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Synthesis of diethylaminoethyl dextran hydrogel and its heavy metal ion adsorption characteristics

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ABSTRACT

Epichlorohydrin-crosslinked diethylaminoethyl dextran (DEAE-D/ECH) hydrogel was synthesized by intermolecular side-chain reaction of DEAE-D hydroxyl groups with monomeric crosslinking agent, ECH. Swelling ability, adsorption capacity and metal removal of the hydrogel were profoundly determined and some structural parameters for the hydrogel such as volume of non-swollen gel, percentages of gellation, swelling ratio and equilibrium water content were evaluated in this study.

The ability of removing heavy metal ions from Orontes River by the synthesized hydrogel, thoroughly characterized by photometric spectrometer and the adsorption characteristics of metal ions, was investigated as well as surface morphologies of the hydrogel before and after metal adsorption were examined by SEM.

Structure of DEAE-D/ECH gel was analyzed by FTIR, TGA, and DSC. Gellation point of binary system reaction between DEAE-D and ECH was determined via monitoring viscosity changes during reaction. The order of affinity based on amount of metal ion uptake was found as follows: $Zn^{2+} > Mn^{2+} > Pb^{2+} > Cd^{2+}$.

1. Introduction

Natural polymers like cellulose, starch, dextran and chitosan have increased usage in low-cost water purification technologies for the removal of metal ions from water systems. These polymers enrich or separate metal ions by binding through adsorption, chelation and ion exchange processes. Chemical modification of crosslinked starch with various reactive monomers yields ionomers used to remove heavy metal ions from wastewater (Chauhan, Singh, Chauhan, Verma, & Mahajan, 2005). Due to synthetic ion exchange resins are quite expensive so, novel materials have been examined constantly.

The removing of heavy metals from water systems has received much attention in recent years (Abd El-Rehim, Hegazy, & El-Hag Ali, 2000; Hegazy, Abd El-Rehim, & Shawky, 1999; Molina, Gomez-Anton, Rivas, Mayurana, & Pierola, 2001; Salih, Pekel, & Güven, 2000; Wang, Chen, & Chang, 2002). Metal ion chelating polymers are called as polychelatogens or chelating exchangers in general. Coordinating polymers, containing one or more electron-donor atoms (Lewis base) such as N, S, O and P can form coordinated bonds with the most of toxic heavy metals (Lewis acid) (Warshawasky, 1987). Hydrogels are water–swollen network of hydrophilic homopolymers or copolymers with crosslinked structure. These polymers acquire a great interest due to their facility of incorporating different chelating groups into the polymeric networks (El-Hag Ali, Shawky, Abd El Rehim, & Hegazy, 2003). Hydrogels containing amide, amine, carboxylic acid, and ammonium groups can bind metal ions and be usable as polychelatogens for water purification applications (Lee & Yuan, 2000).

There are several traditional treatment techniques for removing toxic metal ions from waste water such as chemical treatment, ultrafiltration or combination of chemical treatment and ultrafiltration. Thereby these techniques are not enough to remove a sufficient contaminant in pollution control limit interval (El-Hag Ali et al., 2003).

Hydrogels are capable of undergoing a volume phase transition in response to a change in external parameters such as pH, temperature and ionic strength (Chen et al., 2005; Zhang, Wu, & Chu, 2004; Zhao, Su, Fang, & Tan, 2005). They also have a wide range of application areas from biotechnology to water purification technologies (Bajpai & Johnson, 2005; Döker, Malcı, Doğan, & Salih, 2005; Hoffman, 2002; Li, Zhao, Teasdale, & John, 2002; Nguyen & West, 2002; Wasikiewicz, Nagasawa, Tamada, Mitomo, & Yoshii, 2005). As it was referred above hydrogels are water–swollen crosslinked network of hydrophilic polymers (Taleb, Elsingeny, & Ibrahim, 2007). The swelling degree of a hydrogel is strongly related to the degree of crosslinker, ionic strength of the solution, temperature, pH (Hernandez & Mijangos, 2009), the presence and the extent of hydrophilic groups such as $-OH$, $-COOH$, $-NH_2$, $-CONH_2$,

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—SO_3H (Chern, Lee, & Hsieh, 2004). These functional groups in the hydrogel networks can be utilized for the toxic metal ion removal (Cavuş & Gürdag, 2008; Sahiner, 2008).

Effective removal of lead ions from industrial wastewater has a great scientific and practical interest. Nowadays, various technologies including chemical precipitation, membrane separation, solvent extraction, ion-exchange and adsorption have been developed (Ahluwalia & Goyal, 2007; Dean, Bosqui, & Lanouette, 1972; Patterson, 1985). Adsorption is a promising technique among these techniques because of its high adsorption efficiency, easy handling, and the availability of different adsorbents (Brown, Gill, & Allen, 2000; Nurchi & Villaescusa, 2008). In the past few decades, a large number of cross-linked polymeric materials and chemically modified biosorbents have been reported to be used as adsorbents for removal of lead ions from aqueous solutions. These adsorbent materials usually incorporate various metal-complexing ligands including carboxyl, amide, amino acid, amidoxime, imidazole, thiol, pyridine and triazole functional groups (Denizli, Şanlı, Garipcan, Patır, & Alsancak, 2004; Duran, Soylak, & Tuncel, 2008; Giannakopoulos et al., 2006; Jin & Bai, 2002; Kara, Uzun, Besirli, & Denizli, 2004; Kavaklı & Güven, 2004; Naeem, Woertz, & Fein, 2006; Yantasee et al., 2007; Yordanov & Roundhill, 1998).

According to the scientific and technological information, toxic metal contamination is a serious problem (Jang, Jeonga, Mina, Lyoob, & Lee, 2008; Zhou, Wang, Liu, & Huang, 2009; Zhou, Nie, White, He, & Zhu, 2009) it threats human health since heavy metal ions Pb^{2+}, Cd^{2+}, Hg^{2+} and Ni^{2+} are toxic and carcinogenic even at very low concentrations (Liu, Bai, & Ly, 2008). Because of environmental pollutants resulting from the industries' waste products, novel polymeric materials have been researched and become popular to remove and separate heavy metal ions by complexation and ion exchange mechanism (Atia, Donia, & Yousif, 2003; Debbaudt, Ferreira, & Gschaider, 2004; Katime & Rodriguez, 2001; Trimukhe & Varma, 2008; Yetimoğlu, Kahraman, Ercan, Akdemir, & Apohan, 2007). DEAE-D is a polycationic derivative of dextran and it is chosen as an adsorption agent for heavy metal ions.

DEAE-D is a chemically derivatize dextran produced by reacting diethylaminoethyl chloride with dextran. Its degree of substitution corresponds to approximately one DEAE substituent per three glucose units (0.33 mole DEAE per 1 mol glucose) (Icoz & Lokini, 2007). DEAE-D contains three basic groups with different pK_a values. One of them (2-(diethyl amino) ethyl, *A*) consists of a tertiary amino group with a pK_a of 9.5. The other two moieties are 2-[[2-(diethyl amino) ethyl]-diethyl ammonium] ethyl, *B*) a tertiary amino group with a pK_a of 5.7 and the strongest basic quaternary ammonium group with a pK_a of 14. The pH value and ionic strength influences the dissociation behaviour and the conformational change of DEAE-D (Heinze, Liebert, Heublein, & Horning, 2006) (Scheme 1).

The Orontes or Asi, which runs through Lebanon, Syria and Turkey, is a river that works as the only source of irrigation water for many Antakya districts, south of Turkey. Additionally the Orontes River allows some fish species to live. Currently, zinc and manganese concentrations of the Orontes River are very high, what threatens seriously the human health. These concentrations have been increasing due to the daily contaminated water disposals that proceed from factories.

In this study, DEAE-D/ECH hydrogel was prepared via intermolecular side chain reaction of DEAE-D with ECH in aqueous solutions in the presence of sodium hydroxide and was used as an chelating agent for the removal of Zn^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+} ions. The structures of monomer, crosslinker and the hydrogel were characterized by FTIR analysis. Thermal behaviours of both, monomer and the hydrogel, were investigated with TGA and DSC. The morphologies of the dry and swollen hydrogel sample were examined by SEM. In addition, the viscosity of crosslinking reaction products was also recorded continuously as a function of time. The percentage of gellation and pH-dependent swelling of the hydrogel were determined gravimetrically.

2. Materials and methods

2.1. Materials

DEAE-D hydrochloride (M_w: 500,000 g/mol) used in this study was supplied by Sigma (Denmark). The crosslinked agent, ECH, was supplied by Merck. The accelerator agent *N*,*N*,*N*′,*N*′-tetramethyl ethylene diamine (TEMED) was supplied by Merck. Sodium hydroxide was used in the preparation of alkaline medium for the crosslinking reactions and it was supplied by Merck. Acetone was used as non-solvent agent and it was supplied by Merck. The water samples were obtained from the Orontes River in Antakya and used for adsorption studies.

2.2. Synthesis of the DEAE-D/ECH hydrogels

Synthesis of the DEAE-D/ECH hydrogel was accomplished in aqueous solutions by intermolecular side-chain reaction of DEAE-D hydroxyl groups with ECH in the presence of sodium hydroxide and TEMED. Mixture was stirred magnetically for 20 min at 55 °C. Resulting hydrogel was soaked in distilled water for 2 days to get rid of DEAE-D (uncrosslinked) and/or ECH (crosslinkers) and then hydrogel was dried in oven until no further weight loss occurs.

2.3. Characterization of DEAE-D/ECH hydrogel

Fourier Transform Infrared (FTIR) spectra of the DEAE-D and DEAE-D/ECH hydrogel were recorded on a Perkin Elmer RX-1 Spectrometer in the 4400–400 cm^{-1} by the grinding of the DEAE-D, and its gel with KBr. The surface morphology of DEAE-D and DEAE-D/ECH hydrogel was examined using Scanning Electron Microscopy (SEM), (JSM 5500, JEOL). Differential Scanning Calorimeter (DSC) analysis of DEAE-D and its hydrogel were carried out with a DSC 60 (Shimadzu) in dynamic nitrogen atmosphere at a heating rate of 10 °C/min and temperature interval between 0 and 500 °C. Thermogravimetric analysis (TGA) of DEAE-D and its hydrogel were carried out with Thermogravimetric Analyzer (Shimadzu) in dynamic nitrogen atmosphere at a heating rate of 10 °C/min and temperature interval between 0 and 500 °C.

2.4. Viscosity measurements

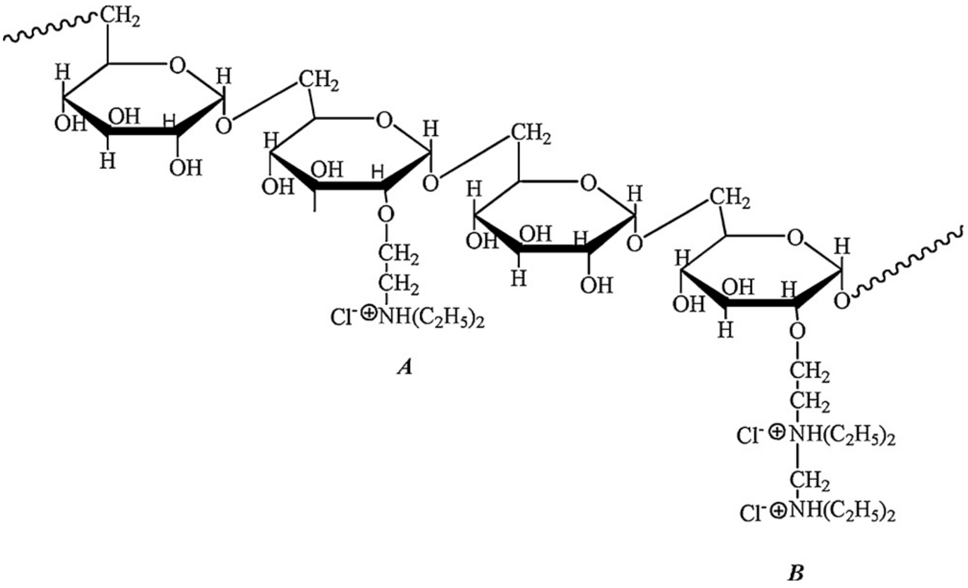
The gellation behaviour between DEAE-D and ECH was studied by measuring the solution viscosity of samples at basic medium as a function of time by using a Fungilab Rotary Cylinder Viscometer (Premium Series) equipped with low viscosity adapter (LCP) supplied with spindle at 55 °C. Experiments were carried out at least three times.

2.5. Determination of DEAE-D/ECH hydrogel volume

Bulk density of hydrogel was filled with non-solvent, acetone. The bulk density was expressed by the following equation:

$$V_{nonswollen\,gel} = \frac{w_{in\quad air} - w_{in\quad acetone}}{\rho_{acetone}}$$

where $V_{nonswollen\,gel}$ is the volume of hydrogel sample before swelling, $w_{in\,air}$ and $w_{in\,acetone}$ are weights of the hydrogel in air and in acetone respectively, and $\rho_{acetone}$ describes the density of acetone.



Scheme 1. Structure of DEAE-D containing 2-(diethylamino)ethyl (A) and 2-[[2-(diethylamino)ethyl]diethylammonium]ethyl (B) groups.

2.6. Swelling experiments of the DEAE-D/ECH hydrogel in water

Hydrogels were immersed in deionized water for one day to wash out any unreacted monomers and initiators, and then dried in a vacuum oven at 35 °C for several days until achieving constant weight (w_i). Pre-weighed dry hydrogel were immersed into 50 mL of deionized water at 20.0 ± 0.1 °C until it swelled. The swollen hydrogel sample was taken out, dried in vacuum oven and reweighed (w_d). Experiments were carried out at least three times. The percentage of gellation was determined gravimetrically by the following equation:

$$\text{gellation}\,(\%) = \frac{w_d}{w_i} \times 100$$

Pre-weighed dry hydrogel was immersed in water at 20.0 ± 0.1 °C until it swelled to equilibrium with the intention of determining the swelling ratio of DEAE-D/ECH hydrogel. It was confirmed that approximately 24 h were enough to reach the swelling equilibrium of the sample. The swollen sample was taken and immediately weighed (after the superficial water was wiped off using absorbent paper). Equilibrium water content (g H_20/g hydrogel) was calculated from the following equation:

$$\text{equilibrium water content}\,(\%) = \frac{w_e - w_i}{w_e} \times 100$$

where w_e *is* the weight of the swollen state of the sample at equilibrium and w_i is the weight of the dry state of the sample (initial weight). The swelling ratio was calculated as a function of time by the following equation:

$$\text{swelling ratio}\,(\%) = \frac{w_t - w_i}{w_i} \times 100$$

where w_t represents the weight in the swollen state of gel sample at a given time (t).

2.7. Swelling of the DEAE-D/ECH hydrogel in different pH mediums

In order to follow the pH response of the DEAE-D/ECH hydrogel samples were allowed to swell till equilibrium in three different pH mediums (pH 2.0; pH 9.2 and river water at pH 7.4) at 20°C ± 0.1 °C. Swelling experiments were carried out at least three times.

2.8. Adsorption studies and swelling of the metal loaded DEAE-D/ECH hydrogel

Metal ion adsorption studies, in competitive conditions, were conducted with concentration of 200 mg/L of the DEAE-D/ECH hydrogel in river water sample at pH 7.4 in a controlled temperature bath at 20.0 ± 0.1 °C by magnetic stirrer. The equilibrated supernatant was filtered from the hydrogel. The concentration of nonadsorbed heavy metal ions (Zn^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+}) in solution was measured by photometric spectrometer (Merck Spectroquant Nova 60). The instrument response was periodically checked with known heavy metal solution standards.

Adsorption capacity, q_t, is the maximum metal ion concentration adsorbed per weight unit of the hydrogel (mg metal ion/g dry hydrogel) at time *t*. It was calculated from the following mass balance equation:

$$q_t\,(\text{mg/g}) = \frac{(C_o - C_t)V}{w}$$

where C_o and C_t (mg/L) are concentrations of the metal ions in the aqueous phase before-adsorption and after-adsorption at time *t*, respectively; *V* is the volume of the aqueous phase (mL), and *w* is the weight of used dry hydrogel (mg).

The percent removal was calculated according to the following equation:

$$\text{percent removal} = \frac{C_o - C_t}{C_t} \times 100$$

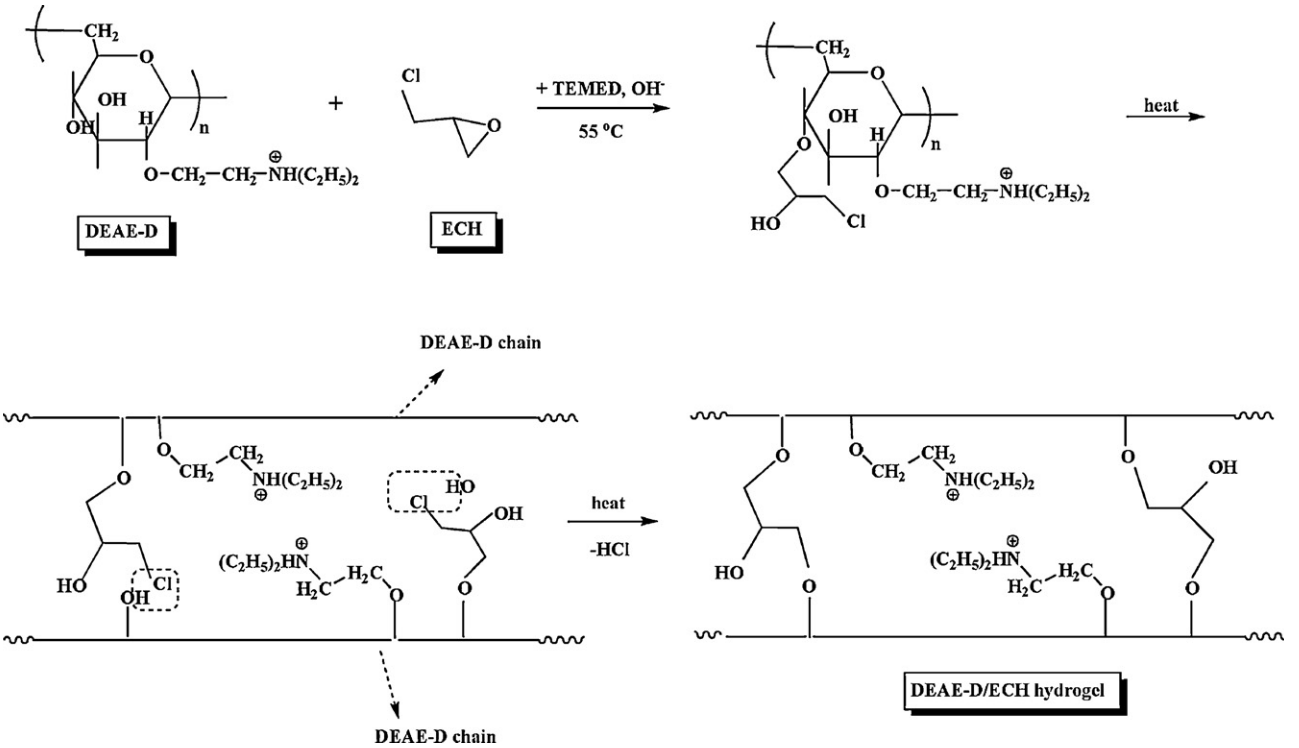
3. Results and discussion

3.1. Synthesis of the DEAE-D/ECH hydrogel

The synthesis conditions of DEAE-D/ECH hydrogel are given in Table 1. This reaction was proceeded in the presence of NaOH, which is acceptor for HCl-product of dehydrochlorination (removing HCl) of chlorohydrin. In the DEAE-D/ECH/NaOH system, DEAE-D was used as a polyether polyol and general scheme of crosslinking reaction corresponded to known reaction of ECH to DEAE-D macromolecules in the basic aqueous medium which is a molecular reaction passing via the side chain alcoholate (DEAE-D-ONa) formation stage. The chlorohydrine fragments can easily be

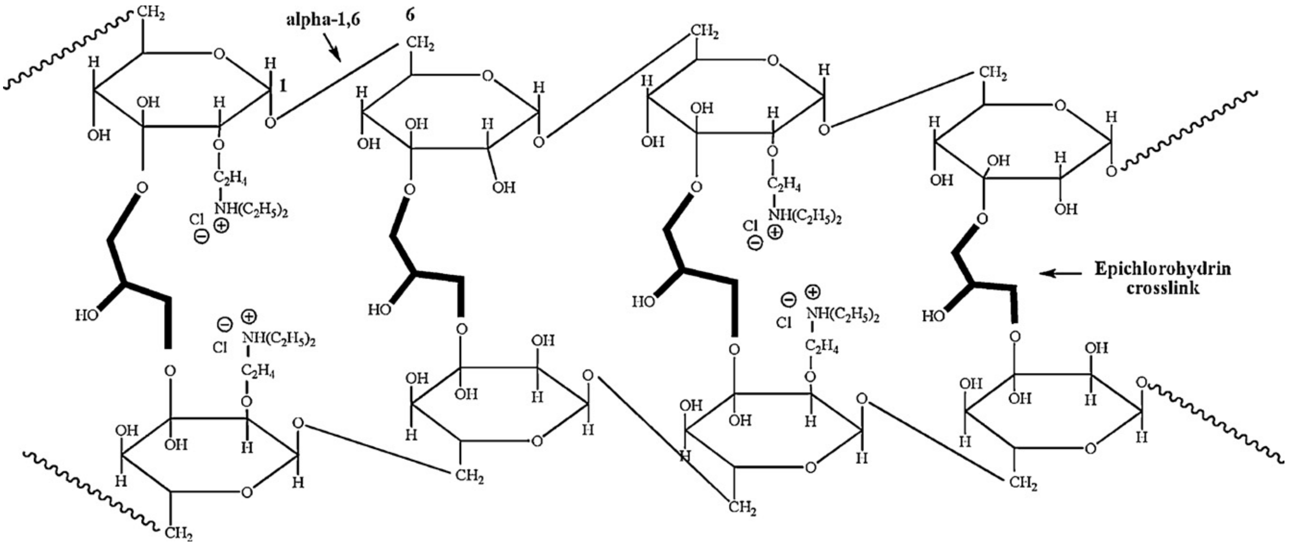
Table 1
Synthesis conditions of DEAE-D/ECH hydrogel.

Monomer	Crosslinker	Accelerator	Temperature (°C)	Time (min)	pH of medium
DEAE-D	ECH	TEMED	55	20	~13–14



Scheme 2. Side-chain reaction suggested for crosslinking reaction of DEAE-D with ECH.

transformed into epoxy group by dehydrochlorination in the presence of NaOH. In the first stage of the reaction between DEAE-D and ECH, the opening of epoxy groups with formation of free chlorohydrine fragments in the side chain of linear macromolecules was proceeded. Then, dehydrochlorination reaction between two macromolecules containing OH^- and Cl-substitute was realized providing formation of crosslinking structure (Guner, Akman, & Rzaev, 2001). The proposed mechanism for crosslinking reaction is illustrated in Scheme 2. Schematic representation of the epichlorohydrin-crosslinked diethylaminoethyl dextran hydrogel is shown in Scheme 3. Yield of hydrogel was obtained as 87.8%.



Scheme 3. Schematic representation of the epichlorohydrin-crosslinked diethylaminoethyl dextran hydrogel.

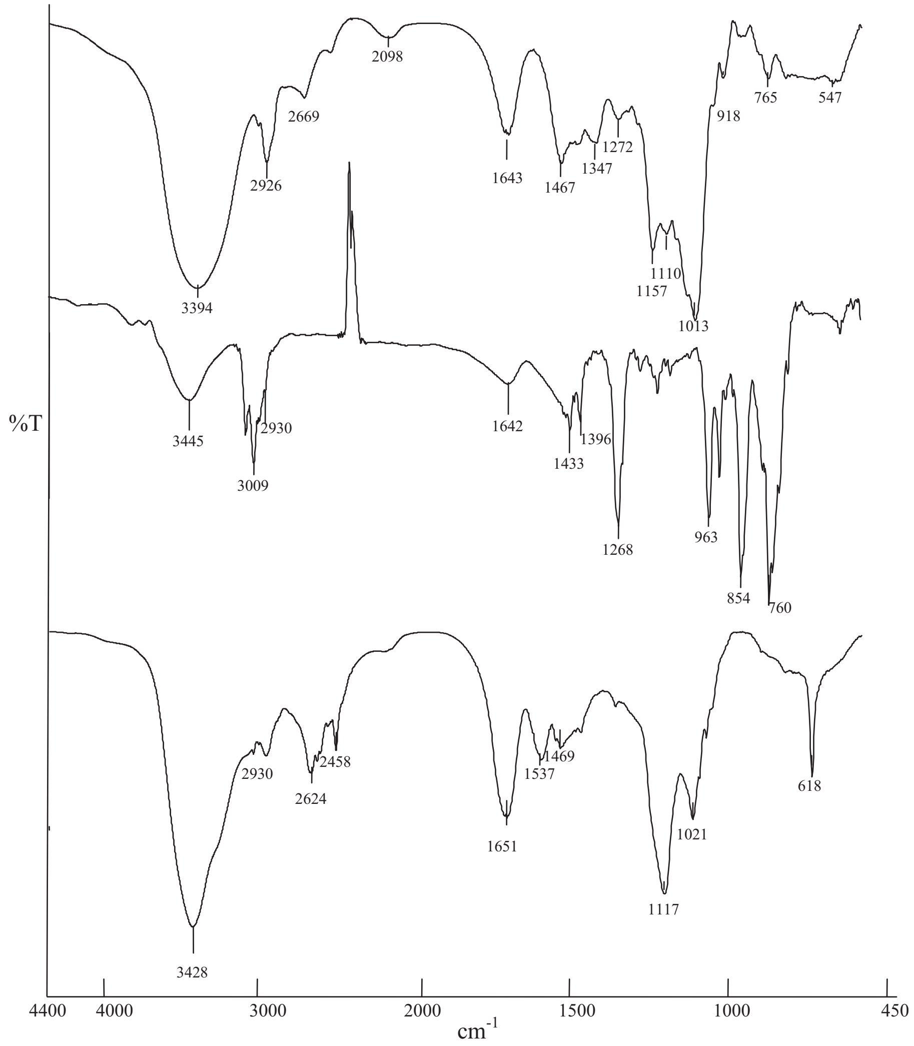


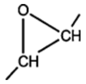
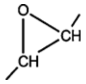
Fig. 1. The FT-IR spectra (a) DEAE-D, (b) ECH, (c) DEAE-D/ECH hydrogel.

3.2. FTIR spectroscopy

Infrared Spectra of DEAE-D; ECH, and DEAE-D/ECH hydrogel are presented in Fig. 1. The changes in position and intensities of main absorption bands are summarized in Table 2.

Spectral results indicate that crosslinking occurs through the side-chain reactions of DEAE-D hydroxyl groups with chloride group of ECH. The band at 1117 cm^{-1} was ascribed to C—O stretching; same functional group was seen at 965 cm^{-1} of ECH. Decreasing intensity of 1269 cm^{-1} and 853 cm^{-1} (epoxy ring) was

Table 2
The changes in position and intensities of band observed from the FTIR spectra of ECH, DEAE-D, and DEAE-D/ECH hydrogel.

Wavenumber, cm^{-1}			Functional group
DEAE-D	ECH	DEAE-D/ECH	
3394 $^{(s)}$	–	3428 $^{(s)}$	N—H stretching, free and H-bonded O—H
2926 $^{(w)}$	3010 $^{(m)}$	2930 $^{(w)}$	C—H stretching
1643 $^{(m)}$	–	1651 $^{(m)}$	N—H bonding
1467 $^{(w)}$	1436 $^{(w)}$	1470 $^{(w)}$	C—C stretching
–	1269 $^{(sp)}$	di	Epoxy ring 
1157 $^{(w)}$	–	1117 $^{(sp)}$	C—O—C stretching
1013 $^{(m)}$	–	1022 $^{(w)}$	C—N stretching
918 $^{(w)}$	965 $^{(sp)}$	di	C—O stretching
–	853 $^{(sp)}$	di	Epoxy ring 
765 $^{(w)}$	753 $^{(w)}$	618 $^{(m)}$	C—Cl stretching

s, strong; *sp*, sharp; *w*, weak; *m*, medium; *di*, decreased intensity.

Table 3
The temperature starting to decompose, weight loss percent and humidity of DEAE-D and DEAE-D/ECH hydrogel determined from TGA.

	Td_1 (°C)	Td_2 (°C)	Weight loss (%)					Moisture content (%)
			200 °C	260 °C	267 °C	400 °C	800 °C	
DEAE-D	150	260	10	55.48	–	70	87	13
DEAE-D/ECH hydrogel	180	267	20	–	49.51	75	90	–

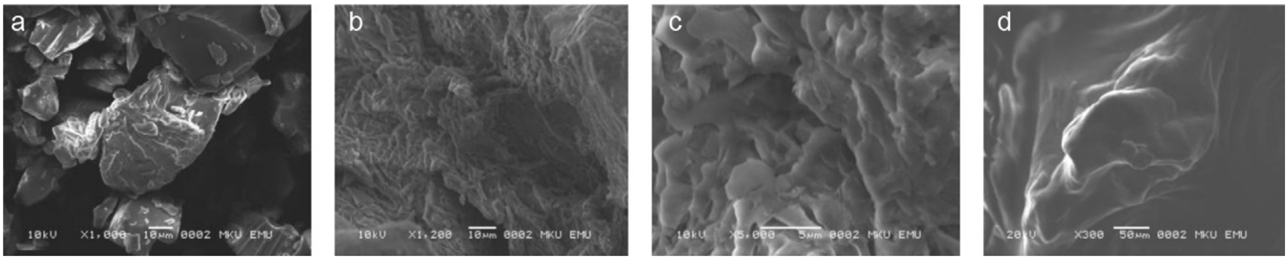


Fig. 2. SEM images (a) DEAE-D polymer, (b) pre-adsorption DEAE-D/ECH hydrogel (at magnification 1200×), (c) pre-adsorption DEAE-D/ECH hydrogel (at magnification 5000×), (d) DEAE-D/ECH hydrogel adsorbed metal.

showed opening of ring at structure of gel. Intensities of bands at 760, 853, and 965 cm^{-1} of ECH were considerable decreased with gel formation. In addition, asymmetrical peak at 3445 cm^{-1} evidenced presence of hydrogen-bond in structure. These values are in harmony with values in literature (Guner et al., 2001; Sahin, Kocak, Arslan, & Ucan, 2010).

3.3. Thermal analysis

The data of TGA of DEAE-D and DEAE-D/ECH hydrogel were obtained between 0 and 900 °C and under N_2 atmosphere. The temperature starting to decompose, percents of weight loss and moisture content of DEAE and hydrogel are given in Table 3. While thermal degradation of DEAE-D was occurred at one step, degradation of hydrogel was at two steps. The maximum weight loss is at 260 °C for DEAE-D and 267 °C for its gel (Guner et al., 2001; Spychaj & Bartkowiak, 1998). According to TGA results, gel is more stable than polymer. Weight loss of hydrogel is approximately 75% at 500 °C.

DEAE-D and DEAE-D/ECH hydrogel samples were also evaluated by DSC. There are two-endothermic peak at 94 °C and 243 °C on the thermograms of DEAE-D and DEAE-D/ECH hydrogel (Table 4). The glass transition temperatures (T_g) of polymer and hydrogel were found at 174 °C and 228 °C respectively. It was shown that thermal stability of gel is higher according to polymer. It was observed that the hydrogel T_g increased and crosslinking decreased the segment's motion. Moreover it was observed the peak of melting temperature (T_m) at 448 °C on the DSC thermogram of DEAE-D. After crosslinking, melting endothermic peak was vanished. It supports that hydrogel is not crystal.

3.4. SEM analysis

SEM images of DEAE-D, before-adsorption hydrogel and hydrogel adsorbed metal are given in Fig. 2a–d respectively. DEAE-D is porous as seen in Fig. 2a. The SEM images of pre-adsorption hydrogel were given at magnification 1200× and 5000× in Fig. 2b and c respectively. As seen in these figures, gel is porous, crosslinked and a matrix which shaped fibre. Pores are mostly smooth and shaped ellipse rod per unit area. SEM image of hydrogel adsorbed metal is given in Fig. 2d. After loaded metal, gel is more rigid, orderly and thick; pores are filled with metal ions after interacting with metal ions in river water (Kartha & Srivastava, 1985a, 1985b; Sahin et al., 2010; Spychaj & Bartkowiak, 1998).

Table 4
The glass transition temperature of DEAE-D and DEAE-D/ECH hydrogel determined from DSC.

	Td_1 (°C)	Td_2 (°C)	T_g (°C)	T_m (°C)
DEAE-D	94	243	174	448
DEAE-D/ECH hydrogel	136	257	228	–

3.5. Viscosity studies

Viscosity values of gellation reaction between DEAE-D and ECH were measured with dilute solution viscometer as a function of time. Gellation point in the binary system reaction between DEAE-D and ECH was determined by digital rotational viscometer. Time-viscosity curve of gellation reaction is given in Fig. 3. It is clearly seen that the viscosity of reaction was increased by time, but after a certain period, it was observed constant viscosity behaviour. While viscosity is 71.58 cP at $t = 0$ s, it is accessed maximum value (250.17 cP) at the 20th min. The sharp increase in the viscosity was shown completed of gellation reaction. This point completed of reaction is gellation point. It was observed partially gelatinized condition through 20 min at the reaction between DEAE-D and ECH (Kartha & Srivastava, 1985a, 1985b).

3.6. Structural parameters calculated from swelling of the DEAE-D/ECH hydrogel in water and acetone

Structural parameters (volume of non-swollen gel in acetone (nonsolvent) and percent gellation; percent swelling ratio, percent equilibrium water content calculated from swelling of the hydrogel in water) are given in Table 5. The swelling ratio of hydrogel is 1291% in pure water. This ratio indicates that attractive interactions between polymer chain and water molecule dominate over the attraction between the polymer chains. The equilibrium swelling ratio of hydrogel was determined as 420.86%. These results demonstrated that the ability of swelling of hydrogel is high and it is

Table 5
Structural parameters calculated corresponding DEAE-D/ECH hydrogel.

Volume of non-swollen gel (cm^3)	Percent gellation	Percent swelling ratio	Percent equilibrium water content
0.0199	84.56	1291	420.86

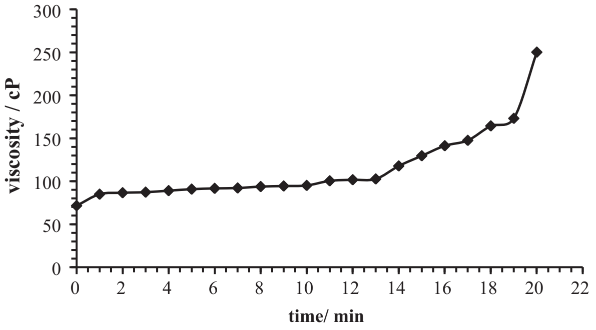


Fig. 3. Viscosity values of gellation reaction between DEAE-D and ECH as a function of time.

highly hydrophilic with a high degree of water uptake and high equilibrium water content.

3.7. *Poly-electrolyte behaviour of the DEAE-D/ECH hydrogel in different pH mediums*

Kinetic curves of swelling of DEAE-D/ECH hydrogel in the different pHs (at pH 2.0; pH 9.2 and river water at pH 7.4) are given in Fig. 4. As can be seen in Fig. 4, the values of the swelling of hydrogel are strongly depending on the pH. Swelling (water uptake) capability of dry hydrogel at all pHs was increased by time and hydrogel shows constant swelling behaviour after a short time (equilibrium time of gels was seen as approximately 1400 min), so process was equilibrated. Maximum swelling capability of hydrogel was varied in range 1088, 883 and 788% at pH 2; 7.4 and 9.2 respectively. Water content of gel is higher at the acidic medium than basic medium.

The swelling of DEAE-D/ECH hydrogel, consistently with polyelectrolyte systems, is strongly dependent on pH and ionic strength of polymer. During gellation process, N^+ group of DEAE-D transfers to structure contains unpaired electron thereby self-donating excess hydrogen. Increasing of $-CH_2-CH_2-\overset{\oplus}{N}H_2-(C_2H_5)_2$ groups in the structure, promotes electrostatic attraction, hence network structure expands and increases swelling. An increase from pH = 2 to 9.2 has decreased swelling percentage of the hydrogel. The reason of reaching maximum swelling of hydrogel at pH 2 is that protonization of amine groups of DEAE-D is completed at this pH value (Kavaklı, Yılmaz, & Sen, 2007).

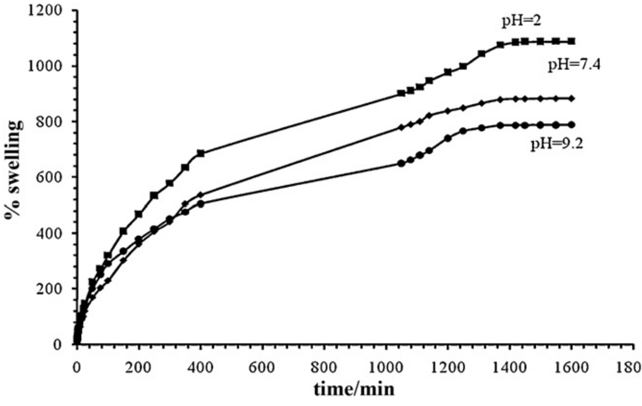


Fig. 4. Kinetic swelling curves of DEAE-D/ECH hydrogel in different pHs.

3.8. *Adsorption of metal ions onto the DEAE-D/ECH hydrogel*

Since various ions are present in the wastewater, it is essential to investigate the competitive binding affinity of these ions towards hydrogel. Different factors such as hydrogel structure, metal combination, level of metal concentration, uptake time and experimental conditions affect the interaction between the metal ion and the reactive sites of hydrogel (Caykara & Inam, 2003; El-Hag Ali et al., 2003; Kasgoz, Ozgumus, & Orbay, 2005; Katime & Rodriguez, 2001; Ozay, Ekici, Baran, Aktas, & Sahiner, 2009; Sag, 2001). In this study, crosslinked DEAE-D/ECH hydrogel was used as adsorbent and multi-component heavy metal adsorption study was carried out. It was thought that metal ions were adsorbed competitively in waste water. It was considered there are three different possibility modifications in structure of gel interacting by metal ions. Absorption by substitution of active functional groups can acquire metal ions or a simple chelating or adsorption possibility due to opening of polymer matrix (Chauhan et al., 2005). Structure of polymer skeleton is an important factor affected adsorption of metal ion (Kavaklı et al., 2007). It was thought that diethylaminoethyl group increases adsorption of metal ions.

Adsorption ability of polyvalent metal cations (Zn^{2+}, Mn^{2+}, Pb^{2+}, and Cd^{2+} ions) with hydroxyl groups of crosslinked DEAE-D/ECH hydrogel was found with photometric spectrometer. The photometric spectra results are given in Tables 6 and 7.

Adsorption capacity was calculated from equation given in Experimental Part and results are submitted in Table 6. According to the obtained results from Table 6, interaction with Zn^{2+}, Mn^{2+} and Pb^{2+} ions of gel are higher than Cd^{2+} ions. The decreasing order of metal removal strength of gel is as follows: $Mn^{2+} > Zn^{2+} > Pb^{2+} > Cd^{2+}$. From this order, it was determined that DEAE-D/ECH hydrogel have abilities absorption of water and adsorption of metal ions (except for Cd^{2+}) in river water.

Maximum values permitted for heavy metal ion concentrations in irrigation water (Pratt, 1972) and heavy metal ion concentrations in river water used in this study are compared in Table 7. According to these results, concentration of Zn^{2+}, Mn^{2+} and Cd^{2+} ions are over limitations. Because of this, it was thought that Orontes River water is aggregate with respect to Zn^{2+}, Mn^{2+} and Cd^{2+} ions usage by aim of irrigation. It was concluded that DEAE-D/ECH hydrogel synthesized in this study is substantially adsorbed other ions (Zn^{2+}, Mn^{2+} and Pb^{2+}) except for Cd^{2+} ion.

Interactions occurred between DEAE-D/ECH hydrogel and metal ions are shown thereby draw a model in Scheme 4. When OH^- was added to DEAE-D/ECH hydrogel system, H_2O liberates and OH^- groups convert into O^-, $-CH_2-CH_2-\overset{\oplus}{N}H_2-(C_2H_5)_2$ group transforms to $-CH_2-CH_2-\ddot{N}H_2-(C_2H_5)_2$ form thereby H_2O and H^+ ion give. In this case, hydrogel structure becomes appropriate to bond metal. The probabilities of interaction between DEAE-D/ECH

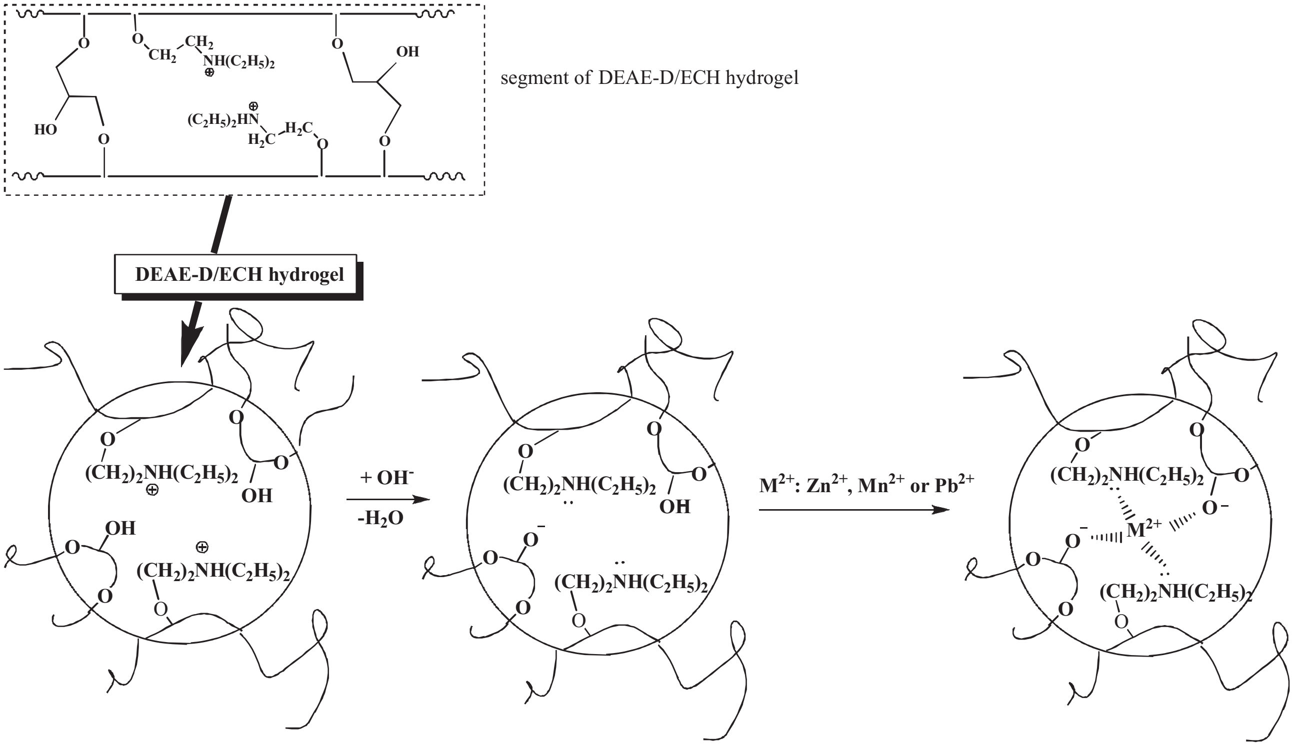
Table 6
Adsorption capacity, metal removal, percent metal ion concentrations determined from photometric spectrometer analysis.

	Zn^{2+}	Mn^{2+}	Pb^{2+}	Cd^{2+}
Concentration of metal ion in the Orontes River (mg/L)	3.46	0.75	0.42	0.113
Concentration of desorbed metal ions *(metal ions in solution)*	1.23	0.17	0.27	0.102
Concentration of adsorbed metal ions *(metal ions in hydrogel)*	2.23	0.58	0.15	0.011
Adsorption capacity (q_t) (mg/g)	509.83	132.60	34.29	2.51
Percent removal	64	77	36	10

Table 7
The comparison of maximum values permitted for heavy metal ion concentrations in irrigation water and heavy metal ion concentrations in Orontes River.

	Zn^{2+}	Mn^{2+}	Pb^{2+}	Cd^{2+}
Maximum values permitted for heavy metal ion concentrations in irrigation water (mg/L)[a]	2.0	0.20	5.0	0.01
Heavy metal ion concentration in Orontes River (mg/L)	3.46	0.75	0.42	0.113

[a] Adapted from Pratt (1972).



Scheme 4. Interaction probabilities of DEAE-D hydrogel with metal.

hydrogel and metal ions are given in Scheme 4 (Kavaklı et al., 2007; Thomas, Namdeo, Mohan, Bajpai, & Bajpai, 2008).

The removal of heavy metal ions by hydrogel was occurred in the order of $Zn^{2+} > Mn^{2+} > Pb^{2+} > Cd^{2+}$. Among the ions investigated in this work, the lowest adsorption on hydrogel was observed with Cd^{2+} ions. It can be concluded that diethylaminoethyl (DEAE) groups have less affinity for binding of Cd^{2+} ions in comparison to that for the Zn^{2+}, Mn^{2+} and Pb^{2+} ions.

4. Conclusions

It was synthesized epichlorohydrin-crosslinked diethylaminoethyl dextran hydrogel with side-chain reaction of DEAE-D with ECH in this study while it was used commercial microspheres of DEAE-D in several studies in literature. The crosslinking reaction of DEAE-D in the given conditions was confirmed by FTIR, TGA, DSC and SEM as well as by structure-property relationship of crosslinked macromolecules.

Consequently it was proposed that DEAE-D/ECH hydrogel can be used, by aim of removing unwanted water or some chemical substances in environment and controlled release of fertilizer and pesticide in agricultural area.

In conclusion, it may be suggested that this hydrogel promise to be potential sorbents for the removal of heavy metal ions (Zn^{2+}, Mn^{2+} and Pb^{2+} ions) from waste water and aqueous effluents.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2012.06.068.

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