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Preparation and utilization of ionic exchange resin via graft copolymerization of β-CD itaconate with chitosan

Mohammed A. Gaffar, Safaa M. El-Rafie, Khaled F. El-Tahlawy*

Textile Research Division, National Research Center, Dokki, Cairo, Egypt

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Abstract

Ionic exchange resin was prepared via grafting of β-cyclodextrin itaconate (CDI) onto chitosan. CDI was prepared by esterification of β-cyclodextrin with itaconic acid using a semidry process. The esterification reaction of β-CD was carried out using [IA]; 2 mol/mol of CD, *M*/*L* ratio; 1:0.6, temperature 100 °C, [catalyst]; 0.5 mol/2 mol IA and in the absence of catalyst. The double bonds of CDI were utilized in grafting copolymeriziation onto chitosan using ceric ammonium nitrate (CAN) as a redox initiation system. The optimum conditions of the polymerization reaction were held as follows: [chitosan], 1 g; $Ce^{(IV)}$, 0.02 mol/l; temperature, 50 °C; and H_2O, 90 ml. At the end of the grafting reaction, the resultant product was subjected to crosslinking using different concentrations of glutraldehyde. Crosslinked chitosan/poly (CDI) graft copolymer (CCPCDI) was successively used for the removal of some hazardous pollutants currently found in textile waste water such as Maxilon Blue 4 GL (basic dye), Iragalon Rubine RL (acid dye) and Brilliant Red M5B R-2 (hydrolyzed reactive dyes).

Keywords: Chitosan; Copolymerization; Cyclodextrins

1. Introduction

Cyclodextrins (α, β, and γ) are series of oligosaccharides produced by *Bacillus macerans* during the enzymatic degradation process of starch and related compounds. Because of the chemical structures and overall shapes of those cyclodextrins, one of the most important characteristics of CDs is the formation of inclusion complexes with various guests in which the guest molecules are included in their cavities (Bender & Komiyama, 1978; Kobayashi, Ueno, & Osa, 1981). β-Cyclodextrin complexes have great stability when the guest molecule can adopt on orientation in the CDs that allows maximal interaction with groups lining the interior of the ring.

Chitin is one of the most abundant structural biopolymers, which mainly consists of *N*-acetyl-D-glucose amine units. Chitin is rapidly hydrolyzed by biological degradation processes, although it is highly resistant to chemical and physical degradation. Thus, its actual utilization is restricted owing to the low stability and compatibility that are ascribed to its strong crystalline structure.

Chitosan is a polyaminosaccharide, normally obtained by alkaline deacetylation of chitin which is very abundant naturally occurring polymeric materials (Roberts, 1992). Chitosan and its derivatives have become useful polysaccharides in the biomedical area because of its biocompatible, biodegradable, and non-toxic properties (Ha, Jae, & Sohk, 1999; Xiao, Yun, Dong, Zhi, & Kang, 2001).

Graft copolymerization is anticipated to be quite promising for developing sophisticated functions; it would enable a wide variety of molecular designs to afford novel types of tailored hybrid materials composed of natural polysaccharides, i.e. chitosan (Yoshikawa, Takayama, & Tsubokawa 1998), cyclodextrin (Casper, Glockner, & Ritter, 2000; Lee, Yoon, & Ko, 2001) and synthetic polymers.

Many attempts were carried out to prepare cyclodextrin-grafted chitosan in the literature. Sreenivasan used diisocyanate as a crosslinking agent (Sreenivasan, 1998), and Michel Morcellet have studied the reaction of cyclodextrin

* Corresponding author.
E-mail address: ktahlawy@hotmail.com (K.F. El-Tahlawy).

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monochlorotriazinyl derivative with chitosan (Martel et al., 2001).

Linking of CDs to chitosan is getting one of our interest areas as a result of the unique properties of the resulting graft copolymer. The present work was therefore undertaken to link chitosan to CD. Systematic studies were carried out to find out the optimum conditions for the preparation of CD itaconate (CDI) vinyl monomer. Further studies were extended for grafting of CDI vinyl monomer onto chitosan using ceric ammonium nitrate as a redox initiation system.

Crosslinked chitosan/poly(CDI) (CCPCDI) was evaluated as a new adsorbent for three classes of dyes (acid, basic, and hydrolyzed reactive), since CCPCDI has three different active groups, which are carboxyl groups, amino groups and CD-ring hosting molecule. The adsorption experiments were conducted under different conditions with a view to establish the appropriate conditions for dye adsorption.

2. Experimental

2.1. Materials

β-cyclodextrin (β-CD) was kindly supplied by Cerestor Co. (USA). Chitosan was kindly supplied by Pronova Biopolymer, Inc (USA). It is degree of deacetylation and molecular weight were determined as 85% and 50,000, respectively. Itaconic acid (IA) sodium hypophosphite (SHP), trisodium citrate (TSC), diammonium hydrogen phosphate (DAHP), nitric acid, and ceric ammonium nitrate (CAN) are laboratory grade chemicals.

2.2. Synthesis of β-cyclodextrin itaconate

Cyclodextrin itaconate was prepared using a semidry reaction method by physical mixing of 2 g of β-CD with a definite amount of water/ethanol (75/25) containing different IA concentrations (0.5–3 mol/mol CD) in the presence and absence of a curing catalyst. The reaction mixture was allowed to react in a circulating air oven at different reaction temperatures (80–140 °C) for 2 h. The cured samples were purified by washing with isopropyl alcohol using soxhlet for 6 h in order to remove unreacted ingredients, followed by drying at 60 °C for 24 h.

2.3. Synthesis of chitosan/poly(CDI) graft copolymer (CPCDI)

The grafting reaction was carried out in a three-necked flask with a magnetic stirrer. One gram of chitosan was dissolved in equivalent amount of nitric acid, followed by addition of different concentrations of CAN (0.005–0.03 M) dissolved in 1% nitric acid. The reacting ingredients were stirred for 20 min in the presence of oxygen. The flask was placed in a thermostatic water bath and heated at different reaction temperature (40–70 °C). To complete the material to liquor ratio 1: 15, a definite amount of water containing 5 g of CD-itaconate was injected to the reaction mixture to start the polymerization reaction. At the end of the reaction, the grafted samples were precipitated by addition of Na_2CO_3 (0.2 N). The samples were thoroughly washed with distilled water till pH 7 to ensure the removal of all unreacted ingredients. Finally the samples were washed with acetone, then oven dried at 60 °C for 24 h.

2.4. Crosslinking of chitosan/poly(CDI)

At the end of polymerization, crosslinked chitosan/poly (CDI) was prepared by adding different amounts of glutraldehyde (0.4–0.8 ml)/1 g CPCDI (solid content). The reaction mixture was allowed to stir for 4 h at 50 °C. At the end of crosslinking, the resulting samples were precipitated by adding Na_2CO_3 (0.2 N), filtered and washed thoroughly with distilled water till pH 7. Finally the crosslinked samples were washed with acetone and dried at 50 °C for 24 h.

2.5. Testing and analysis

The carboxyl content of the prepared CD-itaconate was assessed using acid-base titration according to reported method (Yang & Wang, 2000).

2.6. Double bond content

The resultant product of the esterification reaction was evaluated via determining the double bond content (DBC), expressed in mequiv./100 g CDI. The DBC was estimated according to a method reported by Wallace & Young (1966). Dried sample (0.5 g) was added to stoppered flask containing 10 ml of frozen KBr/$KBrO_3$ mixture, followed by addition of 5 ml H_2SO_4 (2 N). The liberated Br_2 was added to the double bond of the CDI samples. Back titration of the excess Br_2 was carried out using Iodometric titration (Wallace & Young, 1966). The double bound content (DBC) was calculated by the following equation:

$$\mathrm{DBC(mequiv./100\ g\ CDI)} = (V_B - V_S) \times 0.1 \times 100/W$$

where W is weight of the sample (0.5 g); V_B the volume of sodium thiosulfate (0.1 N) equivalent to the liberated Br_2 in the blank titration (ml); V_S the volume of sodium thiosulfate used in the sample titration (ml),

The graft yield was calculated mathematically via determining the decrement in the nitrogen content of the grafted samples according to the procedure described by Kjeldal Vogel (1966).

2.7. Acid hydrolysis susceptibility of CD itaconate (CDI)

The susceptibility of CDI (5 g) towards acid hydrolysis (50 ml of 1% nitric acid) was evaluated by measuring the DBC at interval times of hydrolysis using material to liquor ratio 1:10 at 60 °C. The CD and CDI in the aliquots were precipitated with 100 ml of isopropanol, filtered, washed with isopropanol to insure the removal of hydrolyzed IA, and then dried.

2.8. Ceric ion content

About 15 ml of 0.01 N of ferrous ammonium sulfate solution was added to 5 ml of reaction medium to convert $Ce^{(IV)}$ to $Ce^{(III)}$, then the excess ferrous ammonium sulfate was titrated against 0.01 N ceric sulfate using 2% *o*-phenanthroline solution as indicator (Myung, Yoon, & Ko, 2000).

2.9. Dye adsorption

The adsorption percent of basic, acid and hydrolyzed reactive dyes from their solutions onto crosslinked chitosan/poly(CDI) was studied by adding definite amounts of CCPCDI to different dye concentrations at pH ranges (Bender & Komiyama, 1978; Casper et al., 2000; Ha et al., 1999; Lee et al., 2001; Martel et al., 2001; Roberts, 1992; Sreenivasan, 1998; Xiao et al., 2001; Yoshikawa et al., 1998) and material to liquor ratio 1:200. The adsorption experiments were conducted under continuous stirring 150 rpm at room temperature. The adsorption percent was monitored at different duration by measuring the optical density of the dye solution before and during the adsorption experiments. The optical densities were measured at λ_{max} 550 nm for acid dye, λ_{max} 610 nm for basic dye, and λ_{max} 440 nm for hydrolyzed reactive dye. Calibration curves for dyes were used to calculate the percent dye adsorption.

3. Results and discussions

3.1. Preparation of β-CD Itaconate (β-CDI)

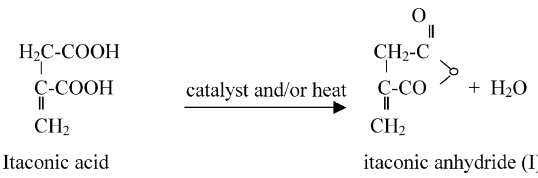
Chemically reactive cyclodextrin was prepared via its reaction with IA to obtain vinyl monomer that can be grafted onto chitosan. IA was selected, since it is a versatile monomer which has a vinyl group capable of undergoing addition polymerization and carboxylic groups capable of undergoing esterification reaction, depending on the reaction conditions used.

3.2. Tentative mechanism

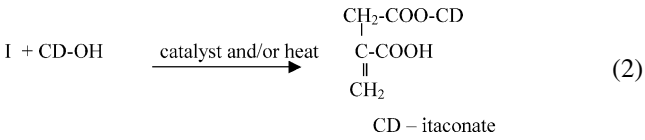
Cyclodextrin containing vinyl groups could be prepared via esterification reaction of cyclodextrin with IA in presence and absence of catalyst.

This suggests that, esterification of β-CD by IA in presence of catalyst can be explained according to the cyclic anhydride reactive intermediate mechanism as follows:

(i) Formation of IA anhydride (Yang & Wang, 1996)



(ii) Esterification of cyclodextrin



3.3. Catalyst type and concentration

To study the effect of catalyst type and concentration on the esterification efficiency of β-CD samples treated with IA, IA concentration was held constant at 2 mol/mol CD, whereas the concentration of selected three different catalysts namely, SHP, TSC, and $NH_4H_2PO_4$ was changed with respect to IA concentration. For a given set of conditions, it is clear that incorporation of the catalyst in the esterification formulation brings about a significant improvement in the carboxyl content and DBC (Fig. 1), irrespective of the catalyst used.

This can be associated with the role of phosphorus-based catalyst (SHP, $NH_4H_2PO_4$) and TSC in (a) catalyzing esterification reaction of hydroxyl containing polymers (such as CD) with dicarboxylic acid (Gaffar, 2000; Welch & Andrews, 1989), (b) swelling of β-CD (i.e. higher accommodation of IA as well as higher availability of its hydroxyl to esterification) under the alkaline effect of these catalysts.

Regardless of the catalyst used, increasing the amount of the catalyst incorporated in the esterification formulation is accompanied by a significant improvement in the functional groups (carboxyl and DBCs) attached to the CD structure.

Beyond a ratio of 0.5 mol catalyst/2 mol IA, there is a marginal increase in the values of carboxyl content and DBCs which can be associated with (a) the depletion of both CD hydroxyls (available for esterification reaction) and/or consumption of IA. (b) saponification of ester linkage of β-CDI under the more alkaline conditions (Rowlond & Brannon, 1968).

Further examination of Fig. 1 reveals that, when esterification reaction was carried out using IA of concentration 2 mol, along with any of the three salts, SHP, TSC and SDHP, the first salt proves to be the optimum catalyst regarding to double bond content, TSC,

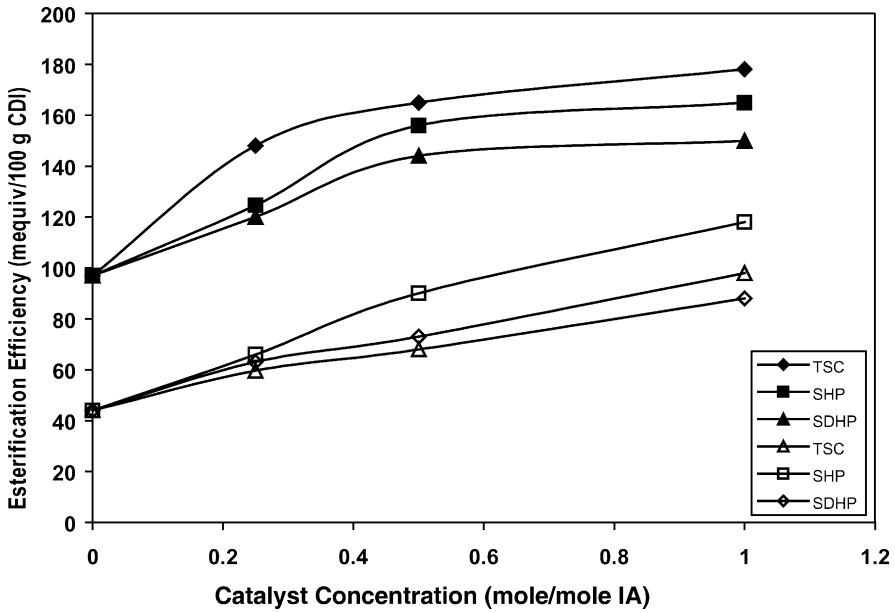
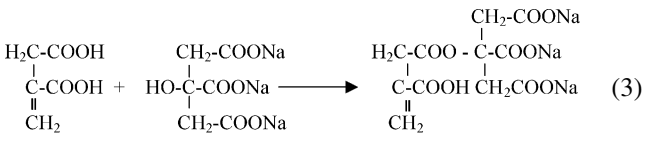


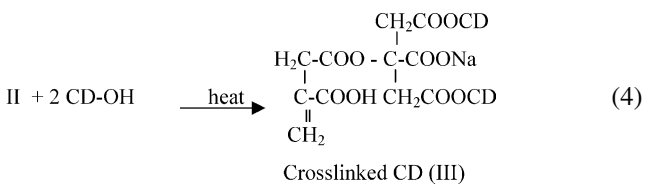
Fig. 1. Effect of [Catalyst] on the Esterification Efficiency of CD-itaconate [IA], 2 mol/mol CD; *M*/*L*-ratio 1:0.6; temperature 100 °C, time 2 h filled legands; carboxyl content, unfilled legands; double bond content.

however, is the superior for introducing carboxyl content. However, the effectiveness of these catalysts, regarding to carboxyl contents can be arranged descendingly as follows: TSC > SHP > SDHP > absence of catalyst. Regarding to DB content: SHP > SDHP > TSC > absence of catalyst, reflecting the difference among these esterification catalysts in Gaffar (2000): (i) extent of dissociation, (ii) pH of esterification formulation medium, (iii) extent of modification of β-CD structure, and mode and mechanism of catalysis, e.g. SHP and SDHP serves as a catalyst only, while TSC serving as a catalyst as well as a citric acid donor (Andrews & Morris, 1993), as the following mechanism:



Itaconyl citrate sodium salt (II) (3)

The formed high polycarboxylic acid sodium salt (II) can react with CD hydroxyl groups in similar manner of those shown by reactions 1 and 2 (Welch, 1990). The direct result of those reactions is the formation of reactive β-CD carrying high amount of carboxyl groups with moderate quantity of double bonds. The equation that can summarize these results can be written as follows:



Crosslinked CD (III) (4)

3.4. Curing temperature

Fig. 2 shows the effect of curing temperature on the esterification efficiency of β- CD using [IA]; 2 mol/mol of CD, *M*/*L* ratio; 1:0.6, [catalyst]; 0.5 mol/2 mol IA and in the absence of catalyst. It can be seen that, irrespective of catalyst used, increasing the temperature from 80 to 120 °C for 2 h is accompanied by marginal increase in the esterification extent, expressed as DBC. On the other hand, the esterification extent (expressed as carboxyl content) shows a significant increase by raising the esterification reaction temperature up to 120 °C. This behavior could be attributed to the positive impact of raising temperature in (a) dehydration of IA resulting in the formation of reactive cyclic anhydride intermediate (reaction (1)) and (b) esterification of β- CD hydroxyl. The data in Fig. 2, also shows that a further increase in reaction temperature beyond 120 °C has practically no effect on DBC of the treated samples with a negative impact on the carboxyl content of TSC catalyzed reaction. The little decrease in the carboxyl content of TSC catalyzed samples beyond 120 °C may be attributed to the accompanied increase in the extent of esterification crosslinking of β-CD with TSC-itaconate terpolymer at such high temperature. The ester crosslinking reaction consumes the carboxyl groups. It could be concluded that the optimum conditions for preparation of a reactive β-CDI carrying both free carboxyl groups and double bonds is [IA]; 2 mol/mol CD, reaction time; 2 h, reaction temperature; 100 °C and at material-to-liquor ratio of 1:0.6.

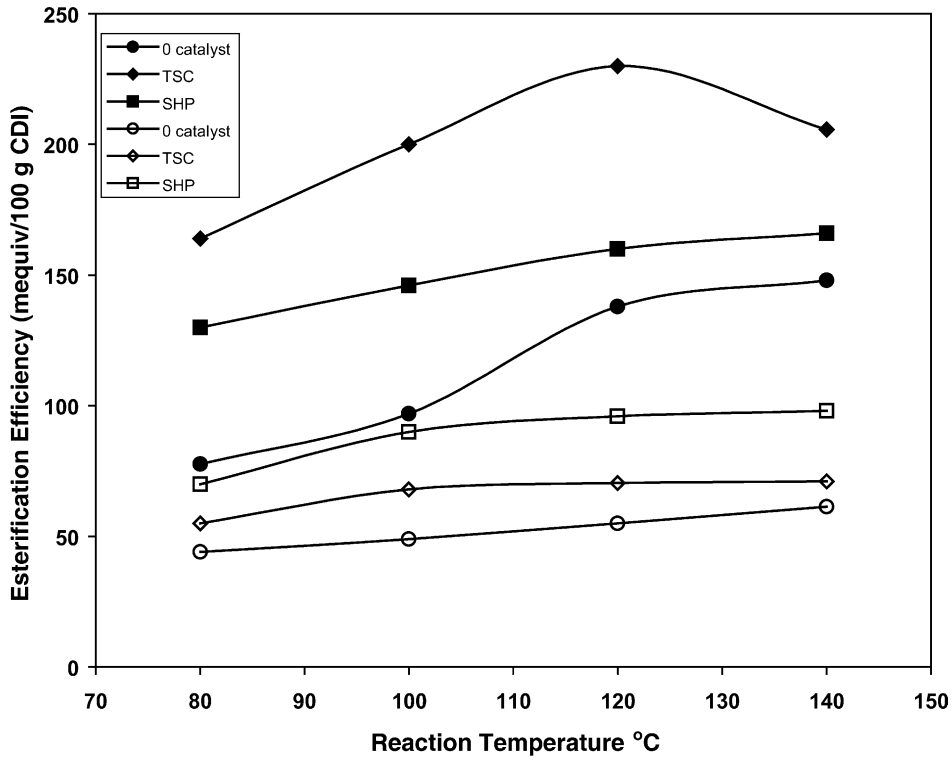


Fig. 2. Effect of Reaction Temperature on the esterification efficiency of CD-itaconate [IA], 2 mol/mol CD; *M*/*L*-ratio 1:0.6; [catalyst]; 0.5 mol/2 IA, time 2 h. Filled legands; carboxyl content, unfilled legands; double bond content.

3.5. Itaconic acid concentration

Fig. 3 shows the effect of IA concentration on the esterification efficiency of β- CD, when the reaction was carried out using material-to-liquor ratio; 1:0.6, reaction temperature 100 °C in the presence (0.5 mol/2 mol IA) and absence of SHP. It is clear that, for a given treatment conditions, increasing IA concentration up to 3 mol/mol CD in estrification formulation brings about: (i) a significant increase in the carboxyl content of β-CD treated samples which may be attributed to the increase in the amount of free carboxyl groups fixed onto CD rings, (ii) a noticeable improvement in the double bond content (DBC) of the treated samples as a direct consequence of increasing the extent of fixation of itaconate moiety via esterification reaction, (iii) significant improvement in the esterification reaction in presence of SHP compared with that in its absence which is a direct consequence of catalytic action of SHP in the esterification of β-CD with IA.

3.6. Graft copolymerization of CDI onto chitosan

To our knowledge the mechanism of graft copolymerization of vinyl monomer onto chitosan using ceric ions as initiator has not been established. A somewhat the reaction mechanism has been reported (El-Alfy, Khalil, & Hebeish, 1981; Hebeish, El-Aref, & El-Rafie, 1979), for the grafting of vinyl monomers onto cellulose and modified cellulose, where the ceric ion (Ce^{IV}) in acidic solution forms a chelate with the cellulose molecules, probably by reaction through the hydroxyl groups and carbon C_2–C_3 of the anhydroglucose ring. Electron transfer from cellulose to the Ce^{IV} ion reduces this to Ce^{III}, followed by the release of Ce^{III} ion and anhydroglucose ring cleavage at C_2–C_3 bond with the formation of a free radical on the cellulose backbone, which is capable of initiating graft copolymerization.

Although graft copolymerization of vinyl monomers onto chitosan has been reported by a group of researchers (Inaki, Otsuru, & Takemoto, 1980; Myung, Yoon, & Ko, 2001), the grafting of CDI monomer onto chitosan has not been reported. In the present article, ceric redox initiator was selected as it can be carried out at lower reaction temperatures with reduced homopolymer formation and relatively simple.

3.7. Stability of CDI towards acid hydrolysis

Graft copolymerization of different vinyl monomers using CAN initiator is carried out in acidic medium (HNO_3). To evaluate the stability of β-CDI towards treatment in acidic medium, 5 g of β-CDI (DBC 102 mequiv./100 g CDI) was treated with 50 ml of 1% nitric acid solution at different reaction duration (30, 60, 90 and 120 min) at 60 °C. The results obtained indicate that the acid treatment of β-CDI at 60 °C for 2 h was accompanied by a slight decrease in the DBC (from 102 to 95 mequiv./100 g CDI). The data obtained reflects the good stability of ester bonds linking itaconate moiety onto

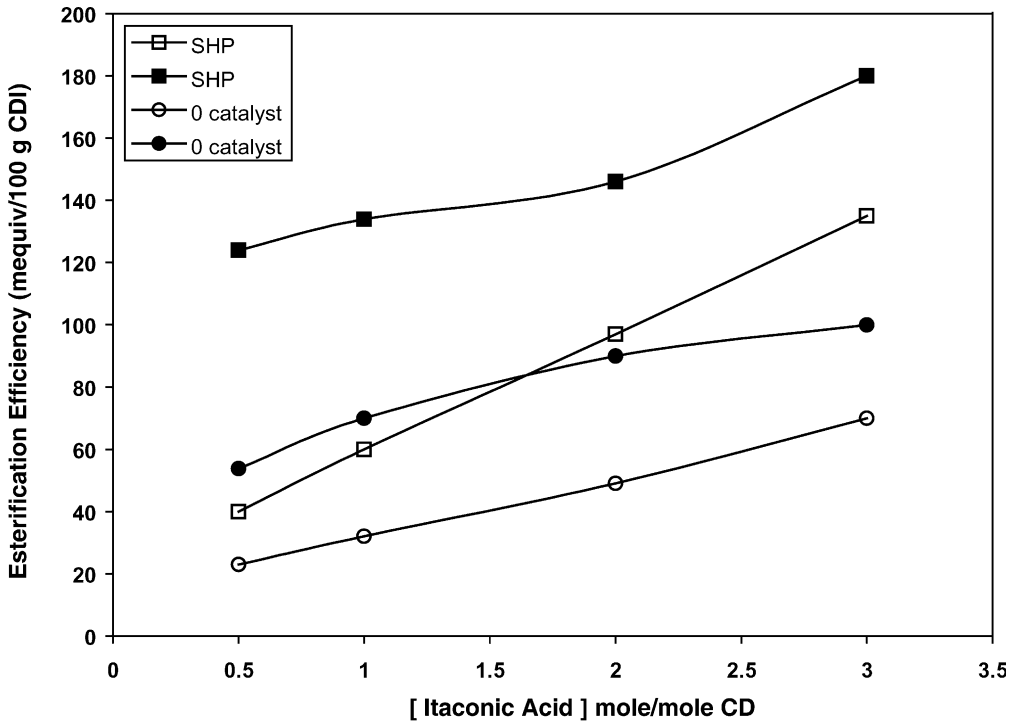


Fig. 3. Effect of reaction temperature on the esterification efficiency at CD-itaconate [SHP], 0.5 mol/2 mol IA; *M*/*L*-ratio 1:0.6; temperature, 100 °C time 2 h, filled legands; carboxyl content, unfilled legands; double bond content.

β-CD macromolecule towards acid hydrolysis. Smith, Koonce, and Hudson (1993) have synthesized vinyl monomer containing β-CD by reacting *N*-methylolacrylamide (NMA) with CD in acid medium. It was found that the prepared NMA-CD vinyl monomer has a weak stability towards acid hydrolysis of nitric acid.

3.8. Ceric consumption

The rate of ceric consumption during treatment of CD, CDI, and chitosan with 0.01 mol/l CAN dissolved in 1% HNO_3 (2% in case of chitosan) was studied individually, when 5 g of the sample was added to ceric solution at 60 °C for different reaction duration. The rate of consumption of $Ce^{(IV)}$ was evaluated by determining the residual ceric ion concentration in the reaction medium. The results (Fig. 4) indicate that, (a) extensive complexation of $Ce^{(IV)}$ with chitosan occurred within 10 min., whereas the rate of consumption of $Ce^{(IV)}$ by CDI was carried out within 20 min, which is much slower compared to chitosan. The rate of consumption of $Ce^{(IV)}$ shows that it is much faster in case of CDI compared with pure CD. It could be concluded that, the prepared monomer (CDI) is stable to CAN treatment. The formation of radicals on chitosan backbone, before the addition of CDI to the reaction mixture was thought to be advantageous for grafting. Therefore it was preferred in our study to add CDI 20 min later after mixing chitosan and CAN solution under the desired reaction temperature.

In order to investigate the effect of the reaction medium on the prepared CDI of the proper sequence of addition of the reactants. The stability of CDI towards the effect of addition of nitric acid in the reaction medium was studied via following up the change in the DBC of CDI. Preliminary experiments were performed to study the rate of CAN consumption in the presence of CD, CDI, and chitosan separately, to find the proper sequence of addition of the reactants.

As already indicated, the present study is concerned with grafting of CDI onto chitosan using CAN as initiator. The polymerization reaction was carried out under different

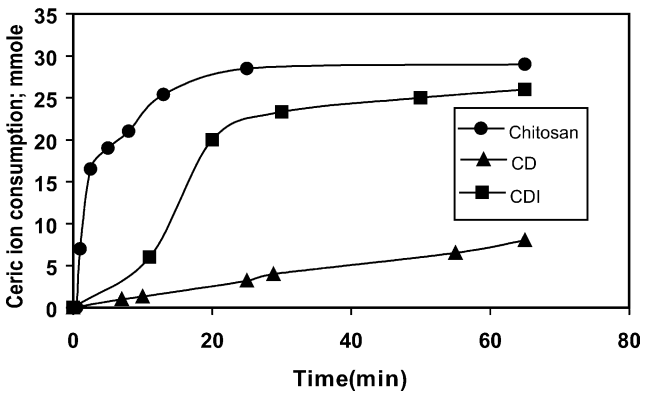


Fig. 4. Ceric ion consumption rate profile of CD, CDI and chitosan. [CAN]; 0.01 mol/l, [HNO_3]; 1% *M*/*L*; 1:15, temp.; 60 °C. (—●—), Chitosan; (—▲—), CD; (—■—) CDI.

conditions including CAN concentration, reaction temperature, monomer concentration, and DBC of CDI.

3.9. Initiator concentration

Graft copolymerization of CDI onto chitosan is an interesting way for providing chitosan with a new functional inclusion polymer. The grafting reaction was carried out at 50 °C, [CDI] (DBC; 102 mequiv./100 CDI); 5 g/1 g chitosan, [HNO_3]; 1%, using material to liquor ratio 1:15 and different CAN concentrations. The polymerization reaction was studied with respect to the graft yield percent (G.Y.%) at the end of the polymerization process.

The data indicated that, the G.Y.% of CDI increases by increasing the concentration of CAN from 0.005 to 0.03 mol/l. The enhancement in the G.Y.% with increasing CAN concentration could be attributed to the increment in the number of free radical sites formed on the chitosan backbone, which are initially involved in the grafting reaction. Also it is noted that, the huge molecular weight of CDI vinyl monomer increases the probability of formation of short side chains rather than formation of long chain polymer which may also illustrate the unexpected improvement in the G.Y.% at higher CAN concentration.

3.10. Effect of reaction temperature

The effect of polymerization temperature on grafting of CDI vinyl monomer onto chitosan was studied at various reaction temperatures at 40, 50, 60, and 60 °C, when the CDI was allowed to polymerize using the following conditions: [chitosan]; 1 g, [CDI]; 5 g, [HNO_3]; 1%, and material to liquor ration 1:15 at two different CAN concentrations (0.01 and 0.02 mol/l).

It is obvious from the data (Fig. 5) that, the extent of grafting, expressed as G.Y.%, increases by raising the reaction temperature from 40 to 50 °C. Further increase in the reaction temperature is accompanied by a significant decrease in the G.Y.%. The data indicated also that, the polymerization temperature plays an important function during the polymerization reaction, since elevation of the reaction temperature could enhance (a) initiation and propagation steps, (b) homogeneity of the reactants, (c) mobility, availability and accessibility of the CDI, and (d) solubility of CDI in the reaction medium. The decrease in the extent of grafting at higher temperature could be attributed to increasing the rate of termination of the growing chains or chain transfer.

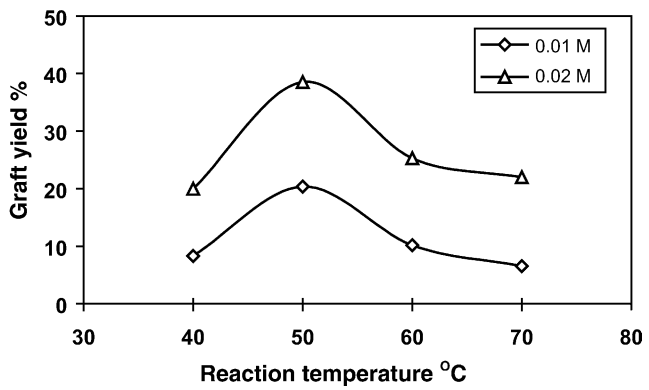


Fig. 5. Effect of reaction temperature on the graft yield percent. [CDI]; 5 g (DBC; 102 mequiv./100 g CDI)/g chitosan; 90 ml of 2% [HNO_3], time 2 h.

3.11. Effect of monomer concentration

Fig. 6 shows the relation between the monomer (CDI) concentration and the extent of grafting, expressed as G.Y.%, when the polymerization was conducted using [chitosan], 1 g; $Ce^{(IV)}$, 0.02 mol/l; temperature, 50 °C; and H_2O, 90 ml. It is depicted from the data that, increasing CDI concentration from 1 to 5 g [having 102 mequiv. DBC/100 CDI]/1 g chitosan is accompanied by a significant increase in the G.Y.%, further increment beyond this concentration is followed by a marginal increase in the G.Y.%. The enhancement in the grafting reaction could be associated with increasing the availability of CDI in the vicinity of chitosan active sites. Also the marginal enhancement in the G.Y % beyond 5 g CDI/1 g chitosan could be ascribed to (1) the increase in the concentration and viscosity of the reaction medium, (2) the decrease in the solubility of CDI and thereby a decrease in the homogeneity of the reactants and (3) chain transfer reaction.

3.12. Effect of extent of esterification

CDI having different esterification extents, expressed as DBC, have been grafted onto chitosan to evaluate the effect of DBC towards grafting. Fig. 7 shows that increasing DBC in CDI leads to an increment in its affinity to graft onto chitosan up to 150 mequiv./100 g CDI. Further increase

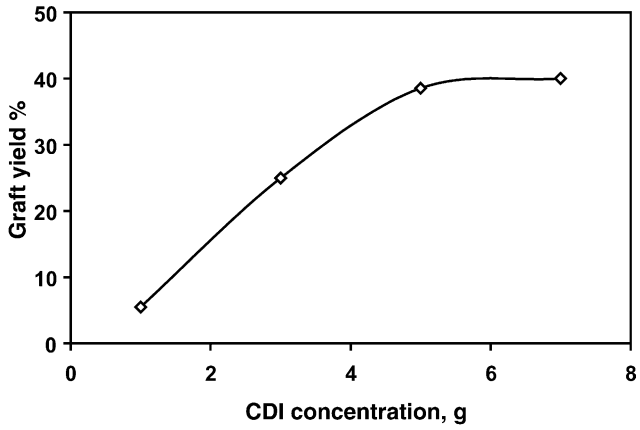


Fig. 6. Effect of [CDI] on the graft yield percent. [CAN]; 0.02 M; chitosan, 1 g; 90 ml of 2% [HNO_3]; temperature; 50 °C, time 2 h; DBC, 102 mequiv./100 g CDI.

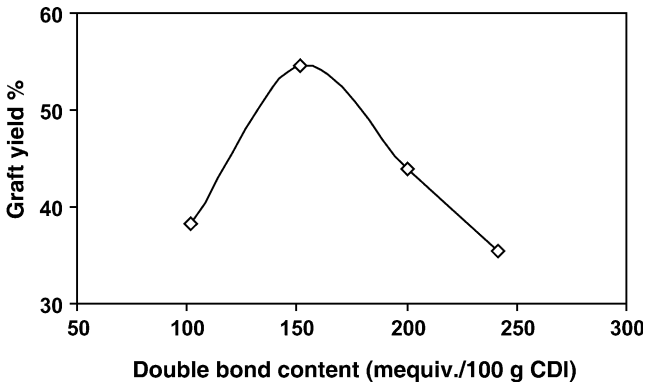


Fig. 7. Effect of double bond content on the graft yield % [CAN]; 0.02 M; [CDI], 3 g/g chitosan; 90 ml of 2% [HNO_3], temperature; 50 °C, time 2 h.

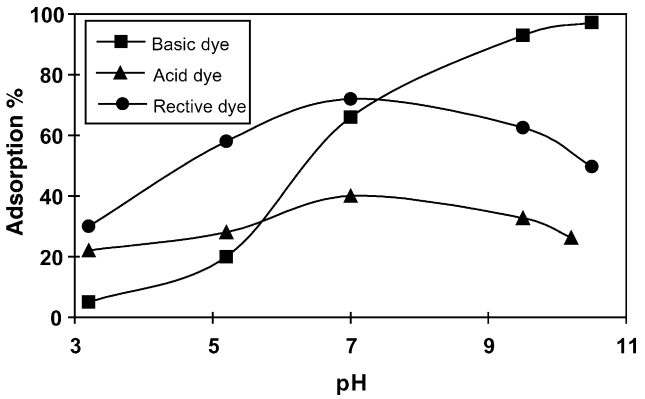


Fig. 8. Effect of pH on the adsorption % of CCPCDI. [Dye], 50 mg/l; *M/L* ratio 1:200; [glutaraldehyde], 0.6 m/g CPCDI; agitation speed, 150 rpm, temperature, 25 °C; time, 2 h. (■), Basic dye; (▲), acid dye; (●), reactive dye.

above this limit results in a significant decrement in its affinity towards grafting. The unexpected decrement in the graft yield % could be ascribed to (a) the increase in the molecular weight of CDI and thereby a decrement in its movability in the reaction medium, (b) increase in the recombination reaction in the growing polymer chains and chain transfer reaction.

3.13. Utilization of crosslinked chitosan/poly(CDI) graft copolymer as adsorbent for dyes from their solutions

Chitosan is well known sorbent for dyes in diluted effluents (Carlough, Hudson, Smith, & Spadgenske, 1991; Easton & Lincoln, 1999). The adsorption capacity for the dyes depends on the amino group concentration of chitosan. Grafting of specific functional groups (CD-itaconate) onto chitosan backbone allows sorption performance to be improved due to the appearance of new sorbting functional groups.

Crosslinked chitosan/poly(CDI) graft copolymers (CCPCDI) were used for removal of some hazardous pollutants currently found in textile waste water. The studied pollutants were basic, acid and hydrolyzed reactive dyes from aqueous medium. Also it is understandable that the adsorption capacity of the dyes from their solutions depends on both the properties of CCPCDI and the conditions of exhaustion of the dye bath. Therefore the adsorption experiments were carried out under various conditions. Variables studied were pH, concentration of dye, duration and extent of crosslinking. Given below are the results obtained along with their appropriate discussion.

3.14. Effect of pH

Fig. 8 shows the effect of pH on the adsorption % of anionic dyes namely Iragalon Rubine RL (acid dye), Brilliant Red M5B R_2 (hydrolyzed reactive), and cationic dye namely, Maxilon Blue 4 GL (Basic dye) of a concentration of 50 mg dye/l at different pH's using material-to-liquor ratio of 1:200, for 90 min. and shaking rate of 150 rpm. For a given set of conditions, it is clear (Fig. 8) that incorporation of the crosslinked chitosan poly(CDI) (CCPCDI) in the dye solution is accompanied by removal of some dyes (under investigation) irrespective of pH of the decolorization medium. This suggests that the CCPCDI has an amphoteric character. The amphoteric nature may be due to the presence of both free carboxylate anion and protonated amino groups (cationic in nature) in the polymer backbone. The protonated amino groups can bind some anionic groups (acid or reactive dyes), whereas the carboxylate anion can bind a positively charged basic dye molecules.

Further examination of Fig. 13, reveals that the alkaline medium favours the basic dye removal and the more the alkalinity is the higher the percent removal will be. The following mechanism can explain this phenomena:

$$^{+}NH_3\text{-}Q\text{-}CH_2\text{-}CH(O^{-}\text{-}C=O)\text{-}CH_2\text{-}COOCD \underset{^{-}OH}{\rightleftharpoons} NH_2\text{-}Q\text{-}CH_2\text{-}CH(O^{-}\text{-}C=O)\text{-}CH_2\text{-}COOCD + H_2O \quad (5)$$

CCPCDI

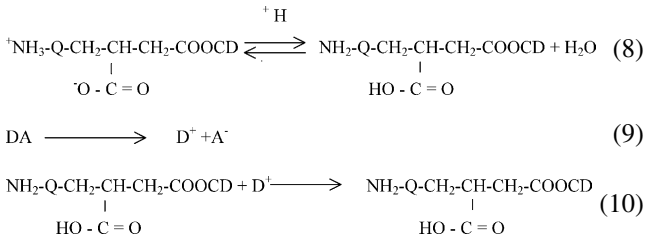
$$DA \longrightarrow D^{+} + A^{-} \quad (6)$$

$$NH_2\text{-}Q\text{-}CH_2\text{-}CH(O^{-}\text{-}C=O)\text{-}CH_2\text{-}COOCD + D^{+} \longrightarrow NH_2\text{-}Q\text{-}CH_2\text{-}CH(D^{+}O^{-}\text{-}C=O)\text{-}CH_2\text{-}COOCD \quad (7)$$

The dissociation of CCPCDI and the basic dye is shown by Eqs. (5) and (6), respectively, where D^{+} is the coloured portion of the dye, and the removal of the basic dye by CCPCDI is shown by Eq. (7). Obviously, increasing the pH results in shifting the equilibrium of reaction represented in Eq. (5) to the right hand side, i.e. towards more formation of CCPCDI anions, and consequently shifts the equilibrium of reaction to the direction of more dye uptake by CCPCDI.

The data shown in Fig. 8 represent the adsorption % of anionic dyes (acid or hydrolyzed reactive) using CCPCDI at different pH values. The data obtained shows that, the optimum pH for anionic dye uptake was at pH of 6, reflecting the role of β-CD annuli found in the CCPCDI backbone in the anionic dye uptake. The chemical

adsorption of anionic dye using CCPCDI can be represented according to the following equations.



(8)

(9)

(10)

Eqs. (8) and (9) represent the dissociation of CCPCDI and the anionic dyes, whereas Eq. (10) shows the removal of dye anion by CCPCDI. It is obvious that, the acidic pH enhances the anionic dye uptake.

On the other hand, the β-CD annuli present in the CCPCDI backbone form host–guest inclusion complex with anionic dye molecules. The stability of β-CD annuli-aromatic compound complexes is known to be established under slightly acidic condition. Shenai (1990). Such higher complex stability under slightly acidic solution can be accompanied by a noticeable enhancement in adsorption % of aromatic compound under such pH conditions. At pH of 6, the anionic dye uptake may be being chemically (via anion–cation interaction) and physically (via complex formation).

It is evident, (Fig. 8) that, at the same pH of dye solution, the adsorption % of the Iragalon Rubine RL (acid dye) is higher than that of Brilliant Red M5B R-2(hydrolyzed reactive), which can be attributed to variation of these dyes with respect to purity, molecular size and weight, chemical structure and functionality.

3.15. Effect of shaking time

Fig. 9 shows the effect of shaking time on adsorption % of the basic dye (at pH 10), acid and hydrolyzed reactive (at pH 6) using CCPCDI as adsorbent, each dye concentration was held constant at 50 mg/l.

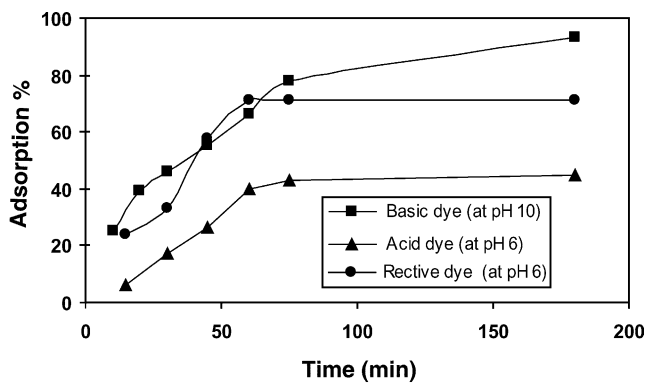


Fig. 9. Effect of duration on the adsorption % CCPCDI. [Dye], 50 mg/l; *M/L* ratio 1:200; [glutaraldehyde], 0.6 m/g CPCDI; agitation speed, 150 rpm, temperature, 25 °C. (■), Basic dye (at pH 10); (▲), acid dye (at pH 6); (●), reactive dye (at pH 6).

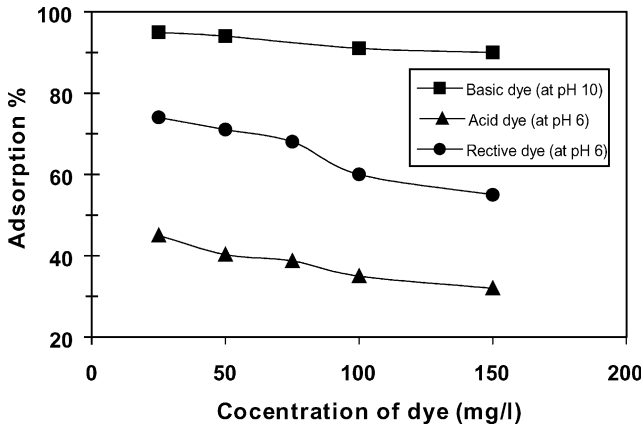


Fig. 10. Effect of [dye] on the adsorption % of CCPCDI *M/L* ratio 1:200; [glutaraldehyde], 0.6 m/g CPCDI; agitation speed, 150 rpm, temperature, 25 °C. (■), Basic dye (at pH 10); (▲), acid dye (at pH 6); (●), reactive dye (at pH 6).

It is clear that the adsorption % of the used dye increases significantly by increasing the duration up to 75 min, then levels off. The fast uptake of the dyes at the initial stage could be attributed to the higher availability of active sites (carboxylate anion, protonated amino groups and CD annuli) of the adsorbent and the dye molecules at earlier stages of the process than the latter stage.

3.16. Dye concentration

Fig. 10 shows the effect of dye concentration on adsorption % using CCPCDI as adsorbent. The material-to liquor-ratio was held constant at 1:200 and the concentration of the dye (basic, acid or hydrolyzed reactive) was changed from 25 mg/l up to 150 mg/l at optimum pH's for each dye.

The data indicates that, the adsorption % decreases on increasing the concentration. The slow down in the extent of removal on increasing the concentration could be ascribed to the accompanying increase in dye aggregation and/or depletion of accessible active sites on the CCPCDI structure (Crini et al., 1998).

3.17. Effect of extent of crosslinking

Fig. 11 shows the effect of three different levels of crosslinked chitosan/poly(CDI) (CCPCDI) with glutaraldehyde (0.4, 0.6 and 0.8 ml/g CPCDI) on the percent removal of the basic, acid and hydrolyzed reactive at the optimum removal conditions. Fig. 11 shows that, the increase in the extent of crosslinking is accompanied by a decrease in the dye uptake in case of acid and basic dye. This can be associated with accompanying decrease in active site (protonated amino groups), accessibility, and swellability of the adsorbent by increasing the level of crosslinking.

Fig. 11 shows also that, the adsorption % of hydrolyzed reactive dye is enhanced slightly by increasing the crosslinking

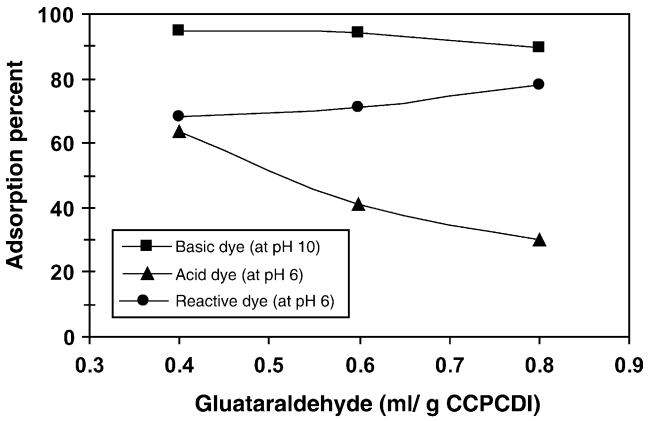


Fig. 11. Effect of extent of crosslinking on the adsorption% [dye], 50 mg/l; *M*/*L* ratio 1:200; agitation speed, 150 rpm, (■), Basic dye (at pH 10); (▲), acid dye (at pH 6); (●) reactive dye (at pH 6).

extent. This can be explained by the fact that, not only does CD annuli, protonated amino groups and carboxylate anions play an important role in the sorption mechanism, but there are also other interactions, probably physical adsorption and/or hydrogen bond interactions, due to the crosslinking agent, and /or hydrophobic guest–guest interactions (Roberts, 1992).

4. Conclusions

β-Cyclodextrin-grafted chitosan was prepared by grafting of CDI vinyl monomer onto chitosan using ceric ammonium nitrate as a redox initiation system. CDI was prepared by esterification of β-cyclodextrin with IA in a semidry process and then the pendent double bonds of CDI were utilized in graft copolymeriziation onto chitosan. The ester link of CDI shows a good stability against acid hydrolysis (HNO_3) in the polymerization medium. Crosslinked chitosan/poly(CDI) graft copolymer (CCPCDI) was used for removal of some hazardous pollutants currently found in textile waste water. The studied pollutants were Maxilon Blue 4 GL (basic dye), Iragalon Rubine RL (acid dye) and Brilliant Red M5B R-2 (hydrolyzed reactive dyes) from aqueous medium.

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