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SYNTHESIZED COPOLYMER DERIVATIVE OF POLY(STYRENE-ALT-MALEIC ANHYDRIDE) AS A NEW CHELATING RESIN TO REMOVE HEAVY METAL IONS FROM AQUEOUS SOLUTION

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Abstract. Chelating resin as a new copolymer for metal ions removal was prepared using 3-(4-hydroxyphenyl) cyclopropane-1,1,2,2-tetracarboxylic acid and 1,2-diaminoethane on the poly(styrene-alt-maleic anhydride). Parameters of sorption behavior were investigated under various conditions. Kinetics studies revealed that the adsorption process confirmed the pseudo-second-order kinetics and adsorption data were well fitted to Langmuir isotherm.

Keywords: adsorption, chelating resin, 3-(4-hydroxyphenyl)cyclopropane-1,1,2,2-tetracarboxylic acid, metal ions, poly(styrene-alt-maleic anhydride).

1. Introduction

Environmental pollution and contamination of water resources by heavy metal ions have become a severe environmental issue. They cause damage to the environment and affect human health and plants' life.[1-4] Therefore, there is a need to remove heavy toxic metal ions such as copper, cadmium, cobalt, chromium, lead, zinc, and iron from the wastewater before releasing it into the environment. Previously to remove heavy metal ions from aqueous effluents such methods as membrane separation, chemical precipitation, ion exchange and adsorption have been utilized.[5-8] Among the various methods, the adsorption process is generally preferred due to its high efficiency, simplicity, low cost, selectivity, and good stability.[9-11] Hence, the efforts have been made to synthesize and design new organic chelating adsorbent with good adsorption performance. Chelating functional groups on the adsorbent surface not only dominate the adsorption mechanism but also affect the sorption selectivity. There are several organic chelating agents that can be placed on the surface of different support polymers such as carboxylate, tetrazole, amine, imine, hydroxyl, maleic acid, and phosphonic, mainly owing to high absorption of a heavy toxic metal ion in aqueous solutions.[12-15] The carboxylic acid-containing adsorbent is known for the formation of stable chelating compounds with various metal ions in aqueous media. Immobilization of new carboxylic acid functional group on different synthetic supporting polymers is drawing comprehensive attention since chelating functional groups amend metal ion sorption.[16-18] Accordingly, we attempted to synthesize novel chelating copolymer containing various carboxylic acid ligands, with high adsorption capacity values in comparison with the similar polymer compounds,[19-23] which can be used to purify different types of wastewater.

Recently, the synthesis of graft copolymer materials with synthetic and natural polymeric materials of maleic anhydride copolymers, which can chemically bind metal ions from aqueous solutions, has been reported.[24,25] The present research aims to investigate the adsorption characteristics of the prepared chelating resin toward Pb(II), Cu(II), and Zn(II) under different experimental conditions. For this propose first SMA copolymer was synthesized by free radical polymerization and prepared linear copolymer was modified with 3-(4-hydroxyphenyl)cyclopropane-1,1,2,2-tetracarboxylic acid(HPC) as grafting and 1,2 diamino ethane as a cross-linking agent to obtain new chelating copolymer with

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multi-carboxyl cyclopropane functionalities in the pendant group. The obtained chelating resins dispersed in various aqueous solutions of metal ions, and their metal adsorption capacity value was measured by AAS.

2. Experimental

2.1. Characterization Techniques

The IR spectra were measured with a Fourier transform infrared spectrophotometer in the region of 4000–400 cm^{-1} (Brucker TENSOR27, Germany). The concentration of metal ions in the aqueous solution was measured by an atomic absorption spectrophotometer (nova AA 400 Analytik Jena, Germany) at 298 K in aqueous solution. Thermal Gravimetric Analysis of prepared resin both before and after the metal sorption was determined by Linseis L81A1750 (Germany) by scanning at 873 K with the heating rate of 10 K/min. The gel permeation chromatography (GPC) measurements were conducted at 298 K with a gilent 1100 instrument. The columns used were packed with a polystyrene/divinyl benzene (PL gel MIXED-B from Polymer Laboratories), and tetrahydrofuran (THF) was used as fluent at a flow rate of 1 ml/min. The inherent viscosity value was measured by using an Ostwald viscometer at 298 K. Elemental analysis of the resins was conducted with a EURO EA 3000 (Italy).

2.2. Materials

p-Hydroxybenzaldehyde (Merck) was recrystallized from distilled water containing a small amount of H_2SO_4 and dried under vacuum. Organic chemicals such as maleic anhydride, styrene, malononitrile, 1,2-diamino ethane (EDA), methanol, triethylamine (TEA), ethyl acetate and the inorganic chemicals including NaOH, HNO_3 were purchased from Merck (Germany) or Aldrich. Cyanogen bromide was prepared as described by Hartman *et al.*[26] Analytical-reagent grade of metal nitrate salts were obtained from Merck (Germany) or Aldrich and used as received. The aqueous solutions (200 $mg\cdot L^{-1}$) of Cu(II), Pb(II), and Zn(II) were prepared by the dissolution of metal salts in deionized water.

2.3. Preparation of HPC

3-(4-Hydroxyphenyl)-1,1,2,2-tetracarboxylic acid cyclopropane (A) was synthesized based on reported reference.[27] A solution of A (3.27 g, 0.014 mol) in 30 mL of methanol and 20 mL of 20 % aqueous NaOH were refluxed for three hours. The methanol solvent was removed under a vacuum condition, and the residual liquid extracted with 10 mL of diethyl ether to remove non-acidic products. The resulting solution was acidified with dilute HCl and once again extracted with 10 mL of diethyl ether. The concentration of the solution on reduced pressure was solidified in distillated water and dried to give 3.56 g of the final product (81.7 % yield).[28]

FT-IR (KBr): 3493(-OH carboxyl), 1703(C=O carboxyl).

2.4. Synthesis of Cross-linked SMA-HPC (CSMA-HPC)

The CSMA-HPC chelating resin was synthesized by simultaneous reaction of the SMA polymer with HPC as a grafting agent,[25,29] 1,2-diaminoethane as a crosslinking agent, and TEA as a catalyst in the process. The molar ratio of SMA, HPC, and 1,2-diaminoethane was 1:0.5:0.25. The resulting mixture was stirred for 6 h at 363 K. The obtained resin was filtered, washed thoroughly with ethanol, and dried at 333 K in an oven overnight. The yield of the reaction was 83 %. The elemental analysis of CSMA-HPC resin was conducted and showed 69.27 % C, 3.31 % H and 2.19 % N. FT-IR (KBr): 3250-3520 (acidic OH + NH amide), 3030 (aromatic CH), 2879-2981 (aliphatic CH), 1741 (C=O ester), 1695 (C=O acid), 1644 (C=O amide), 1516 (NH), 1461 (C=C substituted benzene), 1388 (C–N), 1241 (C–N–H), 1168 (C–O), 1030 (C–H monosubstituted benzene).

2.5. Batch Sorption Experiment

Batch adsorption experiments were performed to study the adsorption process of Cu(II), Pb(II) and Zn(II) on chelating resins. The SMA-HPC and CSMA-HPC (0.05 g) were stirred with excess metal salt (200 $mg\cdot L^{-1}$) at a room temperature. Besides, the pH values of the metal ions solution were adjusted to 2, 3, 5, and 7 by adding 0.01M NaOH or HNO_3. The kinetics of metal ions adsorption was carried out by taking 0.05 g of CSMA-HPC with 30 mL (200 $mg\cdot L^{-1}$) of metal ion solutions. The effect of temperature was obtained by controlling the temperature at 298, 313, and 328 K to investigate the adsorption thermodynamics. The chelating resin sorption rate for metal ions was obtained by shaking the mixture of adsorbent (0.05 g) and 30 mL (200 $mg\cdot L^{-1}$, pH = 5.0) of metal ion solutions, at different time intervals at 298 K.

The combinations were varied for six hours to ensure that the adsorption process reached complete equilibrium, and the filtrates were collected to measure the final metal ion concentration by AAS.

Desorption behavior of the prepared resin was studied according to the method presented by Hosseinzadeh.[25]

The sorption capacities of resin (mg·g^{-1}) were calculated as follows (Eq. 1):

$$q = \frac{(C_0 - C_f) \cdot V}{W} \qquad (1)$$

where q is the amount of adsorption, mg·g^{-1}; C_0 and C_f are the value of the initial and final concentrations of the metal ion in the solution, respectively, mg·L^{-1}; V is the volume of the metal ions solution submitted to sorption, L; W is the weight of polymer (0.05 g).

3. Results and Discussion

3.1. Characterization of the SMA Derivative Copolymers

The SMA was prepared by the procedure described by Henry *et al.*[29] Fig. 1 displays the FT-IR spectra of the prepared copolymers. Fig. 1a shows the FT-IR spectrum of the SMA copolymer. In this spectrum the peaks at 1789 and 1851 cm^{-1} appear due to anhydride groups. The resulting copolymer was soluble in DMF, acetone, and insoluble in ether, water, chlorinated, and aromatic hydrocarbons. The intrinsic viscosity of the SMA copolymer was computed with an Ostwald viscometer at 298 K in acetone solvent, and 0.39 dL/g was obtained. The SMA-HPC was synthetized by the esterification reaction of SMA anhydride moieties. The hydroxyl group of HPC reacted with maleic anhydride repeating functional groups in the copolymer backbone in the presence of TEA to form chelating copolymer bearing carboxylic pendant groups. The comparison of Figs. 1a and 1b reveals that the intensity of anhydride peaks has decreased and instead, the absorption peaks of C=O carboxyl at 1698 cm^{-1} and ester carbonyl groups at about 1739 cm^{-1} have appeared. The results indicate that the grafting process was efficient (Scheme 1). The number and weight average molar masses (M_n and M_w) of the resulting copolymer were found to be 2.012·10^4 and 3.36·10^4 g·mol^{-1}, respectively, with the distribution index of 1.67.

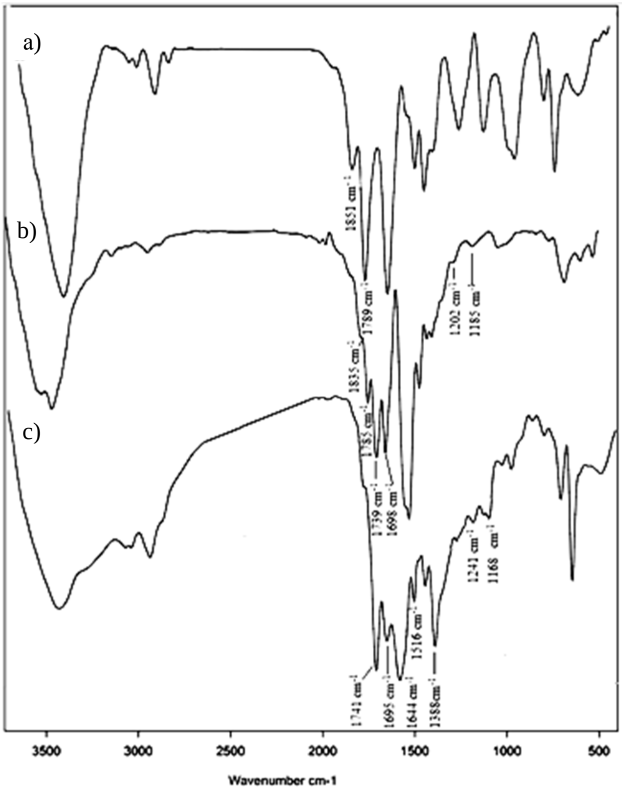
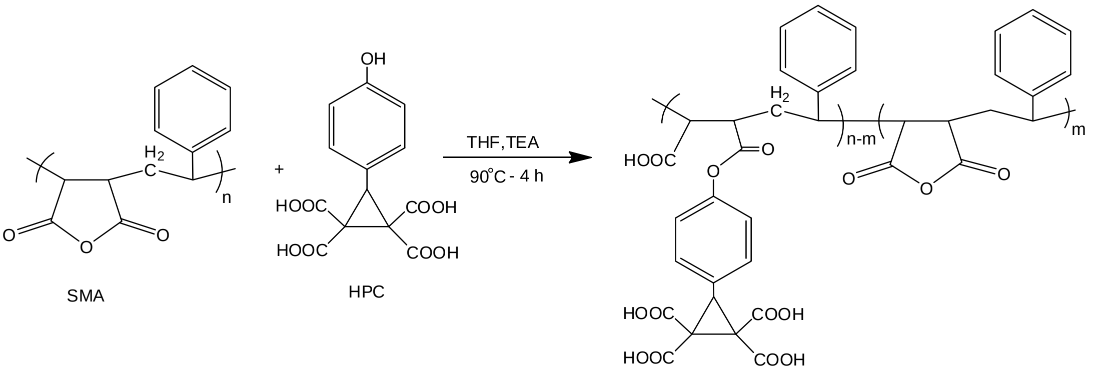


Fig. 1. FT-IR spectra of SMA (a), SMA-HPC (b) and CSMA-HPC (c)



Scheme 1. Synthesis of SMA-HPC

To prepare cross-linked CSMA-HPC resin, the process was performed as the one-pot reaction of the SMA polymer with HPC as a grafting agent, 1,2-diaminoethane as a cross-linking agent and TEA as a catalyst.

Figure 1c displays the FT-IR spectrum of CSMA-HPC. The comparison of Figs. 1b and 1c shows that the anhydride group peaks have completely disappeared, but we see the peaks at about 1644 cm^{-1} due to the formation of amide groups carbonyl, at 1516 cm^{-1} due to N–H bending and at 1388 cm^{-1} due to C–N stretching.

3.2. Effect of pH and Sorption Mechanism

Table 1 presents adsorption capacities of the prepared resins for Cu(II), Pb(II), and Zn(II) elimination at the pH values from 2 to 7. It can be seen that the CSMA-HPC show a high tendency for metal ions compared with a non-cross-linked sample. The adsorption capacity of metal ions for both resins is as follows in the order: Cu(II) > Zn(II) > Pb(II). The Cu(II) ion adsorption capacities of resulting copolymers were higher than other selected metal ions. The Cu(II) ion has the smallest ionic radius. Thus, it can enter into the pores of prepared resins easier than other selected ions.

The adsorption of selected metal ions at pH values below 3 is low. This is due to the fact that a high concentration of proton ions, carboxylic acid, and amine groups are protonated, and metal ion sorption is decreased consequently. Carboxylic acid groups containing copolymers are under carboxylate form, which is appropriate for metal ions complexation when pH value is higher than 3, so the metal adsorption is done intensively. The adsorption of all heavy metal ions on the obtained resins was more favorable at the solution pH value of 5.

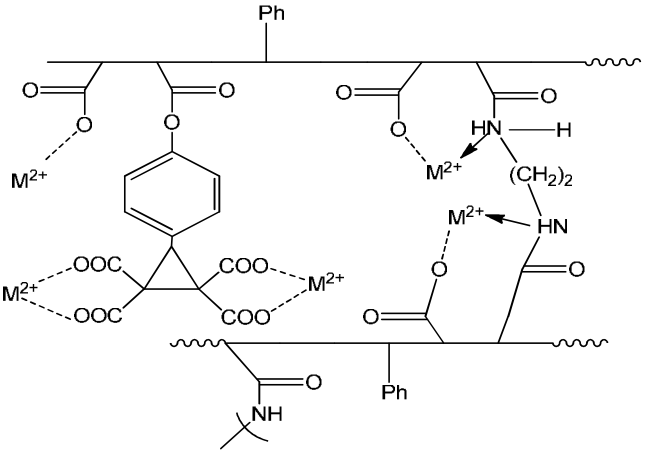
Table 1. Adsorption capacity of the chelating copolymers for single metal ions at different pH

Chelating copolymer	Metal ions	Adsorption capacity, $mg \cdot g^{-1}$			
		pH = 2	pH = 3	pH = 5	pH = 7
SMA-HPC	Cu(II)	59	87	155	154
	Zn(II)	44	72	108	110
	Pb(II)	31	54	65	67
CSMA-HPC	Cu(II)	78	106	197	197
	Zn(II)	55	84	47	146
	Pb(II)	42	63	88	89

Note: metal ions 200 $mg \cdot L^{-1}$, copolymer 0.05 g.

Above pH value of 2.6, the carboxylic acid groups take a carboxylate form, therefore, the strong sorption of resulting copolymers to selected metal ions occurred by electrostatic attractions forces mechanism. Scheme 2 shows the mechanism of metal binding onto the chelating resin. The adsorption mechanisms process is mainly assigned to the metal ion-binding carboxylate organic ligand (–COO^-) and the electrostatic attractions forces between metal ions and oxygenic groups. The metal sorption capacities of the resulting copolymers were measured by AAS method.

The FT-IR spectra of prepared resins after metal ions adsorption are shown in Fig. 2.



Scheme 2. Adsorption mechanism of resin for metal ions

In the case of SMA-HPC, anhydride functional groups still exist in the backbone of the related polymer. So, after metal ions sorption by the resin in solution, hydrolysis of residual anhydride functional groups happened. Therefore, the absorption peaks of anhydride groups in the FT-IR spectrum of chelated form decreased. In this spectrum, the carbonyl stretching of the carboxylate functional group shifts towards lower frequency values, owing to the charge transfer process from the carbonyl oxygen to the metal ions.[30] This indicates that metal ions formed complexes with the acidic carboxyl groups in the resulting copolymer.

In the FT-IR spectra of CSMA-HPC, it can be observed that the peak at 1388 cm^{-1} of C–N bending shifted to a lower frequency after metal ions adsorption by the resin. Meantime, the intensity of amidic carbonyl group increased and shifted towards higher wavenumber. These changes may be due to nitrogen ion pair incorporation of the amide group in the chelating reaction process.

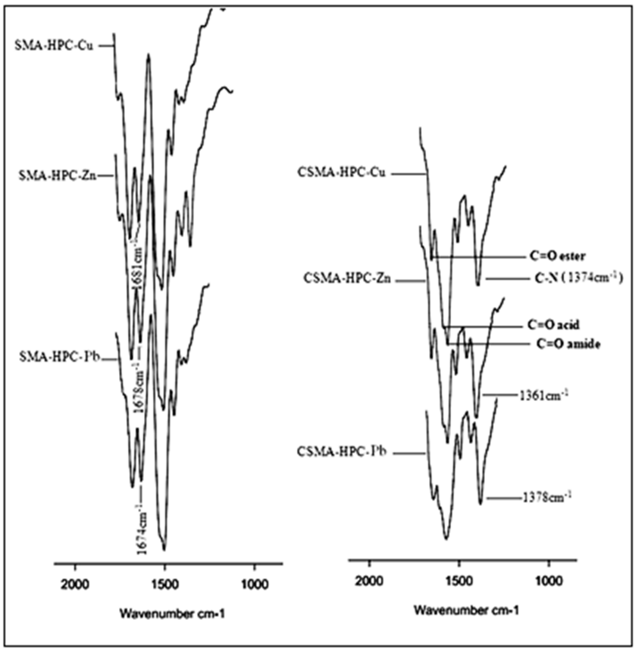


Fig. 2. FT-IR spectra of SMA-HPC
and CSMA-HPC
after complexation with selected metal ions

3.3. Effect of Contact Time and Kinetic Modeling

The influence of time on the sorption capacity value of the CSMA-HPC for selected metal ions was measured, and the obtained results are presented in Fig. 3. The results demonstrate that the rate of metal sorption process by resin was rapid and attained equilibrium within about 30 min. It can be assigned to the sufficient exposure of different active sites, large surface area of the resin and high surface reactivity.

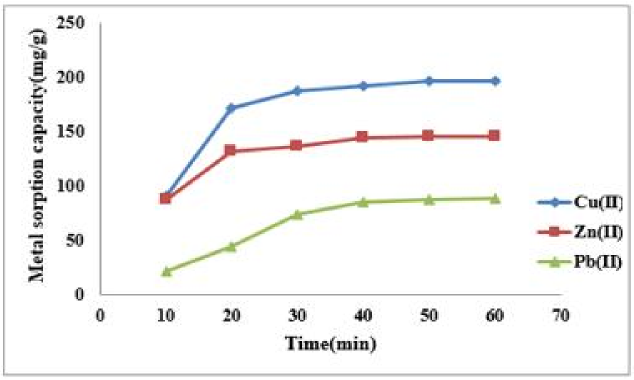


Fig. 3. Effect of contact time on metal ion adsorption onto CSMA-HPC adsorbent: $m = 0.05$ g; $V = 30$ mL; $T = 298$ K; pH = 5

Kinetic models of the pseudo-first order and pseudo-second order show the adsorption mechanisms of CSMA-HPC; they were calculated as following equations.[31,32]

$$\log\,(q_e - q_t) = \log q_e - \left(\frac{k_1 t}{2.303}\right) \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where q_t and q_e are the amounts of ion adsorbed on the resin at time t and equilibrium time, respectively, mg·g^{-1}; k_1 and k_2 are respectively the rate constants of the pseudo-first order and the pseudo-second order reactions, min^{-1} and g·mg^{-1}·min^{-1}, respectively.

Kinetic studies were performed at 298 K and the experimental data are summarized in Table 2. The pseudo-second order kinetic values fitted perfectly well with experimental adsorption data of the removal of all three metal ions by the resin according to the values of correlation coefficients (R^2).

Table 2. Kinetics of metal ions sorption onto CSMA-HPC

Metal	Pseudo-first order model			Pseudo-second order model		
	q_e, mg·g^{-1}	k_1, min^{-1}	R^2	q_e, mg·g^{-1}	k_1, min^{-1}	R^2
Cu(II)	186.3	7.5·10^{-2}	0.939	206	1.37·10^{-3}	0.996
Zn(II)	138.6	7.1·10^{-2}	0.963	156	1.15·10^{-3}	0.993
Pb(II)	98.2	6.67·10^{-2}	0.961	96	0.93·10^{-3}	0.986

3.4. Effect of Concentration and Isotherm Modeling

The result of initial concentration on metal ions removal is investigated by varying concentrations in the ranges from 10 to 200 mg·L^{-1} at the optimum pH value (pH = 5) as shown in Fig 4. The sorption capacity value of metals by the resin was increased with the increase in initial metal concentration. This can be explained with the high driving force for mass transfer.[33] Sorption isotherms of selected metal ions by CSMA-HPC are obtained at pH =5, as shown in Table 3. The Langmuir and Freundlich isotherms are described according to Eqs. (4) and (5), respectively.[34,35]

$$\frac{1}{q_e} = \left(\frac{1}{q_m} bC_e\right) + \frac{1}{q_m} \qquad (4)$$

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \qquad (5)$$

where C_e is the metal ions equilibrium concentration, mg·L^{-1}; q_m is the maximum sorption capacity value of CSMA-HPC, mg·g^{-1} ; b is Langmuir constant that indicates the heat of adsorption, L·mg^{-1}; K_f and n are respectively the Freundlich constant due to the adsorption capacity and sorption at equilibrium concentration, mg$^{1\text{-}n}$·L^{n}·g^{-1}, respectively.

By comparing the R^2 values for the applied Langmuir and Freundlich models, we can see that the Langmuir isotherm provides a slightly better fit to the experimental adsorption data than the Freundlich equation for the adsorption of selected metal ions. It indicates that the surface of the resulting resin was made of homogeneous sorption patches with all the sorption sites having equal adsorbate tendency, and monolayer surface coverage of CSMA-HPC is the main sorption mechanism based on the assumption of Langmuir model.

Table 3. Adsorption isotherm parameters for the sorption of metal ions onto CSMA-HPC

Freundlich isotherm			Langmuir isotherm			Metal
R^2	n	K_f, mg$^{1\text{-}n}$·L^{n}·g^{-1}	R^2	b, L·mg^{-1}	q_m, mg·g^{-1}	
0.970	3.89	38.01	0.987	0.091	201	Cu(II)
0.937	2.63	26.79	0.982	0.068	152	Zn(II)
0.939	2.91	27.35	0.957	0.092	85	Pb(II)

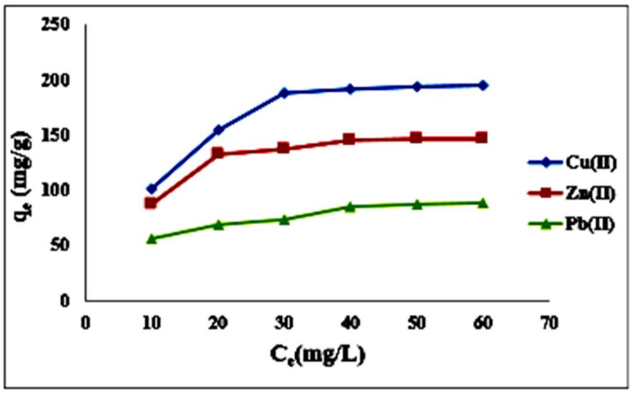


Fig. 4. Effect of concentration on metal ion adsorption onto CSMA-HPC adsorbent: m = 0.05 g; V = 30 mL; T = 298 K; pH = 5

3.5. Effect of Temperature

The result of temperature effect on the adsorption capacity for selected metal ions is considered as one of the essential factors that can determine the efficiency of the adsorption process. Fig. 5 shows that the adsorption process of metal ions increases with the increasing temperature value from 298 to 328 K, confirming that the sorption reaction on to resin is an endothermic process and is significantly affected by the temperature.

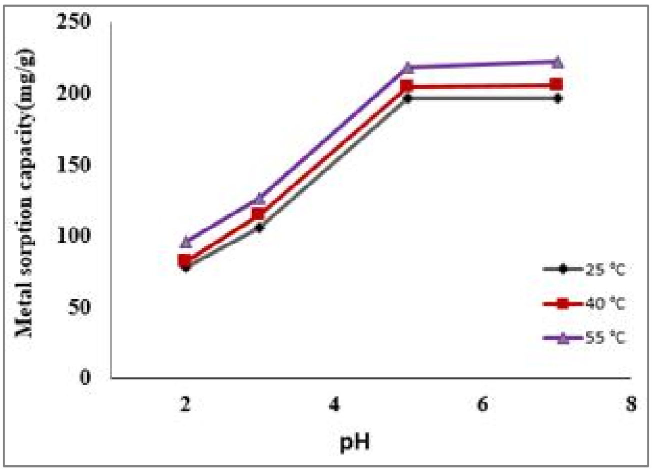


Fig. 5. Adsorption isotherms of Cu(II) on CSMA-HPC at different temperatures (time is 60 min)

3.6. Desorption Study

The desorption of selected metal ions from the resins was also investigated in a batch experimental status.

The resulting copolymer beads, which were charged by the maximum amounts of the related metal ions in pH, five were placed in 1M HCl for 60 min. The number of desorbed metal ions in solution was measured, and the results were listed in Table 4. The results indicate that all selected metal ions have a desorption ratio of over 88 %.

Table 4. Percent of desorption for single metal ions

Copolymer	Percent of desorption		
	Zn(II)	Cu(II)	Pb(II)
SMA-HPC	91.3	92.8	88.3
CSMA-HPC	91.6	92.4	89.8

3.7. Removal of Metal Ions under Competitive Conditions

It was estimated that in a mixture of various metal ions in aqueous solution, only one metal could be selectively adsorbed by a resin. The adsorption selectivity value of chelating resins for metal ion, as well as pH value, is mainly affected by the presence of other metal ions competing for the various active sites in the resulting resin. For this reason, it is inconceivable to distribute the order of metal adsorption selectivity value or to outline the amount of the adsorbed metals according to the conclusions obtained under non-competitive conditions. In this work, metal ion adsorption of the CSMA-HPC resin under competitive conditions as a function of pH value for Cu(II), Pb(II) and Zn(II) ions were specified. The results are presented in Fig. 6. The maximum sorption of the resin for selected metal ions under competitive conditions belongs to Cu(II) at pH = 5. The selectivity for Cu(II) was 1.4 times higher in comparison with Zn(II) and 3.06 – in comparison with Pb(II).

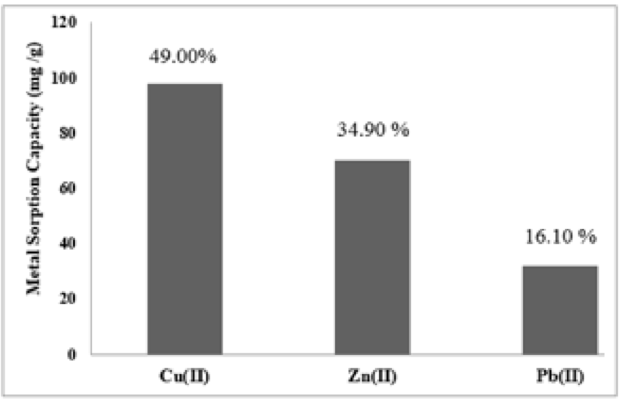
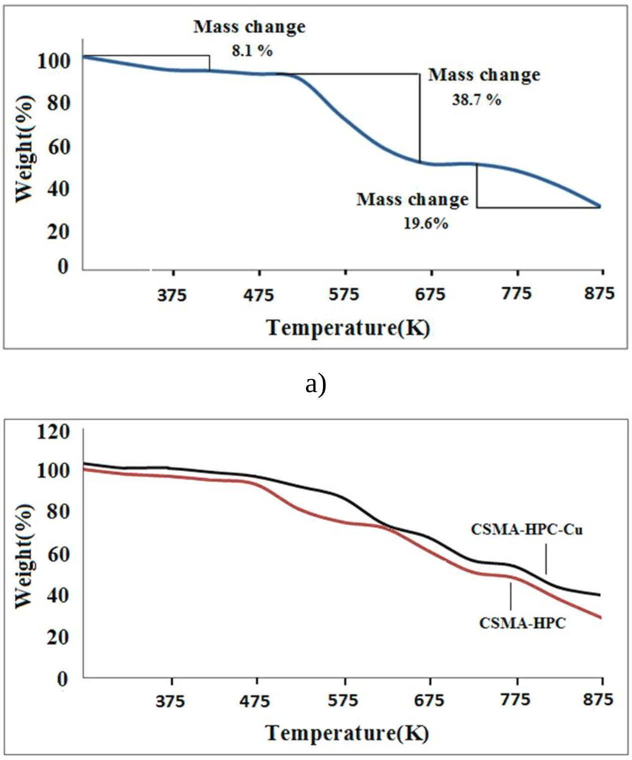


Fig. 6. The adsorption capacities and selectivity (%) of CSMA-HPC under competitive conditions at pH 5 (total metal ion adsorption capacity = 200 mg·g^{-1})

3.8. Thermal Gravimetry Analysis

The thermal degradation analysis of copolymers and their copper complexes was conducted with the heating rate of 10 K/min in the atmosphere of nitrogen. The decomposition behavior of prepared copolymers is shown in Fig. 7. The thermograms indicate that SMA-HPC (Fig 7a) are decomposed within three stages: 298–483 K (8.1 % mass change) could be assigned to the loss of adsorbed moistures, 503–663 K (38.7 % mass change) due to the degradation of grafted groups and 733–873 K (19.6 % mass change) relates to the degradation of the remaining copolymer chains. For CSMA-HPC, the initial weight loss at the temperature of about 503 K was assigned to the formation of acid anhydride functional group from the carboxyl groups with loss of water.[25] The second and last stage of weight loss attributed to the decomposition of aromatic groups, modifying, and cross-linking agents. The weight loss model of CSMA-HPC and its copper complex with maximum metal ion adsorption values up to 493 K was approximately the same, but between 503 and 873 K resin was decomposed stronger than the copper-resin complex (Fig. 7b). There remained mass CSMA-HPC-Cu complex (38 wt %) at 873 K related to the formation of copper oxide.



a)

b)

Fig. 7. TGA curves of SMA-HPC (a), CSMA-HPC and CSMA-HPC-Cu (b). Numbers represent pH at which maximum metal sorption was obtained

4. Conclusions

Chelating resins based on SMA were prepared by functionalization of the polymer by HPC as grafting agent and 1,2-diaminoethane as cross-linking agent for the removal of heavy metal ions such as Zn(II), Cu(II), and Pb(II) from aqueous solution. The adsorption behavior of resulting resins for selected metal ions was favored at the pH value of 5. Also, it can be seen that CSMA-HPC demonstrates high affinity for metal chosen ions regarding SMA-HPC at various pH values. The carboxylic acid group-containing resins could be applied for efficiently removing metal ions by electrostatic attractions forces and metal-binding organic ligand mechanisms. The comparative experiments between CSMA-HPC and similar adsorbent (CSMA-HPCA)[25] have been performed to demonstrate excellent CSMA-HPC adsorption performance. FT-IR and TGA studies on metal-resin complexes acknowledged the presence of metal in the cross-linking copolymer. The adsorption rate of prepared resins under specified conditions (pH = 5, temperature 298 K) was high, and the most considerable fraction of the adsorbed metal was attained within 30 min. It was found that sorption isotherms were better described by the Langmuir model, and the rate of adsorption obeyed the pseudo-second order rate equation. The prepared resin is reusable sorbent for the highly efficient adsorption of selected metal ions, which indicates that it is a good candidate for reuse in the removal of different metal ions from wastewater treatment systems.

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СИНТЕЗОВАНИЙ КОПОЛІМЕРНИЙ ПОХІДНИЙ ПОЛІ(СТИРЕН-АЛЬТ-МАЛЕЇНОВИЙ АНГІДРИД) ЯК НОВА ХЕЛАТИВНА СМОЛА ДЛЯ ВИДАЛЕННЯ ЙОНІВ ВАЖКИХ МЕТАЛІВ З ВОДНОГО РОЗЧИНУ

Анотація. *Хелатову смолу як новий кополімер для видалення йонів металів готували з використанням 3- (4-гідроксифеніл)циклопропан-1,1,2,2-тетракарбонової кислоти, 1,2-діаміноетану та полі(стирен-альт-малеїнового ангідриду). Параметри сорбційної поведінки досліджувались в різних умовах. Дослідження кінетики показали, що процес адсорбції підтвердив кінетику псевдодругого порядку, і дані адсорбції добре відповідали ізотермі Ленгмюра.*

Ключові слова: *адсорбція, хелатна смола, 3-(4-гідроксифеніл)циклопропан-1,1,2,2-тетракарбонова кислота, йони металів, полі(стирен-альт-малеїновий ангідрид).*