Hydrogel based on chitosan, itaconic acid and methacrylic acid as adsorbent of Cd^{2+} ions from aqueous solution

Nedeljko B. Milosavljević[a], Mirjana Đ. Ristić[a], Aleksandra A. Perić-Grujić[a], Jovanka M. Filipović[a], Svetlana B. Štrbac[b], Zlatko Lj. Rakočević[c], Melina T. Kalagasidis Krušić[a,*]

[a] Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia
[b] ICTM-Institute of Electrochemistry, University of Belgrade, P.O.B. 815, 11001 Belgrade, Serbia
[c] INS Vinča, Laboratory for Atomic Physics, University of Belgrade, P.O.B. 522, Mike Alasa 12-14, 11001 Belgrade, Serbia

ARTICLE INFO

ABSTRACT

A hydrogel has been synthesized by ionic crosslinking of chitosan (Ch) with itaconic acid (IA), followed by a free radical polymerization and crosslinking of Ch/IA network by adding methacrylic acid and the crosslinker. The resulting material (Ch/IA/MAA hydrogel) was characterized by spectral (Fourier transform infrared (FTIR)), thermal (thermogravimetric analysis (TGA)) and structural (SEM/EDX and atomic force microscopy (AFM)) analyses. The prepared hydrogel was investigated as potential adsorbent for removal of Cd^{2+} ions from aqueous solution. The effect of various physico-chemical parameters such as pH, adsorbent dosage, adsorbate concentration and contact time was studied in batch experiments. The results of spectral analyses of Cd-loaded hydrogel have shown that active functional groups are –NH$_2$, –OH and –COOH. SEM/EDX analysis and AFM surface topography and phase images indicated that apart from the adsorption on the surface of the hydrogel, sorption takes place in the bulk, as well. The experimental kinetic and equilibrium data were better fitted by pseudo-second order kinetic model and Langmuir adsorption isotherm. The parameters obtained in thermodynamic studies showed that the adsorption of Cd^{2+} on Ch/IA/MAA hydrogel was spontaneous and exothermic in nature. Desorption studies were carried out using acid leaching (HNO$_3$) and it has been shown that the regenerated hydrogel can be reused three times without any loss of adsorption capacity. The maximum adsorption of 285.7 mg/g has been obtained at pH 5.5 and the results of adsorption/desorption experiments implies that the Ch/IA/MAA hydrogel may be used as efficient sorbent for removal of Cd^{2+} ions from aqueous solution.

1. Introduction

Trace elements, especially heavy metals, are considered to be one of the main sources of pollution in the environment, since they have a significant effect on its ecological quality [1]. Unlike most other toxic pollutants, metals can accumulate throughout the food chain due to their nonbiodegradability and thus have potentially detrimental effects on all living species. Therefore, methods for the removal of toxic heavy metals from polluted and wastewater are of great importance. The most widely used methods for removing heavy metals from wastewater are coagulation and precipitation, adsorption, ion exchange treatment and co-precipitation/adsorption. In comparison with the other processes for the treatment of polluted aqueous effluents, the sorption process possesses some advantages, such as flexibility in design and operation, producing superior effluent suitable for reuse without

other pollutants [2]. With the selection of a proper adsorbent, the adsorption process can be a promising technique for the removal of certain types of contaminants. For recovery and removal of heavy metal cations, polymeric adsorbents are more effective due to their structure, cost effectiveness, availability of different sorbents, easy handling, reusability, and chemical and mechanical strength [3,4].

In recent years, special attention has been given to hydrogels [2]. Among them, pH-sensitive hydrogels are very interesting because they possess ionic functional groups and are widely studied as adsorbents for the removal and separation of metal ions or ionic dyes from wastewater.

Chitosan is currently in the focus of increasing scientific and economic interest among all polysaccharides because of its significance in nature and technology [5]. In the literature, a number of data regarding the chitosan application for toxic ion (heavy metals, fluoride, etc.) removal have been reported [6–10]. Also, the numerous chitosan based beads have already been examined as adsorbent for removal of cadmium ions from water solutions [11–13].

Cadmium is released to the environment through wastewater, and diffuse pollution is caused by contamination from fertiliz-

* Corresponding author. Tel.: +381 11 3303730; fax: +381 11 3370387.
E-mail address: meli@tmf.bg.ac.rs (M.T. Kalagasidis Krušić).

ers and local air pollution. The health effects of Cd(II) on human include nausea, vomiting, diarrhea, muscle cramp, salivation, loss of calcium from bones, yellow coloration of teeth (cadmium ring formation), reduction of blood cells, damage of bone marrow, hypertension, kidney failure following oral ingestion, lung irritation, chest pain, and loss of smell after inhalation [14]. Because of the toxicity and bioaccumulation, cadmium is considered as a priority pollutant by the US Environmental Protection Agency.

In this study, a hydrogel composed of chitosan, itaconic acid and methacrylic acid was synthesized and used for the removal of Cd^{2+} ions from aqueous solutions. Chitosan was ionically crosslinked with itaconic acid and then a free radical polymerization and crosslinking of Ch/IA network was performed by adding methacrylic acid and the crosslinker. The swelling behavior of hydrogel was measured. The hydrogel was characterized using thermogravimetric analysis (TGA) scanning electron microscopy/energy dispersive X-ray (SEM/EDX), Fourier transform infrared (FTIR) and atomic force microscopy (AFM) analyses. The influence of initial pH of Cd solution, adsorbent dosage and initial concentration on the Cd^{2+} ions uptake was studied.

2. Experimental

2.1. Materials

Methacrylic acid (MAA, Fluka A.G.) was vacuum distilled at 63 °C/12 mm Hg, prior to use, in order to remove the inhibitor. The cross-linking agent, N,N′-methylenebisacrylamide (MBA, Acros), potassium persulfate (KPS, Merck, p.a.), potassium pyrosulfate (KPyS, Merck p.a.), itaconic acid (IA, Fluka, p.a.) and chitosan (Ch, Fluka, middle viscous) were used without further purification. Cadmium stock solution (1000 mg/L) was prepared by dissolving a calculated amount of $Cd(NO_3)_2 \cdot 4H_2O$ (Merck, p.a.). Double distilled deionized water was used through the research.

2.2. Preparation of hydrogel

The hydrogel was synthesized by ionic crosslinking of Ch and IA, according to the procedure described previously [15], followed by free radical polymerization and crosslinking with MAA (Scheme 1). Ch/IA/MAA weight ratio was 1:1.56:7.5, while the crosslinking agent concentration was 0.2 wt.% with respect to the total weight of the reaction mixture. The redox pair KPS ($K_2S_2O_8$) and KPyS ($K_2S_2O_7$), both 0.2 wt.% with respect to the total weight of the reaction mixture, was used as initiator.

Double distilled deionized water was used as a solvent. Nitrogen was bubbled through the mixture for 20 min to remove the dissolved oxygen. Finally, the reaction mixture was placed between two glass plates (20 cm × 5 cm × 0.4 cm) sealed with a rubber spacer (2 mm thick). Polymerization was carried out at 50 °C for 3 h. After completion of the reaction, the gels were cut into discs and immersed in water, which was changed daily for one week, in order to remove the unreacted monomers. After washing, the hydrogels were left to dry at room temperature. The thickness of dried disks was 1.25 ± 0.02 mm with 6.53 ± 0.01 mm in diameter.

2.3. Characterization

2.3.1. Swelling studies

In order to study the swelling behavior, the disk samples were immersed in buffer solution (pH 2.2 and 6.8) at 25 °C. The progress of the swelling process was monitored gravimetrically and the degree of swelling (q) was calculated from the following equation:

$$q = \frac{W_t}{W_o} \times 100 \tag{1}$$

where W_o and W_t are the weights of dried and swollen hydrogel at time t, respectively.

2.3.2. Instruments

FTIR spectra of unloaded and loaded hydrogel were recorded on a Bomem MB 100 FTIR spectrophotometer as KBr pellets.

Thermogravimetric analysis (TGA) of hydrogels was performed by a Perkin Elmer TGS-2 thermogravimetric analyzer. All analyses were performed with a 3 mg sample in aluminum pans under a dynamic nitrogen atmosphere between 0 and 650 °C at a heating rate of 10 °C/min.

SEM/EDX was used to investigate the morphology of the prepared hydrogel. Measurements were taken on a JEOL JSM-5800 scanning electron microscope. Before SEM measurements, hydrogels were lyophilized. In order to keep the pores of the hydrogels intact for imaging, the hydrogels were left in liquid nitrogen and then broken.

The surface topography changes were observed by AFM, while the changes in surface composition were detected using phase imaging AFM. Multimode quadrex SPM with Nanoscope IIIe controller (Veeco Instruments, Inc.), operated under ambient conditions was used to simultaneously acquire surface topography and phase images. Standard AFM tapping mode was explored using a commercial Veeco RTESP AFM probe. All measurements were performed in one series using the same cantilever and with the same value of the drive amplitude set at 32.2 mV, the drive frequency was 246.830 kHz, while the amplitude set point was 2.7 ± 0.1 V.

The aqueous phase concentration of Cd^{2+} cation was determined by ICP-MS Agilent Technologies 7500ce system.

The flasks were agitated on a thermostatted mechanical shaker (WNB-14, Memmert).

2.3.3. Adsorption experiments

The effect of pH on adsorption was studied by batch adsorption process varying the initial pH of solution from 2.2 to 6.8. Experiments were carried out by mixing approximately 0.035 g of hydrogel with 50 mL of cadmium nitrate aqueous solution with the desired concentration and appropriate pH and shaking for 48 h in a thermostatic shaker bath at 25 °C. Then the aqueous samples were filtered through 0.45 μm filters and the concentrations of Cd^{2+} in filtrate were analyzed using the ICP MS.

The batch kinetics experiments were conducted at room temperature with 0.035 g of hydrogel in a 50 mL solution of Cd^{2+} ions.

The amount of cadmium adsorbed at equilibrium (q_e) was calculated using the following equation:

$$q_e = (C_0 - C_e)\frac{V}{W} \tag{2}$$

where C_0 (mol/L) and C_e (mol/L) are the initial and the final concentration of cadmium, V is the volume of the solution (mL) and W is the weight of the hydrogel (g).

Adsorption isotherm experiments were performed with solutions of different initial cadmium concentrations. The range of concentration of cadmium solution prepared from stock solution was varied between 5 and 750 mg/L at pH 5.5. The adsorption experiments were repeated three times and the mean values are reported. The reproducibility and the relative standard deviation were of the order ±0.5% and ±3% respectively.

2.3.4. Desorption studies

In order to determine the potential reusability of the hydrogels, consecutive sorption–desorption cycles were repeated three times using the sorbent prepared following the procedure described in adsorption experiments.

Desorption was done with HNO_3 and CH_3COOH (mass of loaded sorbent 0.035 g; volume of solution 50 mL, concentration 0.01 and
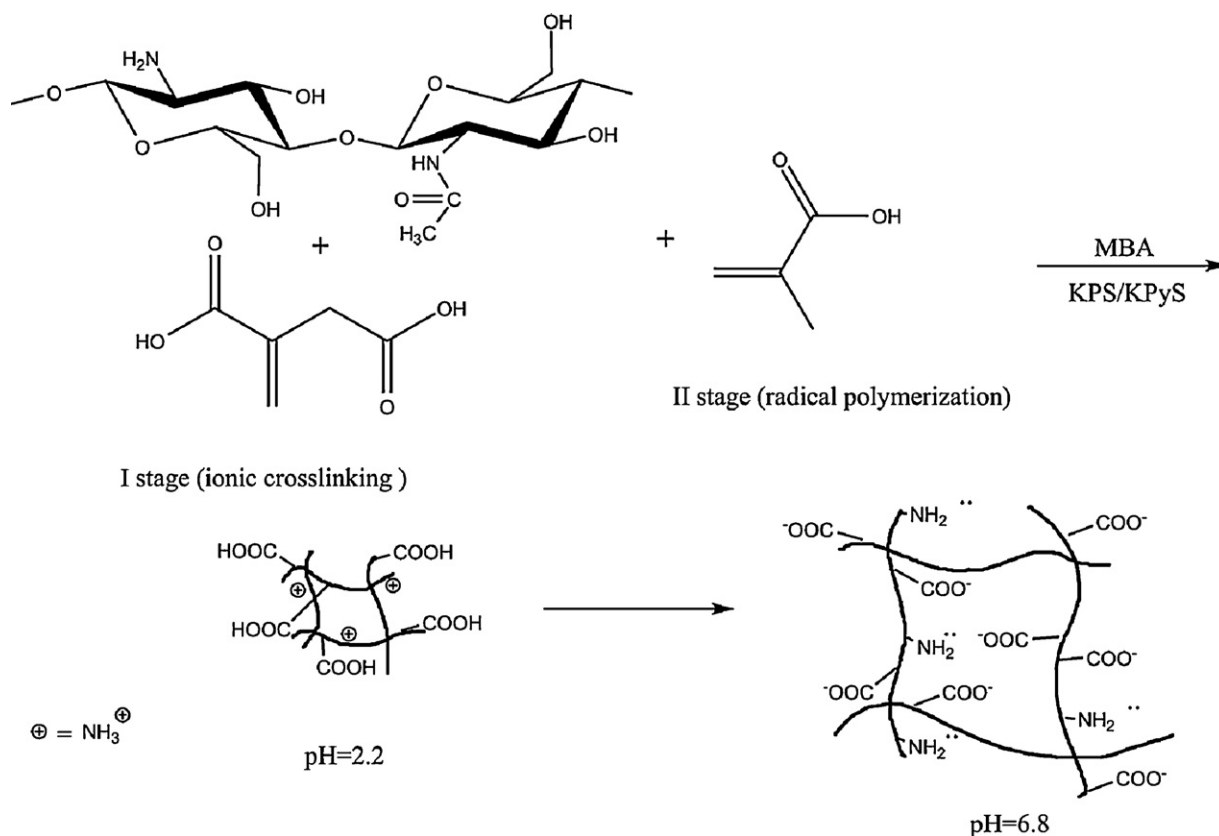
Scheme 1. Formation of the three-dimensional network structure of Ch/IA/MAA hydrogel.

0.1 mol/L; duration of process 24 h). The sorption/desorption cycles were repeated for three times using 0.035 g of the sorbent and 750 ppm of Cd solution in total volume of 50 mL.

3. Results and discussion

3.1. Preparation and properties of hydrogels

In this study a novel Ch/IA/MAA hydrogel was synthesized. The swelling behavior of hydrogels is strongly dependent on crosslinking density and the pH value of the swelling medium. The hydrogel shows high swelling degree at pH 6.8 and low swelling degree at pH 2.2.

To determine the swelling behavior of hydrogel, buffer solutions of pH 2.2 and 6.8 were chosen as the swelling media. The weight increase with time was monitored and the corresponding graphs were illustrated in Fig. 1.

The degree of swelling is strongly dependent on the pH of the external media. By increasing the pH from 2.2 to 6.8, the degree of swelling significantly increases. At pH 2.2 the acid groups, as well as a part of chitosan amino groups incorporated into network are not ionized and the degree of swelling is low (Fig. 1). At pH value of 6.8 degree of swelling increases significantly due to the ionization of MAA and IA present in hydrogel and strong electrostatic repulsion, but the time necessary to attain the equilibrium is longer in comparison with pH 2.2 (Fig. 1). Probably relatively slow dissociation of ionic crosslinks takes place and the system reaches equilibrium slowly.

3.1.1. FTIR studies

Fig. 2 shows the FTIR spectra of chitosan, copolymer hydrogel IA/MAA and Ch/IA/MAA hydrogel. The FTIR spectrum of chitosan (Fig. 2a) exhibits characteristic peaks around 896 and 1157 cm^{-1}

(antisymmetric stretching of the C–O–C bridge) corresponding to the saccharide structure. The absorption peaks at 1635 and 1322 cm^{-1} are characteristic of chitin and chitosan and have been reported as amide I and amide III peaks, respectively. The sharp peaks at 1379 and 1421 cm^{-1} were assigned to the CH$_3$ symmetrical deformation mode, while the broad peaks at 1074 and 1030 cm^{-1} indicate the C–O stretching vibration in chitosan. The intense band at around 3430 cm^{-1} should be assigned to the stretching vibration of O–H and/or N–H, as well as to intermolecular hydrogen bonding within the polysaccharide [15]. Peaks at 2876 and 2920 cm^{-1} are the typical C–H stretch vibrations [16]. Fig. 2c shows FTIR spectrum of copolymer hydrogel of MAA and IA. There are three significant signals; at 3300–3500 cm^{-1} due to C–O–H stretching of the hydroxyl group, at 1715 cm^{-1} corresponding to
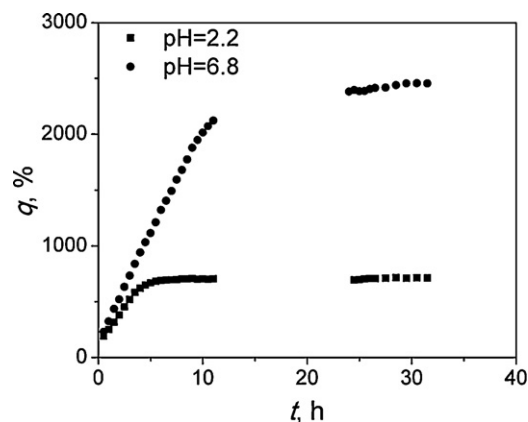

Fig. 1. Swelling (%) as a function of time for Ch/IA/MAA hydrogel in buffers of pH values 2.2 and 6.8.
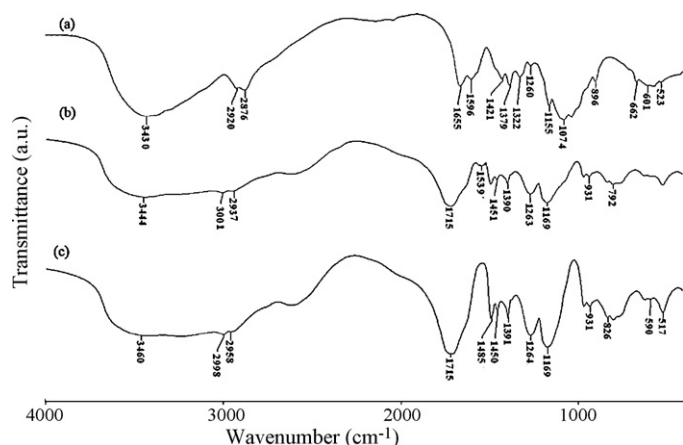
Fig. 2. FTIR spectra of the (a) chitosan, (b) Ch/IA/MAA, (c) IA/MAA.

the C=O stretching vibration of the carboxylic group and finally, at 2950–3000 cm^{-1} which is attributed to the CH$_2$ stretching. In the FTIR spectra of Ch/IA/MAA samples (Fig. 2b), the peak of carbonyl group appeared at 1715–1718 cm^{-1} with a predominant shoulder at 1638 cm^{-1}, which was assigned to symmetric deformation of ammonium ion, confirming the presence of Ch in the matrix. A new peak at 1539 cm^{-1}, was found in the FTIR spectrum of Ch/MAA/IA, probably due to the ionic interaction between Ch and the acids.

3.1.2. Thermogravimetric analysis

Among other properties, thermal stability is very important for the application of hydrogel. Therefore, thermal properties of the Ch/IA/MAA hydrogel were studied and the corresponding TGA and DTG thermograms are presented in Fig. 3. The thermal stability of chitosan is also presented for comparison.

The weight loss curve for chitosan is characterized by two stages. The first one, at 60 °C with a weight loss of 7%, can be assigned to the loss of water, while the second starts at 220 °C and reaches a maximum at 280 °C with a weight loss of 52.5%. This corresponds to the main degradation of chitosan with the elimination of volatile products. On the other hand, three stage decomposition mechanisms have been observed for Ch/IA/MAA hydrogel. The first stage started at lower temperature compared to chitosan due to the presence of IA [17], but the rate of decomposition with respect to temperature was slower. Hence, it is evident that the presence of acids has induced lower thermal stability in the networks. Considering the potential application, it was found that Ch/IA/MAA hydrogel has a good thermal stability. The higher final decomposition temper-

ature of Ch/IA/MAA hydrogel can be explained by the cyclization reactions of polymers at high temperature.

3.2. Adsorption studies

3.2.1. Effects of different experimental parameters and kinetics of Cd^{2+} sorption

The effects of initial pH and adsorbent dosage on the uptake capacity are shown in Fig. 4.

Determination of the pH effects on the adsorption of Cd^{2+} ion was performed by adding 0.035 g of the Ch/IA/MAA hydrogel into 50 mL of 10 mg/L cadmium nitrate solution. Sorption of Cd^{2+} on Ch/IA/MAA hydrogel was strongly influenced by pH value of the solution, since pH affects the metal speciation in aqueous solution, the degree of ionization and the hydrogel performance by influencing its swelling and charge of functional groups.

The influence of the pH on the adsorption capacity of Cd^{2+} ions is shown in Fig. 4a. At pH 2 the sorption of Cd^{2+} ions was near zero because most of the NH$_2$ groups are protonated and do not bind metal ions. Also, at this pH value, the removal capacity was negligible due to low dissociation of the carboxylic groups and competition between H$^+$ and Cd^{2+} ions for the same sorption site. The adsorption capacity of hydrogel increased with increasing pH, and the maximum q_e was obtained at pH 5.5. In the pH range 3–5.5 the ionization of carboxylic groups takes place (pK_a = 3–6) and increased Cd^{2+} ions sorption is a result of electrostatic attraction of cadmium. The high uptake of cadmium at pH 5.5 could be attributed to electrostatic attractions between Cd^{2+} ions and negatively charged binding sites, since ligands such as carboxyl, hydroxyl and amino groups are free to promote interaction with metal cations. Also the swelling degree is improved at higher pH values and thus increases the adsorption capacity. On further increase of pH, adsorption decreases probably due to the formation of cadmium hydroxide which lowers the adsorption of cadmium ion on Ch/IA/MAA hydrogel. The same trend has also been reported in the removal of Cd^{2+} ions by activated alumina because the dominant metal species are M(OH)$_2$ at pH > 6 and M^{2+} and M(OH)$^+$ at pH < 6 [14]. Based on the obtained results, further adsorption studies were carried out at pH 5.5.

The effect of adsorbent dosage in terms of adsorption capacity (mg/g of adsorbent dosage) on the removal of Cd^{2+} ion is represented in Fig. 4b. The amount of adsorbent varied in the range of 0.025–0.300 g and the contact time was 48 h. For adsorbent dosage higher than 0.035 g Cd^{2+} ion removal significantly decreases because the surface metal ion concentration and the solution metal concentration comes to equilibrium with each other [18].

Fig. 5 shows plot of amount of Cd (mg) adsorbed per gram of Ch/IA/MAA hydrogel at various times versus contact time (0–48 h)
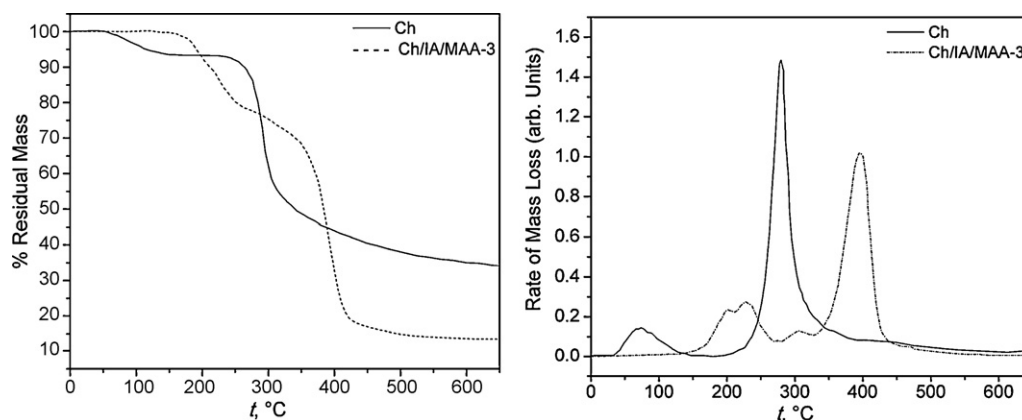

Fig. 3. TGA and DTG thermograms of chitosan and Ch/IA/MAA hydrogel.
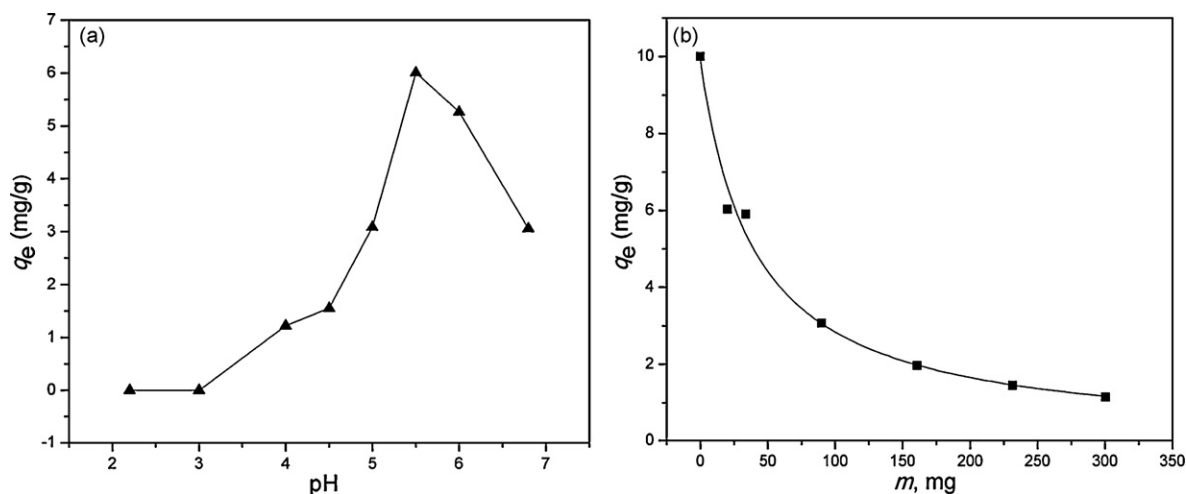
Fig. 4. Effects of initial pH (a) and adsorbent dosage (b) on the adsorption capacity of Cd^{2+} ions onto Ch/IA/MAA hydrogel. *Experimental conditions*: (a) C_0 10 mg/L; amount of sorbent 0.035 g; volume of solution 50 mL; pH range: 2–6.8; temperature: 25 °C; contact time 48 h; (b) C_0 10 mg/L; initial pH 5.5; volume of solution 50 mL; temperature 25 °C; contact time 48 h.
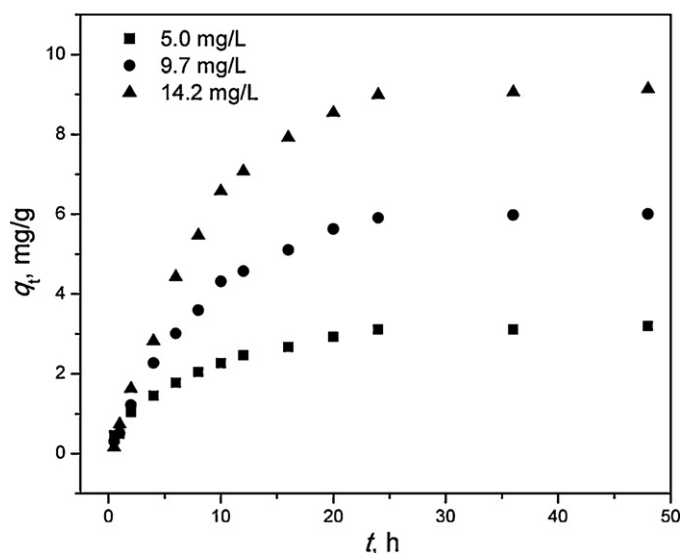

Fig. 5. Adsorption kinetics for Cd(II) onto Ch/IA/MAA hydrogel at different initial Cd(II) concentrations. *Experimental conditions*: Amount of sorbent 0.035 g; volume of the solution 50 mL; initial pH 5.5; temperature 25 °C; contact time 0.5–48 h.

for different initial metal ion concentrations of 5, 10 and 15 mg/L. It can be seen from Fig. 5a that the adsorption capacity varied with the initial concentration of cadmium. The increase in the initial concentration led to an increase in the metal ion adsorbed onto Ch/IA/MAA hydrogel. This indicated that the initial concentration plays an important role in the adsorption capacity of Cd^{2+} ions onto Ch/IA/MAA hydrogel. The extent of adsorption increased with time and attained equilibrium for all concentrations studied at 40 h. The contact time of 48 h was chosen for the further sorption experiments.

The results obtained from the experiments were used to study the kinetics of Cd^{2+} ion adsorption. The rate constants of sorption process were determined using pseudo-first order equation proposed by Lagergren [19] and pseudo-second order proposed by Ho and MsKay [20]. The kinetic models and its parameters are summarized in Table 1. The correlation coefficients, R^2, showed that the pseudo-second order model fits better with the experimental data than pseudo-first model. Moreover, the calculated q_e values ($q_{e,cal}$) obtained with pseudo-second order kinetic model are more consistent with the experimental q_e values ($q_{e,exp}$), which also indicated that the adsorption process of Cd^{2+} ions on Ch/IA/MAA hydrogel can be well described by the pseudo-second order model. Processes that were found to comply with the pseudo-second order kinetic model include different sorption mechanism such as surface complexation, ion-exchange and dissolution/precipitation [21–23]. The rate limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate [20].

3.3. Characterization of Cd^{2+}-Ch/IA/MAA hydrogel

The Cd^{2+} loaded hydrogel was characterized using FTIR spectral analysis, SEM/EDX analysis and AFM surface topography and phase imaging.

The FTIR spectra (400–4000 cm^{-1}) of the Ch/IA/MAA hydrogel, free and metal-loaded, was taken and compared with each other to obtain information on the nature of the possible adsorbent–metal ion interactions. The obtained results are presented in Fig. 6. Broad peak at 3435 cm^{-1} (Fig. 6a) is caused by the symmetrical amine N–H vibration and C–O–H stretching of the hydroxyl group. The intensity of this band decreases and shifts to lower wave numbers in the FTIR spectrum of cadmium-loaded Ch/IA/MAA hydrogel (Fig. 6b) indicating that these two groups are possibly involved in
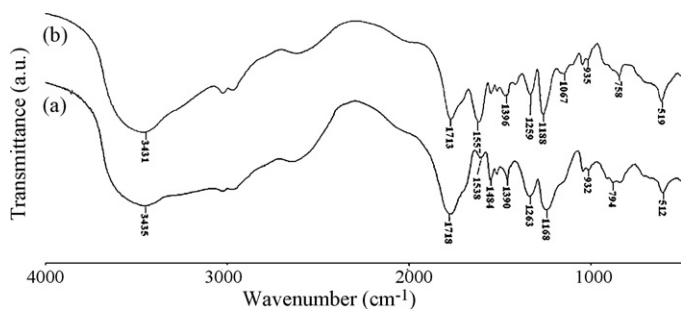
Table 1
The rate constants of Ch/IA/MAA hydrogel toward Cd^{2+} ions.

Initial Cd^{2+} concentration (mg/L)	$q_{e,exp}$ (mg/g)	Rate constant					
		Pseudo-first order			Pseudo-second order		
		k_1 (min^{-1})	$q_{e,cal}$ (mg/g)	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e,cal}$ (mg/g)	R^2
5	3.19	1.86	2.71	0.9379	10.4	3.62	0.9971
10	6.01	2.57	7.26	0.9774	4.16	7.14	0.9962
15	9.14	2.39	10.5	0.9680	2.79	10.0	0.9798

Fig. 6. FTIR spectra of the Ch/IA/MAA hydrogel before (a) and after (b) adsorption.

the adsorption. The strong absorption band at $1718\,cm^{-1}$ (Fig. 6a) assigned to C=O stretching vibration from carboxylic groups obviously weakened (Fig. 6b) and shifted to the lower wave number ($1713\,cm^{-1}$) in the metal loaded spectrum. The absorption band at $1538\,cm^{-1}$ (Fig. 6a), assigned to the ionic interaction between Ch and the acids, as well as the absorption band at $1168\,cm^{-1}$, assigned to the deformation absorption bands of –OH groups, were obviously enhanced and shifted to higher wave numbers after cadmium adsorption (Fig. 6b). These results reflects that –NH$_2$ and –OH groups are involved in binding the Cd^{2+} ions. FTIR spectra of the Ch/IA/MAA hydrogel before and after Cd adsorption indicates that –NH$_2$, –OH and –COOH groups in the hydrogel were all involved in the adsorption process.

The SEM image of Ch/IA/MAA hydrogel before and after adsorption is shown in Fig. 7. Fig. 7a shows that the structure of the unloaded hydrogel is highly porous. Fig. 7b shows that cadmium adsorption causes significant changes in hydrogel structure. EDX was employed to confirm whether the electron dense part on the

hydrogel is made up of cadmium ions. Typical EDX spectra of the unloaded hydrogel and the cadmium-adsorbed hydrogel are presented in Fig. 7a′ and b′. The EDX spectrum for the intact hydrogel did not show the characteristic peak of cadmium. On the other hand, the EDX spectrum of cadmium-loaded hydrogel showed clearly the peak of cadmium which intensity is proportional to the metal concentration. Hence, the existence of cadmium ion on the Ch/IA/MAA hydrogel is confirmed by EDX spectra.

Characteristic three dimensional (3D) surface topography and phase AFM images (500 nm × 500 nm) of the reference sample and of ones modified by absorbed Cd, are presented in Fig. 8. Grains of various sizes randomly aggregated can be seen in Fig. 8a. Due to the contrast enhancement in phase images, particular grains are clearly highligted in Fig. 8b. Upon Cd adsorption, a significant change in surface topography is obtained. Larger grains of the reference sample are broken into a higher number of smaller grains agglomerated into chain-like structures giving thus a flattened Cd/ref surface, as illustrated in Fig. 8c. Presence of cadmium containing phase on the surface is indicated by a light contrast of small grains in phase image, Fig. 8d. The better agglomeration of even smaller grains resulting in a relatively rough surface morphology is more pronounced in the case when Cd is absorbed from more concentrated solutions, as can be seen from the topography AFM image given in Fig. 8e. On the other hand, the homogenization in surface composition can be seen in a corresponding phase image given in Fig. 8f.

3.4. Adsorption isotherms

The adsorption isotherms for the removal of Cd^{2+} ion were studied over a large initial concentration range (5–$750\,mg\,L^{-1}$) for a fixed amount of sorbent (0.035 g). The influence of C_e on
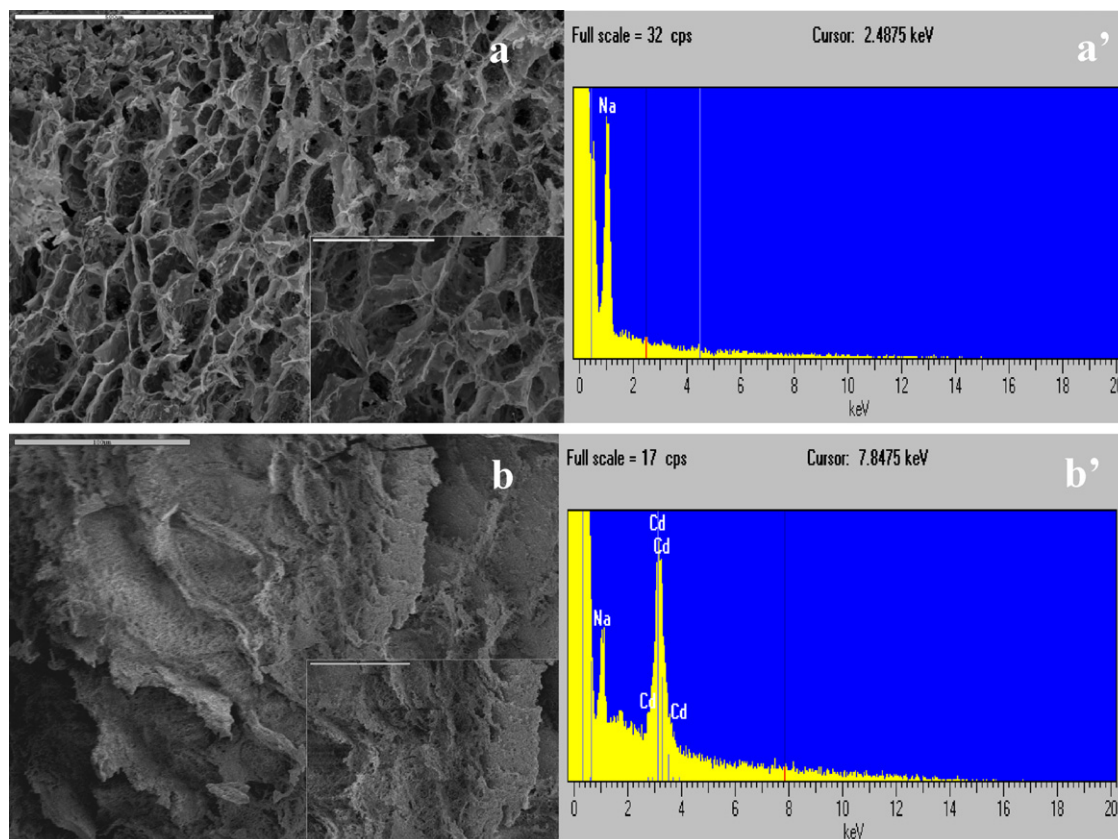

Fig. 7. (a) SEM micrograph 'bar' 500 μm, 90×; zoom 'bar' 200 μm, 300× and (a′) EDX spectra of intact Ch/IA/MAA hydrogel (b) SEM micrograph 'bar' 100 μm, 400×; zoom 'bar' 50 μm, 1000× and (b′) EDX spectra of Ch/IA/MAA hydrogel after loading of cadmium from nitrate solution (300 mg/L).
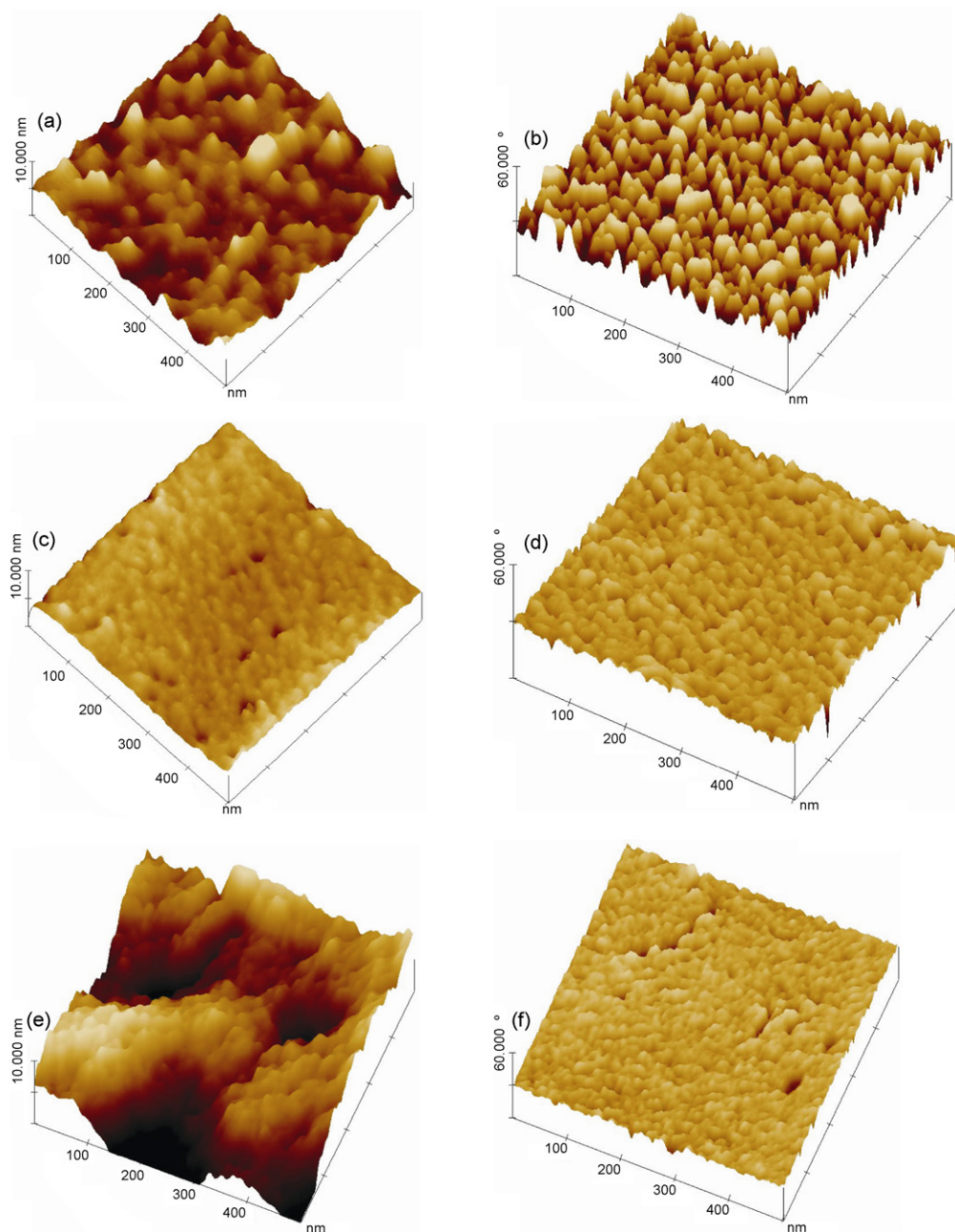
Fig. 8. AFM images (500 nm × 500 nm) showing: (a) the morphology of the reference sample and (b) the corresponding phase image; (c) the morphology of the same sample after Cd^{2+} ions adsorption (initial concentration 80 mg L^{-1}) and (d) the corresponding phase image; (e) the same sample containing Cd absorbed (initial concentration 320 mg L^{-1}) and (f) the corresponding phase image. For surface morphology images z-range is 10 nm, while for phase images z-range is 60°.

adsorption capacity (q_e) is shown in Fig. 9. The equilibrium adsorption data were subjected to Langmuir and Freundlich adsorption isotherms. The parameters of these adsorption isotherms, evaluated from linear plots are presented in Table 2, along with the correlation coefficient. Comparing the linear correlation coefficients listed in Table 2, it is concluded that the adsorption of Cd^{2+} ions on Ch/IA/MAA hydrogel follows the Langmuir isotherm equation under the concentration range studied.

Weber and Chakraborti [24] expressed the essential characteristics and the feasibility of the Langmuir isotherm in terms of a dimensionless constant separation factor or equilibrium parameter R_L, which is defined as:

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

where C_0 is the initial concentration of Cd^{2+} (in mg/L) and b is the Langmuir constant (L/mg).

According to McKay et al. [25], R_L values between 0 and 1 indicate favorable adsorption. The calculated R_L values for the adsorption of Cd^{2+} ions on Ch/IA/MAA hydrogel for highest initial concentration used in this study (C_0 = 750 mg/L), was 0.147 indicating that the adsorption was favorable.

The studies relating the effect of temperature on adsorption were carried out at three different temperatures (25, 37 and 45 °C) at optimum pH value of 5.5 and adsorbent dosage level of 0.035 g. The equilibrium contact time was 48 h.

The Langmuir constant K_L is related to the energy of adsorption and the free energy change, ΔG, of adsorption is given by:
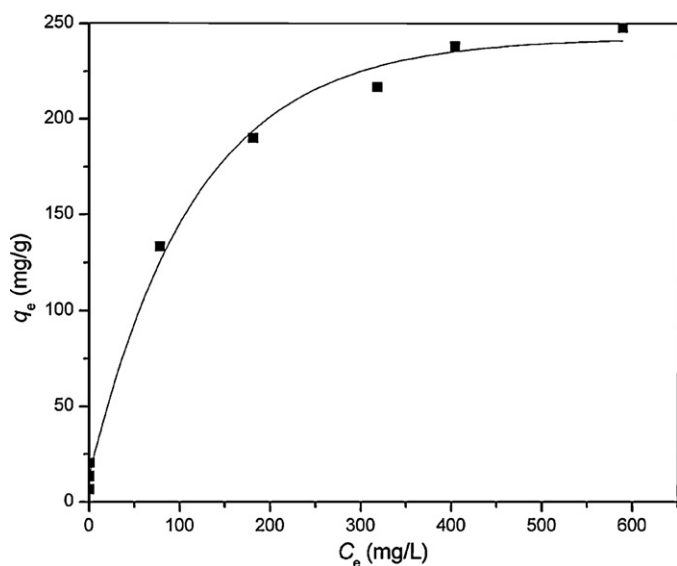
$$\Delta G = -RT \ln K_L \tag{4}$$

Fig. 9. Sorption isotherm for Cd^{2+} onto Ch/IA/MAA hydrogel. *Experimental conditions*: Initial pH of solution 5.5; sample dose: 0.035 g; volume of solution 50 mL; temperature: 25 °C; equilibrium time: 48 h.

where R is the universal gas constant (8.314 J/mol K) and T is the temperature.

The influence of temperature on Cd^{2+} ion adsorption on Ch/IA/MAA hydrogel was evaluated using equation:

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{5}$$

The enthalpy (ΔH) and entropy (ΔS) were calculated from the slope and intercept of a plot $\ln K_L$ versus $1/T$.

The negative values of ΔG obtained (-23.01, -22.84 and -22.67 kJ/mol at 25, 37 and 45 °C, respectively) indicate that the process of Cd^{2+} ion adsorption on Ch/IA/MAA hydrogel is spontaneous.

The enthalpy change, ΔH, and the entropy change, ΔS, values obtained were -27.9 kJ/mol and -16.6 J/mol K, respectively. Obviously, the reaction is exothermic (ΔH is negative) and there is randomness decreasing at the solid/solution interface and a decrease in the degree of freedom of the adsorbed species (ΔS is negative).

Adsorption capacities of chitosan and modified chitosan sorbents, reported in the literature, are included in Table 3 along with the values obtained in this study. The Ch/IA/MAA hydrogel exhibits higher adsorption capacity comparing to most modified forms. The incorporation of active functional groups –NH$_2$, –OH and –COOH, that can gain metal ions by exchange or by simple chelatation or adsorption due to opening of polymer matrix, results in high adsorption capacity of Ch/IA/MAA hydrogel. Vuković et al. reported that oxygen introduced groups and amino groups were responsible for cadmium uptake [29]. Apart from the adsorption on the surface of the hydrogel, sorption takes place in the bulk, thus confirmed by

Table 2
Langmuir and Freundlich isotherm parameters for Cd^{2+} ions adsorption on Ch/IA/MAA hydrogel.

Model	Parameter	Value
Langmuir	q_{max} (mg/g)	285.7
	K_L (L/g)	10.85
	R^2	0.9940
Freundlich	K_F (L/g)	7.2417
	n	1.84
	R^2	0.9751

Table 3
Maximum adsorption capacity of different chitosan based adsorbents for Cd^{2+} ions.

Adsorbent	q_{max} (mg/g)	Reference
Pristine CTS vs. CdSO$_4$	382.2	Wu et al. [26]
Pristine CTS vs. Cd(NO$_3$)$_2$	96.7	Wu et al. [26]
CCTSL	58.4	Krishnapriya and Kandaswamy [13]
HQS-GLA-CTS	32.6	Vitali et al. [27]
Cs-GLA-CTS	357.4	Sankararamakrishnan et al. [28]
Ch/IA/MAA	285.7	Present study

SEM/EDX analysis and AFM surface topography and phase images. The Ch/IA/MAA hydrogel showed appropriate swelling properties and extent of the water uptake affects cadmium ion adsorption in the bulk of the network.

3.5. Desorption studies

When a 0.01 mol/L CH$_3$COOH and 0.1 mol/L CH$_3$COOH solutions were used as the desorbing agents, 28.5% and 81.3% desorption efficiency was obtained, respectively. Both HNO$_3$ solutions, 0.1 and 0.01 mol/L, appeared to be effective for cadmium ion desorption (100.0%), and the 0.01 mol/L HNO$_3$ solution was used in further sorption/desorption studies. No significant loss of the capacity was observed during three cycles of adsorption–desorption.

4. Conclusions

The properties of the Ch/IA/MAA hydrogel, as well as its ability for the removal of Cd^{2+} ions from water solution, has been investigated. It was found that the swelling degree and adsorption capacity of the hydrogel increased with pH, while the optimum pH for cadmium adsorption was 5.5. The results of the adsorption kinetics and isotherms have shown that the adsorption process of Cd^{2+} ions on Ch/IA/MAA hydrogel can be fitted by the pseudo-second order equation and the Langmuir equation, respectively. From the dimensionless equilibrium parameter (R_L) and thermodynamic parameters, it has been concluded that the adsorption is favorable, spontaneous and exothermic. The examined new material exhibits high adsorption capacity and cadmium can be efficiently desorbed with 0.01 mol/L HNO$_3$.

References

[1] J. Sastre, A. Sahuquillo, M. Vidal, G. Rauret, Determination of Cd, Cu, Pb and Zn in environmental samples: microwave-assisted total digestion versus aqua regia and nitric acid extraction, Anal. Chim. Acta 462 (2002) 59–72.
[2] X. Wang, Y. Zheng, A. Wang, Fast removal of copper ions from aqueous solution by chitosan-g-poly(acrylic acid)/attapulgite composites, J. Hazard. Mater. 168 (2009) 970–977.
[3] A. Kara, L. Uzun, N. Beşirli, A. Denizli, Poly(ethylene glycol dimethacrylate-n-vinyl imidazole) beads for heavy metal removal, J. Hazard. Mater. 106B (2004) 93–99.
[4] A. Duran, M. Soylak, S. Ali Tuncel, Poly(vinyl pyridine-poly ethylene glycol methacrylate-ethylene glycol dimethacrylate) beads for heavy metal removal, J. Hazard. Mater. 155 (2008) 114–120.
[5] D. Kumar Mishra, J. Tripathy, A. Srivastava, P. Kant Pandey, K. Behari, Synthesis and characterization of chitosan-g-methacrylic acid and studies of its additional physicochemical properties, such as swelling, metal-ion sorption, and flocculation behavior, J. Appl. Polym. Sci. 113 (2009) 2429–2439.
[6] L. Zhao, H. Mitomo, Adsorption of heavy metal ions from aqueous solution onto chitosan entrapped cm-cellulose hydrogels synthesized by irradiation, J. Appl. Polym. Sci. 110 (2008) 1388–1395.

[7] M.A. Sharaf, H.A. Arida, S.A. Sayed, A.A. Younis, A.B. Farag, Separation and preconcentration of some heavy-metal ions using new chelating polymeric hydrogels, J. Appl. Polym. Sci. 113 (2009) 1335–1344.

[8] S. Jagtap, D. Thakre, S. Wanjari, S. Kamble, N. Labhsetwar, S. Rayalu, New modified chitosan-based adsorbent for defluoridation of water, J. Colloid. Interface Sci. 332 (2009) 280–290.

[9] N. Viswanathan, S. Meenakshi, Enriched fluoride sorption using alumina/chitosan composite, J. Hazard. Mater. 178 (2010) 226–232.

[10] D. Thakre, S. Jagtap, N. Sakhare, N. Labhsetwar, S. Meshram, S. Rayalu, Chitosan based mesoporous Ti–Al binary metal oxide supported beads for defluoridation of water, Chem. Eng. J. 158 (2010) 315–324.

[11] M. Kumar, B.P. Tripathi, V.K. Shahi, Crosslinked chitosan/polyvinyl alcohol blend beads for removal and recovery of Cd(II) from wastewater, J. Hazard. Mater. 172 (2009) 1041–1048.

[12] R. Chanthateyanonth, S. Ruchirawat, C. Srisitthiratkul, Preparation of new water-soluble chitosan containing hyperbranched-vinylsulfonic acid sodium salt and their antimicrobial activities and chelation with metals, J. Appl. Polym. Sci. 116 (2010) 2074–2082.

[13] K.R. Krishnapriya, M. Kandaswamy, Synthesis and characterization of a crosslinked chitosan derivative with a complexing agent and its adsorption studies toward metal(II) ions, Carbohydr. Res. 344 (2009) 1632–1638.

[14] T.K. Naiya, A.K. Bhattacharya, S.K. Das, Adsorption of Cd(II) and Pb(II) from aqueous solutions on activated alumina, J. Colloid Interface Sci. 333 (2009) 14–26.

[15] N.B. Milosavljević, Lj.M. Kljajević, I.G. Popović, J.M. Filipović, M.T. Kalagasidis Krušić, Chitosan, itaconic acid and poly(vinyl alcohol) hybrid polymer networks of high degree of swelling and good mechanical strength, Polym. Int. 59 (2010) 686–694.

[16] T. Wang, M. Turhan, S. Gunasekaran, Selected properties of pH-sensitive, biodegradable chitosan–poly(vinyl alcohol) hydrogel, Polym. Int. 53 (2004) 911–918.

[17] M. Kalagasidis Krušić, D. Danković, M. Nikolić, J. Filipović, Macromol. Chem. Phys. 205 (2004) 2214–2220.

[18] I.N. Jha, L. Iyengar, A.V.S. Prabhakara Rao, Removal of cadmium using chitosan, J. Environ. Eng. 114 (1988) 962–974.

[19] S.S. Lagergren, Zur theorieder sogennanten adsorption gelöster stoffe, K. Sven. Vetenskapsakad. Handl. 24 (1988) 1–39.

[20] Y.S. Ho, G. McKay, Pseudo-second order model for adsorption processes, Process Biochem. 34 (1999) 451–465.

[21] M. Šljivić, I. Smičiklas, I. Plećaš, M. Mitrić, The influence o equilibration conditions and hydroxyapatite physico-chemical properties onto retention of Cu^{2+} ions, Chem. Eng. J. 48 (2009) 80–88.

[22] K. Chojnacka, Equilibrium and kinetic modelling of chromium(III) sorption by animal bone, Chemosphere 59 (2004) 315–320.

[23] N. Bektas, S. Kara, Removal of lead from aqueous solutions by natural clinoptilolite: equilibrium an kinetic studies, Sep. Purif. Technol. 39 (2004) 189–200.

[24] T.W. Weber, R.K. Chakraborti, Pore and solid diffusion models for fixed bed adsorbents, AIChE J. 20 (1974) 228–238.

[25] G. McKay, H.S. Blair, J.R. Gardener, Adsorption of dyes on chitin I. Equilibrium studies, J. Appl. Pol. Sci. 27 (1982) 3043–3057.

[26] F.-C. Wu, R.-L. Tseng, R.-S. Juang, A review and experimental verification of using chitosan and ites derivatives as adsorbents for selected heavy metals, J. Environ. Manage. 91 (2010) 798–806.

[27] L. Vitali, M.C.M. Laranjeira, N.S. Goncalves, V.T. Favere, Spray dried chitosan microspheres containing 8-hydroxyquinoline-5-sulfonic acid as a new adsorbent for Cd(II) and Zn(II) ions, Int. J. Biol. Macrmol. 42 (2008) 152–157.

[28] N. Sankararamakrishnan, A.K. Sharma, R. Sanghi, Novel chitosan derivative for the removal of cadmium in the presence of cyanide from electroplating wastewater, J. Hazard. Mater. 148 (2007) 353–359.

[29] G.D. Vuković, A.D. Marinković, M. Čolić, M.Đ. Ristić, R. Aleksić, A. Perić-Grujić, P.S. Uskoković, Removal of cadmium from aqueous solutions by oxidized and ethylenediamine-functionalized multi-walled carbon nanotubes, Chem. Eng. J. 157 (2010) 238–248.