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Use of β-cyclodextrin and starch based polymers for sorption of Congo red from aqueous solutions

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Abstract

Two starch-based and a β-cyclodextrin (β-CD)-based polymers were synthesized using 4,4′-methylene-bis-phenyldiisocyanate (MDI) or hexamethylenediisocyanate (HMDI) as a cross linking agent in dry dimethylformamide and used as a sorbent for the removal of Congo red from aqueous solutions. The cross-linked polymers were characterized by Fourier transform infrared spectroscopy, thermogravimetric and differential scanning calorimetric analysis. The dye adsorption experiments were carried out by using batch and recycling column procedure. The effects of initial pH (pH_0), the contact time and the initial dye concentration were changed to obtain the best experimental conditions. The pH_0 of the dye solution strongly affected the chemistry of both the dye molecules and polymer **3** in an aqueous solution. The effective pH_0 was 7.0 for adsorption on polymer **3**. The equilibrium adsorption data were interpreted using Langmuir and Freundlich models. The adsorption of Congo red was better represented by the Freundlich equation.
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1. Introduction

Textile industry provides many quantities of wastewater as a result of many intermediate stages using water [1]. Moreover, each intermediate stage provides different wastewater, so the final wastewater can be considered as a mixture of intermediate wastewater, containing mainly unfixed dyes as well as other impurities such as, polyvinyl alcohol, starches, surfactants, pesticides, biocides and relatively high salinity [2]. However, the increased color intensity is the most serious problem of the wastewater provided by the textile industries because many of the commercial azo dyes can produce hazardous aromatic amines, as well as other highly toxic by-products through metabolic processes in plants and animals or directly after the disposal in lakes, rivers or sea [3–6]. Concerning the reactive dyes which are mainly used for textile dying processes, it is known that 30% of the initial amount of the dye is released in the wastewater due to hydrolysis side reaction, resulting in limited degree of fixation [7]. Moreover, azo dyes which are syn-

thetic products, show rather low biodegradability, firstly because of lack of natural biodegradation paths and secondly because of stereochemical interferences concerning the accession of the reductant or oxidant molecule to the azo-group [8,9]. As a result, traditional biological processes are not able to fully decolorize azo dye wastewater [10–15]. Removal of toxic substances from water has been a challenge since long time and adsorption technique has proved best to minimize this task [16,17]. It is now well established that for the wastewater treatment, adsorption is a much better process than other physical techniques like, flocculation, froth flotation, etc. because of its efficacy and economy [18–22]. Moreover, ability of adsorption to remove toxic chemicals without disturbing the quality of water or leaving behind any toxic degraded products has augmented its usage in comparison to electrochemical, biochemical or photochemical degradation processes [23]. Recovery of costly toxic substances from the wastewater is an added advantage of the adsorption procedure [24]. With these methods a number of non-conventional, low cost adsorbents have been tried for dye removal. These include wood [25], Fuller's earth and fired clay [26], fly ash [27], biogas waste slurry [28–32], waste orange peel [33], banana pith [34,35], peat [36], chitin [37], chitosan [38], silica [39], starch and starch derivatives [40–43].

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In recent years, much attention has been paid to chemical separation techniques and the design and synthesis of new extraction reagents for ions and molecules. This attention results in part from environmental concerns, efforts to save energy and recycling at the industrial level. In this respect, the supramolecular chemistry has provided a much better solution to the search for molecular structures that can serve as building blocks for the production of sophisticated molecules by anchoring functional groups oriented in such a way that they delineate a suitable binding site. This was achieved with the development of macrocyclic molecules such as synthetic crown ethers, cryptands, spherands [44], calixarenes [45,46] and natural cyclodextrins [47,48]. Cyclodextrins (CDs) are glucose-based molecules and produced from the enzymatic degradation of starch by bacteria. They are cyclic oligosaccharides consisting of 6 (α), 7 (β), 8 (γ) glucopyranose units, which are joined together by α (1–4) linkage forming a torus-shaped ring structure. These compounds when crosslinked with suitable crosslinkers form an insoluble resin which exhibits specific adsorption based on inclusion complex formation [43,49–52]. The most characteristic feature of CDs is the ability to form inclusion compounds with various organic molecules through host-guest interactions: the interior cavity of the molecule provides a relatively hydrophobic environment into which an apolar pollutant can be trapped. Several review articles were devoted to the detailed description of the industrial applications of CDs [53,48,40,54,55]. β-Cyclodextrin based materials were used as sorbent in the wastewater by the Crini and Peindy [47]. They found β-cyclodextrin based materials exhibited high adsorption capacities toward phenolic molecules and dyes. In particular, the β-cyclodextrin based polymers are very different in removing acid, direct, disperse and reactive dyes from solutions. Recently, they prepared β-cyclodextrin based polymers containing carboxyl groups from reticulation of β-CD using epichlorohydrin in the presence of carboxymethyl cellulose for the sorption of C.I. Basic Blue 9 [47].

We now report the removal abilities of two cross-linked starch polymers and a β-cyclodextrin-based polymer as an adsorbent for dyes with a model system of aqueous Congo red solutions. The effects of contact time, initial dye concentration, and pH on the sorption capacity are investigated in detail.

2. Materials and methods

2.1. Reagents

β-Cyclodextrin (CD) was purchased from Fluka and used without further purification. The anionic dye, Congo red (1-naphthalenesulfonic acid, 3,3-(4,4-biphenylenebis(azo)) bis (4-amino-) disodium salt) was obtained from Merck (Darmstadt, Germany)., with analytical grade and it was used without further purification. Congo red contains NH_2 and SO_3 functional groups (see Fig. 1). It has a maximum absorbency at wavelength 496 nm on a UV-vis spectrophotometer. The chemical formula and molecular weight of Congo red is $C_{32}H_{22}N_6Na_2O_6S_2$ and 696.7 g mol^{-1}, respectively. The coal-based granular activated carbon (AC) was purchased from Fluka. The AC had an average
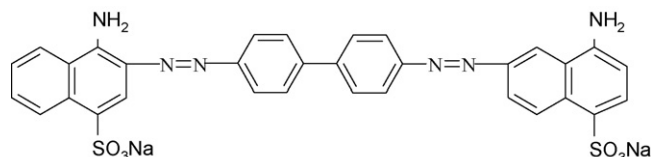

Fig. 1. Structure of Congo red.

diameter of 2.5 mm and a density of 2 g mL^{-1}. Its BET surface area was 1600 m^2 g^{-1}. Solvents were dried by storage over molecular sieves (Aldrich; 4 A°, 8–12 mesh). All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

2.2. Apparatus

IR spectra were recorded with a Perkin-Elmer 1605 FTIR spectrometer as KBr pellets. UV-vis spectra were obtained with a Shimadzu 160 A UV- vis recording spectrophotometer. TGA was carried out with Perkin-Elmer Pyris 1 thermogravimetric analyzer. The sample weight was 13–15 mg. Analysis was performed from room temperature to 800 °C at a heating rate of 20 °C min^{-1} in nitrogen.

2.2.1. Preparation of polymers

The polymer **3** was prepared according to the reported procedures [56]. The cross-linked polymer **1** and **2** have been prepared in one step by starch using hexamethylene diisocyanate (HMDI) or 4,4-methylene-bis-phenyldiisocyanate (MDI). The synthetic procedure has already been described in detail [57]. A typical reticulation reaction was carried as follows (polymer **1–2**). Starch (2.0 g) was dissolved in 10 ml of dry DMF in 100 ml round bottom flask at room temperature. Then 6.55 mmol of hexamethylenediisocyanate (HMDI) for polymer **1** or 4,4-methylene-bis-phenyldiisocyanate (MDI) for polymer **2**, were added dropwise. Then the solution of polymer was stirred at 70 °C for 4 h. At end of this period, the product was precipitated by the addition of acetone/ethanol and was filtered and washed acetone and water several times. The product was dried in vacuo for 24 h (Table 1).

2.3. Sorption studies

2.3.1. Batch experiments

Batch adsorption experiments were carried out by agitating 10 ml of dye solution with 25 mg of adsorbent in glass bottles at 180 rpm at room temperature (25 ± 2 °C) using a shaker machine. The dye solution was separated from the adsorbent by centrifugation at 2200 rpm for 5 min. The dye removal was estimated spectrophotometrically by monitoring the absorbance changes at the wavelength of maximum absorption (496 nm) using a UV-Vis spectrophotometer (Model Shimadzu 160A). For studies on the effect of pH upon dye removal, the initial pH of the dye solution was varied from 2 to 10. In the pH range 5.8–10 there was no change in absorbance with pH. But in acidic conditions (pH range 2.0–5.5) the absorbance of the dye changed.

Table 1
Experimental conditions of the synthesis and characteristics of the polymers used during this study

Polymer	Starch (g)	HMDI or MDI (mol)	N (%)[a]	HMDI or MDI[b]
Polymer 1	2.0	6.55	8.07	2.86
Polymer 2	2.0	6.55	5.80	2.07
Polymer 3	2.0[c]	6.55[d]	6.07	2.17

[a] Nitrogen content from elemental analysis.

[b] HMDI or MDI content in mmol $1g^{-1}$ polymer from elemental analysis.

[c] β-CD is used.

[d] MDI is used.

Hence, the percent removal of the dye was determined from absorbance values of dye solutions after adjusting the final pH to 5.8. Batch tests were carried out to compare the adsorptive capacity and intensity of activated carbon-commercial grade. The data for Langmuir and Freundlich adsorption isotherms were taken from batch adsorption experiments.

2.3.2. 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. The column was eluted using only water until the flow rate became constant. For the recycling system column, the experimental conditions are the following: concentration of 2×10^{-5} in water for Congo red, flow rate of 1.5 ml min^{-1}; and a column filled with the insoluble polymer with respect to organic 50 mg of polymer. 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. Results and Discussion

3.1. Characterization of sorbents

Structures of two starch and a β-CD-based polymers are shown in Scheme 1. The synthesis of polymer **3** was based on reported procedure [56] and by addition of MDI as crosslinking agents. The cross-linked starch polymers were prepared by reaction of starch with HMDI or MDI.

The polymers were insoluble in water, as well as most of organic solvents. Consumption of the isocyanate reactant was followed by observing the disappearance in absorbance of the −N=C=O anti-symmetric stretching band at 2275 cm^{-1} for polymer **2** and at 2295 cm^{-1} for polymer **1**. A band at 3319 cm^{-1} for polymer **2** and 3310 cm^{-1} for polymer **1** due to the free NH and OH stretching absorption for the starch and urethane groups developed as the polymerization progressed. Upon completion of 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} polymer **2**.

The thermal stability of starch polymer **1** and **2** was evaluated by thermal gravimetric analysis (TGA). It was found that the polymer undergoes three-step thermal degradation. The first step arises from decomposition of starch, while the second and third are due to the polymer. According to the literature [58], starch starts to decompose at temperatures ranging from 290 to 300 °C. The onsets of degradation for starch polymers were found to occur at 320 °C for polymer **1** and for polymer **2** at 345 °C. This is quite high compared to conventional polyurethanes, which generally begin to decompose around 200–220 °C. The enhanced thermal stability of starch polymers are attributed to their cross-linked nature, since it is well-known that cross-linking leads to increased thermal stability. Since polymer **2** contains aromatic bridges showed more thermal stability than the polymer **1**. A weight loss maximum of 44–45% for polymer **1** and 30–35% for polymer **2** during the first stage of thermal decomposition results from cleavage of the urethane linkage and volatilization of the resultant decomposition products.
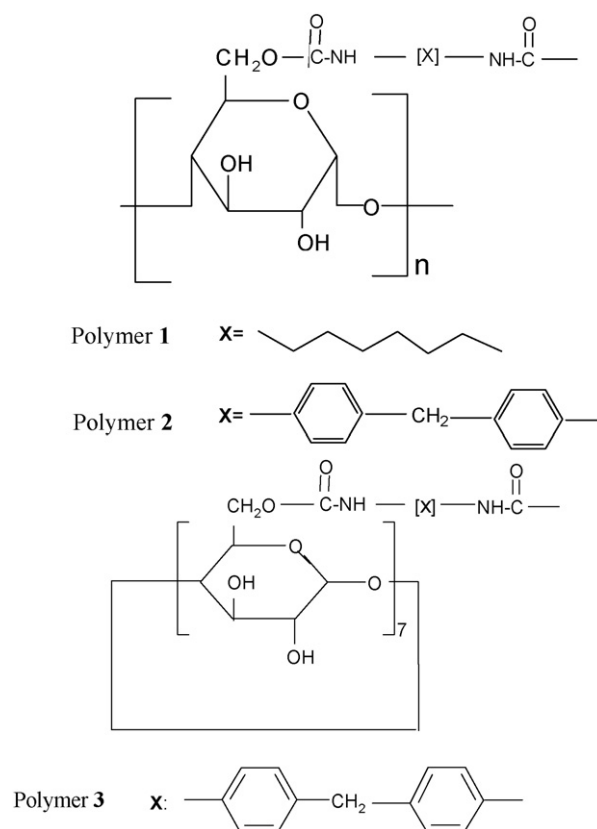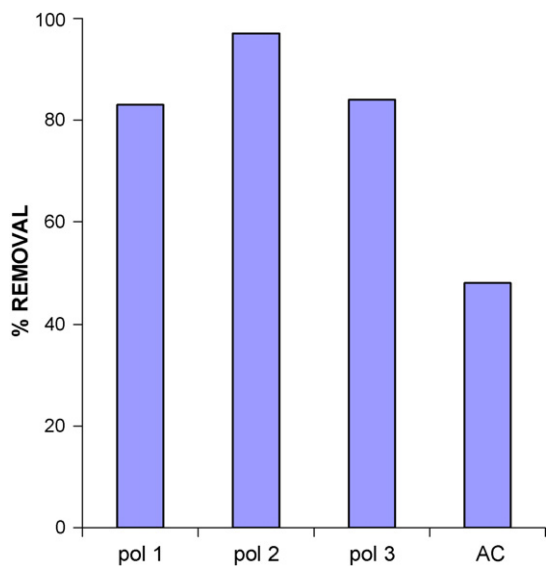

Scheme 1.

Fig. 2. Sorption percentages of the Congo red with polymers 1–3, and AC (polymer dose 25 mg, contact time 1 h, concentration 2×10^{-5} mol L^{-1}, pH 5.8).

3.2. Sorption studies

3.2.1. Batch studies

The adsorption capacity was expressed in percentage uptake (in %) which represents the ratio between the amount of sorbed dye and the starting amount of dye. The experiments were performed in triplicate under identical conditions. Batch sorption studies were carried out to examine the influence of various parameters such as initial concentration of dye, sorbent dosage, time of sorption and influence of pH on the removal of Congo red. The optimum wavelengths for maximum absorption of Congo red was 496 nm, at the natural pH of the solutions i.e. 5.8. The results of sorption experiments in terms of percentage removal, with time using sorbent (dosing 25 mg) for Congo red solution at pH 5.8 are shown in Fig. 2. Sorption capacity of cross-linked starch polymers (1 and 2) was compared with the β-CD based polymer (polymer 3). Among the sorbents, it was observed that polymer 2 was effective and efficient extractant than the others. The polymer 2 which contains rigid aromatic bridge showed higher affinity of the guest compounds than polymer 1 which contains flexible hexamethylene bridges. This observation clearly demonstrated the presence of hydrophobic–hydrophobic (dye–dye) interactions in the sorption mechanism. So an aggregation mechanism could be also included.

Sorption experiments were performed to allow for comparison of solid-liquid batch sorption results for the starch and β-CD-based polymers (1–3) with the activated carbon. The results shown in Fig. 2 clearly establish that starch and β-CD-based polymers are better sorbents for Congo red than the activated carbon.

3.2.2. Influence of the pH on the sorption capacity

The adsorptive treatment of dye containing water is pH dependent. However, pH is also known to affect the structural
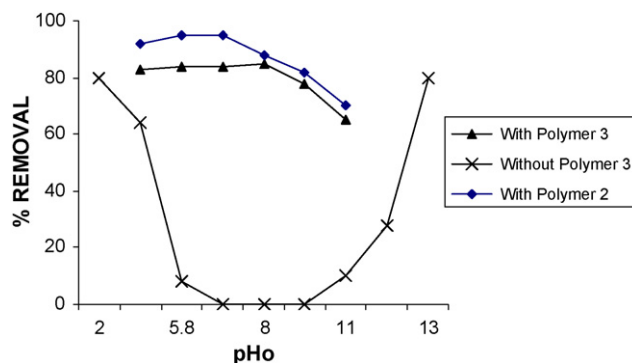

Fig. 3. Effect of pH$_0$ on the removal of Congo red with and without polymer 2 and 3 (polymer dose 25 mg, contact time 1 h, dye concentration 2×10^{-5} mol L^{-1}).

stability of Congo red and, therefore, its color intensity. Hence, the effect of pH$_0$ was studied with blank Congo red solutions of concentration 2×10^{-5} mol L^{-1} having the natural pH$_0$ 6.8. The solution was kept for 1 h after the pH adjustment and, thereafter, the absorbance of solution was found out. It is found that the color is stable at pH$_0$ around 7. Fig. 3 shows the color removal without polymer 2 and 3 over a pH$_0$ range of 2–13. pH reduced the color below pH$_0$ 6 and above pH$_0$ 10, however, color change is negligible over a pH$_0$ range of 6–10. Maximum color removal is at pH$_0$ 2 and 13. Color removal due to pH change alone may be due to the structural changes being effected in the dye molecules [59,60].

Effect of pH$_0$ on the removal of Congo red with polymer 2 and 3 is also shown in Fig. 3. More than 80% color removal is observed in the pH$_0$ range 4–9.

In the aqueous solution, the acid dye is first dissolved and the sulfonate groups of the acid dye (Dye-SO$_3$Na) are dissociated and converted to anionic dye ions. Congo red is a relatively large molecule and negatively charged for much of the pH range (>5).

$$Dye\text{-}SO_3Na \rightarrow Dye\text{-}SO_3^- + Na^+$$
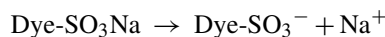
It was observed that the percentage of color removed was 92% for polymer 2, 83% and for polymer 3 when the dye solution pH was 4.0 and they attained minimum to 70% for polymer 2 and 65% for polymer 3 when dye solution pH increased to 11. As the pH of the system increase, the number of negatively charged site increases and the number of positively charged surface site decreases. Also, lower adsorption of Congo red at high alkaline pH (>9) is due to the presence of excess HO$^-$ ions competing with the dye anions for the adsorption sites. A negatively charged site on the adsorbent does not favor the adsorption of dye anions due to electrostatic repulsion. A similar trend was observed for the adsorption of Congo red and acid violet on coir pith carbon [61–64]. However, for pH values ranging from 4.0 to 8.0, the sorption could be explained taking into account other sorption mechanisms, such as hydrogen bonds or Π–Π stacking interactions.
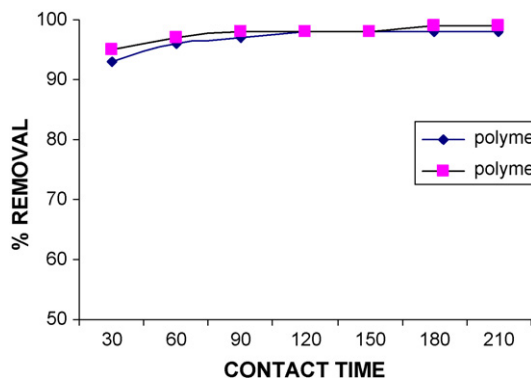
Fig. 4. Effect of contact time on percent adsorption of Congo red by the polymers (concentration 2×10^{-5} mol L^{-1} pH 5.8).

3.3. Column studies

In a kind of experiment, we used recycling column and tried to saturate the polymer using a significant amount of solution containing the azo dye. The aim was to confirm that not only does β-CD play a role in the sorption, but also does the polymer network introduced by hexamethylene or 4,4′-methylenebisphenyl bridging groups. In this work, as described above Congo red exhibits the best interaction with these sorbents (polymer **2** and **3**). Fig. 4 shows the amount of Congo red 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 1.0 and 2.5 mL min^{-1}. 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. Fig. 4 shows the amount of dye sorbed for polymer **2** and **3** in the recycling column experiment was higher than the batchwise technique.

3.4. Adsorption isotherms

The Freundlich isotherm is the earliest known relationship describing the sorption equation [65]. The application of the Freundlich equation suggests that sorption energy exponentially decreases on completion of the sorptional centers of an adsorbent. This isotherm is an empirical equation employed to describe heterogeneous systems and is expressed by the following equation [65,66]:

$$q_e = K_F C_e^{(1/n)} \tag{1}$$

where q_e is the equilibrium dye concentration on adsorbent (mg g^{-1}), C_e is the equilibrium dye concentration in solution (mg L^{-1}), K_F is Freundlich constant (L g^{-1}), and $1/n$ is the heterogeneity factor. The capacity constant K_F and the affinity constant n are empirical constants dependent on several environmental factors. A linear form of the Freundlich expression can be obtained by taking logarithms of Eq. (2):

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \tag{2}$$

Therefore, the plot of $\ln q_e$ versus $\ln C_e$ was employed to generate the intercept value of K_F and the slope of $1/n$. The results are given in Fig. 5(a). The fit is well for the adsorption system under the concentration range studied (correlation coefficient, $R^2 > 0.994$). The value of R^2 is higher than the Langmuir isotherm value and the value of n was >1, reflecting the favorable adsorption. Apparently, the plots in Fig. 5a demonstrate that the Freundlich equation provides a reasonable description of the experimental data. The Langmuir sorption isotherm is the most widely used for the sorption of a pollutant from a liquid solution assuming that the sorption takes place at specific homogeneous sites within the adsorbent [66–68]. The application of the Langmuir model suggests that the sorptional energy is constant and does not depends on the degree of occupation of the active centers of an adsorbent. It also assumes that once a dye occupies a site, no further sorption can take place at that site. All sites are energetically equivalent and there is no interaction between molecules adsorbed on neighboring sites. The linearized equation of Langmuir is represented as follows:

$$q_e = \frac{x}{m} = \frac{K_L C_L}{1 + a_L C_L} \tag{3}$$

where x is the amount of dye adsorbed (mg); m is the amount of adsorbent used (g); C_e (mg L^{-1}) and q_e (mg g^{-1}) are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium, respectively; K_L (L g^{-1}) and a_L (L mg^{-1}) are the Langmuir isotherm constants. The Langmuir isotherm constants, K_L and a_L are evaluated through linearisation of Eq.
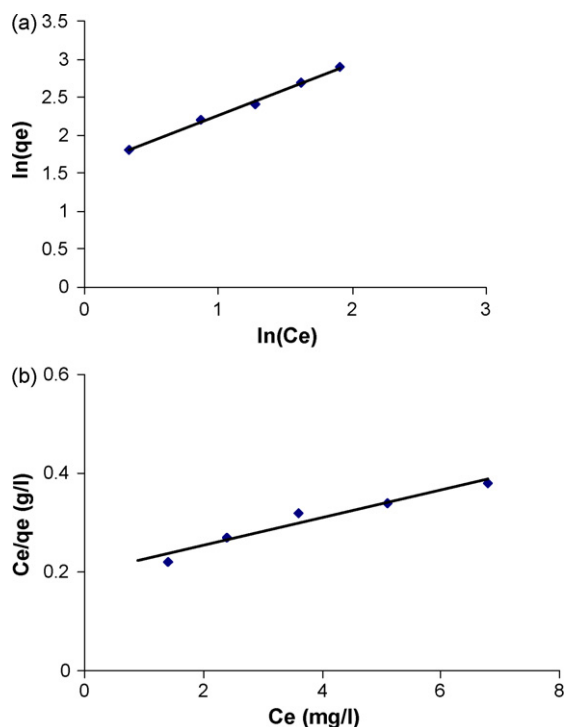

Fig. 5. Adsorption isotherms for Congo red by polymer **3** sorbent: (a) Freundlich isotherm; (b) Langmuir isotherm.

Table 2
Summary of the isotherm constants and the correlation coefficients for different isotherms

Freundlich isotherm			Langmuir isotherm				
K_F (L g^{-1})	n	R^2	K_L (L g^{-1})	a_L (L mg^{-1})	R^2	q_0 (mg g^{-1})	K_L
4.81	1.45	0.994	5.07	0.14	0.946	36.2	0.33

(4):

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L C_e} \tag{4}$$

Hence by plotting C_e/q_e against C_e it is possible to obtain the value of K_L from the intercept which is $1/K_L$ and the value of a_L from the slope, which is a_L/K_L. The theoretical monolayer capacity is q_0 (or q_{max} the maximum adsorption capacity of the adsorbent) and is numerically equal to K_L/a_L. The Langmuir equation is applicable to homogeneous sorption, where the sorption of each molecule onto the surface has equal sorption activation energy. Alternatively, at high adsorbate concentrations, the model predicts a constant monolayer adsorption capacity [66]. The plot of equilibrium concentrations of Congo red in the solid and liquid phases, that is C_e/q_e versus C_e is presented in Fig. 5(b) and Table 2. The value of the monolayer saturation capacity demonstrates that the β-CD-based adsorbent exhibit interesting sorption properties toward anionic dye. Compared with some recent data in the literature [69–74] the results also reveal the potential of this material to be an effective sorbent for removing basic dyes. From correlation coefficients, equilibrium adsorption data of Congo red did not fit to the Langmuir isotherm well it is evident that the Freundlich model is better than the Langmuir model. This suggests that some heterogeneity in the surface or pores of the polymer **3** will play a key role in dye adsorption and that the heterogeneous adsorption model will be better for isotherm simulation. Comparison of monolayer sorption capacity (Q_0) for the adsorption of Congo red by non-conventional adsorbents are presented in Table 3.

Further, the essential characteristics of the Langmuir isotherm can be described by a separation factor R_L; which is defined by the following equation [75,76].

$$R_L = \frac{1}{(1 + bC_i)} \tag{5}$$

Where, C_i is the initial concentration of dye (in mg L^{-1} or ppm) and b is the Langmuir constant (in g L^{-1}). The separation fac-

Table 3
Comparison of monolayer sorption capacity (Q_0) for the adsorption of Congo red by non-conventional adsorbents

Adsorbents	Q_0 (mg g^{-1})	Ref.
Waste orange peel	22.44	[33]
Commercial activated carbon	0.60	[59]
Activated carbon	1.87	[59]
Coir pith	6.72	[61]
β-CD polymer	36.20	Present work

tor R_L, indicates the shape of the isotherm and nature of the adsorption process as given below:

R_L values	Nature of the process
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

In the present study, the computed values of R_L (Table 2) were found to be in the range of 0–1, indicating that the adsorption process was favorable for polymer **3**.

The polymers were easily regenerated using ethanol as washing solvent by soxhlet extraction. It was observed that the sorption capacity was not changed after this treatment. This showed that the chemical stability of the polymers and reproducibility of the values.

4. Conclusion

This study was carried out to synthesize water insoluble a β-CD and two starch-based polymers. These materials have been evaluated for the extraction of Congo red from aqueous solution.

The following results can be summarized as:

- Indigenously prepared polymers show relatively high sorption capacity for dye (Congo red) compared to AC.
- The pH affects the adsorption capacity and the effective pH range for the sorption was found to be 4–8. Lower sorption of Congo red at high alkaline pH (>9) is due to the presence of excess HO$^-$ ions competing with the dye anions for the adsorption sites. A negatively charged site on the adsorbent does not favor the adsorption of dye anions due to electrostatic repulsion.
- The separation factor (R_L) was found to be favorable ($0 < R_L < 1$)
- The isotherm data could be well described by the Freundlich and Langmuir. The Freundlich equation showed a somewhat better fit than does the Langmuir for adsorption of Congo red using polymer
- It was concluded that adsorption mechanism mainly electrostatic interactions between adsorbent and adsorbate. Beside, hydrogen bonding, hydrophobic interactions (pollutant–polymer and pollutant–pollutant interactions), complexation were also occurred.

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