

# Removal of Pb<sup>2+</sup> from aqueous solution by P(HEA/IA) hydrogels

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## Abstract

A series of poly(2-hydroxyethyl acrylate-co-itaconic acid), P(HEA/IA), hydrogels with different HEA/IA ratio, were synthesized using free radical crosslinking/copolymerization and investigated as sorbents for Pb<sup>2+</sup> from aqueous solutions. Hydrogels were characterized using DMA, FTIR, DSC, SEM and AFM. The adsorption was found to be highly dependent on hydrogel composition, solution pH, sorbent weight, ionic strength and contact time. Five isotherm models, Langmuir, Freundlich, Redlich–Peterson, Temkin and Dubinin–Radushkevich, were applied to the sorption data. The best fit was obtained with Redlich–Peterson isotherm. The separation factor,  $R_L$ , value indicated favorable sorption for Pb<sup>2+</sup>. The maximum sorption capacities were 392.2 and 409.8 mg/g for P(HEA/2IA) and P(HEA/10IA), respectively. Kinetic data showed best fit with pseudo-second-order model. Thermodynamic studies revealed that the reaction was exothermic and proceeds with a decrease in entropy. Moreover, P(HEA/IA) hydrogel showed the most pronounced sorption toward Pb<sup>2+</sup> from environment containing Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> and Co<sup>2+</sup>. Sorption/desorption experiments, showed that the P(HEA/IA) hydrogels could be reused without significant loss of the initial properties even after three adsorption–desorption cycles.

**Keywords:** hydrogel, itaconic acid, reusability, lead removal.

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The increasing level of heavy metals such as lead, that are discharged into the environment as industrial wastes, represent a serious threat to human health, living resources, and ecological system [1,2]. Lead is an important element used as an intermediate in processing industries such as plating, paint and dyes, glass operations, and lead batteries. The toxicity of lead comes from its ability to mimic biologically important essential metals, mainly calcium, iron, and zinc. Lead inhibits some enzymes that cause poisoning in humans [3]. Therefore, lead has been classified as priority pollutant by the US Environmental Protection Agency (EPA) and the maximum contaminant level (MCL) of lead ions in drinking water has been set at a low level of 0.015 mg/l by EPA [4]. Various technologies have been applied to remove lead from water. These include chemical precipitation, ion exchange, membrane filtration and reverse osmosis [5]. Among them, adsorption has been recognized as a cost-effective alternative for removing metal ions existing in wastewater [6–10].

Hydrogels are cross-linked hydrophilic polymers which, when immersed in water can uptake large amount of water. Environmentally sensitive or “smart” hydrogels are able to change their volume by more than one order of magnitude in response to different

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parameters such as temperature, pH value, light, ion, and substance concentrations [11]. Due to characteristic properties such as tailored swelling and ability to incorporate different functional groups into polymeric network, hydrogels have found a great application as sorbents for heavy metal ion removal from wastewater [12].

Hydrogels based on 2-hydroxyethyl acrylate (HEA) were previously investigated regarding their sorption characteristics [13–17]. All studies clearly indicate that hydrogels based on HEA are promising sorbents for removal of heavy metal ions from aqueous solutions. Itaconic acid (IA) is a water soluble monomer having two carboxylic acid groups. Due to its double functionality, IA polymers offer interesting possibilities as functional polymers for wastewater treatment.

In this study, pH sensitive hydrogels, based on 2-hydroxyethyl acrylate and itaconic acid, were synthesized by free radical crosslinking/copolymerization and used as sorbents to remove Pb<sup>2+</sup> from aqueous solution. With regard to good sorption capabilities of both HEA and IA, it was assumed that HEA/IA copolymers would show improved sorption compared to corresponding homopolymers. Besides, in many papers dealing with Pb<sup>2+</sup> sorption high values of sorption capacities were obtained for low initial concentrations of metal ions, but there is a lack of papers presenting good sorption performance for high initial concentrations of heavy metal ions. The hydrogels were characterized using differential scanning calorimetry (DSC),

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scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM) analyses. The influence of initial pH of the solution, adsorbent dosage, temperature and ionic strength on the lead ions adsorption on P(HEA/IA) hydrogels were studied. Furthermore, the adsorption kinetics and isotherms of Pb<sup>2+</sup> by P(HEA/IA), as well as the competitive ion adsorption were also analyzed. Finally, desorption and reusability of P(HEA/IA) hydrogels were investigated.

## EXPERIMENTAL

### Materials

2-hydroxyethyl acrylate (HEA), ethylene glycol dimethacrylate (EGDMA), potassium persulfate (KPS) and *N,N,N',N'*-tetramethylethylenediamine (TEMED) were purchased from Sigma–Aldrich, Germany. Itaconic acid (IA) was supplied from Fluka, Germany. Lead stock solution (1000 mg/L) was prepared by dissolving Pb(NO<sub>3</sub>)<sub>2</sub> (Merck, Germany). Deionized water was used for all polymerizations and solution preparations. Ratio of water and ethanol in water/ethanol mixture (H<sub>2</sub>O/C<sub>2</sub>H<sub>5</sub>OH) was 1:1.

### Hydrogel synthesis

The P(HEA/IA) hydrogels were synthesized as described in the literature [16,18–22], with IA mole fractions of 2.0, 5.0, 7.0, and 10.0, respective to monomer. 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).

### Characterization techniques

The hydrogels were characterized before and after lead adsorption. Fourier transform infrared (FTIR) spectra of the hydrogels were recorded in the transmission mode using a Bomem 100 FTIR spectrophotometer. Before recordings, xerogels were crumbled into powder and mixed with potassium bromide (Merck IR spectroscopy grade) in the proportion 1:100, and then compressed into a 12-mm semi-transparent disk under pressure (Pressure gage, Shimadzu). 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), in the temperature range of –50 to 150 °C to eliminate any residual water. Scanning electron microscope (SEM) was used to investigate the hydrogels morphology. Measurements were taken on a JEOL JSM-5800 scanning electron microscope. Hydrogel samples, swollen to equilibrium in distilled water and

lead solution, were freeze-dried using a Modulyo Freeze Dryer System Edwards, lyophilized, fractured and finally, covered with gold vapor before scanning. Atomic force microscopy (AFM, AutoProbe CP Research, TM microscopes) in non-contact mode was used to investigate the surface topography of the hydrogels. 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.

The aqueous phase concentration of Pb<sup>2+</sup> 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.

### Sorption experiments

To investigate the effects of pH, sorbent dosage, contact time, ionic strength, temperature, initial metal ion concentration, and presence of other metal ions batch sorption experiments were carried out. All experiments were carried out in 80 ml flasks containing 50 ml of aqueous solution of heavy metal ions and around 0.03 g of hydrogel. The solutions were stirred with a constant speed of 100 rpm for 48 h.

pH of the aqueous phase was adjusted with dilute NaOH or HNO<sub>3</sub> and measured with a Hanna pH meter using a combined glass electrode. In order to investigate the effect of temperature and sorbent dosage on sorption process, the equilibrium sorption measurements were carried out 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 sorption, ionic strengths of the solutions were adjusted with NaCl concentration range from 0–0.3 mol/L.

The amount of sorbed heavy metal ions, *q* (mg/g) and sorption efficiency (%) were calculated using Eqs. (1) and (2):

$$q = \frac{V(c_0 - c_e)}{m_s} \quad (1)$$

$$\text{Sorption efficiency (\%)} = \frac{100(c_0 - c_e)}{c_0} \quad (2)$$

where *c*<sub>0</sub> (mg/L) and *c*<sub>e</sub> (mg/L) are the initial and final concentration of heavy metal ions, *V* (L) is the volume of the solution, and *m*<sub>s</sub> (g) is the weight of dry hydrogel. All experiments were carried out in triplicate and average results are reported.

### Competitive sorption

Competitive heavy metal ion sorption from artificial water (containing Pb<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Co<sup>2+</sup>) 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.

### Desorption and regeneration experiments

Desorption efficiency and regeneration potential of P(HEA/IA) hydrogel were also studied. In order to determine the most effective desorption medium, desorption was examined with different concentrations of CH<sub>3</sub>COOH, HCl and HNO<sub>3</sub>. To determine the potential reusability of the hydrogels, desorption process was carried out in a 0.1 M HNO<sub>3</sub> aqueous solution, and consecutive sorption–desorption cycles were repeated three times using the same adsorbent. Desorption efficiency was calculated using the following equation:

$$\begin{aligned} \text{Desorption efficiency (\%)} &= \\ &= 100 \frac{\text{Amount of desorbed metal ions}}{\text{Amount of sorbed metal ions}} \end{aligned} \quad (3)$$

### Sorption kinetics

To evaluate the kinetics of the sorption process, pseudo-first order [23] and pseudo-second order [24] models were tested to interpret the experimental data. The linear forms of those kinetic equations can be expressed as:

Pseudo-first order equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

Pseudo-second order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where  $q_e$  and  $q_t$  (mg/g) are the sorption capacities at equilibrium, and at time  $t$  (h), respectively;  $k_1$  (h<sup>-1</sup>) is the pseudo-first order rate constant and  $k_2$  (g/mg h) is the pseudo-second order rate constant. 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.

### Sorption isotherms

Sorption of Pb<sup>2+</sup> by P(HEA/IA) hydrogel was modeled using five adsorption isotherms: Langmuir, Freundlich, Redlich–Peterson, Temkin and Dubinin–Radushkevich. The linear forms of listed models are presented in Table 1.

### Thermodynamic parameters

The thermodynamic parameters can be determined from the thermodynamic equilibrium constant,  $K_c$  (or the thermodynamic distribution coefficient). The standard Gibbs energy change  $\Delta G^\circ$  (kJ/mol), standard enthalpy change  $\Delta H^\circ$  (kJ/mol), and standard entropy change  $\Delta S^\circ$  (J/(mol K)) were calculated using the following equations:

$$K_c = \frac{c_s}{c_e} \quad (6)$$

$$\Delta G^\circ = -RT \ln K_c \quad (7)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

where  $K_c$  is the equilibrium constant,  $c_s$  is the amount of metal ions sorbed at equilibrium (mg/L),  $c_e$  is the amount of metal ions remained in the solution (mg/L),  $R$  is the universal gas constant (kJ/(mol K)), and  $T$  is the solution temperature (K) [25]

Values for  $\Delta S^\circ$  and  $\Delta H^\circ$  are obtained from the slope and intercept of a plot  $\ln K_c$  vs.  $1/T$  according to Eq. (8) and the  $\Delta G^\circ$  values were calculated from the two parameters using Eq. (7).

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

Isotherm	Equation	Reference
Langmuir	$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \frac{1}{c_e}$	[40]
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e$	[41]
Redlich–Peterson	$\ln \left( K_R \frac{c_e}{q_e} - 1 \right) = \beta \ln c_e + \ln a_R$	[42]
Temkin	$q = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln c_e$	[43]
Dubinin–Radushkevich (D–R)	$\ln q_e = \ln q_m - \beta \varepsilon^2$	[44,45]

## RESULTS AND DISCUSSION

The FTIR spectra of P(HEA/10IA) hydrogels, pure and metal loaded are presented in Fig. 1. Sorption of Pb<sup>2+</sup> onto P(HEA/10IA) hydrogel caused changes in intensity and position of some absorption peaks. The broad peak at 3424 cm<sup>-1</sup>, assigned to stretching vibration of –OH bond, is shifted to 3416 cm<sup>-1</sup> after Pb<sup>2+</sup> sorption. Strong peak, assigned to C=O stretching vibration from carboxylic groups, was shifted from 1720 to 1731 cm<sup>-1</sup>. The new peak at 1554 cm<sup>-1</sup> appeared after Pb<sup>2+</sup> sorption, which might be a result of interactions between Pb<sup>2+</sup> and C=O. These results indicate that –OH and –COOH groups in the P(HEA/IA) hydrogel might be involved in the sorption process. The probable interactions might be electrostatic interactions between Pb<sup>2+</sup> and carboxylic groups. In order to further investigate this assumption we performed DSC analysis.

Differential scanning calorimetry (DSC) was used to determine the glass transition temperature ( $T_g$ ) of P(HEA/IA) hydrogel before and after Pb<sup>2+</sup> sorption. For all copolymeric networks a single  $T_g$  value was clearly observed, indicating that all the samples are copolymers. The observed glass transition temperatures of metal-free and metal loaded hydrogels are presented in Table 2. The increase of the  $T_g$  value after metal adsorption could be explained by the reduced mobility of polymer chains after the metal ion adsorption due to the additional crosslinking by Pb<sup>2+</sup> [14].

The change of the  $T_g$  value after lead adsorption additionally confirms the assumption of the existence

of interactions between the P(HEA/IA) hydrogel and the Pb<sup>2+</sup>. It could be expected that these interactions influence the hydrogel morphology, so the influence of the lead ions on morphology was examined by SEM and AFM analysis. Changes in morphology of unloaded and metal loaded samples are presented in Fig. 2.

Inner morphology of metal free and metal loaded P(HEA/10IA) hydrogels was examined by cross sectional SEM analysis. The resulting micrographs are presented in Fig. 2. The structure of the unloaded sample (Fig. 2c) is highly porous with a characteristic honey-comb structure with open pore 3D structure. The reduction of the pores can be observed after sorption of lead ions (Fig. 2d). Upon sorption Pb<sup>2+</sup> interact with COO<sup>-</sup> present in the hydrogel. The electrostatic repulsive forces are diminished, which leads to decrease in the swelling degree and reduction of hydrogel pores [26].

Characteristic three-dimensional (3D) images of the hydrogel surface before and after metal sorption were recorded using AFM. Fig. 2a shows a predominantly hill-valley-structured surface with irregular pores of P(HEA/10IA) hydrogel before metal sorption. A visible change in surface topography is obtained after sorption of lead. Larger hill-structures of the reference sample are broken into smaller structures. Fig. 2b shows smoother surface of hydrogel after lead sorption, indicating the interaction between lead ions and the hydrogel.

The mechanical strength and stability are among the most important properties of hydrogels considering their application in wastewater treatment. Hydrogels

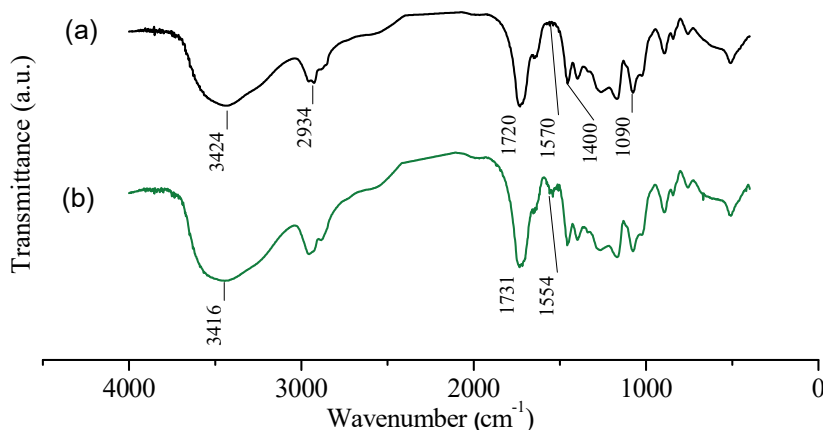


Figure 1. FTIR spectra of P(HEA/10IA) hydrogel: a) before and b) after Pb<sup>2+</sup> sorption.

Table 2. Values of glass transition temperatures ( $T_g$ ) of P(HEA/IA) hydrogels free and lead loaded and plateau storage modulus of P(HEA/IA) hydrogels swollen in deionized water and in Pb<sup>2+</sup> solution (10 mg/L)

Parameter	P(HEA/2IA)	P(HEA/5IA)	P(HEA/7IA)	P(HEA/10IA)
$T_g$ / °C (unloaded)	19.5	27.0	32.0	41.0
$T_g$ / °C (lead loaded)	21.0	28.0	33.5	42.0
Plateau storage modulus (deionized water), kPa	1.13	2.18	3.26	4.13
Plateau storage modulus (Pb <sup>2+</sup> solution), kPa	2.04	3.07	4.45	4.92

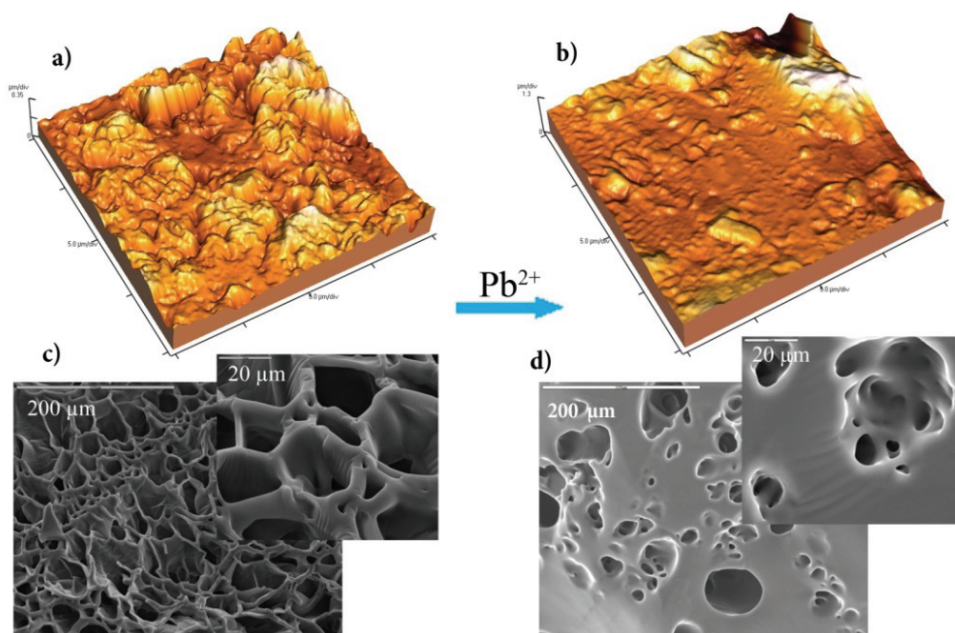


Figure 2. AFM images of the top surface of P(HEA/10IA) hydrogel: a) before sorption, b) after Pb<sup>2+</sup> sorption. SEM micrographs: cross section morphology of: c) P(HEA/10IA) lead free and d) P(HEA/10IA) hydrogel lead loaded.

should have good mechanical properties in swollen state in order not to crumble apart during exploitation. Therefore, it is of great importance to investigate hydrogel's mechanical properties in conditions in which they are used. The storage modulus ( $G'$ ) for P(HEA/IA) hydrogels, swollen to equilibrium in deionized water and in Pb<sup>2+</sup> solution were measured and presented in Table 2, in order to determine the sample with the best mechanical strength. Frequency independent values of storage modulus are obtained for all samples in applied frequency range. Storage modulus is higher for samples swollen in solution of lead than for those swollen in deionized water, which indicates that embedding of Pb<sup>2+</sup> reinforce the polymeric network. The reinforce of Pb<sup>2+</sup> is a consequence of the fact that Pb<sup>2+</sup> are electrically bonded to two carboxylic anions and act as cross-linker point.

Also, with the increase of IA content in the sample  $G'$  increases, improving the mechanical properties of hydrogel. The increase of  $G'$  is more pronounced in samples swollen in deionised water because the influence of itaconic acid is partly screened in samples swollen in Pb<sup>2+</sup> solution due to sorption on Pb<sup>2+</sup>.

### Sorption experiments

The initial pH of the aqueous solution is an important parameter in the sorption process because it influences the protonation of the sorbent functional groups as well as the solution chemistry of the heavy metal ions [27–29]. Figure 3 presents the effects of the solution pH (2.0 to 7.0) on the sorption capacity of Pb<sup>2+</sup> for P(HEA/IA) hydrogels. As it was expected, the sorption of lead ions is low in acidic medium (pH 2–3) due to the low dissociation of carboxylic groups of itaconic

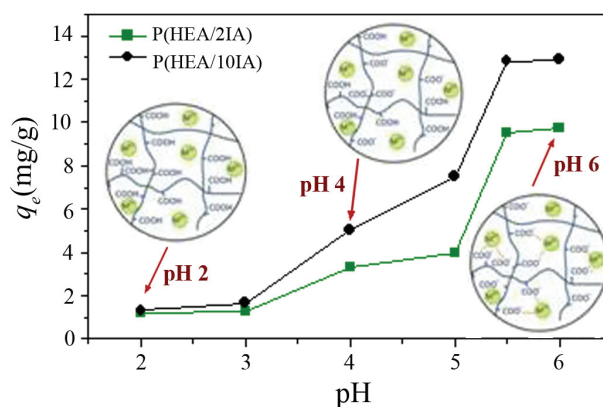


Figure 3. The effect of initial pH on the sorption capacity of Pb<sup>2+</sup> onto P(HEA/IA) hydrogels.

acid. However, the uptake of Pb<sup>2+</sup> was found to increase sharply when the pH value was increased from 3.0 to 6.0. At pH > 5.5, ionization of both carboxylic groups of itaconic acid took place, the negative charge density on the sorbent increases, and increased sorption of lead ions is a result of electrostatic attraction between metal ions and negatively charged binding sites. In order to avoid the precipitation of metal ions and to achieve high efficiency, further experiments were carried out at pH 5.5.

The effect of sorbent weight on the sorption capacity and removal efficiency of Pb<sup>2+</sup> is shown in Fig. 4a. According to the results presented, the sorption capacity decreased with the increase of the sorbent weight, while the removal efficiency increased. This behavior is expected due to fact that the increase of sorbent weight increases the number of binding sites on the hydrogel surface available for the sorption of metal ions. Although the sorption efficiency of lead increased with the increase in the hydrogel mass due to the higher amount of active sites, the sorption capacity was reduced. These results were expected, and reported for many other sorption systems [30,31].

Ionic strength is a very important variable in the sorption process since high levels of various salts are often present in wastewater. Ions can have two opposite functions: they may screen the electrostatic interaction of opposite charges of sorbents and sorbate molecules, so the amount of metal adsorbed in presence of salts is reduced, or they may enhance the degree of dissociation of the sorbate molecules and facilitate the amount of pollutant adsorbed [32]. The effect of ionic strength on the sorption of Pb<sup>2+</sup> by P(HEA/IA) hydrogel was analyzed over the NaCl concentration range from 0 to 0.3 mol/L. As shown in Fig.4b, along with ionic strength increasing, the sorption capacity of hydrogel decreased. Therefore, it is obvious

that the addition of salt screens the electrostatic interactions of hydrogel with metal ions and makes the polymer chains shrink [33].

### Sorption kinetics

The sorption kinetic curves are presented in Fig. 5. The sorption capacity for Pb<sup>2+</sup> increased rapidly at the beginning of the adsorption process: more than 80 % of the sorbed Pb<sup>2+</sup> occurred within first 10 h. The kinetic data were analyzed using pseudo-first order and pseudo-second order models. As it can be seen from the Table 3, correlation coefficients for the pseudo-first order kinetic model were much lower, and the calculated equilibrium sorption capacities ( $q_{e,cal}$ ) deviated considerably from the experimental data. This is because in many cases, the pseudo-first order equation does not fit well to the whole range of contact time and is generally applicable only over the initial stage of the sorption process [34]. The results showed that the sorption process of Pb<sup>2+</sup> onto P(HEA/IA) hydrogel followed the pseudo second-order kinetic model and that the sorption is probably controlled by the chemical process [35,36].

### Sorption isotherms

Sorption of Pb<sup>2+</sup> by P(HEA/IA) hydrogel was modeled using the Langmuir, Freundlich, Redlich–Peterson, Temkin and Dubinin–Radushkevich isotherms. The applicability of the isotherm models to describe the sorption process was judged by the correlation coefficient,  $R^2$ . The obtained characteristic parameters of evaluated isotherm models are summarized in Table 4.

As it can be seen from the Fig. 6, all applied sorption models result in nonlinear curve. The best interpretation of the experimental data showed the Redlich–Peterson isotherm compared to the other four isotherms.

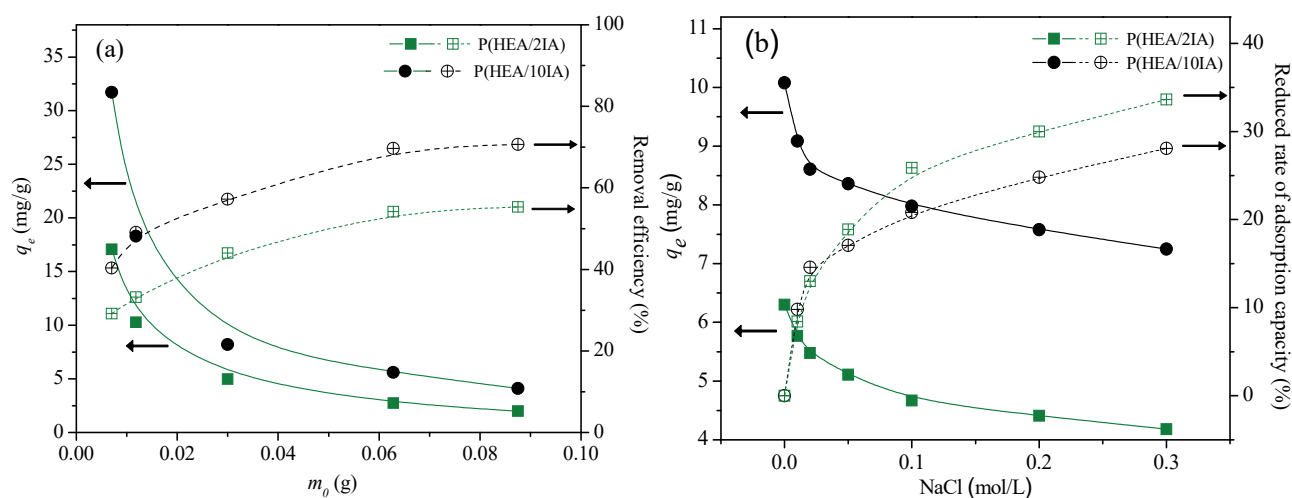


Figure 4. The effect of: a) the sorbent weight and b) ionic strength on the Pb<sup>2+</sup> removal from the aqueous solution onto P(HEA/IA) hydrogels.



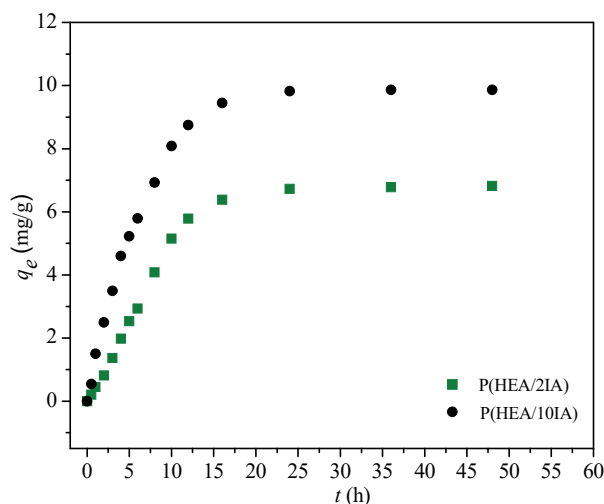


Figure 5. Sorption kinetics of Pb<sup>2+</sup> on P(HEA/IA) hydrogels ( $c_0 = 10 \text{ mg L}^{-1}$ ,  $m_0 = 0.03 \text{ g}$ , volume of solution  $0.05 \text{ L}$ , pH 5.5,  $T = 25 \text{ }^\circ\text{C}$ , contact time: 0.5–48 h).

Dubinin–Radushkevich and Temkin models have lower agreement with experimental data than the first three models for Pb<sup>2+</sup>. The values of the sorption capacity obtained by D–R equation are higher than  $q_m$  values obtained by Langmuir model, which is expected, since D–R model takes into account porous structure of a sorbent.

Very important characteristic of the Langmuir model is 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. (9):

$$R_L = \frac{1}{1 + K_L c_0} \quad (9)$$

where  $c_0$  is the maximal initial metal ion concentration ( $\text{mg L}^{-1}$ ) [37].

The values of the separation factors  $0 < R_L < 1$  and the value for Freundlich exponent  $n > 1$  (Table 4) indicate that the sorption of Pb<sup>2+</sup> onto investigated hydrogels is favorable. Moreover, the calculated  $R_L$  values for all investigated concentrations (Table 5) point out that sorption is more favorable at higher initial metal ion concentrations. Sorption capacities for Pb<sup>2+</sup> on different sorbents reported in the literature are presented in Table 6. It is obvious that the  $q_m$  values, obtained for the P(HEA/IA) hydrogels, are higher compared to the most of the previously investigated sorbents.

Table 3. Parameters of the applied kinetic models for sorption of Pb<sup>2+</sup> onto P(HEA/IA) hydrogels and correlation coefficients ( $c_0 = 10 \text{ mg/L}$ ;  $m_0 = 0.03 \text{ g}$ ; volume of solution  $0.05 \text{ L}$ ; pH 5.5;  $T = 25 \text{ }^\circ\text{C}$ )

Sample	$q_{e,\text{exp}} / \text{mg g}^{-1}$	Pseudo first-order model			Pseudo second-order model		
		$k_1 / \text{h}^{-1}$	$q_{e,\text{cal}} / \text{mg g}^{-1}$	$R^2$	$k_2 / \text{g mg}^{-1} \text{h}^{-1}$	$q_{e,\text{cal}} / \text{mg g}^{-1}$	$R^2$
P(HEA/2IA)	7.32	0.166	9.14	0.9243	0.855	9.712	0.9707
P(HEA/10IA)	9.87	0.256	17.94	0.9388	2.314	11.1894	0.9917

Table 4. Parameters of investigated sorption models for sorption of Pb<sup>2+</sup> from aqueous solution onto P(HEA/IA) hydrogels ( $c_0 = 10\text{--}520 \text{ mg/L}$ ,  $m_0 = 0.03 \text{ g}$ , volume of solution:  $0.05 \text{ L}$ , pH 5.5,  $t = 48 \text{ h}$ ,  $T = 25 \text{ }^\circ\text{C}$ )

Model	Parameter	P(HEA/2IA)	P(HEA/10IA)
Langmuir	$K_L / \text{L g}^{-1}$	3.39	5.76
	$q_m / \text{mg g}^{-1}$	392.20	409.84
	$R^2$	0.9914	0.9927
Freundlich	$K_F$	1.98	3.63
	$\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$		
	$n$	1.21	1.28
Redlich–Peterson	$R^2$	0.9915	0.9881
	$K_R / \text{L g}^{-1}$	1.34	1.98
	$B$	0.89	0.93
Dubinin–Radushkevich	$a_R / \text{L mol}^{-1}$	0.0060	0.0016
	$R^2$	0.9984	0.9991
	$q_m / 10^6 \text{ mg g}^{-1}$	0.462	0.068
Temkin	$E / \text{kJ mol}^{-1}$	0.616	0.72
	$\beta \times 10^6$	1.32	0.96
	$R^2$	0.8016	0.7983
Freundlich	$K_T / \text{L g}^{-1}$	0.105	0.14
	$B$	54.62	68.33
	$b / \text{J mol}^{-1}$	45.36	36.26
Dubinin–Radushkevich	$R^2$	0.8635	0.8775
	$q_m / 10^6 \text{ mg g}^{-1}$	0.462	0.068
	$E / \text{kJ mol}^{-1}$	0.616	0.72
Freundlich	$\beta \times 10^6$	1.32	0.96
	$R^2$	0.8016	0.7983

#### Thermodynamic parameters

The effect of temperature on the removal efficiency of Pb<sup>2+</sup> was investigated and presented in Table 7. An increase in temperature resulted in a decreased of Pb<sup>2+</sup> sorption on P(HEA/10IA) hydrogel. The decrease of sorption of lead ions by the P(HEA/10IA) hydrogel at higher temperature indicates that the adsorption is an exothermic process. The values of  $\Delta G^0$  for Pb<sup>2+</sup> are negative indicating sorption is spontaneous and the degree of spontaneity of the reaction decreases with the temperature increase. The negative value of  $\Delta H^0$  suggests that the sorption processes is exothermic, which is supported by the decrease of the sorption of metal ions with increase of temperature. The negative value of  $\Delta S^0$  suggest there is a decrease in the randomness at the solid-solution interface of Pb<sup>2+</sup> and P(HEA/10IA) hydrogel [38].

#### Competitive adsorption study

The existence of multiple ionic species in the solution may affect the sorption capacity of hydrogel for

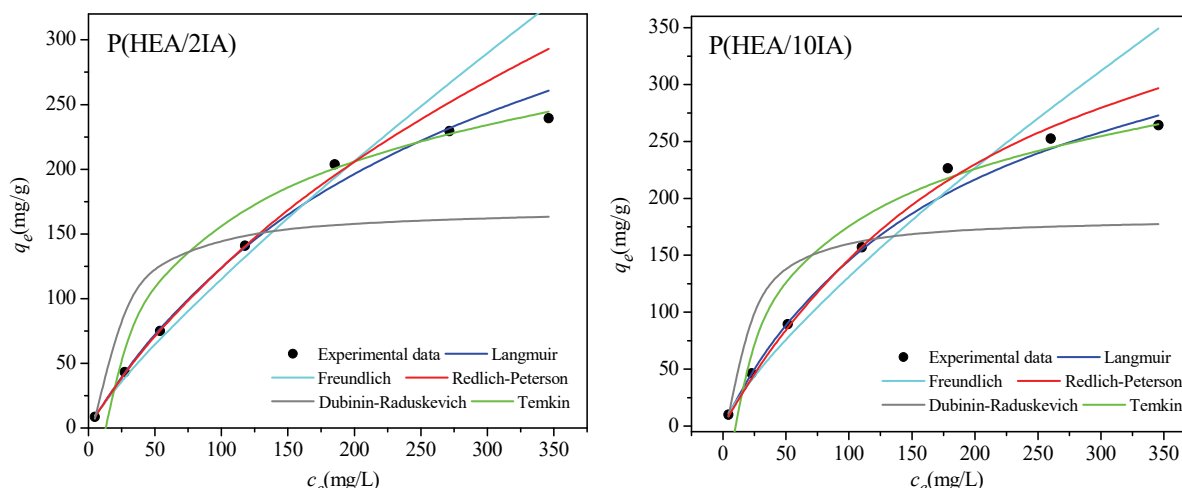


Figure 6. Comparison of five isotherm models applied in this work for the Pb<sup>2+</sup> adsorption onto P(HEA/IA) hydrogel.

Table 5. The  $R_L$  values for the P(HEA/2IA) and P(HEA/10IA) hydrogels at 25 °C

$c_0 / \text{mg L}^{-1}$	P(HEA/2IA)	P(HEA/10IA)
10.00	0.9672	0.9455
53.13	0.8558	0.7774
98.72	0.7404	0.6267
202.24	0.5943	0.4631
307.53	0.4878	0.3592
427.11	0.4135	0.2932
518.06	0.3637	0.2516

each ion species. In this section, the competitive sorption behaviour of Pb<sup>2+</sup> on the P(HEA/IA) hydrogel was evaluated using solutions containing a mixture of various metal ions (Pb<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Co<sup>2+</sup>). The concentration of all ions was the same (10 mg L<sup>-1</sup>). The results are presented in Fig. 7. The sorption capacity for lead ions decreased under competitive conditions. Also, with the increasing number of various metal ions in the system, the sorption of Pb<sup>2+</sup> decreased even more. Compared to the results under non-competitive conditions, the sorption capacity of Pb<sup>2+</sup> decreased by 5.27% in the binary system and by 11.10% in the system containing three metal ions. The reason for sorption decrease could be the competition

for the chelation sites on the hydrogel and/or a screening effect by the other metal ions [39]. The results showed that through the metal uptake, the sorption of Pb<sup>2+</sup> was barely affected by the presence of other metal ions in the solution. The higher ion selectivity observed for Pb<sup>2+</sup> might be attributed to the bigger ionic radius of Pb<sup>2+</sup> (1,19 Å) [37].

Table 7. Thermodynamic parameters for sorption of Pb<sup>2+</sup> onto P(HEA/10IA) hydrogel

$t / ^\circ\text{C}$	$q_{e,\text{exp}}$ mg/g	$\Delta G^0$ kJ/mol	$\Delta H^0$ kJ/mol	$\Delta S^0$ J/(mol K)
10	10.04	-0.800	-3.315	-8.785
25	9.87	-0.721	-	-
50	9.11	-0.454	-	-

#### Desorption and reusability studies

The obtained results for Pb<sup>2+</sup> desorption from P(HEA/IA) hydrogel are presented in Table 8. The Pb<sup>2+</sup> desorption was increased by increasing in extractant concentration. Maximum desorption for Pb<sup>2+</sup> was achieved at 0.1 M HNO<sub>3</sub> and it was found to be 95.2. Results of three consecutive adsorption–desorption cycles showed that by the end of the third cycle, more than 88% of the initial adsorption capacity was obtained.

Table 6. Comparison of maximum sorption capacities for Pb<sup>2+</sup> on different sorbents

Hydrogel	$q_m / \text{mg g}^{-1}$	Reference
HEA/AMPS	76.5	[13]
HEA/MALA	80.8	[14]
Fe <sub>3</sub> O <sub>4</sub> -P(Cys/HEA)	23.5	[15]
C-g-AA	825.7	[37]
Chitosan(chitin)/cellulose composite biosorbents	26.3	[46]
Magnetic p(AMPS) hydrogels	140.8	[47]
HEA/2IA	392.2	Present work
HEA/10IA	409.8	Present work



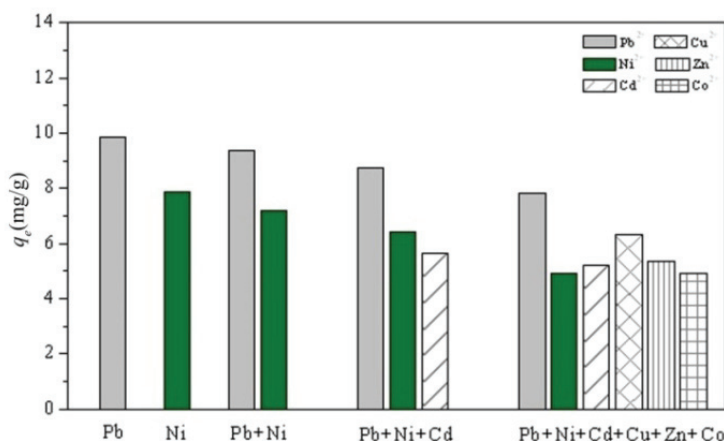


Figure 7. Adsorption capacity of Pb<sup>2+</sup> on P(HEA/IA) under noncompetitive and competitive conditions.

Table 8. The percentages of Pb<sup>2+</sup> desorption after third cycle by different desorption agents from P(HEA/10IA) in various concentrations

HNO <sub>3</sub>			HCl			CH <sub>3</sub> COOH		
0.001 M	0.01 M	0.1 M	0.001 M	0.01 M	0.1 M	0.001 M	0.01 M	0.1 M
64.7	89.8	95.2	48.7	63.3	84.6	42.4	57.8	80.3

## CONCLUSIONS

In this study, the ability of P(HEA/IA) hydrogels for removal of Pb<sup>2+</sup> from aqueous solution has been investigated. FTIR spectra of the investigated hydrogels indicate that –OH and –COOH groups are involved in the sorption process. The sorption of Pb<sup>2+</sup> on P(HEA/IA) followed a pseudo-second-order kinetics and showed the best fit with Redlich-Peterson isotherm model. It is found that the initial concentration of metal ions, solution pH, the adsorbent mass, ionic strength and the temperature have significant influence on sorption process. The priority order in multi-component adsorption was Pb<sup>2+</sup> > Cu<sup>2+</sup> > Zn<sup>2+</sup> > Cd<sup>2+</sup> > Ni<sup>2+</sup> > Co<sup>2+</sup>. Desorption studies showed that desorption of P(HEA/IA) hydrogel is pH dependent and hydrogels can be successfully desorbed with 0.1 mol/L HNO<sub>3</sub>. In addition, hydrogels could be reused without significant losses of the initial properties after three adsorption-desorption cycles performed. Our findings suggest that the P(HEA/IA) hydrogel is a favorable sorbent with great potency for the removal and recovery of lead ions from wastewater.

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## REFERENCES

- [1] X. Huang, M. Sillanpää, B. Duo, E.T. Gjessing, Water quality in the Tibetan Plateau: Metal contents of four selected rivers, *Environ. Pollut.* **156** (2008) 270–277.
- [2] H. Ren, Z. Gao, D. Wu, J. Jiang, Y. Sun, C. Luo, Efficient Pb(II) removal using sodium alginate-carboxymethyl cellulose gel beads: Preparation, characterization, and adsorption mechanism, *Carbohydr. Polym.* **137** (2016) 402–409.
- [3] R. Company, A. Serafim, B. Lopes, A. Cravo, T.J. Shepherd, G. Pearson, M.J. Bebianno, Using biochemical and isotope geochemistry to understand the environmental and public health implications of lead pollution in the lower Guadiana River, Iberia: A freshwater bivalve study, *Sci. Total Environ.* **405** (2008) 109–119.
- [4] L.H. Keith, Analysis of organic water pollutants, *Environ. Sci. Technol.* **13** (1979) 1469–1471.
- [5] U. Kumar, M. Bandyopadhyay, Sorption of cadmium from aqueous solution using pretreated rice husk, *Biores. Technol.* **97** (2006) 104–109.
- [6] G. Zhang, Z. He, W. Xu, A low-cost and high efficient zirconium-modified-Na attapulgite adsorbent for fluoride removal from aqueous solutions, *Chem. Eng. J.* **183** (2012) 315–324.
- [7] U. Yildiz, Ö.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.
- [8] 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 Interf. Sci.* **315** (2007) 87–93.
- [9] G. Zhou, J. Luo, C. Liu, L. Chu, J. Ma, Y. Tang, Z. Zeng, S. Luo, A highly efficient polyampholyte hydrogel sorbent

- based fixed-bed process for heavy metal removal in actual industrial effluent, *Water Res.* **89** (2016) 151–160.
- [10] P.M. Spasojević, V.V. Panić, M.D. Jović, J. Marković, C. van Roost, I.G. Popović, S.J. Velicković, Biomimic hybrid polymer networks based on casein and poly(methacrylic acid). Case study: Ni<sup>2+</sup> removal, *J. Mater. Chem., A* **4** (2016) 1680–1693.
- [11] A.E. English, E.R. Edelman, T. Tanaka, *Experimental Methods in Polymer Science: Modern Methods in Polymer Research and Technology* Academic Press, New York, 2000.
- [12] E. Ramírez, S.G. Burillo, C. Barrera-Díaz, G. Roa, B. Bilyeu, Use of pH-sensitive polymer hydrogels in lead removal from aqueous solution, *J. Hazard. Mater.* **192** (2011) 432–439.
- [13] Y.W. Z. Li, 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.
- [14] 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.
- [15] 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.
- [16] 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 Cd<sup>2+</sup> ion removal from aqueous solution, *Appl. Surf. Sci.* **338** (2015) 178–189.
- [17] Q. Zhu, Z. Li, Hydrogel-supported nanosized hydrous manganese dioxide: Synthesis, characterization, and adsorption behavior study for Pb<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup> and Ni<sup>2+</sup> removal from water, *Chem. Eng. J.* **281** (2015) 69–80.
- [18] M.M. Babić, B.Đ. Božić, K.M. Antić, J.S. Jovašević Vuković, M.D. Perišić, J.M. Filipović, S.Lj. Tomić, Design of novel multifunctional Oxaprozin delivery system based on dual-sensitive poly(2-hydroxypropyl acrylate/itaconic acid) hydrogels, *Mater. Lett.* **147** (2015) 64–68.
- [19] M.M. Babić, B.Đ. Božić, B.Đ. Božić, J.M. Filipović, G.S. Uščumlić, S.L. Tomić, Evaluation of novel antiproliferative controlled drug delivery system based on poly(2-hydroxypropyl acrylate/itaconic acid) hydrogels and nickel complex with oxaprozin, *Mater. Lett.* **163** (2016) 214–217.
- [20] M.M. Babić, B.Đ. Božić, B.Đ. Božić, J.M. Filipović, G.S. Uščumlić, S.Lj. Tomić, Evaluation of poly(hydroxyethyl acrylate/itaconic acid) hydrogels for controlled delivery of transition metal complexes with Oxaprozin as potential antiproliferative agents, *J. Mater. Sci.* **50** (2015) 6208–6219.
- [21] M.M. Babić, K.M. Antić, J.S.J. Vuković, B.Đ. Božić, S.Z. Davidović, J.M. Filipović, S.Lj. Tomić, Oxaprozin/poly(2-hydroxyethyl acrylate/itaconic acid) hydrogels: morphological, thermal, swelling, drug release and antibacterial properties, *J. Mater. Sci.* **50** (2014) 906–922.
- [22] J.S. Vuković, M.M. Babić, K.M. Antić, M.G. Miljković, A.A. Perić-Grujić, J.M. Filipović, S.Lj. Tomić, A high efficacy antimicrobial acrylate based hydrogels with incorporated copper for wound healing application, *Mater. Chem. Phys.* **164** (2015) 51–62.
- [23] Y.S. Ho, Citation review of Lagergren kinetic rate equation on adsorption reactions, *Scientometrics* (2004) 171–177.
- [24] Y.-S. Ho, Review of second-order models for adsorption systems, *J. Hazard. Mater.* **136** (2006) 681–689.
- [25] 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.
- [26] N. Milosavljević, A. Debeljković, M.K. Krušić, N. Milašinović, O.B. Uzum, E. Karadağ, Application of poly(acrylamide-co-sodium methacrylate) hydrogels in copper and cadmium removal from aqueous solution, *Environ. Prog. Sustain.* **33** (2014) 824–834.
- [27] 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. Hazard. Mater.* **181** (2010) 836–844.
- [28] 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.
- [29] 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 nano mesoporous silica, *Chem. Eng. J.* **153** (2009) 70–79.
- [30] 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.
- [31] 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.
- [32] 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.
- [33] D. Ceylan, O. Okay, Macroporous Polyisobutylene Gels: A Novel Tough Organogel with Superfast Responsivity, *Macromolecules* **40** (2007) 8742–8749.
- [34] Y.S. Ho, G. McKay, The sorption of lead(II) ions on peat, *Water Res.* **33** (1999) 578–584.
- [35] Y. Zheng, S. Hua, A. Wang, Adsorption behavior of Cu<sup>2+</sup> from aqueous solutions onto starch-g-poly(acrylic acid)/sodium humate hydrogels, *Desalination*, **263** (2010) 170–175.
- [36] 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 Surfaces, A* **380** (2011) 143–151.

- [37] L.Z.Y. Zhou, S. Fu, L. Zheng, H. Zhan, Adsorption behavior of Cd<sup>2+</sup>, Pb<sup>2+</sup> and Ni<sup>2+</sup> from aqueous solutions on cellulose-based hydrogels, *Bioresources* **7** (2012) 2752–2765.
- [38] 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.
- [39] R. Coşkun, A. Delibas, Removal of methylene blue from aqueous solutions by poly(2-acrylamido-2-methylpropane sulfonic acid-co-itaconic acid) hydrogels, *Polym. Bull.* **68** (2012) 1889–1903.
- [40] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* (1918) 1361–1403.
- [41] C.-H. Yang, Statistical Mechanical Study on the Freundlich Isotherm Equation, *J. Colloid Interf. Sci.* **208** (1998) 379–387.
- [42] D.P.O. Redlich, A useful adsorption isotherm, *J. Phys. Chem.* **63** (1959) 1024–1026.
- [43] O. Çelebi, Ç. Üzümlü, T. Shahwan, H.N. Erten, A radio-tracer study of the adsorption behavior of aqueous Ba<sup>2+</sup> ions on nanoparticles of zero-valent iron, *J. Hazard. Mater.* **148** (2007) 761–767.
- [44] R.T.Y.N.D. Hutson, Theoretical basis for the Dubinin–Radushkevitch (D–R) adsorption isotherm equation, *Adsorption* **3** (1997) 189–195.
- [45] 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.
- [46] L.Z. J. Zhou, Q. Deng, X. Wu, Synthesis and characterization of cellulose derivatives prepared in NaOH/urea aqueous solutions, *J. Polym. Sci., A: Polym. Chem.* **42** (2004) 5911–5920.
- [47] P. Miretzky, C. Muñoz, Enhanced metal removal from aqueous solution by Fenton activated macrophyte biomass, *Desalination*. **271** (2011) 20–28.

## IZVOD

### UKLANJANJE Pb<sup>2+</sup> IZ VODENIH RASTVORA POMOĆU P(HEA/IA) HIDROGELA

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(Naučni rad)

Hidrogelovi na bazi 2-hidroksietil-akrilata i itakonske kiseline su sintetisani polimerizacijom preko slobodnih radikala i ispitana je mogućnost njihove primene kao sorbenata za uklanjanje Pb<sup>2+</sup> iz vodenih rastvora. P(HEA/IA) kopolimeri sa različitim udelom itakonske kiseline su karakterisani pomoću DMA, FTIR, DSC, SEM i AFM analize. Ispitan je uticaj pH, mase sorbenta, jonske jačine, vremena sorpcije i početne koncentracije jona olova na proces sorpcije. Analizirano je pet modela adsorpcionih izoterma (Langmuir, Freundlich, Redlich–Peterson, Tjorkin i Dubinin–Radushkevitch). Najbolje slaganje sa eksperimentalnim vrednostima pokazuje Redlich–Petersonova izoterma. Maksimalni sorpcioni kapaciteti za P(HEA/2IA) i P(HEA/10IA) hidrogelove su bili 392,2 i 409,8 mg/g, redom. Kinetička analiza sorpcije je pokazala najbolje slaganje eksperimentalnih vrednosti sa pseudo-drugim redom reakcije. Ispitivanje termodinamičkih parametara je pokazalo da je reakcija sorpcije olova egzotermna i odigrava se uz smanjenje entropije. Takođe, P(HEA/IA) hidrogel je pokazao najveći afinitet prema Pb<sup>2+</sup> prilikom sorpcije iz rastvora koji je sadržao smešu Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> i Co<sup>2+</sup>. Eksperimenti sorpcije/desorpcije su pokazali da se P(HEA/IA) hidrogel može ponovno koristiti bez značajnih gubitaka čak i nakon tri ciklusa sorpcije/desorpcije.

**Ključne reči:** Hidrogel • Itakonska kiselina  
• Ponovna upotreba • Uklanjanje olova