

Accepted Manuscript

Title: Preparation and characterization of novel P(HEA/IA) hydrogels for Cd²⁺ ion removal from aqueous solution

Author: Katarina M. Antić Marija M. Babić Jovana J. Jovašević Vuković Dana G. Vasiljević-Radović Antonije E. Onjia Jovanka M. Filipović Simonida Lj. Tomić



PII: S0169-4332(15)00449-3
DOI: <http://dx.doi.org/doi:10.1016/j.apsusc.2015.02.133>
Reference: APSUSC 29813

To appear in: *APSUSC*

Received date: 27-10-2014
Revised date: 11-2-2015
Accepted date: 22-2-2015

Please cite this article as: K.M. Antić, M.M. Babić, J.J.J. Vuković, D.G. Vasiljević-Radović, A.E. Onjia, J.M. Filipović, S.Lj. Tomić, Preparation and characterization of novel P(HEA/IA) hydrogels for Cd²⁺ ion removal from aqueous solution, *Applied Surface Science* (2015), <http://dx.doi.org/10.1016/j.apsusc.2015.02.133>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Preparation and characterization of novel P(HEA/IA) hydrogels for Cd²⁺ ion removal from aqueous solution

Katarina M. Antić¹, Marija M. Babić¹, Jovana J. Jovašević Vuković¹, Dana G. Vasiljević-Radović², Antonije E. Onjia³, Jovanka M. Filipović¹, Simonida Lj. Tomić^{1,*}

¹ Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia

² Institute for Chemistry, Technology and Metallurgy, University of Belgrade, Njegoseva 12, Belgrade, Serbia

³ Vinca Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, Belgrade, Serbia

*Corresponding author: Tel: +381-11-3303-703; Fax: +381-11-3370-387;
e-mail: simonida@tmf.bg.ac.rs

ABSTRACT

Series of novel hydrogels based on 2-hydroxyethyl acrylate (HEA) and itaconic acid (IA), P(HEA/IA) copolymers, were prepared by free radical cross-linking copolymerization and investigated as potential adsorbents for Cd²⁺ removal from aqueous solution. The hydrogels before and after Cd²⁺ adsorption were characterized using FTIR, DSC, SEM/EDX, AFM and DMA analysis. The swelling results showed that these hydrogels are pH and temperature sensitive. In order to evaluate adsorption behavior of samples various factors affecting the Cd²⁺ uptake behavior, such as: contact time, temperature, pH, ionic strength, adsorbent weight, competitive ions and initial concentration of the metal ions were investigated. Five adsorption isotherms and two kinetic models were studied. The adsorption behavior can be very well described by the pseudo-second order kinetic model and Langmuir isotherm. Multicomponent adsorption studies revealed that adsorption of cadmium depends on the type of metal ions present in the system. Desorption studies showed that hydrogel can be reused three times with only 15% loss of adsorption capacity. All results indicate that the sample with the highest IA content is the most promising adsorbent for Cd²⁺ removal.

Keywords: Hydrogel, Cadmium adsorption, Surface topography, Isotherm, Multicomponent adsorption, Reusability

1. Introduction

Discharges of effluents containing heavy metals, even in low concentrations, has resulted in a number of environmental problems. Unlike organic pollutants, heavy metal ions are not biodegradable. They tend to accumulate in the organisms and enter the food chains through various pathways, which cause serious harm to human health [1-5].

Cadmium is considered to be an extremely toxic metal without known biological function [6]. It has been released to the environment through combustion of fossil fuels, metal production, application of phosphate fertilizers, and the manufacturing of batteries, pigments and screens [7]. Cadmium may cause serious damage to living organisms, even at very low concentrations. Because of the toxicity and bioaccumulation, US Environment Protection Agency has classified cadmium as group B1 carcinogen. The World Health Organization (WHO) has set a maximum guideline concentration of 0.003 mg L^{-1} for Cd in drinking water [8].

There are various methods for removing heavy metals from aqueous solution, including adsorption, chemical precipitation, ion exchange, membrane filtration and reverse osmosis [9]. Among them, adsorption is one of the most effective methods for heavy metals removal, due to its high efficiency, ease of operation, cost effectiveness and no secondary pollution [10-12].

Recently, hydrogels have attracted much attention, because when compared with conventional solid adsorbents they have many advantages, such as biocompatibility, biodegradability, lack of toxicity, ability of incorporating different functional groups into the polymeric networks, easy handling and reusability [13, 14]. 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 [15-18] or ionic dyes from wastewater [19, 20].

Although many works have focused on adsorption of heavy metals on hydrogels, only few authors investigated application of hydrogels based on 2-Hydroxyethyl acrylate (HEA) in metal ions removal from aqueous solutions [21-24].

In this study, a novel poly(2-hydroxyethyl acrylate/itaconic acid) (P(HEA/IA)) hydrogels were synthesized by free radical copolymerization/crosslinking, and used in removal of Cd^{2+} ions from water for the first time. The structure of P(HEA/IA) hydrogels was confirmed by FTIR spectroscopy and the samples were also characterized using differential scanning calorimetry

(DSC), scanning electron microscopy (SEM/EDX), atomic force microscopy (AFM) and dynamic–mechanical analysis (DMA) spectroscopy. The influence of initial pH of the solution, adsorbent dosage, temperature and ionic strength on the Cd^{2+} ion adsorption on P(HEA/IA) hydrogels were studied. Furthermore, pseudo-first order and pseudo-second order kinetics as well as five adsorption isotherm models were applied to verify the mechanism and kinetics of the adsorption process. In addition, the adsorption of cadmium was studied in a multicomponent heavy metal ion experiment. Finally, desorption and reusability of hydrogels were investigated.

2. Materials and methods

2.1 Materials

2-hydroxyethyl acrylate (HEA), ethylene glycol dimethacrylate (EGDMA), potassium persulfate (KPS) and N,N,N',N'-tetramethylethylene diamine (TEMED) were purchased from Sigma-Aldrich. Itaconic acid (IA) was supplied from Fluka. All reactants were of analytical grade and used as received. Cadmium stock solution (1000 mg L^{-1}) was prepared by dissolving $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck, p.a.). Buffer solutions with different pH values were prepared using hydrochloric acid (La Chema), potassium chloride (Fluka), potassium mono- and dihydrogenphosphate (Fluka) and sodium hydroxyde (Fluka). Deionized water was used for all polymerizations, preparation of solutions and buffers.

2.2 Hydrogel synthesis

The P(HEA/IA) hydrogels were synthesized via free radical polymerization/cross-linking, with IA mole fractions of 2.0, 5.0, 7.0, and 10.0 (Scheme 1). In all polymerizations, ethylene glycol dimethacrylate (EGDMA) was used as cross-linking agent, potassium persulfate (KPS), as initiator, and N,N,N',N'- tetramethylethylene diamine (TEMED), as activator. All reactants were dissolved in water/ethanol mixture and the reaction mixture was degassed and placed between two glass plates sealed with a rubber spacer (2-mm thick). The reaction was carried out at $50 \text{ }^\circ\text{C}$ for 24 h. After the reaction, the gels were cut into disks and immersed in water for a week to

remove unreacted chemicals, by changing water daily. The disks were dried to xerogels at room temperature. The dimensions of the xerogel disks used in each experiment were 0.450 ± 0.010 cm (average in diameter) and 0.150 ± 0.010 cm (average in thickness).

2.3 Characterization

2.3.1 Swelling studies

Swelling measurements were carried out in buffers, in a pH range of pH (2.20, 3.85, 5.45 and 6.80) at 25 °C, and in the temperature range of 10-50 °C at pH 6.80. Swelling of the hydrogels was also investigated in deionized water and in Cd^{2+} ion solution. Hydrogels were immersed in the swelling medium and left for 48 h to attain swelling equilibrium. The equilibrium degree of swelling was calculated as follows:

$$Q_e = \frac{m_e - m_0}{m_0} \quad (1)$$

where m_e is the weight of the hydrogel swollen at equilibrium and m_0 is the weight of the xerogel. The mean values of three swelling measurements are presented.

2.3.2 Hydrogel characterization

The hydrogels were characterized before and after cadmium adsorption. Dynamic-mechanical analysis (DMA) was performed on Discovery Hybrid Rheometer HR2 (TA Instruments) operating in shear mode, parallel plate geometry. Diameter of the plates was 25 mm. The storage modulus, G' , was measured as a function of frequency (varied from 0.1 to 100 rad/s) at a shear strain of 1 % at 25 °C. Fourier transform infrared (FTIR) spectra of the hydrogels were recorded in the transmission mode using a Bomem 100 FTIR spectrophotometer, as KBr pellets. Scanning electron microscope (SEM/EDX) was used to investigate the hydrogels morphology. Measurements were taken on a JEOL JSM-5800 scanning electron microscope. Atomic force microscopy (AFM, AutoProbe CP Research, TM microscopes) in non contact mode was used to investigate the surface topography of the hydrogels. The glass transition

temperatures of P(HEA/IA) hydrogels were determined with a DSC (TA Instruments Q2000 system). The DSC was calibrated with metallic indium standards (99.9 % purity). The hydrogel samples were desiccated for 24 h at 40 °C in vacuum, and tested in crimped aluminium pans at a rate of 20 °C/min, under nitrogen gas flow (50 mL min⁻¹), in the temperature range of -50 to 150 °C to eliminate any residual water. The aqueous phase concentration of Cd²⁺ was determined by ICP-OES Thermo iCAP 6500 system, equipped with the Thermo iTEVA software, a concentric nebulizer, and a Cyclonic Spray Chamber. Blank and calibration standards were prepared in 2 % nitric acid for all the measurements.

2.4 Adsorption experiments

Batch adsorption experiments were conducted to study the effect of different parameters on the adsorption of Cd²⁺ on P(HEA/IA) hydrogels. All experiments were carried out in 80 ml flasks containing 50 ml of aqueous solution of Cd(NO₃)₂·4H₂O and 0.03 g of hydrogel. The solutions were stirred with a constant speed of 100 rpm for 48 h.

The effect of pH (2.0 to 7.0), adsorption time (0.5 to 48 h) and initial Cd²⁺ ion concentration (10–500 mg L⁻¹) on the adsorption were studied. The pH of the aqueous phase was adjusted with dilute NaOH or HNO₃ and measured with a Hanna pH meter using a combined glass electrode.

In order to investigate the effect of temperature and adsorbent dosage on adsorption process, the equilibrium sorption measurements were carried out in 10 mg L⁻¹ Cd²⁺ ion solutions and pH 5.5, at 10, 25 and 50 °C and hydrogel mass within the range 0.008–0.09 g. To study the influence of ionic strength on the adsorption, ionic strengths of the solutions were adjusted with NaCl concentration range from 0 to 0.3 mol L⁻¹.

Five adsorption isotherm models were used to fit experimental data: Langmuir, Freundlich, Redlich-Peterson, Temkin and Dubinin-Radushkevich (D-R) isotherm. The linear forms of listed models are presented in Table 1.

The Cd²⁺ adsorption capacity q (mg g⁻¹) and adsorption efficiency (%) were calculated from Eqs. (2) and (3):

$$q = \frac{(C_0 - C_e) \cdot V}{m_0} \quad (2)$$

$$\text{Adsorption efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \cdot 100 \quad (3)$$

where C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial and final concentration of cadmium, V (L) is the volume of the solution, and m_0 (g) is the hydrogel weight. All experiments were carried out in triplicate and averaged values are reported.

2.5 Competitive adsorption

Adsorption of Cd^{2+} ions from artificial water (containing Cd^{2+} , Pb^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Co^{2+} ions) was investigated. A series of solutions containing different combinations of heavy metal ions were prepared. The experiments were conducted as described above, with initial concentration of each metal 10 mg L^{-1} .

2.6 Desorption and regeneration experiments

Desorption efficiency and regeneration potential of P(HEA/10IA) hydrogel were studied. The hydrogels at adsorption equilibrium, once loaded with Cd^{2+} ions (separated from 10 mg L^{-1} ions solution), were placed in the volume of 100 ml of the desorption medium and shaken at 100 rpm for 48 h. In order to determine the most effective desorption medium, desorption was done with 0.1 M solution of CH_3COOH , HCl and HNO_3 . To investigate the influence of desorption medium pH on desorption efficiency, pH values of the solutions were adjusted, from 1.5 to 5.5 using dilute HNO_3 . To determine the potential reusability of the hydrogels, desorption process was carried out in a 0.1M HNO_3 aqueous solution, and consecutive sorption–desorption cycles were repeated three times using the same adsorbent. Desorption efficiency was calculated using the following equation:

$$\text{Desorption efficiency (\%)} = \frac{\text{amount of desorbed metal ions}}{\text{amount of adsorbed metal ions}} \cdot 100 \quad (4)$$

3. Results and discussion

3.1 Swelling studies

Swelling behavior was investigated in buffers in the pH range of 2.20-6.80, at 25°C. As can be seen from Table 2, the equilibrium degree of swelling is strongly dependent on the pH of the surrounding media and on IA content. IA is a weak acid that has two COOH groups with different pK_a values. These two COOH groups do not behave in the same way, the primary one is more reactive and easily ionizes whereas the secondary COOH group undergoes dissociation rather slowly. At pH below pK_a values ($pK_{a1}= 3.85$ and $pK_{a2}=5.45$) carboxylic groups of itaconic acid are not ionized and the degree of swelling is low. As the pH value of the surrounding media rises above first and second pK_a value, the electrostatic repulsive forces among the carboxylic anion groups become dominant driving force in the swelling process. As a result the degree of swelling increases significantly and this phenomenon is most expressed for the sample with the highest IA content. The swelling behavior of hydrogels was also investigated in deionized water as well as in Cd^{2+} solutions used for adsorption measurements. As it can be seen from the Table 2, in these media the hydrogels swelling degree changes in the opposite way compared to swelling in buffer solutions (above pH 5.45). The decrease in swelling in deionized water with the increase in IA content could be explained by the formation of intermolecular hydrogen bonds, which results in an increase in the overall crosslinking density of the hydrogel network. The results for Q_e values in Cd^{2+} solution were reduced in comparison with those measured in deionized water. Generally, the swelling ability of "anionic" hydrogels in salt solutions is noticeably decreased compared to the swelling in deionized water. This decrease of Q_e may be attributed to a "charge screening effect" of the additional cations which causing a non-perfect anion-anion electrostatic repulsion. Also, in salt solution the osmotic pressure difference between the hydrogel and external salt solution is reduced, leading to decrease in swelling [31].

The influence of solution temperature on swelling was studied at four different temperatures (10, 25, 45 and 50 °C) in a buffer 6.8. It is observed that the Q_e decreases with the temperature increase from 10 to 50 °C. The temperature sensitivity of P(HEA/IA) hydrogels is associated with hydrogen bonding of hydroxyl groups from HEA with water hydroxyl groups and

hydrophobic interactions [32]. Hydrogels swell more at low temperatures of surrounding media, since hydrogen bonds in the hydrogel during interaction with water considerably lower the free energy of mixing. However, at higher temperatures, the hydrogen bonds weaken; at the same time, the system tends to minimize the contact between the water and hydrophobic groups, so that the interactions between the hydrophobic groups increase and water is expelled from the hydrogels [33].

3.2 Mechanical properties

Mechanical strength and stability of hydrogels are very important properties for environmental application and wastewater treatment. Therefore, it is of great importance to investigate their mechanical properties in conditions in which they are applied, in this case the aqueous solution of cadmium. The storage modulus (G') was measured in order to determine whether the samples are stable for this specific application. The plateau storage modulus for P(HEA/IA) hydrogels, swollen to equilibrium in deionized water and in Cd^{2+} ion solution are given in Table 3. It is obvious that modulus depends on IA content in the hydrogel. Increase of IA content in the sample resulted in increase of G' and thus improved mechanical properties of hydrogel. Also, storage modulus is higher for samples swollen in solution of cadmium than for those swollen in deionized water, which means that embedding of Cd^{2+} ions reinforce the polymeric network. The obtained results are in accordance with the swelling results (Table 2).

Further experiments were performed for two hydrogels: P(HEA/2IA) and P(HEA/10IA), as samples with lowest and highest q_e value, in order to stress the pH sensitivity i.e. the influence of IA content on adsorption properties of P(HEA/IA) hydrogels.

3.3 FTIR spectra

Spectral characterization was performed in order to detect chemical structure and bonds of synthesized hydrogels. Fig. 1 shows the FTIR spectra of P(HEA/10IA) hydrogel, free and cadmium loaded. The FTIR spectrum of P(HEA/10IA) (Fig. 1(a)) exhibits several characteristic peaks at 3424, 2934 and 1720 cm^{-1} . The broad peak at 3424 cm^{-1} corresponds to stretching vibration of -OH bond, as well as peak intensities at 1400 and 1180 cm^{-1} . Peaks at 2871 and 2934

cm^{-1} are the typical C–H stretch vibrations [34]. Carboxylic groups show a characteristic peak at 1720 cm^{-1} , assigned to the C=O stretching vibration.

In order to notice shifting of characteristic peaks, the FTIR spectra was recorded for P(HEA/10IA) hydrogels loaded from two initial concentrations of cadmium, 10 mg L^{-1} and 100 mg L^{-1} and the results are presented in Fig 1 (b, c). The FTIR spectra of the hydrogels after Cd^{2+} ion adsorption showed all the above characteristic peaks with a slight shift to lower or higher wavenumbers. The intensity of the peak at 3424 cm^{-1} weakened and shifted to 3420 and 3418 cm^{-1} , for hydrogels loaded with 10 and 100 mg L^{-1} , respectively, indicating –OH group is possibly involved in the adsorption. Strong peak at 1720 cm^{-1} , assigned to C=O stretching vibration from carboxylic groups, was shifted to 1726 and 1729 cm^{-1} , for hydrogels loaded with 10 and 100 mg L^{-1} , respectively. This change suggests the possible interaction between cadmium ions and COO^- . The weak absorption band at 1570 cm^{-1} , assigned to asymmetric stretching vibration of C=O was sharpened and shifted to 1562 and 1557 cm^{-1} , for hydrogels loaded with 10 and 100 mg L^{-1} , respectively [35]. The shift of peaks at 3424 , 1720 and 1570 cm^{-1} before and after cadmium adsorption indicates that –OH and –COOH groups in the hydrogel are most likely involved in the adsorption process.

3.4 Morphology

Morphological features of lyophilized P(HEA/IA) samples, with and without adsorbed metal, were performed by observing cross-section and surface by SEM. The resulting micrographs are presented in Fig. 2. The cross-sectional image of P(HEA/2IA) (Fig. 2(a)) shows that the structure of the unloaded sample is highly porous with a characteristic honey-comb structure. The unloaded P(HEA/10IA) (Fig. 2(b)) sample has similar structure as P(HEA/2IA), but with slightly smaller pores, as expected, which is consistent with its lower equilibrium degree of swelling. The SEM micrographs of P(HEA/2IA), swollen at equilibrium in highly acidic ($\text{pH}=2.0$) (Fig. 2(c)) and weakly acidic ($\text{pH}=6.0$) (Fig. 2(d)) shows that the structure of P(HEA/IA) samples strongly depends on pH. At low pH compact structure with small non-uniformly distributed ellipsoidal pores can be observed, while at pH 6 much larger pore sizes are visible. This is in agreement with the swelling results, revealing low swelling at low pH and high swelling at pH 6. The sorption of cadmium ions causes significant reduction in the P(HEA/2IA) hydrogel pore size and

the change in pore structure (Fig. 2 (e)). Upon sorption metal ions interact with carboxyl groups, leading to diminished electrostatic repulsive forces between COO^- groups, and consequently to the reduction of hydrogel pores [36]. EDX analysis confirmed the presence of cadmium ions inside the hydrogel, as well as on the hydrogels surface.

3.5 Surface topography

To observe morphological properties such as surface porosity, texture and roughness, micrographs of the surface of P(HEA/IA) samples before and after metal adsorption were registered by using AFM. Fig. 3(a) shows a predominantly hill-valley-structured surface with irregular pores of P(HEA/10IA) hydrogel before cadmium adsorption. A visible change in surface topography is obtained after cadmium adsorption. Larger hill-structures of the reference sample are broken into smaller structures giving thus a flattened surface, as illustrated in Fig. 3(b). Fig. 3(c) represents AFM image of the sample in the case when cadmium is absorbed from more concentrated solutions. This image shows even smoother surface of the hydrogel than that in Fig. 3(b), indicating that most of the surface is covered with a layer of adsorbed cadmium ions which fill the roughness and pores on the sample surface.

3.6 Thermal properties

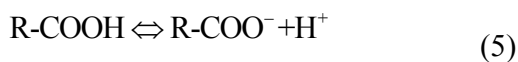
DSC thermograms of P(HEA/2IA) and P(HEA/10IA) hydrogels are presented in Fig. 4. For both hydrogels a single T_g value was clearly observed, showing that tested samples are copolymers. As seen from Fig. 4, T_g values depend on IA content, higher T_g values were obtained for hydrogel with higher IA content. On the other hand, after adsorption of Cd^{2+} ions T_g value increased. This increase of the T_g value could be explained by the reduced mobility of polymer chains due to metal complexation with the polymer chains.

3.7 The effect of different experimental parameters on adsorption properties of P(HEA/IA) hydrogels

3.7.1 Effect of pH

pH of the aqueous solution is one of the most important parameters affecting the adsorption process. It can influence the protonation of the adsorbent functional groups as well as the solution chemistry of the heavy metal ions [37-39]. The adsorption of heavy metal ions, on a polymer backbone containing acidic pendant groups, is usually a strong function of the pH because the acidic pendant groups release protons in response to changes in pH. Additionally, metal ions in the aqueous solution may undergo solvation and hydrolysis. Cadmium is present in aqueous solutions in the forms of Cd^{2+} , $\text{Cd}(\text{OH})^+$, $\text{Cd}(\text{OH})_2^0$ and $\text{Cd}(\text{OH})_{2(s)}$, which depends on the pH of the solution [40]. Cd^{2+} , is the only ionic species present in the solution at $\text{pH} < 6.0$, and the dominant cadmium species at $\text{pH} < 8.0$ is Cd^{2+} and $\text{Cd}(\text{OH})^+$, and at $\text{pH} > 8.0$ is $\text{Cd}(\text{OH})_2$ [41, 42]. In the alkaline range, precipitation plays the main role in the removal of cadmium attributed to the formation of precipitate of $\text{Cd}(\text{OH})_{2(s)}$. In order to avoid the hydrolysis and precipitation of cadmium ions, the pH range was chosen to be 2.0–7.0.

The influence of the pH on the adsorption capacity of Cd^{2+} ions is shown in Fig. 5. The observed lower adsorption capacity in acidic media (pH 2–3) may be attributed to low dissociation of itaconic acid carboxylic groups which causes competition between H^+ and Cd^{2+} ions for the same sorption site. In the pH range 3–6, ionization of carboxylic groups of itaconic acid takes place, the negative charge density on the adsorbent increases, and increased sorption of cadmium is a result of electrostatic attraction between Cd^{2+} ions and negatively charged binding sites, since ligands such as carboxyl and hydroxyl groups are free to promote interaction with metal cations. Based on the literature [17, 22, 35], the adsorption onto P(HEA/IA) hydrogels at different pH values is assumed to occur through ion-exchange and chelation between positively charged metal cations and nonionized or ionized carboxylic groups within the polymer hydrogels, which can be represented by the following equations:





The aforementioned adsorption mechanism could be confirmed by the following facts: (a) pH variation of the suspension before and after the adsorption. In aqueous solution $-\text{COOH}$ groups from IA dissociate to yield protons by which the solution pH will decrease. During the adsorption experiment pH of the suspension changed from 5.5 to 4.0; (b) FTIR spectra of the P(HEA/10IA) hydrogel before and after cadmium adsorption showed changes in some characteristic adsorption groups that were involved in the adsorption process; (c) SEM images of hydrogel before and after adsorption of cadmium ion showed significant reduction in the hydrogel pore size (Fig. 2 (e)). Upon sorption metal ions interact with carboxyl groups, electrostatic repulsive forces between COO^{-} groups are diminished leading to higher crosslinking degree and consequently to the decrease in hydrogel pore size. All these information suggest that adsorption mechanism may be combined action of ion-exchange and chelation.

Several researchers investigated the effect of pH on adsorption of metal ions on different sorbents [18, 37, 43]. In all cases, they observed a maximum metal ions adsorption between pH 5 and 6. Based on the obtained results, in order to achieve high efficiency and good selectivity, further adsorption studies were carried out at pH 5.5.

3.7.2 Effect of adsorbent weight

The effects of adsorbent weight on the adsorption capacity and removal efficiency for the Cd^{2+} ions are presented in Fig. 6. With the increase of adsorbent weight from 0.008 to 0.09 g, adsorption efficiency of Cd^{2+} ions changed from 28.1 to 62.6 % and from 34.6 to 69.3 % for P(HEA/2IA) and P(HEA/10IA) hydrogels, respectively. This behavior is expected due to the fact that with increasing adsorbent weight the sorbent surface increases, resulting in increase of the number of binding sites on the hydrogel surface available for the sorption of metal ions. On the contrary, the adsorption capacity of hydrogels decreases with the increase of adsorbent dosage due to unsaturation of adsorption sites during the adsorption process [44]. These results were expected, and reported for many other sorption systems [45].

3.7.3 Effect of ionic strength

Study on the influence of salts on metal ions removal is of great importance due to the fact that various salts are often present in wastewater at high levels. The presence of inorganic salts in the solution may either accelerate or slow down the adsorption process. Salts may screen the electrostatic interaction of opposite charges on adsorbent surface and metal ions, and an increase in salt concentration could decrease the adsorption capacity. On the contrary, salts may increase the degree of dissociation of the adsorbate molecules and promote the adsorption [17, 46, 47]. The situation becomes much more significant when both the adsorbate and adsorbent are both charged. In this work, the effect of NaCl concentration on the adsorption process was discussed.

As shown in Fig. 7, with the increase of ionic strength, the adsorption capacity for both hydrogels decreased. With the addition of 0.01 mol L⁻¹ of NaCl, the adsorption capacity of Cd²⁺ ions is reduced by 3.2 % for P(HEA/10IA) and 7.5 % for P(HEA/2IA). Moreover, the adsorption capacity decreases by 28 % for P(HEA/10IA) and 37.2 % for P(HEA/2IA) as concentration of NaCl increases to 0.3 mol L⁻¹. So, the ionic strength is an important factor in the adsorption process. The addition of salt screens the electrostatic interactions of the carboxylic groups of itaconic acid and makes the polymer chains shrink [48, 49].

3.7.4 Effect of temperature

The investigation of the temperature effect on the Cd²⁺ ions adsorption on P(HEA/10IA) hydrogel was conducted at three different temperatures (10, 25 and 50 °C). The adsorption of Cd²⁺ ions decreases slowly as the temperature increases (Table 4).

In order to describe the thermodynamic character of the sorption of Cd²⁺ ions on P(HEA/10IA) hydrogel, the thermodynamic parameters including enthalpy (ΔH°), entropy (ΔS°) and change in free Gibbs energy (ΔG°) have been determined from the Eqs. (8), (9) and (10). Values for ΔS° and ΔH° are obtained from the slope and intercept of a plot $\ln K_c$ vs $1/T$ according to Eq. (10). ΔG° values were calculated from the two parameters using Eq. (9) and the obtained data are presented in Table 4.

$$K_c = \frac{C_{ads}}{C_e} \quad (8)$$

$$\Delta G^{\circ} = -RT \ln K_c \quad (9)$$

$$\ln K_c = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (10)$$

where K_c is the equilibrium constant, C_{ads} is the amount of metal ions adsorbed at equilibrium (mg L^{-1}), C_e is the amount of metal ions remained in the solution (mg L^{-1}), R is the universal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$), and T is the solution temperature (K) [50].

At 10 and 25 °C the values of ΔG° are negative indicating adsorption is spontaneous, while the ΔG° value on 50 °C is positive, meaning that the process on this temperature is non-spontaneous and the degree of spontaneity of the reaction decreases with the temperature increase. The negative value of ΔH° suggests that the adsorption processes is exothermic, which is supported by the decrease of the adsorption of Cd^{2+} ions with increase of temperature. The negative value of ΔS° signify there is a decrease in the randomness at the solid-solution interface of Cd^{2+} onto P(HEA/IA) hydrogel [19].

3.7.5 Adsorption isotherms

The most common way to examine the mechanism of the adsorption and describe how adsorbate could interact with adsorbent is through adsorption isotherms. The obtained experimental data were simulated with linearized forms of five isotherm models Langmuir, Freundlich, Redlich-Peterson, Temkin and Dubinin–Radushkevich, using commercial software Origin Microcal 8.0 (Fig. 8). The applicability of the isotherm models to describe the adsorption process was judged by the correlation coefficient, (R^2) and Chi-square analysis (χ^2). The obtained characteristic parameters of evaluated isotherm models are summarized in Table 5.

The Langmuir and Redlich-Peterson isotherms give very high and close R^2 values that it is difficult to conclude which model gives the best interpretation of experimental data. Moreover, linear equations have different axial settings individually so that would alter the result of a linear regression and influence the determination process. Due to the resulting correlation coefficients (R^2) of the isotherms that were very close and high, Chi-square test is used to determine best isotherm models. The advantage of using Chi-square test was comparing all isotherms on the same abscissa and ordinate.

The Chi-square test measures the difference between the experimental and model data. The mathematical form of Chi-square is given as [51]:

$$\chi^2 = \sum \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \quad (11)$$

Where, $q_{e,exp}$ is experimental equilibrium capacity data and $q_{e,cal}$ is the equilibrium capacity from isotherm model. If data from the model are similar to experimental data, χ^2 will be small and vice versa.

The Langmuir equation relates the coverage of molecules on the solid surface to concentration of a medium above the solid surface at a fixed temperature and adsorption is limited to monolayer coverage, and intermolecular forces decrease with the distance from the adsorption surface. On the other hand, the Freundlich model supposes that the adsorption surface is heterogeneous, that interactions among adsorbed molecules can occur, and that multilayer adsorption is possible. Redlich–Peterson isotherm is a combination of Langmuir and Freundlich model. It approaches the Freundlich model at higher concentration, while for lower concentration it is in accordance with the Langmuir equation. The Langmuir isotherm has the lowest χ^2 value, suggesting that this isotherm provides the best fit to the experimental data.

The Langmuir equation can be expressed in terms of dimensionless separation factor, R_L , which indicates whether the sorption is favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$), and is given by Eq. (12):

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (12)$$

where C_0 is the the maximal initial metal ion concentration (mg L^{-1}) [20].

The values of the separation factors $0 < R_L < 1$ and the value for Freundlich exponent $n > 1$ (Table 5) indicate that the sorption of Cd^{2+} onto investigated hydrogels is favorable. The calculated R_L values for all studied concentrations (Table 6) point out that sorption is more favorable at higher initial metal ion concentrations.

Dubinin–Radushkevich and Tempkin models have lower agreement with experimental data than first three models. The values of the sorption capacity obtained by D–R equation are higher than q_m values obtained by Langmuir model, as expected, because D–R model takes into account porous structure of a sorbent.

Since the swelling and adsorption properties of P(HEA/IA) hydrogels were highly influenced by the presence of ions in the solution, we investigated influence of swelling degree (Q_e) on the adsorption capacity. As shown in Fig. 9, the increase in the initial concentration of Cd^{2+} ions significantly influenced the Q_e as well as q_e for both hydrogels. As presented in Fig. 9, Langmuir isotherm model fits well to experimental data at lower concentrations ($<200 \text{ mg L}^{-1}$). At higher initial Cd^{2+} concentrations swelling was reduced due to the so called “charge screening effect” around ionic groups of opposite charge. At this point the number of available binding sites for sorption of cadmium ions was significantly decreased. With further increase in the initial concentration of Cd^{2+} deviation between experimental and calculated values rose, because isotherm models did not take into account decrease of Q_e . According to R^2 and χ^2 , agreement between the experimental and calculated data was better in the case when the Q_e was less influenced by the initial concentration (the decrease in Q_e was lower for P(HEA/10IA)).

Adsorption capacities for Cd^{2+} ions on the different sorbents reported in the literature are presented in Table 7. It is obvious that the q_m values, obtained for the P(HEA/IA) hydrogels, are higher in comparison with most of the previously investigated sorbents.

3.7.6 Adsorption kinetics

The adsorption kinetic curves are presented in Fig 10. To evaluate the kinetics of the adsorption process, pseudo-first order and pseudo-second order models were tested to interpret the experimental data [52, 53]. The linear forms of pseudo-first order and pseudo-second order models are presented in Eqs. (13) and (14), respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (13)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (14)$$

where q_e and q_t (mg g^{-1}) are the adsorption capacities at equilibrium, and at time t (h), respectively; k_1 (h^{-1}) and k_2 ($\text{g mg}^{-1} \text{ h}^{-1}$) are the pseudo-first and the pseudo-second order rate constants.

The rate constants k_1 and k_2 , as well as predicted q_e values, were determined from the slope and intercept of plots $\ln(q_e - q_t)$ vs. t and t/q_t vs. t , respectively. The obtained results for the

pseudo-first order and pseudo-second order models are presented in Table 8. The correlation coefficients, R^2 , showed that the pseudo-second order model fits better with the experimental data than pseudo-first order model for both hydrogels ($R^2 > 0.99$). In addition, the agreement of the calculated equilibrium adsorption capacities ($q_{e,cal}$) and the experimental data are better in the case of pseudo second-order kinetics, meaning that the adsorption process of Cd^{2+} onto P(HEA/IA) hydrogel is probably controlled by the chemical process [17, 22].

3.8 Multicomponent heavy metal ion adsorption

The investigation of adsorption process in multicomponent heavy metal ion system is very important since the natural and industrial effluents rarely contain a single heavy metal ion, and some of the ions in the effluent may reduce the adsorption of others or may be co-adsorbed along with other ions [42]. The interactive effects of a metal ions mixture on a polymeric matrix are extremely complex phenomena and depend on polymer type, number of metals competing for binding sites, metal combination, concentrations and experimental conditions [54].

In order to investigate the competitive adsorption of Cd^{2+} ions on P(HEA/10IA) hydrogel, the synthetic wastewater containing the same concentrations (10 mg L^{-1}) of Cd^{2+} , Ni^{2+} , Pb^{2+} , Cu^{2+} , Zn^{2+} , and Co^{2+} ions were prepared. The results are presented in Fig. 11. The results show that the adsorption of cadmium ions decreased under competitive conditions. Also, with the increasing number of metals in the system, the adsorption of cadmium ions decreased even more. Compared to the results under noncompetitive conditions, the adsorption capacity of cadmium decreased by 8.51 % in the binary system containing Cd^{2+} and Ni^{2+} and by 24.5 % in the system containing Cd^{2+} and Pb^{2+} , suggesting that Pb^{2+} influenced the adsorption capacity of Cd^{2+} more than nickel. In the system containing of Cd^{2+} , Ni^{2+} , Pb^{2+} , Cu^{2+} , Zn^{2+} , and Co^{2+} , the adsorption capacity of cadmium ions decreased by 38.9 %. Different sorption of the ions in multicomponent system may be ascribed to the differences in their ionic radii. The ionic radius of Pb^{2+} is 119 pm, while that of Cd^{2+} is 95 pm, and that of Ni^{2+} is 69 pm. The ionic radius of Zn^{2+} , Cu^{2+} and Co^{2+} are 74, 73 and 65 pm, respectively. The smaller the ionic radius, the greater its tendency to hydrolyse, which further leads to reduced sorption [55].

3.9 Desorption and reusability experiments

When 0.1 mol L⁻¹ solutions of CH₃COOH and HCl were used as the desorbing agents, 74.2 and 87.3 % desorption efficiency were obtained, respectively. Maximum desorption of Cd²⁺ ions was achieved with 0.1 mol L⁻¹ HNO₃ and it was 94.6 %. Also, desorption was done with different concentrations of HNO₃ in order to investigate the influence of pH of desorption medium on desorption efficiency. Results are presented in Fig. 12. As it was expected, desorption efficiency increased when the pH value of the solution is reduced using HNO₃. Desorption of cadmium was less than 20 % at pH 5.5, increasing gradually up to 94.6 % at pH 1. Results of three consecutive adsorption-desorption cycles show that by the end of the third cycle, more than 85 % of the initial adsorption capacity was obtained.

4. Conclusions

The ability of novel P(HEA/IA) hydrogels for Cd²⁺ ion removal from aqueous solution has been investigated. The adsorption of Cd²⁺ onto P(HEA/IA) hydrogels was found to be highly dependent on hydrogel composition, initial concentration of metal, solution pH, adsorbent mass, ionic strength and temperature. The adsorption kinetics data can be well described by the pseudo-second-order model, and the adsorption isotherm agrees well with the Langmuir model. Competitive adsorption studies revealed that adsorption of cadmium in multicomponent systems is dependent on the type of metal ions in the solution. Desorption studies showed that desorption of P(HEA/IA) hydrogel is pH dependent and hydrogels can be successfully regenerated with 0.1 mol L⁻¹ HNO₃. In addition, hydrogels could be reused without significant losses of the initial properties after three adsorption-desorption cycles performed. The sample with highest IA content, P(HEA/10IA) showed the highest adsorption capacity, as well as the highest plateau storage modulus, meaning that this sample is the most suitable one for application in wastewater treatment. These findings suggest that the P(HEA/10IA) hydrogel is a promising adsorbent for wastewater treatment in weakly acidic media.

Acknowledgments

The authors would like to acknowledge funding from the Ministry of Education, Science and Technological Development of the Republic of Serbia (Projects No. 172062 and 172015).

References

- [1] C. Cheng, J. Wang, X. Yang, A. Li, C. Philippe, Adsorption of Ni(II) and Cd(II) from water by novel chelating sponge and the effect of alkali-earth metal ions on the adsorption, *J. Hazard. Mater.* 264 (2014) 332–341.
- [2] X.W. Lu, L.J. Wang, K. Lei, J. Huang, Y.X. Zhai, Contamination assessment of copper, lead, zinc, manganese and nickel in street dust of Baoji, NW China, *J. Hazard. Mater.* 161 (2009) 1058–1062.
- [3] B. Amzal, B. Julin, M. Vahter, A. Wolk, G. Johanson, A. Akesson, Population toxicokinetic modeling of cadmium for health risk assessment, *Environ. Health Perspect.* 117 (2009) 1293–1301.
- [4] P.C. Nagajyoti, K.D. Lee, T.V.M. Sreekanth, Heavy metals, occurrence and toxicity for plants: a review, *Environ. Chem. Lett.* 8 (2010) 199–216.
- [5] W. Swaddiwudhipong, P. Limpatanachote, P. Mahasakpan, S. Krintratun, B. Punta, T. Funkhiew, Progress in cadmium-related health effects in persons with high environmental exposure in northwestern Thailand: a five-year follow-up, *Environ. Res.* 112 (2012) 194–198.
- [6] F.Y. Wang, H. Wang, J.W. Ma, Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent-Bamboo charcoal, *J. Hazard. Mater.* 177 (2010) 300–306.
- [7] H. K. Boparai, M. Joseph, D. M. O'Carroll, Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles, *J. Hazard. Mater.* 186 (2011) 458–465.
- [8] WHO, Guidelines for Drinking Water Quality: Recommendations, vol. 1, 3rd ed., World Health Organisation, Geneva, 2008.

- [9] U. Kumar, M. Bandyopadhyay, Sorption of cadmium from aqueous solution using pretreated rice husk, *Bioresour. Technol.* 97 (2006) 104-109.
- [10] G. Zhang, Z. He, W. Xu, A low-cost and high efficient zirconium-modified-Naattapulgit adsorbent for fluoride removal from aqueous solutions, *Chem. Eng. J.* 183 (2012) 315–324.
- [11] U. Yildiz, O.F. Kemik, B. Hazer, The removal of heavy metal ions from aqueous solutions by novel pH-sensitive hydrogels, *J. Hazard. Mater.* 183 (2010) 521– 532.
- [12] V.K. Gupta, I. Ali, V.K. Saini, Adsorption studies on the removal of Vertigo Blue 49 and Orange DNA13 from aqueous solutions using carbon slurry developed from a waste material, *J. Colloid. Interface Sci.* 315 (2007) 87–93.
- [13] H. Kasgoz, S. Ozgumu, M. Orbay, Modified polyacrylamide hydrogels and their application in removal of heavy metal ions, *Polymer* 44 (2003) 1785–1793.
- [14] E.S. Abdel-Halim, S.S. Al-Deyab, Hydrogel from crosslinked polyacrylamide/guar gum graft copolymer for sorption of hexavalent chromium ion, *Carbohydr. Polym.* 86 (2011) 1306-1312.
- [15] H.A. Essawy, H.S. Ibrahim, Synthesis and characterization of poly (vinylpyrrolidone-co-methylacrylate) hydrogel for removal and recovery of heavy metal ions from wastewater, *React. Funct. Polym.* 61 (2004) 421–432.
- [16] J. Liu, Y. Ma, T. Xu, G. Shao, Preparation of zwitterionic hybrid polymer and its application for the removal of heavy metal ions from water, *J. Hazard. Mater.* 178 (2010) 1021–1029.
- [17] Y. Zheng, S. Hua, A. Wang, Adsorption behavior of Cu^{2+} from aqueous solutions onto starch-g-poly (acrylic acid)/sodium humate hydrogels, *Desalination* 263 (2010) 170-175.

- [18] N. Milosavljević, M. Ristić, A. Perić-Grujić, J. Filipović, S. Štrbac, Z. Rakočević, M. Kalagasidis Krušić, Hydrogel based on chitosan, itaconic acid and methacrylic acid as adsorbent of Cd²⁺ ions from aqueous solution, *Chem. Eng. J.* 165 (2010) 554-562.
- [19] M.S. Chiou, H.Y. Li, Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads, *Chemosphere*, 50 (2003) 1095-1105.
- [20] H. Yan, W. Zhang, X. Kan, L. Dong, Z. Jiang, H. Li, H. Yang, R. Cheng, Sorption of methylene blue by carboxymethyl cellulose and reuse process in a secondary sorption, *Colloids Surf. A.* 380 (2011) 143–151.
- [21] Z. Li, Y. Wang, N. Wu, Q. Chen, K. Wu, Removal of heavy metal ions from wastewater by a novel HEA/AMPS copolymer hydrogel: preparation, characterization, and mechanism, *Environ. Sci. Pollut. Res.*, 20 (2013) 1511-1525.
- [22] N. Wu, Z. Li, Synthesis and characterization of poly(HEA/MALA) hydrogel and its application in removal of heavy metal ions from water, *Chem. Eng. J.* 215-216 (2013) 894-902.
- [23] J. Tu, J. Zhou, C.F. Wang, Q.A. Zhang, S. Chen, Facile synthesis of N-vinylimidazole-based hydrogels via frontal polymerization and investigation of their performance on adsorption of copper ions, *J. Polym. Sci. Pol. Chem.* 48 (2010) 4005–4012.
- [24] R. Hua, Z. Li, Sulfhydryl functionalized hydrogel with magnetism: Synthesis, characterization, and adsorption behavior study for heavy metal removal, *Chem. Eng. J.* 249 (2014) 189-200.
- [25] Langmuir I, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [26] C.H. Yang, Statistical mechanical study on the Freundlich isotherm equation, *J. Colloid Interface Sci.* 208 (1998) 379–387.

- [27] O. Redlich, D.L. Peterson, A useful adsorption isotherm, *J. Phys. Chem.* 63(6) (1959) 1024–1026.
- [28] O. Celebi, C. Uzum, T. Shahwan, H.N. Erten, A radiotracer study of the adsorption behavior of aqueous Ba^{2+} ions on nanoparticles of zero-valent iron, *J. Hazard. Mater.* 148 (2007) 761–767.
- [29] N.D. Hutson, R.T. Yang, Theoretical basis for the Dubinin–Radushkevitch (D–R) adsorption isotherm equation, *Adsorption* 3 (1997) 189–195.
- [30] B.F. Urbano, B.L. Rivas, F. Martinez, S.D. Alexandratos, Equilibrium and kinetic study of arsenic sorption by water-insoluble nanocomposite resin of poly[N-(4-vinylbenzyl)-N-methyl-d-glucamine]-montmorillonite, *Chem. Eng. J.* 193–194 (2012) 21–30.
- [31] A. Pourjavadi, M. Kurdtabar, Collagen-based highly porous hydrogel without any porogen: Synthesis and characteristics, *European Polymer Journal*, 43 (2007) 877–889.
- [32] V. Ozturk, O. Okay, Temperature sensitive poly(N-t-butylacrylamide-coacrylamide) hydrogels: synthesis and swelling behavior, *Polymer* 43 (2002) 5017–5026.
- [33] S. Tomic, M. Micic, J. Filipovic, E. Suljovrucic, Synthesis, characterization and controlled release of cephalexin drug from smart poly(2-hydroxyethyl methacrylate)/poly(alkylene glycol)(meth)acrylates hydrogels, *Chem. Eng. J.*, 160 (2010) 801–809.
- [34] T. Wang, M. Turhan, S. Gunasekaran, Selected properties of pH-sensitive, biodegradable chitosan–poly(vinyl alcohol) hydrogel, *Polym. Int.* 53 (2004) 911–918.
- [35] Y. Zhou, L. Zhang, S. Fu, L. Zheng, H. Zhan, Adsorption behavior of Cd^{2+} , Pb^{2+} and Ni^{2+} from aqueous solutions on cellulose-based hydrogels, *BioRes.* 7(3) (2012) 2752–2765.
- [36] N. Milosavljevic, A. Debeljkovic, M. Kalagasidis Krusic, N. Milasinovic, Ö.B. Üzüm, E. Karadağ, Application of poly(acrylamide-co-sodium methacrylate) hydrogels in copper and cadmium removal from aqueous solution, *Environmental Progress & Sustainable Energy* 00 (2013) 1–11.

- [37] A. Afkhami, M. Saber-Tehrani, H. Bagheri, Simultaneous removal of heavy-metal ions in wastewater samples using nano-alumina modified with 2,4 dinitrophenylhydrazine, *J. of Hazard. Mater.* 181 (2010) 836–844.
- [38] A.F. Ngomsik, A. Bee, J.M. Siaugue, D. Talbot, V. Cabuil, G. Cote, Co(II) removal by magnetic alginate beads containing Cyanex 272, *J. Hazard. Mater.* 166 (2009) 1043–1049.
- [39] A. Heidari, H. Younesi, Z. Mehraban, Removal of Ni(II), Cd(II), and Pb(II) from a ternary aqueous solution by amino functionalized mesoporous and nanomesoporous silica, *Chem. Eng. J.* 153 (2009) 70–79.
- [40] V.L. Snoeyink, D. Jenkins, *Water Chemistry*, John Wiley & Sons, New York, 1980.
- [41] R. Leyva-Ramos, J.R. Rangel-Mendez, J. Mendoza-Baron, L. Fuentes-Rubio, R.M. Guerrero-Coronado, Adsorption of cadmium(II) from aqueous solution onto activated carbon, *Water Sci. Technol.* 35 (1997) 205–210.
- [42] V.C. Srivastava, I.D. Mall, I.M. Mishra, Adsorption of toxic metal ions onto activated carbon. Study of sorption behaviour through characterization and kinetics, *Chem. Eng. Process.* 47 (2008) 1269–1280.
- [43] 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.
- [44] A. Shukla, Y. H. Zhang, P. Dubey, J. L. Margrave, S. S. Shukla, The role of sawdust in the removal of unwanted materials from water, *J. Hazard. Mater.* 95 (2002) 137-152.
- [45] A. El-Sikaily, A. El Nemr, A. Khaled, Copper sorption onto dried red alga *Pterocladia capillacea* and its activated carbon, *Chem. Eng. J.* 168 (2011) 707–714.

- [46] G. Crini, P.M. Badot, Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: a review of recent literature, *Prog. Polym. Sci.* 33 (2008) 399–447.
- [47] Y. Zheng, A. Wang, Evaluation of ammonium removal using a chitosan-g-poly (acrylic acid)/rectorite hydrogel composite, *J. Hazard. Mater.* 171 (2009) 671–677.
- [48] A. Takahashi, M. Nagasawa, Excluded volume of polyelectrolyte in salt solutions, *J. Am. Chem. Soc.* 86 (1964) 5543–5548.
- [49] D. Ceylan, O. Okay, Macroporous polyisobutylene gels: a novel tough organogel with superfast responsivity, *Macromolecules* 40 (2007) 8742–8749.
- [50] A. Sari, M. Tuzen, D. Citak, M. Soylak, Equilibrium, kinetic and thermodynamic studies of adsorption of Pb(II) from aqueous solution onto Turkish kaolinite clay, *J. Hazard. Mater.* 149 (2007) 283–291.
- [51] H.K. Boparai, M. Joseph, D.M. O’Carroll, Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles, *J. Hazard. Mater.* 186 (2011) 458–465.
- [52] Y.S. Ho, Citation review of Lagergren kinetic rate equation on adsorption reactions, *Scientometrics* 59 (2004) 171–177.
- [53] Y.S. Ho, Review of second-order models for adsorption systems, *J. Hazard. Mater.* 136 (2006) 681–689.
- [54] L. Uzun, D. Türkmen, E. Yilmaz, S. Bektaş, A. Denizli, Cysteine functionalized poly(hydroxyethyl methacrylate) monolith for heavy metal removal, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 330 (2008) 161-167.
- [55] G. Wulfsberg, *Principles of Descriptive Chemistry*. Brooks/Cole Publishing, Monterey CA, 1987.

List of figures

Scheme 1. Hydrogel synthesis

Fig. 1. FTIR spectra of P(HEA/10IA) hydrogel (a) before and (b) after Cd^{2+} adsorption.

Fig. 2. SEM micrographs: cross-section morphology of (a) P(HEA/2IA), (b) P(HEA/10IA) hydrogel swelled in water (pH=6) (bar 200 μm); P(HEA/2IA) swollen in water at (c) pH 2.0, (d) pH 6 (bar 20 μm); SEM and EDX spectra of P(HEA/2IA) hydrogel after loading with cadmium nitrate solution (250 mg L^{-1}) (e) cross-section and (f) surface (bar 200 μm).

Fig. 3. AFM images of the top surface of P(HEA/10IA) hydrogel: (a) before adsorption, (b) after Cd^{2+} adsorption ($C_0=50 \text{ mg L}^{-1}$), (c) after Cd^{2+} adsorption ($C_0=250 \text{ mg L}^{-1}$).

Fig. 4. DSC thermograms of P(HEA/2IA) and P(HEA/10IA) hydrogels free and cadmium loaded.

Fig. 5. The effect of initial pH on the adsorption capacity of Cd^{2+} ions onto P(HEA/2IA) and P(HEA/10IA) hydrogels ($C_0=10 \text{ mg L}^{-1}$; $m_0=0.03 \text{ g}$; volume of solution 0.05 L; pH: 2-7; $T=25^\circ\text{C}$; $t=48 \text{ h}$).

Fig. 6. The effect of the adsorbent weight on the Cd^{2+} removal from the aqueous solution onto P(HEA/2IA) and P(HEA/10IA) hydrogels in terms of equilibrium sorption capacity q_e (solid lines) and adsorption efficiency (dashed lines) ($C_0=10 \text{ mg L}^{-1}$, $m_0=0.008\text{-}0.09 \text{ g}$, volume of solution 0.05 L, pH = 5.5, $t=48 \text{ h}$, $T=25^\circ\text{C}$).

Fig. 7. The effect of ionic strength on the Cd^{2+} removal onto P(HEA/2IA) and P(HEA/10IA) hydrogels in terms of equilibrium sorption capacities q_e (solid lines) and the reduced rate of adsorption capacity (dashed lines) ($C_0=10 \text{ mg L}^{-1}$, $m_0=0.03 \text{ g}$, volume of solution 0.05 L, $C(\text{NaCl})=0\text{-}0.3 \text{ mol L}^{-1}$, pH = 5.5, $t=48 \text{ h}$, $T=25^\circ\text{C}$).

Fig. 8. Comparison of five isotherms applied in this work for the Cd^{2+} adsorption onto (a) P(HEA/2IA) and (b) P(HEA/10IA) hydrogels.

Fig. 9. The effect of the initial Cd^{2+} ion concentration on swelling degree (Q_e) and adsorption capacity (q_e) for P(HEA/2IA) and P(HEA/10IA) hydrogels.

Fig. 10. Sorption kinetics of Cd^{2+} ions on P(HEA/2IA) and P(HEA/10IA) hydrogels ($C_0=10 \text{ mg L}^{-1}$, $m_0=0.03 \text{ g}$, volume of solution 0.05 L , $\text{pH} = 5.5$, $T = 25^\circ\text{C}$, contact time $0.5\text{-}48 \text{ h}$).

Fig. 11. Adsorption capacity of Cd^{2+} ions on P(HEA/10IA) under noncompetitive and competitive conditions ($C_0=10 \text{ g L}^{-1}$ (all metal ions), $m_0=0.03 \text{ g}$, volume of solution 0.05 L , $\text{pH} = 5.5$, $t = 48 \text{ h}$, $T = 25^\circ\text{C}$).

Fig. 12. Desorption of Cd^{2+} from P(HEA/10IA) hydrogels by adjusting the pH values of the solution using HNO_3 .

Highlights

Hydrogels based on 2-hydroxyethyl acrylate and itaconic acid (P(HEA/IA)) were synthesized.

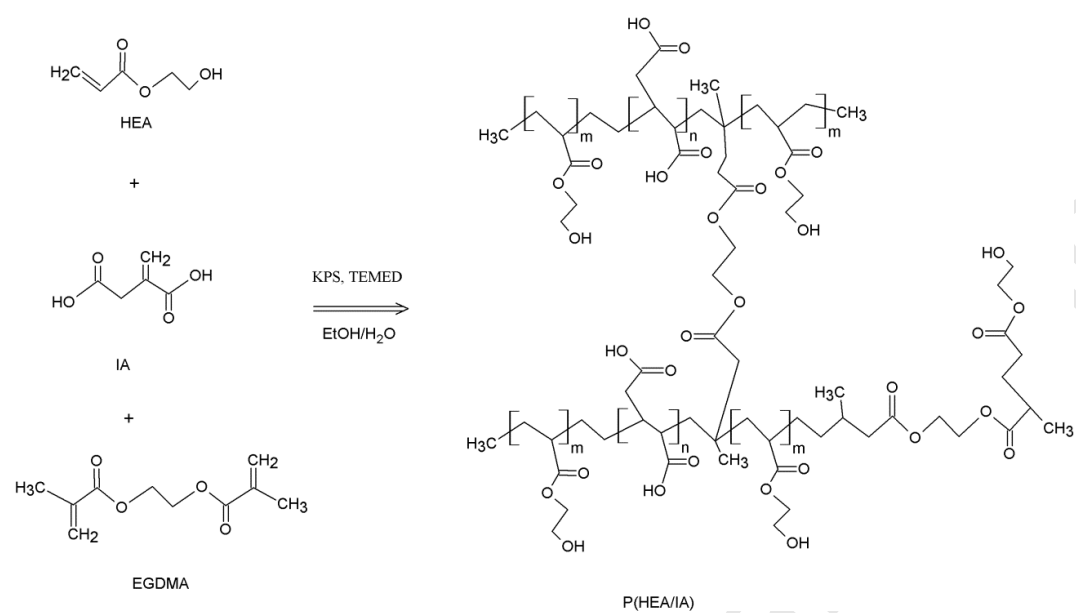
Cd^{2+} ion removal was investigated.

The surface and cross-section of hydrogels were observed by SEM and AFM.

The adsorption kinetics and isotherms of cadmium ions on the hydrogel were studied.

Approximately 95 % of the adsorbed cadmium could be recovered by 0.1 M HNO_3 treatment.

Accepted Manuscript



Scheme 1.

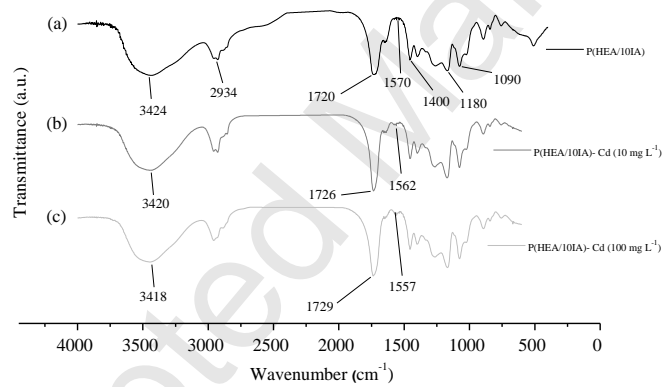
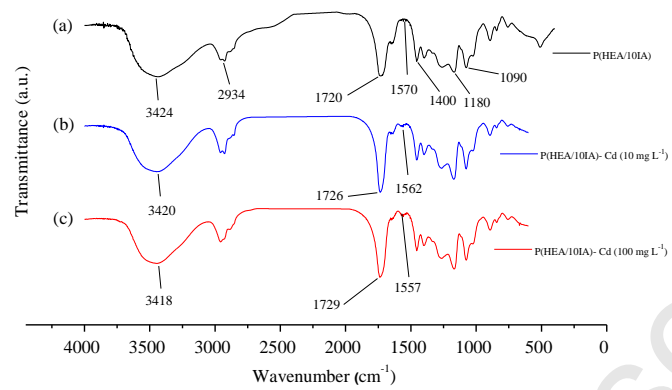
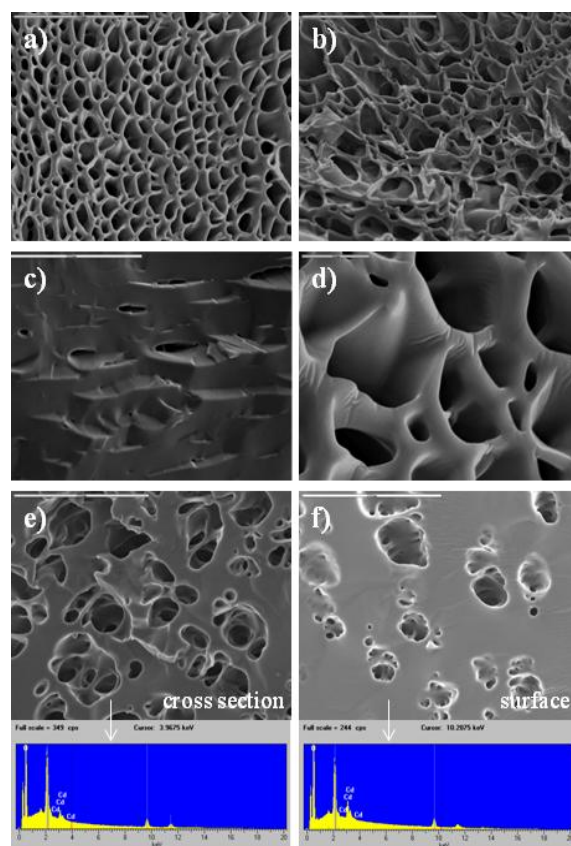


Fig. 1.



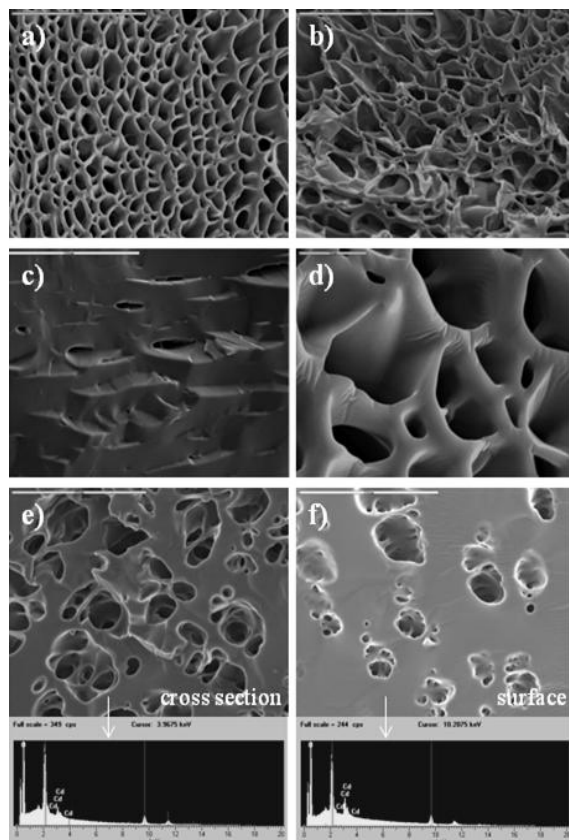


Fig. 2.

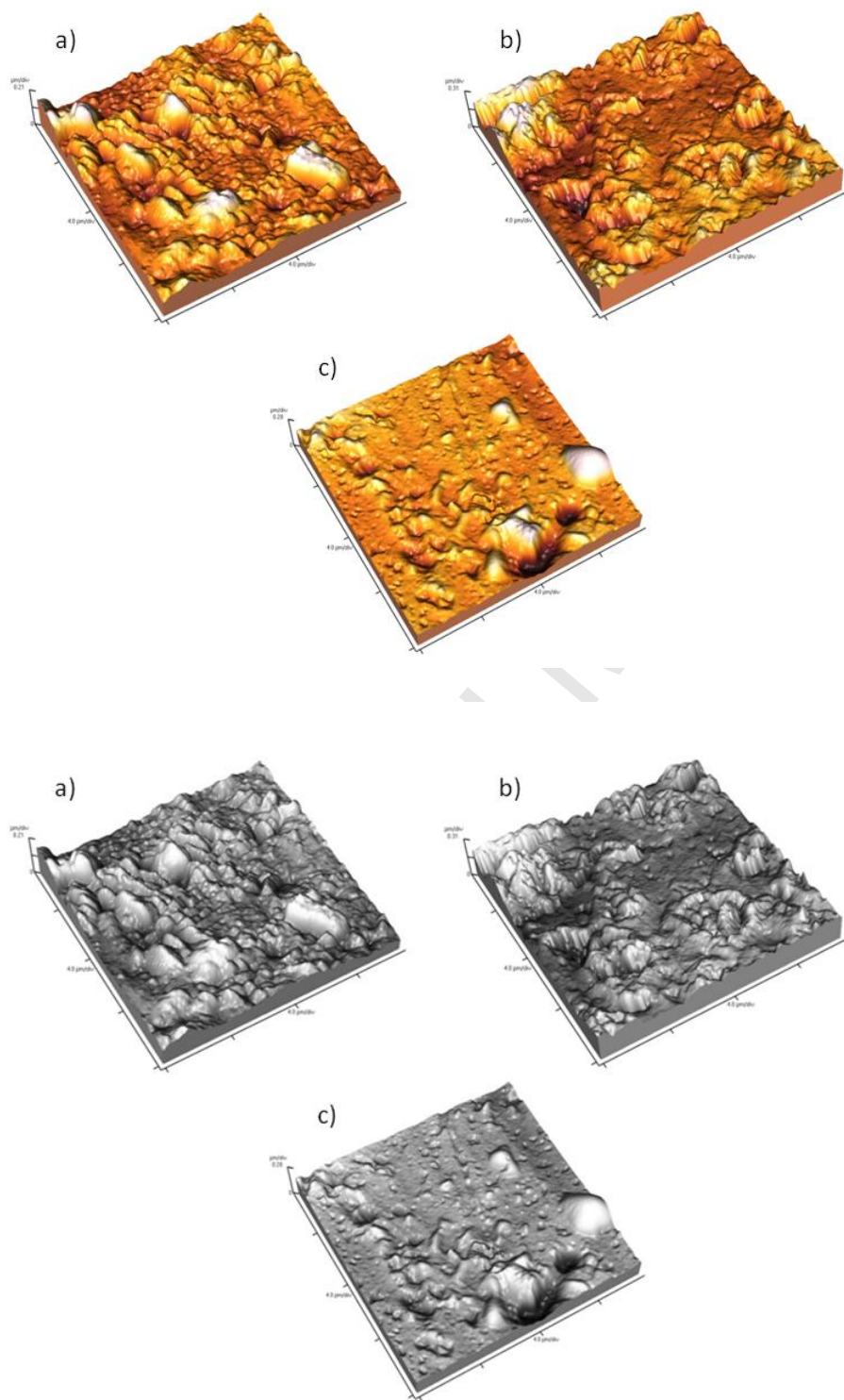


Fig. 3.

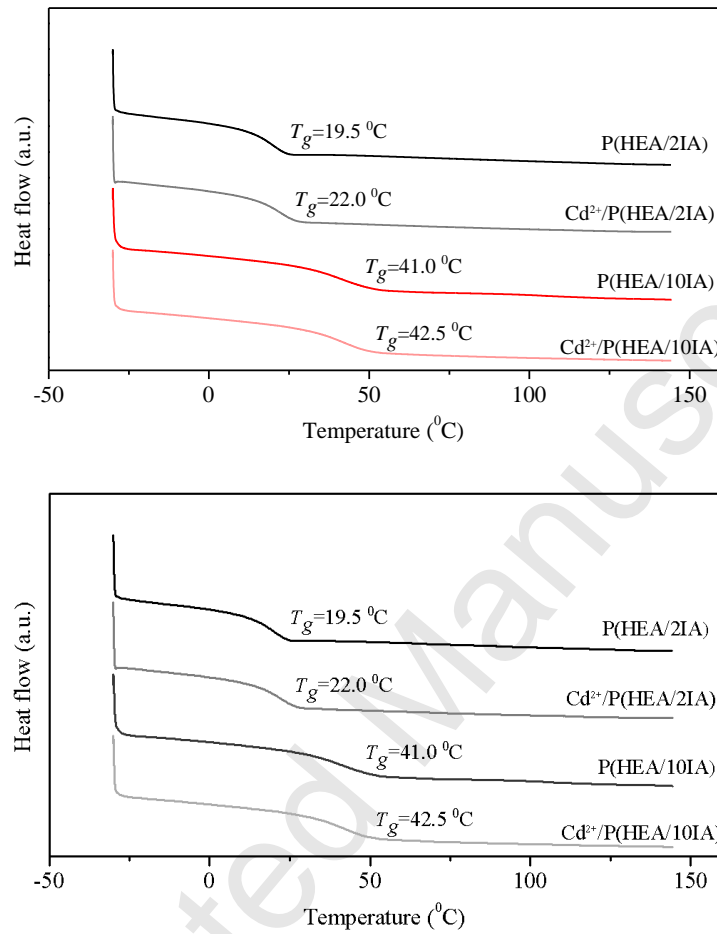


Fig. 4.

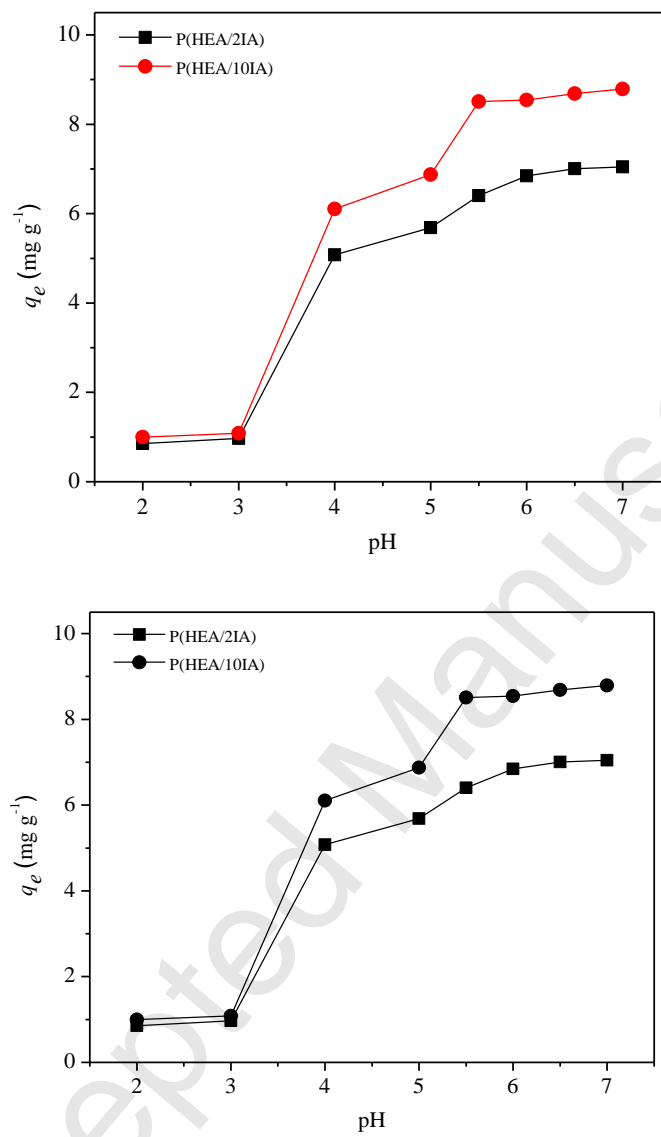


Fig. 5.

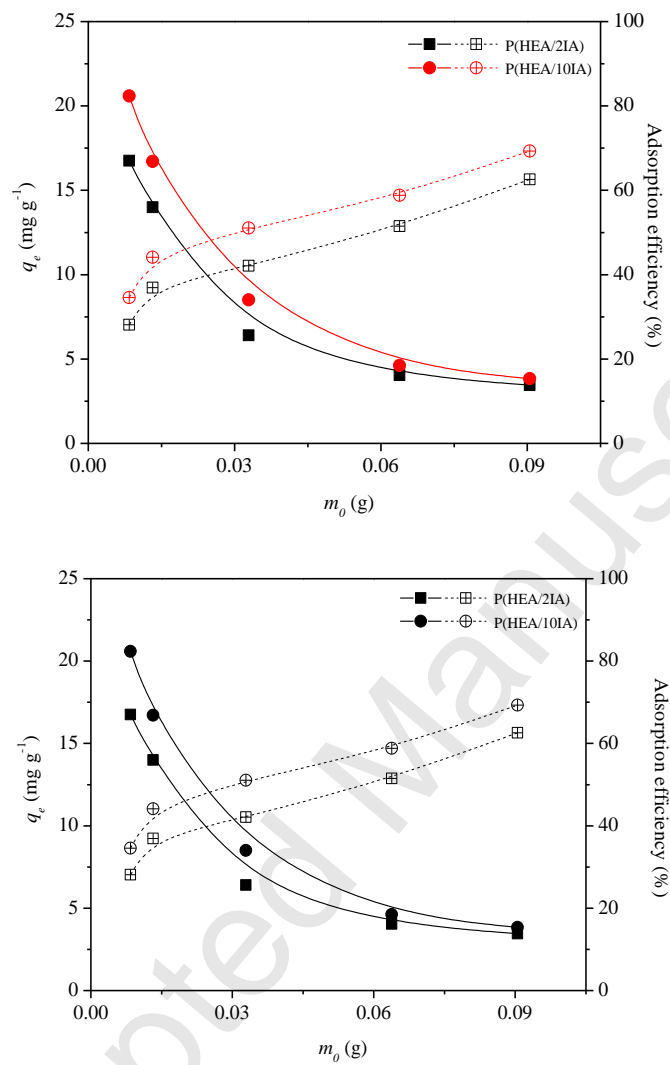


Fig. 6.

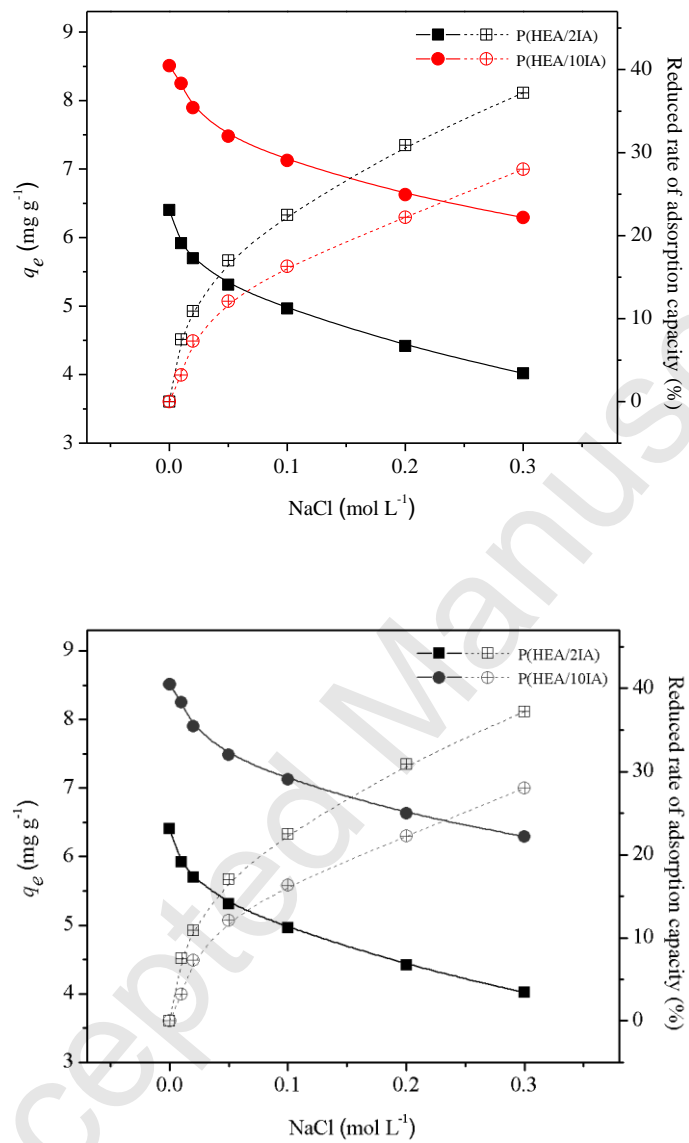


Fig. 7.

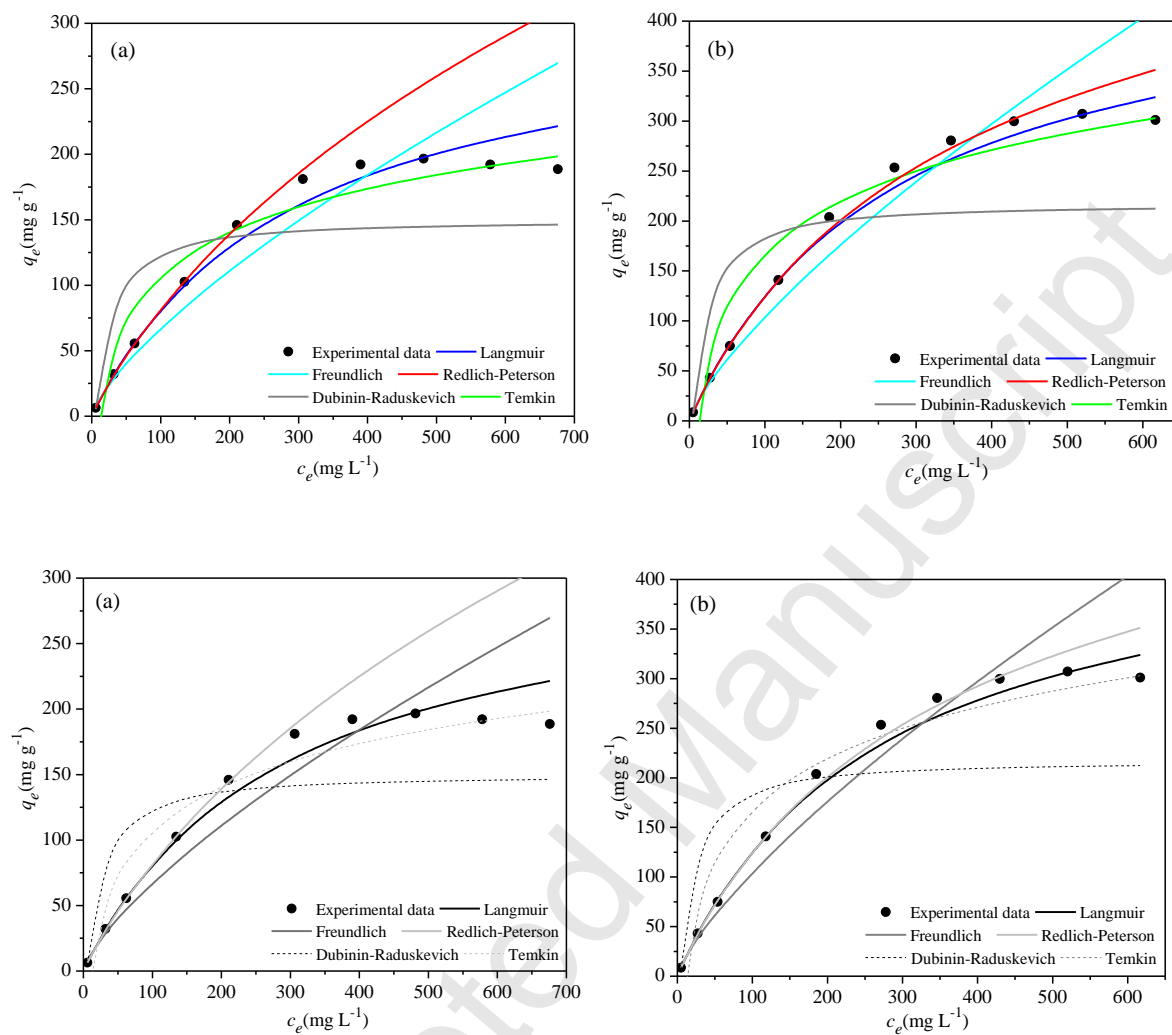


Fig. 8.

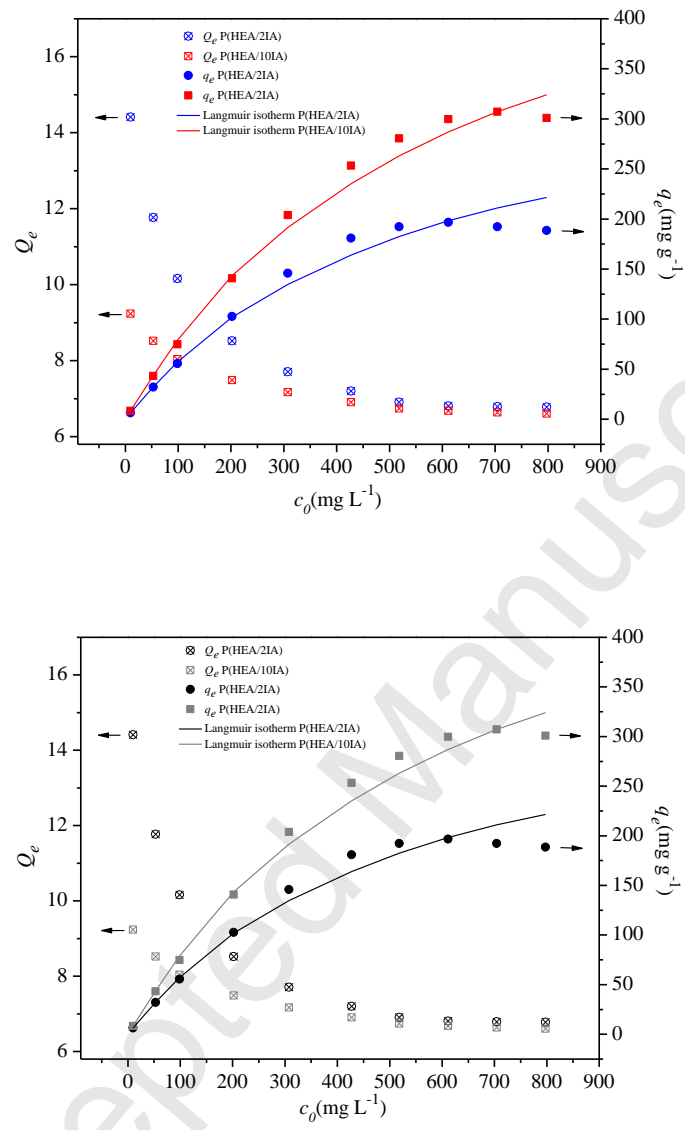


Fig. 9.

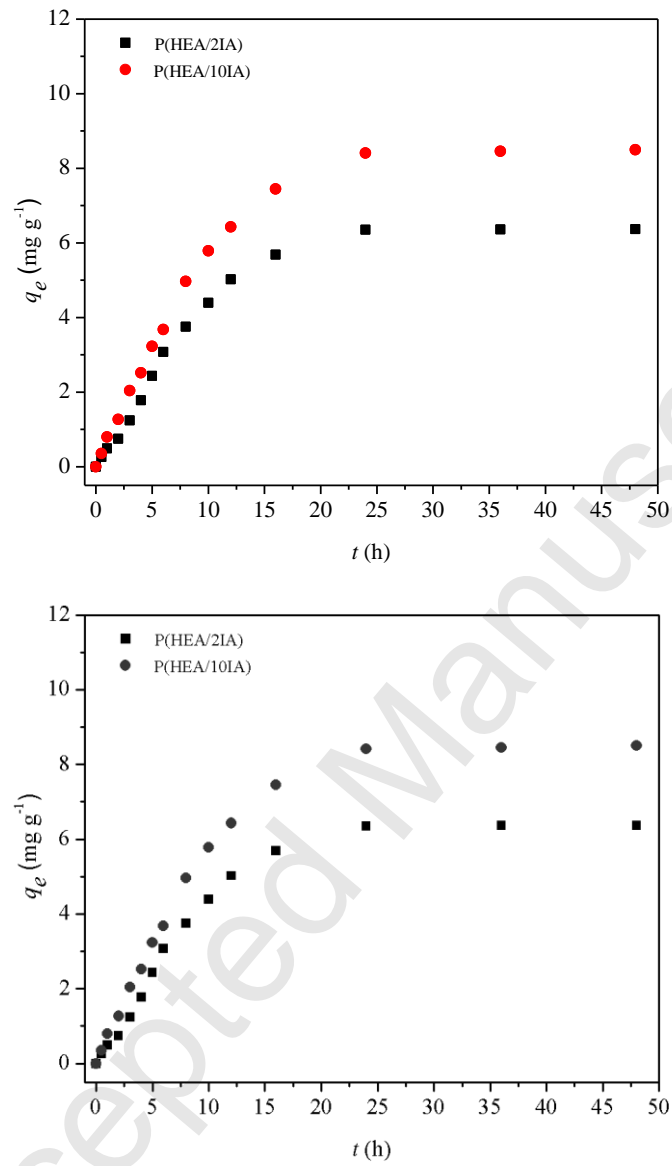


Fig. 10.

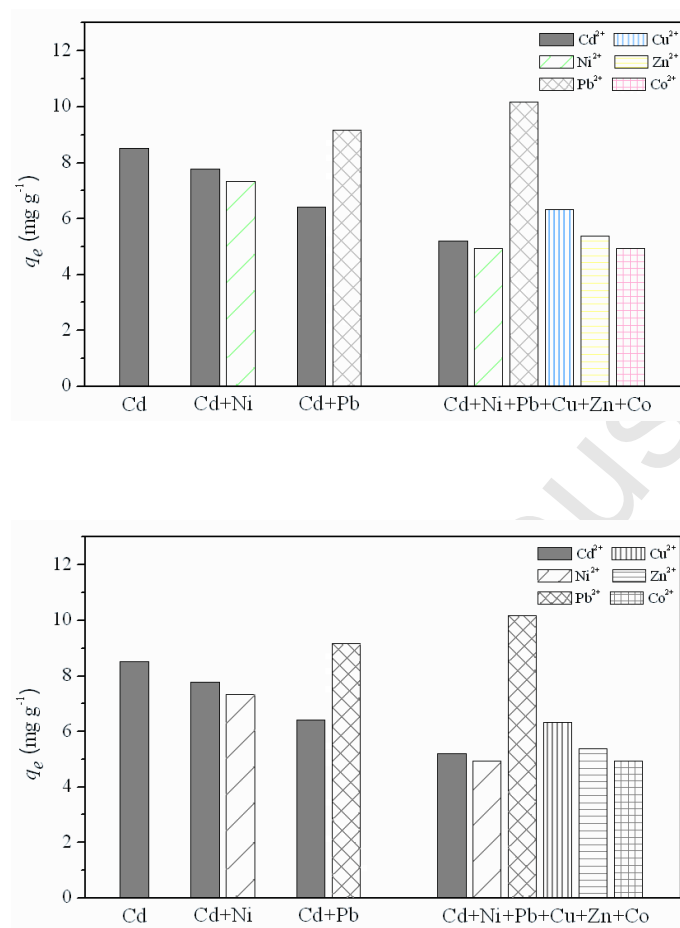


Fig. 11.

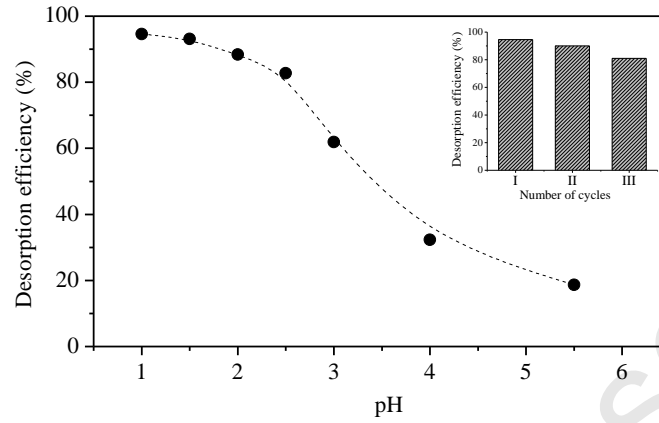


Fig. 12.

Table 1 Adsorption isotherm models used to fit the adsorption experimental data.

Isotherm	Equation	Reference
Langmuir	$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \frac{1}{C_e}$	[25]
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	[26]
Redlich-Peterson	$\ln \left(K_R \cdot \frac{C_e}{q_e} - 1 \right) = \beta \cdot \ln C_e + \ln a_R$	[27]
Temkin	$q = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$	[28]
Dubinin-Radushkevich (D-R)	$\ln q_e = \ln q_m - \beta \varepsilon^2$	[29, 30]

Table 2 Equilibrium degree of swelling for P(HEA/IA) hydrogels as a function of pH, and temperature.

Parameters		P(HEA/2IA)	P(HEA/5IA)	P(HEA/7IA)	P(HEA/10IA)
Q_e (buffers)	pH 2.2	5.98	4.27	3.86	3.21
	pH 3.85	9.77	8.82	7.54	10.84
	pH 5.45	10.71	13.06	16.26	16.77
	pH 6.8	13.24	17.45	19.27	23.23
Q_e (deionized water)		29.22	20.56	15.24	10.17
Q_e (Cd ²⁺ solution)	pH 5.6	14.41	12.92	11.12	9.24
Temperature (°C)	10	13.19	16.31	19.84	23.01
	25	13.28	17.47	19.27	23.28
	45	9.67	14.18	18.13	21.80
	50	9.54	14.16	17.59	21.24

Table 3 Plateau storage modulus of P(HEA/IA) hydrogels swollen in deionized water and in Cd^{2+} solution.

Parameters	P(HEA/2IA)	P(HEA/5IA)	P(HEA/7IA)	P(HEA/10IA)
Plateau storage modulus (deionized water) (kPa)	1.13	2.18	3.26	4.13
Plateau storage modulus (Cd^{2+} solution) (kPa)	2.25	3.34	4.81	5.38

Table 4 Thermodynamic parameters for adsorption of cadmium onto P(HEA/10IA) hydrogel.

Temperature (°C)	$q_{e,exp}$ (mg g ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
10	8.81	-0.272		
25	8.51	-0.104	-10.178	-34.441
50	6.69	1.078		

Accepted Manuscript

Table 5 Parameters of investigated adsorption models for adsorption of Cd^{2+} ions from aqueous solution onto P(HEA/IA) hydrogels ($C_0=10\text{-}520 \text{ mg L}^{-1}$, $m_0= 0.03 \text{ g}$, volume of solution 0.05 L , $\text{pH} = 5.5$, $t = 48 \text{ h}$, $T = 25^\circ\text{C}$).

MODEL	Parameter	P(HEA/2IA)	P(HEA/10IA)
Langmuir	$K_L (\text{L g}^{-1})$	3.60	3.84
	$q_m (\text{mg g}^{-1})$	312.50	460.83
	R^2	0.9998	0.9999
	χ^2	12.511	8.156
Freundlich	$K_F (\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n})$	2.40	3.29
	n	1.38	1.33
	R^2	0.9544	0.9719
	χ^2	60.622	63.857
Redlich-Peterson	$K_R (\text{L g}^{-1})$	1.14	1.78
	β	0.91	0.92
	$a_R (\text{L mol}^{-1})$	0.0058	0.0057
	R^2	0.9827	0.9910
	χ^2	100.053	11.177
Temkin	$K_T (\text{L g}^{-1})$	0.104	0.105
	B	46.67	72.56
	$b (\text{J mol}^{-1})$	53.09	34.14
	R^2	0.9035	0.9025
	χ^2	32.835	52.576
Dubinin-Radushkevich	$q_m (\text{mg g}^{-1}) \times 10^{-6}$	1.04	0.44
	$E (\text{kJ mol}^{-1})$	0.49	0.63
	$\beta \times 10^6$	1.44	1.24
	R^2	0.8095	0.7842

χ^2

141.931

278.407

Accepted Manuscript

Table 6 The R_L values for the P(HEA/2IA) and P(HEA/10IA) hydrogels at 25°C.

C_0 (mg L ⁻¹)	R_L	
	P(HEA/2IA)	P(HEA/10IA)
10.00	0.9674	0.9632
53.13	0.8481	0.8313
98.72	0.7504	0.7262
202.24	0.5951	0.5642
307.53	0.4911	0.4598
427.11	0.4099	0.3800
518.06	0.3642	0.3357
611.34	0.3197	0.2784
704.41	0.2897	0.2508
797.32	0.2649	0.2283

Table 7 Comparison of maximum adsorption capacities for Cd²⁺ ions of different hydrogels.

HYDROGEL	q_m (mg g ⁻¹)	Reference
HEA/MALA	42.60	[22]
HEA/AMPS	167.00	[21]
Fe ₃ O ₄ -P(Cys/HEA)	19.14	[24]
HEMA-MAC	303.00	[54]
AAm/SMA	32.99	[36]
CH/IA/MAA	285.70	[18]
C-g-AA	571.40	[35]
HEA/2IA	312.50	Present work
HEA/10IA	460.83	Present work

Table 8 Parameters of the applied kinetic models for adsorption of Cd²⁺ ions onto P(HEA/IA) hydrogels and correlation coefficients ($C_0=10$ mg L⁻¹; $m_0= 0.03$ g; volume of solution 0.05 L; pH=5.5; $T=25^0$ C).

Sample	$q_{e,exp}$ (mg g ⁻¹)	Pseudo first-order model			Pseudo second-order model		
		k_1 (h ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	R^2	k_2 (g mg ⁻¹ h ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	R^2
P(HEA/2IA)	6.400	0.252	14.171	0.9146	1.274	7.313	0.9902
P(HEA/10IA)	8.510	0.170	21.012	0.9314	1.571	9.856	0.9911