.5	This work
Xylenol Orange	$\gamma$ -CDs-CMC	29.9	[39]
Direct Red 83:1	HP- $\alpha$ -CDs-EPI	23.4	This work
Eriochrome Black T	$\beta$ -CDs-PU	20.1	[40]
Phenolphthalein	Cellulose-EPI	16.9	[11]
2-chlorophenol	$\beta$ -CDs-CS	14.5	[41]
Evans Blue	$\beta$ -CDs-HMDI	10.5	[42]
Brilliant Yellow	HP- $\beta$ -CDs-CS	8.8	[43]

**CA-WF:** citric acid-wood flour, **GO-IPDI:** graphene oxide-isophorone diisocyanate, **g-C<sub>3</sub>N<sub>4</sub>:** graphite carbon nitride, **HMDI:** hexamethylene diisocyanate, **MIPs:** molecularly imprinted polymers, **PU:** polyurethane, **CS:** chitosan.



The best form to compare the adsorption capacity of different polymers is to evaluate the  $q_{\max}$  parameter obtained with the Langmuir isotherm. The deep revision of the literature of different CD-polymers could be observed in Table 6. The wide variety of crosslinking agents and CDs make difficult the comparison, however, the results for EPI polymers are similar, taking into account that different dyes were employed in the related studies.

This finding suggested that the Freundlich model yielded a much better fit than the Langmuir model for the absorption of Direct Red. The fact that the latter model better describes absorption is consistent with the presence of heterogeneous absorption sites on the CDs-EPI surfaces, a reasonable observation taking into account the SEM analysis (Fig. 8). This trend was similar in other articles, for example using chitosan and activated clay [44], in the absorption of methylene blue [45] or in the removal of Congo Red [46]. In the case of the Langmuir isotherm the absorption process is considered favourable or not depending on the results obtained for a dimensionless constant called the separation factor ( $R_L$ ) Fig.7d. Taking into account that  $R_L$  value indicates whether the type of the isotherm is favourable ( $0 < R_L < 1$ ), unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), or irreversible ( $R_L = 0$ ), since the results obtained for  $\alpha$ -CDs-EPI (0.629-0.124) and HP- $\alpha$ -CDs-EPI (0.847-0.316) were between 0-1, indicates that the absorption process is favourable (Table 5).

Finally, the experimental data were analyzed using the Temkin isotherm. The equation of this model assumes that the heat of absorption diminishes linearly due to the interactions between polymer and dye. The plot of  $q_e$  versus  $\ln C_e$  provided the linear form of the isotherm, as well as the parameters  $b_T$  and  $a_T$ , using the slope and the intercept respectively (Fig.7c). The results obtained for these parameters could be observed in Table 5.

It has been stated that the range of binding energies for the mechanism of ionic exchange is between 8 and 16 kJ/mol, whereas these values are lower than -40 kJ/mol for the

physical adsorption process [47]. The  $b_T$  value obtained for  $\alpha$ -CDs-EPI was 0.586 kJ/mol and 0.765 kJ/mol for HP- $\alpha$ -CDs-EPI. Both values indicated that in the adsorption of Direct Red onto the CDs-EPI polymers were involved physical and chemisorption processes. The  $R^2$  values for this model were 0.931 for  $\alpha$ -CDs-EPI and 0.944 for HP- $\alpha$ -CDs-EPI. According to these results, the Temkin isotherm presented a similar adjustment than that observed in the case of the Langmuir isotherm, being the Freundlich model the best isotherm to explain the results of the experimental data.

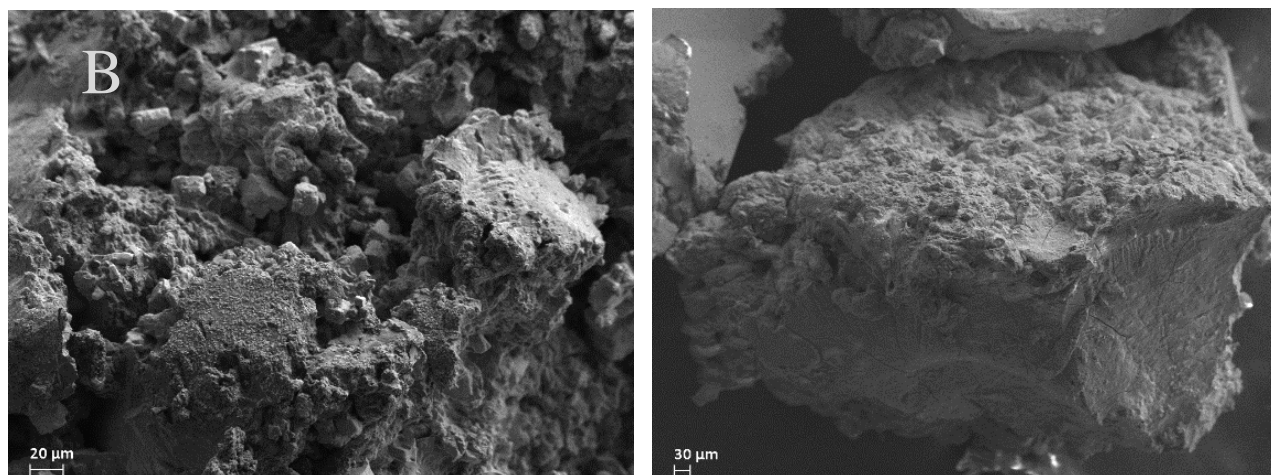
The standard free energy ( $\Delta G^\circ$ ) of the absorption process was calculated at 25 °C, using the following equation (9):

$$\Delta G^\circ = -RT \ln K_L \quad (9)$$

where T is the temperature in Kelvin, R the universal gas constant (8.314 J/mol K) and  $K_L$  is the Langmuir constant. The  $\Delta G^\circ$  values were 0.746 kJ/mol for  $\alpha$ -CDs-EPI and 4.4 kJ/mol for HP- $\alpha$ -CDs-EPI. Positive  $\Delta G^\circ$  values were observed at 25 °C indicating that spontaneity is not favoured at low temperatures. A similar trend has been observed for the removal of methyl orange using a novel  $\beta$ -cyclodextrin functionalized graphene [33] or the removal of Congo red [48].

### 3.4. SEM analysis

The morphology of the CD-based polymers was analysed using SEM technology. Fig.8a showed an unloaded  $\alpha$ -CDs-EPI polymer. This polymer is characterized for its porous and irregular structure. This conformation allows the polymer to entrap the dye molecules. However, the presence of Direct Red 83:1 onto the polymer (Fig.8b) provoked a smoother morphology of the surface. This suggests the accumulation of Direct Red over the polymer surface. The morphological change in surface of the polymer indicates the removal of dye from the aqueous solution through absorption process.



**Fig. 8**

#### **4. Conclusions**

This paper presents for the first time the absorption of Direct Red 83:1 using different CDs polymers. The adsorption capacities of CDs-EPI polymers were enhanced upon working at optimized conditions pH 7.0, using 1 g of polymer and controlling agitation rate (500 rpm). Adsorption reaches equilibrium within 30 min and the kinetics of dye adsorption follows the pseudo-second-order model. The maximum uptake capacities for Direct Red 83:1 were achieved using  $\alpha$ -CDs-EPI, at dye concentrations lower than 200 mg/ml (mean 92.8%), and the equilibrium data are fitted well by the Freundlich model based on the high correlation coefficient ( $R^2 = 0.98$ ). This is also an indication of surface heterogeneity of the polymer responsible for multilayer adsorption due to the presence of energetically heterogeneous adsorption sites. Our results suggest that  $\alpha$ -CDs-EPI can be used as a reusable absorbent for easy, convenient, and efficient removal of Direct Red 83:1 from wastewater.

#### **References**

- [1] Yagub MT, Sen TK, Ang H. Equilibrium, kinetics, and thermodynamics of methylene blue adsorption by pine tree leaves. *Water Air Soil Poll* 2012;223:5267-5282.

- [2] Semeraro P, Rizzi V, Fini P, Matera S, Cosma P, Franco E, García R, Ferrándiz M, Núñez-Delicado E, Gabaldón JA, Fortea I, Pérez E, Ferrándiz M. Interaction between industrial textile dyes and cyclodextrins. *Dyes Pigments* 2015;119: 84-94.
- [3] Rofchahi EM, Gilani AG, Taghvaei V, Karimi R, Ramezanzade N. Synthesis, structural elucidation, solvatochromism and spectroscopic properties of some azo dyes derived from 6-chloro-4-hydroxyquinoline-2 (1H)-one. *J Mol Struct* 2016;1108:623-630.
- [4] Mahmood S, Khalid A, Arshad M, Mahmood T, Crowley DE. Detoxification of azo dyes by bacterial oxidoreductase enzymes. *Crit Rev Biotechn* 2016;36:639-651.
- [5] Cong VH, Sakakibara Y, Komori M, Kishimoto N, Watanabe T, Mishima I, Ihara I, Tanaka T, Yoshida Y, Ozaki H. Recent developments in electrochemical technology for water and wastewater treatments. *J Water Environ Technol* 2016;14:25-36.
- [6] Li X, Jin X, Zhao N, Angelidaki I, Zhang Y. Novel bio-electro-Fenton technology for azo dye wastewater treatment using microbial reverse-electrodialysis electrolysis cell. *Bioresour Technol* 2017;228:322-329.
- [7] Xie M, Shon HK, Gray SR, Elimelech M. (2016). Membrane-based processes for wastewater nutrient recovery: technology, challenges, and future direction. *Water Res* 2016;89:210-221.
- [8] Yilmaz A, Yilmaz E, Yilmaz M, Bartsch RA. Removal of azo dyes from aqueous solutions using calix[4]arene and  $\beta$ -cyclodextrin. *Dyes Pigments* 2007;74:54-59.
- [9] Lucas-Abellán C, Fortea MI, Gabaldón JA, Núñez-Delicado E. Complexation of resveratrol by native and modified cyclodextrins: Determination of complexation constant by enzymatic, solubility and fluorimetric assays. *Food Chem* 2008;111:262-267.
- [10] Lay S, Ni X, Yu H, Shen S. State-of-the-art applications of cyclodextrins as functional monomers in molecular imprinting techniques: a review. *J Sep Sci* 2016;39:2321-2331.

- [11] Udoetok IA, Dimmick RM, Wilson LD, Headley JV. Adsorption properties of cross-linked cellulose-epichlorohydrin polymers in aqueous solution. *Carbohydr Polym* 2016;136:329-340.
- [12] Crini G, Morcellet M. Synthesis and applications of adsorbents containing cyclodextrins. *J Sep Sci* 2002;25:789–813.
- [13] Morin-Crini N, Crini G. Environmental applications of water-insoluble  $\beta$ -cyclodextrin-epichlorohydrin polymers. *Prog Polym Sci* 2013;38:344-368.
- [14] Krause RWM, Mamba BB, Bambo FM, Malefetsa TJ. Cyclodextrin polymers: Synthesis and application in water treatment. *Cyclodextrins: Chemistry and Physics*, Jie Hu (Ed.). 2010;9:185–208.
- [15] Mallard I, Baudelet D, Castiglione F, Ferro M, Panzeri W, Ragg E, Mele A. Polydisperse methyl  $\beta$ -cyclodextrin-epichlorohydrin polymers: variable contact time  $^{13}\text{C}$  CP-MAS solid-state NMR characterization. *Beilstein J Org Chem* 2015;11:2785-2794.
- [16] Renard E, Deratani G, Volet B, Sebille B. Preparation and characterization of water soluble high molecular weight  $\beta$ -cyclodextrin-epichlorohydrin polymers. *Eur Polym J* 1997;33:49-57.
- [17] Kyzas GZ, Sifaka PI, Pavlidou EG, Chrissafis KJ, Bikiaris DN. Synthesis and adsorption application of succinyl-grafted chitosan for the simultaneous removal of zinc and cationic dye from binary hazardous mixtures. *Chem Eng J* 2015;259:438-448.
- [18] Lagergren S. Zur theorie der sogenannten adsorption gelöster stoffe, kungliga svenska vetenskapsakademiens, *Handlingar* 1898;24:1-39.
- [19] Ho YS. Review of second-order models for adsorption systems. *J Hazard Mater* 2006;136:681–689.

- [20] Weber WJ, Morris JC. In: Proc. Int. Conf. Water Pollut. Symp., vol. 2, Pergamon, Oxford, 1962, pp. 231–266.
- [21] Freundlich HZ. Over the adsorption in solution. *J Phys Chem A* 1906;57:385–470.
- [22] Langmuir I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *J Ame Chem Soc* 1918;40:1361-1403.
- [23] Temkin MI, Pyzhev V. (1940). Kinetic of ammonia synthesis on promoted iron catalyst. *Acta Physiochimica USSR* 1940;12:327-356.
- [24] Hameed BH. Evaluation of papaya seeds as a novel non-conventional low-cost adsorbent for removal of methylene blue. *J Hazard Mater* 2009;162:939-944.
- [25] Chanzu HA, Onyari JM, Shiundu PM. Biosorption of malachite green from aqueous solutions onto polylactide/spent brewery grains films: kinetic and equilibrium studies. *J Polym Environ* 2012;20:665-672.
- [26] Hu Z, Chen H, Ji F, Yuan S. Removal of Congo red from aqueous solution by cattail root. *J Hazard Mater* 2010;173:292-297.
- [27] Wanyonyi WC, Onyari JM, Shiundu PM. Adsorption of Congo Red dye from aqueous solutions using roots of *Eichhornia crassipes*: kinetic and equilibrium studies. *Enrgy Proced* 2014;50:862-869.
- [28] Tan P, Hu Y. Improved synthesis of graphene/ $\beta$ -cyclodextrin composite for highly efficient dye adsorption and removal. *J Mol Liq* 2017;242:181-189.
- [29] Vahedi S, Tavakoli O, Khoobi M, Ansari A, Faramarzi MA. Application of novel magnetic  $\beta$ -cyclodextrin-anhydride polymer nano-adsorbent in cationic dye removal from aqueous solution. *J Taiwan Inst Chem E* 2017. In press, <http://dx.doi.org/10.1016/j.jtice.2017.07.039>

- [30] Zhao D, Zhao L, Zhu CS, Huang WQ, Hu JL. Water-insoluble  $\beta$ -cyclodextrin polymer crosslinked by citric acid: synthesis and adsorption properties toward phenol and methylene blue. *J Incl Phenom Macro* 2009;63:195-201.
- [31] Crini G, Peindy HN, Gimbert F, Robert C. Removal of CI Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies. *Sep Purif Technol* 2007;53:97-110.
- [32] Si H, Wang T, Xu Z. (2013). Biosorption of methylene blue from aqueous solutions on  $\beta$ -cyclodextrin grafting wood flour copolymer: kinetic and equilibrium studies. *Wood Sci Technol* 2013;47:1177-1196.
- [33] Yan J, Zhu Y, Qiu F, Zhao H, Yang D, Wang J, Wen W. Kinetic, isotherm and thermodynamic studies for removal of methyl orange using a novel  $\beta$ -cyclodextrin functionalized graphene oxide-isophorone diisocyanate composites. *Chem Eng Res Des* 2016;106:168-777.
- [34] Yuan J, Qiu F, Li P. Synthesis and characterization of  $\beta$ -cyclodextrin-carboxymethyl cellulose-graphene oxide composite materials and its application for removal of basic fuchsin. *J Iran Chem Soc* 2017;14:1827-1837.
- [35] Crini G, Peindy HN. Adsorption of CI Basic Blue 9 on cyclodextrin-based material containing carboxylic groups. *Dyes Pigments* 2006;70:204-211.
- [36] Liu ZG, Xu M, Yang Z, Wang YX, Wang SQ, Wang HX. Efficient removal of organic dyes from water by  $\beta$ -cyclodextrin functionalized graphite carbon nitride composite. *Chem Select* 2017;2:1753-1758.
- [37] Ozmen EY, Yilmaz M. Use of  $\beta$ -cyclodextrin and starch based polymers for sorption of Congo red from aqueous solutions. *J Hazard Mater* 2007;148: 303-310.

- [38] Kyzas GZ, Lazaridis NK, Bikiaris DN. Optimization of chitosan and  $\beta$ -cyclodextrin molecularly imprinted polymer synthesis for dye adsorption. *Carbohydr Polym* 2013;91:198-208.
- [39] Xiong XL, Shao CB. Removal of xylenol orange from solutions by  $\gamma$ -cyclodextrin-grafted carboxymethyl cellulose. *Adv Mater Res* 2011;204: 1180-1183.
- [40] Dong K, Qiu F, Guo X, Xu J, Yang D, He K. Adsorption behavior of azo dye eriochrome black T from aqueous solution by  $\beta$ -cyclodextrins/polyurethane foam material. *Polym-Plast Technol* 2013;52:452-460.
- [41] Zhou LC, Meng XG, Li JM, Hu W, Liu B, Du J. Kinetics and thermodynamics of adsorption of chlorophenols onto  $\beta$ -cyclodextrin modified chitosan. *Acta Phys-Chim Sin* 2012;28:1615-1622.
- [42] Yilmaz E, Memon S, Yilmaz M. Removal of direct azo dyes and aromatic amines from aqueous solutions using two  $\beta$ -cyclodextrin-based polymers. *J Hazard Mater* 2010;174:592-597.
- [43] Jabli M, Hamdaoui M, Jabli A, Ghandour Y, Ben Hassine B. (2014). A comparative study on the performance of dye removal, from aqueous suspension, using (2-hydroxypropyl)- $\beta$ -cyclodextrin-CS, PVP-PVA-CS, PVA-CS, PVP-CS and plain CS microspheres. *J Text I* 2014;105:661-675.
- [44] Chang MY, Juang RS. Adsorption of tannic acid, humic acid, and dyes from water using the composite of chitosan and activated clay. *J Colloid Interf Sci* 2004;278:18-25.
- [45] Yagub MT, Sen TK, Ang M. Removal of cationic dye methylene blue (MB) from aqueous solution by ground raw and base modified pine cone powder. *Environ Earth Sci* 2014;71:1507-1519.



- [46] Dawood S, Sen TK. Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: Equilibrium, thermodynamic, kinetics, mechanism and process design. *Water Res* 2012;46:1933-1946.
- [47] Hu X, Wang J, Liu Y, Li X, Zeng G, Bao Z, Zeng X, Chen A, Long F. Adsorption of chromium (VI) by ethylenediamine-modified cross-linked magnetic chitosan resin: isotherms, kinetics and thermodynamics. *J Hazard Mater* 2011;185:306–314.
- [48] Namasivayam C, Kavitha D. Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. *Dyes Pigments* 2002;54:47-58.

### **Acknowledgements**

This study was supported by the European project “DYES4EVER” (Use of cyclodextrins for treatment of wastewater in textile industry to recover and reuse textile dyes, LIFE12 ENV/ES/000309) within the LIFE+ 2012 “Environment Policy and Governance project application” program.

### **Figure Captions**

**Fig. 1.** Molecular structure of Direct Red 83:1.

**Fig. 2.** UV-Vis spectrum of Direct Red 83:1 in aqueous solution.

**Fig. 3.** Effect of contact time between  $\alpha$ -CDs-EPI (A) and HP- $\alpha$ -CDs-EPI (B) with different concentrations of Direct Red 83:1 25 mg/L (●), 50 mg/L (○), 75 mg/L (■), 100 mg/L (□), 150 mg/L (▲), 200 mg/L (Δ), 250 mg/L (◆) and 300 mg/L (◇).

**Fig. 4.** Pseudo first order model plots for the Direct Red 83:1 absorption onto  $\alpha$ -CDs-EPI (A) and HP- $\alpha$ -CDs-EPI (B) polymers at different concentrations of dye (25 mg/L (●), 50 mg/L (○), 75 mg/L (■), 100 mg/L (□), 150 mg/L (▲), 200 mg/L (Δ), 250 mg/L (◆) y 300 mg/L (◇)).

**Fig. 5.** Pseudo second order model plots for the Direct Red 83:1 absorption onto  $\alpha$ -CDs-EPI (A) and HP- $\alpha$ -CDs-EPI (B) polymers at different concentrations of dye (25 mg/L (●), 50 mg/L (○), 75 mg/L (■), 100 mg/L (□), 150 mg/L (▲), 200 mg/L (Δ), 250 mg/L (◆) y 300 mg/L (◇)).

**Fig. 6.** Intraparticle diffusion model plots for the Direct Red 83:1 absorption onto  $\alpha$ -CDs-EPI (A) and HP- $\alpha$ -CDs-EPI (B) polymers at different concentrations of dye (25 mg/L (●), 50 mg/L (○), 75 mg/L (■), 100 mg/L (□), 150 mg/L (▲), 200 mg/L (Δ), 250 mg/L (◆) y 300 mg/L (◇)).

**Fig. 7.** Absorption isotherms for Direct Red 83:1 by  $\alpha$ -CDs-EPI (●) and HP- $\alpha$ -CDs-EPI (○). (A) Freundlich isotherm, (B) Langmuir isotherm, (C) Temkin isotherm, (D) Separation factor.

**Fig. 8.** SEM analysis of polymer (A) and polymer loaded with Direct Red 83:1 (B).