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Study on adsorption, regeneration, and reuse of crosslinked chitosan graft copolymers for Cu(II) ion removal from aqueous solutions

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ABSTRACT

This study deals with the adsorption, regeneration, and reuse of chitosan-graft-itaconic acid and chitosan-graft-crotonic acid beads for Cu(II) ion removal from aqueous solutions. For this aim, adsorption capacities, adsorption kinetics, and adsorption isotherms of these crosslinked chitosan-graft-copolymeric beads were investigated in detail. The maximum adsorption capacities of chitosan-graft-itaconic acid and chitosan-graft-crotonic acid beads were found to be 0.31 and 0.25 mmol/g, respectively. In addition, it was found that the pseudo-second-order kinetic model is more suitable than pseudo-first-order model for the adsorption of Cu(II) ions onto the beads according to adsorption kinetics data. Adsorption isotherm data were evaluated using Freundlich, Langmuir, Brauner–Emmet–Teller, Dubinin–Radushkevich and Temkin isotherm models. The results revealed that the adsorption of Cu(II) ions onto the beads fits very well Freundlich isotherm model. Then, the beads were regenerated with an acid solution, and they were reused for adsorption of Cu(II) ions. Regeneration study results showed that, the metal ion removal capacity of regenerated beads did not change significantly in the end of the fourth regeneration period compared to the first regeneration period. It was concluded that the crosslinked chitosan-graft-copolymeric beads might be suitable adsorbent for the removal of metal ions from aqueous effluent.

Keywords: Adsorption; Crosslinked copolymers; Graft copolymers; Chitosan; Crotonic acid; Itaconic acid

1. Introduction

The chemical contamination of water with toxic materials such as heavy metals, aromatic molecules, and dyes is an important environmental problem [1,2]. Copper, which is one of the heavy metals, interferes into natural waters with various industrial processes such as mining, metallurgy, and fertilizer industries. Heavy metals can accumulate easily in living tissues. Therefore, the presence of Cu ions in natural waters causes toxic effects for humans and other living organism in the long term [3–5].

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The removal of heavy metal from waters is extremely important because of their toxic effects [6]. Today, there are various treatment methods to remove heavy metal ions and basic dyes from industrial and natural water such as ion-exchange, evaporation, electrodialysis, chemical precipitation, adsorption, and reverse osmosis techniques [6–9]. Since adsorption method is highly effective, inexpensive and easy to operate, it is widely preferred for water treatment processes [10]. In recent years, polymeric adsorbents have been used to remove heavy metal ions and basic dyes from waste waters [4–7,11–15]. In parallel, the use of natural polymers (e.g., cellulose, starch, chitosan, and alginate) and their derivatives for the removal of heavy metal ions from wastewater has become important by reason of their biodegradability [2].

Chitin is a natural polymer based on the polysaccharide of β-(1,4)-2-acetamido-2-deoxy-D-glucopyranose. Chitosan is obtained by deacetylation of chitin under alkaline conditions. Chitosan is a linear polysaccharide composed of glucosamine and N-acetyl glucosamine units linked by (1–4) glycoside bonds. When the content of glucosamine (degree of deacetylation) of chitin is higher than about 50%, it is as named chitosan, and it becomes soluble in an aqueous acidic medium [16,17]. The presence of amino groups in chitosan besides hydroxyl groups is highly advantageous for modification reactions [2,18]. Therefore, several modifications were carried out on the hydroxyl and amino groups on glucosamine units of chitosan previously. Crosslinking on chitosan is an effective way on improving its physical and mechanical properties [2,19]. Chemical resistance is very important property for an adsorbent. The crosslinked chitosan is very stable in acidic and basic solutions [2,5]. For this reason, some cross-linking reagents (e.g., glutaraldehyde, sulfuric acid, epichlorohydrin and ethylene glycol diglycidyl ether) have been used for crosslinking reaction of chitosan [2,5,19].

The grafting of synthetic polymers to chitin and chitosan has attracted worldwide attention for graft copolymerization of these natural polymers. Grafting process provides the synthesis of novel types of hybrid materials composed of natural and synthetic polymers. Graft copolymerization enables the production of new polymeric materials with desired properties. Various side chains can be added into the main structure with grafting and thus, it can be possible to make various molecular designs. The properties of graft copolymers can be controlled by molecular structure, length and number of side chains attached [20,21]. The brief summary of studies about graft copolymerization of chitosan is given below, and properties of chitosan, which have improved by grafting, were clearly emphasized.

In a study of carboxymethyl chitosan-methacrylic acid graft copolymer, water solubility of this copolymer has been improved by grafting [22]. In another study, grafted polymers based on chitosan, which have antioxidant activity, have been synthesized [23,24]. Grafting with hydroxylpropyl groups has provided relatively higher “superoxide anion scavenging ability” to the chitosan structure [25]. The various forms (film and fiber) of chitosan-polyaniline graft copolymer have been also produced with the grafting reaction. In the mentioned study, flexible or brittle products have been obtained depending on feeding ratio of monomers [26]. In addition, thermal stability of chitosan has been improved by the grafting of zwitterionic monomer onto chitosan [27]. Chitosan-poly(N-isopropylacrylamide) graft copolymer has been also investigated. Synthesized this chitosan-based stimuli responsive polymer has exhibited swelling/deswelling changes in response to pH and temperature [21]. In another study, grafting of 2-hydroxyethyl methacrylate onto chitosan has caused a significant decrease in the mechanical strength under wet conditions. On the other hand, grafting reaction has improved swelling property and hydrophilicity of this graft copolymer [28]. Further, modification of chitosan by grafting of vinyl pyrrolidone has been realized. In mentioned study, the solubility of chitosan has decreased after grafting with vinyl pyrrolidone, significantly [29]. Grafted polymer based on chitosan and 2-acrylamido-2-methyl propane sulfonic acid has been also synthesized for use in textile finishing agent [30].

There are many researches about crosslinked chitosan for drug delivery, tissue engineering, anti-microbial agents, and other biomedical applications. However, there are few studies about chitosan derivatives which are used for adsorption of metal ions and wastewater treatment processes. For example, Singh et al. have described the synthesis and application of the poly(methyl methacrylate) grafted chitosan for the removal of azo dyes [1]. Additionally, the graft copolymers such as chitosan-graft-N-vinyl formamide and chitosan-graft-N,N-dimethyl acrylamide have been used in the removal of heavy metal ions from aqueous solutions [31,32]. Grafting of vinyl monomers onto chitosan has improved the adsorption properties (e.g., dye and metal ion adsorption) of chitosan [31]. As mentioned above, although many studies related to the grafting reaction of chitosan exists, there is no study about crosslinked chitosan beads grafted with itaconic acid or crotonic acid in the literature except our previous work [2].

In this study, crosslinked chitosan graft copolymeric beads have been used as an adsorbent for the removal of Cu(II) ions from aqueous solutions. For this aim, adsorption capacities, adsorption kinetics and adsorption isotherms of the beads were investigated and, these beads were reused after regeneration process.

2. Materials and methods

2.1. Materials

The monomers, itaconic acid (IA) and crotonic acid (CA) were obtained from Fluka (USA) and ABCR (Germany), respectively. Epichlorohydrin (ECH) (crosslinking agent) and ammonium persulfate (APS) (initiator) were purchased from Merck (Germany) and chitosan (Ch) was purchased from Aldrich (USA). All solutions and standards were prepared with distilled water.

Chitosan-graft-itaconic acid (Ch-g-IA) and chitosan-graft-crotonic acid (Ch-g-CA) copolymers were synthesized in laboratory within our previous study. The synthesis procedures of these copolymers have been given in our previous article [2]. However, the synthesis method was summarized again below.

2.1.1. Preparation of chitosan beads

Chitosan (2 g) was dissolved in 60 mL of dilute acetic acid (5% v/v). This solution was dropped into a 500 mL 0.5 M NaOH solution. The formed chitosan beads were left in the NaOH solution for 24 h and then washed with distilled water [2,33].

2.1.2. Preparation of crosslinked chitosan beads

The resultant chitosan beads were crosslinked with ECH. A solution of 0.01 M ECH was prepared, and pH of this solution was adjusted to 10 with NaOH solution. Then, chitosan beads were added to ECH solution (ECH/chitosan; 1/1 molar ratio), and this mixture were heated to a temperature between 40 and 50 ℃ for 2 h and stirred continuously. After the reaction, crosslinked chitosan beads were filtered and filtered beads washed to remove unreacted ECH with distilled water [2,5].

2.1.3. Preparation of Ch-g-IA and Ch-g-CA copolymeric beads

Graft copolymerization of monomers (IA and CA) onto the crosslinked chitosan beads were carried out in a glass tube at 60 ℃ using APS initiator. A mixture of crosslinked chitosan beads (1 g), APS (0.5 wt.% based on monomer) and water (12 mL) was stirred to facilitate free radical formation on chitosan under nitrogen atmosphere for 15 min. Then monomer (0.025 mol) was added to the glass tube and graft copolymerization was maintained for 3 h. After the reaction, the grafted crosslinked chitosan beads were filtered out thoroughly washed to remove the unreacted reagents with deionized water and then extracted to dissolve homopolymer with hot water. The percentage of grafting efficiency (GE %) and percentage of add-on (add-on %) were calculated within our previous study [2]. However, these values were presented again in this study. Related equations [34] are given below:

$$\text{GE }\% = (w_2 - w_1/w_3) \times 100 \tag{1}$$

$$\text{add-on }\% = (w_2 - w_1/w_2) \times 100 \tag{2}$$

where w_1 (g) is the weight of pure chitosan; w_2 (g) is the weight of graft copolymer and w_3 (g) is the weight of monomer.

The GE% values of the beads were calculated as 29% and 23% for Ch-g-IA and Ch-g-CA, respectively. The add-on% values were also calculated as 47% and 32% for Ch-g-IA and Ch-g-CA, respectively.

2.1.4. Fourier transform infrared spectroscopy (FTIR) analysis

Crosslinked chitosan-graft-copolymeric beads were characterized by the FTIR technique. FTIR spectra of the beads were taken with Digilab Excalibur-FTS 3000MX model FTIR (Randolph, MA, USA) using KBr pellets.

2.2. Adsorption studies

The Cu(II) ion removal capacities of crosslinked chitosan graft copolymeric beads were determined using aqueous Cu(II) solution. Stock Cu(II) solution (2.5 mmol metal ion/L) was prepared by dissolving metal acetate salt in distilled water. The beads (0.3 g) were added in 50 mL of stock solution and the mixture was stirred with a magnetic stirrer. After desired time periods, the amount of residual metal ion in the solutions was determined by using "Varian SpectrAA FS-220" atomic absorption spectrometer (AAS).

The adsorption capacities (mmol Cu(II) g^{-1} sample) of Ch-g-IA and Ch-g-CA samples were calculated using the following expression:

$$q_e = (C_i - C_e) \times V/m \quad (3)$$

where q_e is the adsorbed amount of Cu(II) ion per gram sample, C_i and C_e are the concentration of metal ion in the initial solution and equilibrium, respectively (mmol L^{-1}), "V" is the volume of the metal ion solution added (mL), and "m" is the amount of the sample used (g). In adsorption kinetic graphics, the q_e symbol is given as q_t that illustrates the amount of Cu(II) per gram of sample for a given time.

2.2.1. Adsorption kinetics

There are different kinetic models to describe the kinetics of adsorption. In this study, the experimental data were analyzed to investigate the mechanism of adsorption process by pseudo-first-order and pseudo-second-order kinetic models.

The first-order rate expression of Lagergren [35] can be formulated as below:

$$\log(q_e - q_t) = \log q_e - (k_1 t/2.303) \quad (4)$$

q_e, the amounts of Cu(II) adsorbed on the beads at equilibrium (mmol g^{-1}); q_t, the amounts of Cu(II) adsorbed on the beads at any time t (mmol g^{-1}); and k_1, the rate constant of first-order adsorption (min^{-1}).

A straight line of t versus log $(q_e - q_t)$ suggests the applicability of this kinetic model to fit the experimental data. The slope and intercept of this plot were used to determine the first order rate constant k_1 and equilibrium adsorption q_e.

The first-order equation of Lagergren cannot be used to the whole contact time, and it represents to the initial stage of the adsorption process [36]. The second-order kinetic model is feasible to predict the behavior of whole adsorption process. Rate controlling step of this model is chemical sorption or electrostatic interaction between ions and adsorbent involve valence forces through sharing or exchanging electrons [37].

Pseudo-second-order kinetic model can be expressed as below:

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (5)$$

q_e, the amounts of Cu(II) adsorbed on the beads at equilibrium (mmol g^{-1}); q_t, the amounts of Cu(II) adsorbed on the beads at any time t (mmol g^{-1}); and k_2, the rate constant of second-order adsorption (g mmol^{-1} min^{-1}).

The slope and intercept of plot of t versus t/q_t was used to determine the second order rate constant k_2 and equilibrium adsorption q_e.

2.2.2. Adsorption isotherms

The adsorption isotherm models were used to characterize the relationship between the adsorbate on the adsorbent and the concentration of adsorbate in the liquid at equilibrium [38,39]. There are many adsorption isotherm models such as Freundlich [38], Langmuir [38], Brauner–Emmet–Teller (BET) [40], Dubinin–Raduschkevich (D–R) [41], and Temkin [41] models. These isotherm models were presented in Table 1.

2.3. Regeneration studies

Crosslinked chitosan-graft-copolymeric beads, which are used for adsorption studies, were regenerated with acid solution (1 M HNO_3), and they were used in heavy metal ion removal again. For this purpose, Cu(II) ion adsorbed beads were dried after adsorption study and added to 50 mL 1 M HNO_3 solution. This solution was continuously agitated at 150 rpm for 48 h. Then the beads were filtered and washed with distilled water until reached neutral pH. It was observed that the shapes and dimensions of rigid and stable beads have not changed after regeneration process. That is, copper adsorbed beads did not swell or collapse in the end of the regeneration process. Regenerated beads were used again for adsorption of Cu(II) ions from aqueous solution. This "regeneration and reuse" cycle was repeated for four times. Adsorption capacities of reused beads were also determined for each cycle.

3. Results and discussion

3.1. FTIR analysis

Structural analyses of crosslinked chitosan-graft-copolymeric beads, were performed with the FTIR technique. FTIR spectra of the beads (Ch-g-IA, Ch-g-CA, crosslinked Ch) and grafting mechanism, which have been given also in our previous article [2], were presented again in Figs. 1 and 2, respectively. Detailed explanations about structural analysis of Ch-g-IA and Ch-g-CA beads and, grafting reaction mechanism between the crosslinked chitosan beads with monomers (IA, CA) were also given below:

As it seen in Fig. 1, the absorption peak corresponding to the CH_2 groups of CH_2OH onto chitosan

Table 1
Adsorption isotherm models

Isotherm models	Equations
Freundlich	$\ln q_e = \ln K_f + 1/n \ln C_e$
q_e	The amount of adsorbate (mg g^{-1})
C_e	Adsorbate equilibrium concentration (mg L^{-1})
K_f	Freundlich constant related to adsorption capacity
n	Freundlich constant related to adsorption intensity
Langmuir	$1/q_e = 1/bq_oC_e + 1/q_o$
q_e	The amount of adsorbate (mg g^{-1})
C_e	Adsorbate equilibrium concentration (mg L^{-1})
q_o	Langmuir constant related to adsorption capacity
b	Langmuir constant related to energy of adsorption
BET	$C_e/(C_s - C_e)\ q_e = 1/(K_bq_m) + (K_b - 1)C_e/K_bq_mC_s$
q_e	The amount of adsorbate (mg g^{-1})
C_e	Adsorbate equilibrium concentration (mg L^{-1})
C_s	The saturation concentration of solute
K_b	BET constant related to adsorption energy
q_m	The amount of solute adsorbed in forming a complete monolayer
Dubinin–Raduschkevich	$\ln q_e = \ln q_m - K_{D-R}\varepsilon^2$
q_e	The amount of adsorbate (mg g^{-1})
C_e	Adsorbate equilibrium concentration (mg L^{-1})
K_{D-R}	DR constant related to adsorption energy
ε	The Polanyi potential [$\varepsilon = RT \ln(1 + 1/C_e)$]
Temkin	$q_e = RT/b_T \ln K_T + RT/b_T \ln C_e$
q_e	The amount of adsorbate (mg g^{-1})
C_e	Adsorbate equilibrium concentration (mg L^{-1})
b_T	Temkin constant related to heat of adsorption
K_T	Temkin constant related to binding energy

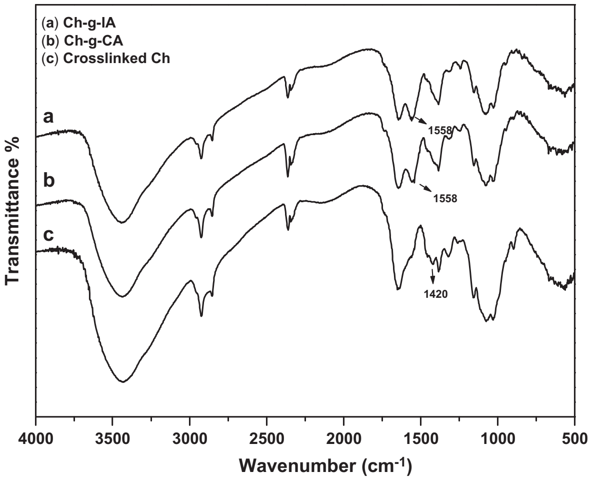

Fig. 1. FT-IR spectra of Ch-g-IA, Ch-g-CA beads and crosslinked chitosan beads [2].

at 1,420 cm^{-1} was observed in the spectrum of the crosslinked Ch but this peak was not observed in the spectra of Ch-g-IA and Ch-g-CA due to the reaction of CH_2OH groups with IA and CA [42,43]. The FTIR spectra of Ch-g-IA and Ch-g-CA showed a new peak at 1,558 cm^{-1}. This new peak was attributed to "the monomer (IA and CA) which reacted with the amino groups of the beads". This peak was confirmed by the formation of secondary amine structure [43]. As known, the absorption peaks approximately at 1,470–1,250 cm^{-1} and 3,500–3,100 cm^{-1} regions in the FTIR spectra of the crosslinked Ch are attributed to CH_2OH groups [2]. Intensity of these peaks has decreased or has become a shoulder (particularly in case of Ch-g-IA). This situation clearly confirms the grafting mechanism presented in Fig. 2.

As a result, we deduced that, IA and CA easily react with NH_2 and CH_2OH groups of the crosslinked chitosan beads and thus, crosslinked chitosan graft structure occurs.

3.2. Adsorption studies

The effect of contact time on the adsorption of Cu(II) onto the Ch-g-IA and Ch-g-CA beads is shown in Fig. 3. The adsorption capacities of Ch-g-IA and Ch-g-CA beads increased with the increase in the adsorption time until it reaches the equilibrium value. The Cu(II) adsorption capacities were found as 0.31 and 0.25 mmol g^{-1} for Ch-g-IA and Ch-g-CA beads, respectively. The Cu(II) adsorption capacity of Ch-g-IA bead is approximately 1.25 times higher than that of Ch-g-CA bead. This situation can be attributed to higher amount of the carboxyl groups of Ch-g-IA bead than that of Ch-g-CA bead. When IA was used instead of CA for grafting, amount of the ionizable carboxyl groups on the grafted bead increased, in parallel. Therefore, interaction between Ch-g-IA beads and Cu(II) ions increased according to the high amount of the carboxyl group on the Ch-g-IA structure. This result showed that the main adsorption mechanism of Cu(II) occurred by the electrostatic

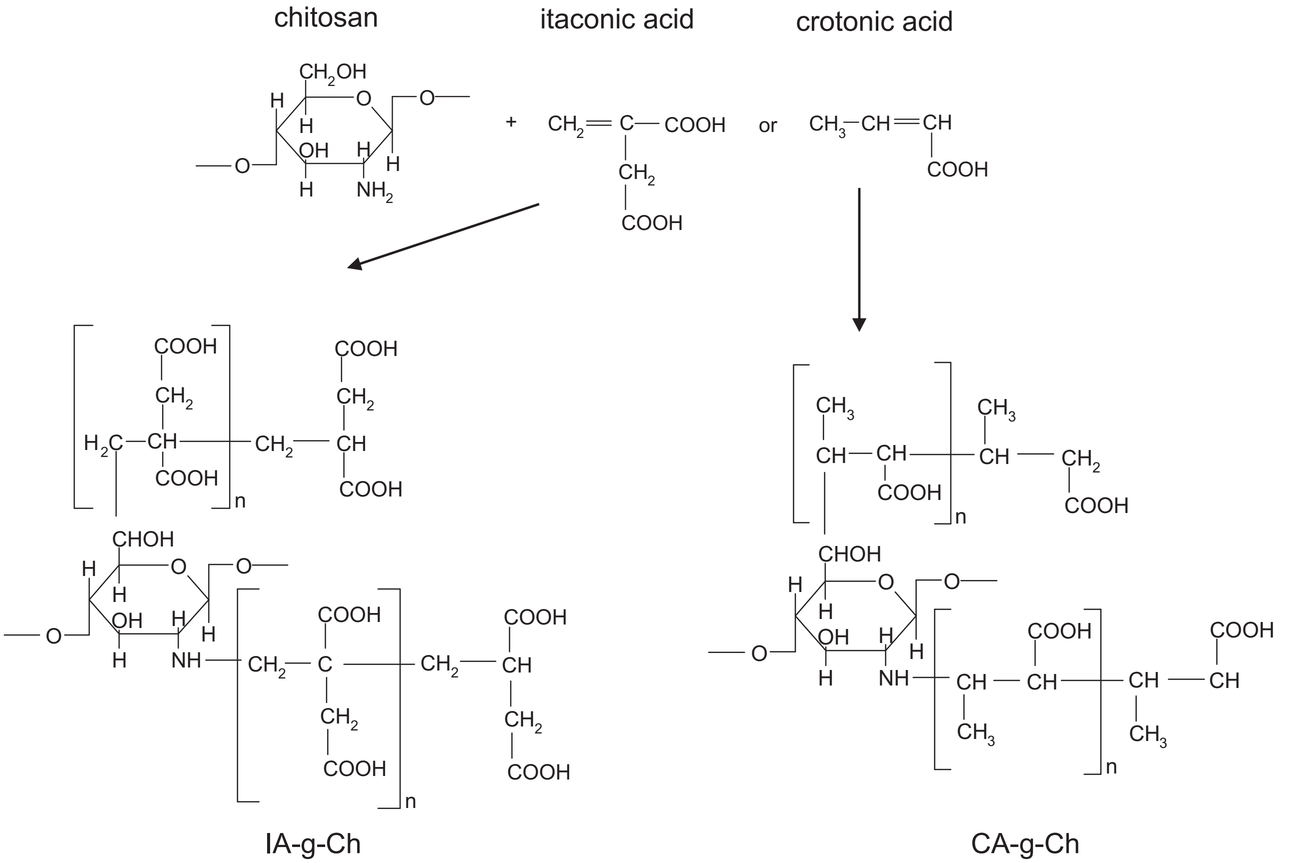

Fig. 2. Grafting mechanism of monomers (IA and CA) onto the croslinked chitosan beads [2].

interactions of negative charges on the beads and positive charge of the Cu(II).

To determine of optimal pH value, the adsorption studies were realized at different pH values. In these preliminary studies, it was observed that Cu(II) ions collapsed at higher pH values than 6. In addition, Ch-g-IA and Ch-g-CA beads have negative charges (ionized form) at natural pH value (approximately 6) of metal ion solution [4]. Therefore, lower pH values than 6 are not suitable for adsorption studies because carboxyl groups of these beads are non-ionized form and, the optimal pH value was determined as "6" according to the preliminary adsorption studies, which were carried out at different pH values. This result was compatible with other results given in the literature [4,11,12]. As it is seen also from the grafting mechanism, which is schematized in Fig. 2, Ch-g-IA and Ch-g-CA have many ionizable groups (–COOH groups). At pH 6, the –COOH groups are ionized, and electrostatic interaction occurs between the –COOH groups of the Ch-g-IA and Ch-g-CA beads and the Cu(II) ions.

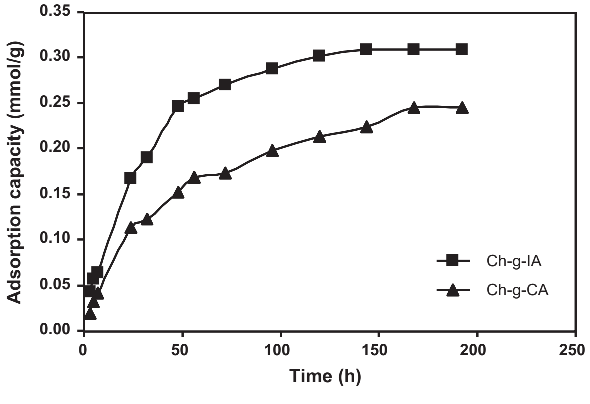

Fig. 3. The effect of the treatment time on the metal ion removal capacity of Ch-g-IA and Ch-g-CA beads.

3.2.1. Adsorption kinetics

Pseudo-first-order and pseudo-second-order kinetic plots for the adsorption of Cu(II) ion onto grafted chitosan beads were drawn, and kinetic parameters were calculated. The parameters (k_1, k_2, calculated q_e, experimental q_e and R^2) obtained from these models are presented in Table 2. Although the

Table 2
Kinetic parameters for the adsorption of Cu (II) onto Ch-g-IA and Ch-g-CA beads

Sample	$q_{e,\text{ exp.}}$ (mmol g^{-1})	Kinetic models					
		Pseudo first order			Pseudo second order		
		k_1 (min^{-1})	$q_{e,\text{ teo.}}$ (mmol g^{-1})	R^2	k_2 (g mmol^{-1} min^{-1})	$q_{e,\text{ teo.}}$ (mmol g^{-1})	R^2
Ch-g-IA	0.30	$5.0 \times 10^{-4} \pm 1.8 \times 10^{-5}$	0.29 ± 0.01	0.9887	$1.61 \times 10^{-3} \pm 8 \times 10^{-5}$	0.37 ± 0.01	0.9960
Ch-g-CA	0.26	$2.68 \times 10^{-4} \pm 2.4 \times 10^{-5}$	0.24 ± 0.01	0.9418	$1.2 \times 10^{-3} \pm 3 \times 10^{-5}$	0.30 ± 0.01	0.9956

experimental q_e values of pseudo-first-order model appear compatible with calculated q_e, the correlation coefficients of second order model are more acceptable.

In conclusion, the adsorption studies results show that the pseudo-second-order kinetic model fitted better than the data obtained from pseudo-first-order model depending on high correlation coefficients ($R^2 = 0.9960$–0.9956).

3.2.2. Adsorption isotherms

Adsorption isotherm studies were realized for all the adsorption models in the room temperature and at natural pH of Cu(II) ion solution. All adsorption experiments were carried out in duplicate. The regression coefficient (R^2) values of different isotherm models for the adsorption of Cu(II) onto Ch-g-IA and Ch-g-CA beads were given in Table 3. When the Langmuir, BET, D–R and Temkin isotherm models were applied for the adsorption of Cu (II) onto Ch-g-IA bead, the R^2 values were found to be 0.5678, 0.6195, 0.8705, and 0.9143, respectively. Similar to, when these isotherm models were applied for the adsorption of Cu (II) onto Ch-g-CA bead, the R^2 values were found to be 0.3688, 0.7875, 0.8932, and 0.9625 for Langmuir, BET, D–R and Temkin isotherm models respectively. Therefore, these four isotherm models are not suitable for describes the adsorption of Cu(II) onto crosslinked chitosan graft copolymeric beads. On the contrary, Freundlich model is more suitable for Cu(II) ion adsorption onto the beads, compared with other models. This model was used successfully to describe the relationship between the amount of Cu(II) adsorbed and its equilibrium concentration in solution.

Table 3
R^2 values of different isotherm models for the adsorption of Cu(II) onto Ch-g-IA and Ch-g-CA beads

Isotherm models	R^2 values of different isotherm models	
	Ch-g-IA	Ch-g-CA
Freundlich	0.9960	0.9965
Langmuir	0.5678	0.3688
BET	0.6195	0.7875
Dubinin and Raduschkevich	0.8705	0.8932
Temkin	0.9143	0.9265

The Freundlich equation [6,44] is the earliest known relationship describing the adsorption equation [6]. This empirical equation is suitable for use with heterogeneous surfaces [40,45]. Freundlich equation is presented in Table 1. As it is seen in Table 1, K_f and n are Freundlich constants related to the "adsorption capacity" and "adsorption intensity," respectively [36,46]. K_f and n can be determined from the linear plot of $\ln C_e$ and $\ln q_e$. The n values between 1 and 10 indicate beneficial adsorption and relatively high K_f values reflect high adsorption capacity [9,14]. The Freundlich isotherm parameters, K_f, n and R^2 were given in Table 4. As seen from this table, Freundlich isotherm fits well with the experimental data ($R^2 = 0.9960$–0.9965) and n values are higher than "1" which demonstrate "beneficial adsorption".

To the purpose of comparison, the results of our study and reported adsorption capacities in the literature for various chitosan-based adsorbents for Cu(II) ion were given in Table 5. These data can be interpreted that, the adsorption capacities of crosslinked chitosan-graft-copolymeric beads for Cu(II) ion were acceptable, compatible, and comparable with the results of other chitosan-based adsorbents that have been given in the literature [46–51].

Table 4
Freundlich constants for the adsorption of Cu(II) onto Ch-g-IA and Ch-g-CA beads

Sample	Freundlich constants		
	K_f	n	R^2
Ch-g-IA	0.4189 ± 0.055	1.10 ± 0.055	0.9960
Ch-g-CA	0.1884 ± 0.050	1.04 ± 0.050	0.9965

Table 5
Adsorption capacities of various chitosan-based adsorbents for Cu(II)ion

Chitosan-based adsorbent	Adsorption capacity		Reference
	mg g^{-1}	mmol g^{-1}	
Crosslinked chitosan acetate crown ether	23.9	0.38	[46]
Crosslinked chitosan diacetate crown ether	31.3	0.49	[46]
Epichlorohydrine crosslinked chitosan	16.8	0.26	[46]
Chitosan PVA beads	45.0	0.71	[47]
Chitosan glutaraldehyde beads (1:1)	31.2	0.49	[48]
Chitosan glutaraldehyde beads (2:1)	19.5	0.31	[48]
Glutaraldehyde crosslinked chitosan	59.7	0.94	[49]
Epichlorohydrine crosslinked chitosan	62.5	0.98	[49]
Ethylene glycol diglycidylether crosslinked chitosan	45.6	0.72	[49]
Epichlorohydrin crosslinked chitosan	34.1	0.54	[50]
N-(4-pyridylmethyl) chitosan	45.1	0.71	[51]
Itaconic acid grafted crosslinked chitosan beads	19.6	0.31	This work
Crotonic acid grafted crosslinked chitosan beads	15.9	0.25	This work

Finally, we can say that Cu(II) ion adsorption capacities of Ch-g-IA and Ch-g-CA beads can be workable for new potential adsorption systems.

3.3. Regeneration and reuse studies

Adsorption capacities of Ch-g-IA and Ch-g-CA beads for Cu(II) before and after regeneration periods were given in Table 6. As it is seen in table, metal ion removal capacities of Ch-g-IA and Ch-g-CA beads have decreased after first regeneration process from 0.25 to 0.13 and from 0.18 to 0.12 mmol/g, respectively. In other words, adsorption capacities of the beads have decreased about 50–60% after first regeneration process. Regeneration processes of the beads have realized relatively difficult because of their high crosslink density, and this crosslinked structure has not allowed regeneration of beads the rate of 100%. Therefore, adsorption capacity values of regenerated beads slightly decreased after first regeneration process. On the other hand, adsorption capacities of the beads have remained stable in 0.08–0.13 mmol/g range for Ch-g-IA and Ch-g-CA beads during the "2, 3 and 4 regeneration processes". Metal ion removal capacity values of regenerated chitosan beads have not changed significantly in the end of the fourth cycle (regeneration period) compared to the first cycle (Figs. 4 and 5). Thereby Ch-g-IA and Ch-g-CA beads can be used again at least 4 times for adsorption with approximately 50% yield.

Table 6
Adsorption capacities of Ch-g-IA and Ch-g-CA beads for Cu(II) before and after regeneration periods

Sample	Adsorption capacity* (mmol/g)	Adsorption capacity* (mmol/g) (after regeneration)			
	Before regeneration	(1) cycle	(2) cycle	(3) cycle	(4) cycle
Ch-g-IA	0.25	0.13	0.11	0.09	0.08
Ch-g-CA	0.18	0.12	0.11	0.10	0.08

Note: * At the end of 48 hours.

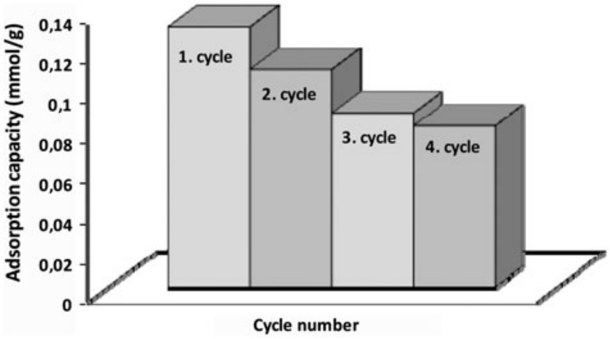

Fig. 4. Adsorption capacities of Ch-g-IA beads for Cu(II) after regeneration periods.

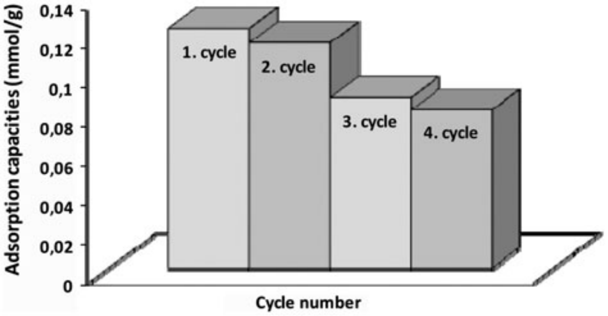

Fig. 5. Adsorption capacities of Ch-g-CA beads for Cu(II) after regeneration periods.

4. Conclusions

This study is about "adsorption and reuse of Ch-g-IA and Ch-g-CA beads for Cu(II) ion removal from aqueous solutions".

Our results show the following:

- Ch-g-IA and Ch-g-CA beads were used as an adsorbent for Cu(II) ions removal from aqueous solutions for the first time.
- The maximum adsorption capacities of Ch-g-IA and Ch-g-CA beads were found to be 0.31 and 0.25 mmol/g respectively.
- Main adsorption mechanism of Cu(II) ions onto Ch-g-IA and Ch-g-CA beads was occurred by the electrostatic interactions of negative charges (–COOH groups) on the beads and positive charge of the Cu(II) ions.
- In order to determine the controlling mechanism of adsorption processes, experimental data were tested using the pseudo-first-order and pseudo-second-order kinetic equations. When second-order-kinetic model was used, R^2 values were obtained in the range of 0.9956–0.9960. In case of pseudo-second-order model, the calculated q_e values are compatible with the experimental q_e values. According to these results, the adsorption data were well expressed by pseudo-second-order kinetics.
- In order to describe the relationship between the amount of adsorbate and the concentration, Freundlich, Langmuir, BET, D–R, and Temkin isotherm models were used. As a result, the Freundlich model was more suitable for Cu(II) ion adsorption onto chitosan beads, compared with other models.
- Metal ion removal capacities of regenerated chitosan beads have not changed significantly in the end of the fourth cycle (regeneration period) compared to the first cycle.
- Ch-g-IA and Ch-g-CA beads can be used again at least four times for adsorption with approximately 50% yield.

It is concluded that Ch-g-IA and Ch-g-CA beads can be used for an alternative adsorbent for water treatment process.

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