Introducing a New Co-polymeric Adsorbent with Fast Sorption Rate and High Sorption Capacity in Removal of Heavy Metal Ions: a Thermodynamic and Kinetic Study

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Highlights:

- A novel heavy metal co-polymeric adsorbent with a fast sorption rate and high sorption capacity was synthesized.
- The adsorption capacity of the synthesized polymer was investigated for Pb$^{2+}$ and Cd$^{2+}$.
- pH was a significant parameter that affects the adsorption of Pb$^{2+}$ and Cd$^{2+}$.
- The thermodynamic of metal adsorptions with various models were studied.
- Characteristic properties of this polymeric adsorbent are reusable.
Abstract
Heavy metal ions have been recognized as the most hazardous contaminants of water sources. In this study, a novel polymeric adsorbent based on 2-hydroxyethyl methacrylate (HEMA), acrylic acid (AA), and 1,4-butanediol dimethacrylate (BDDMA) was successfully synthesized and its efficiency in removal of selected heavy metal ions (Pb$^{2+}$ and Cd$^{2+}$) were investigated. The role of significant parameters such as pH, contact time, adsorbent dose, metal ions concentration and temperature on removing harmful metal ions were logically studied. Results showed that the amount of pH, contact time and polymer adsorbent dose had direct relation in adsorption of metal ions. While increasing metal ion concentrations have no significant effect in metal ions adsorption and that was fixed up to 15 mg/L. Adsorption isothermal process of the new polymeric adsorbent was studied by several selected models and also maximum values of adsorption capacities of the introduced adsorbent for Pb$^{2+}$ and Cd$^{2+}$ ions were characterized. Adsorption /desorption cycles of synthesized polymer adsorbent were around 15 times. According to the modeling of adsorption data, the pseudo-second-order kinetic equation could best describe the adsorption kinetics. According to the intra-particle diffusion studies adsorption of heavy metal ions might be dominated by external diffusion mechanism.

Keywords: Polymeric adsorbent, Heavy metal ions, Isotherm, Kinetic, Thermodynamics,

1. Introduction
Burning in jungles, volcanos, human being activities, industrial waste materials, phosphate fertilizers are some of the contaminant sources for Cd$^{2+}$ [1]. Cd$^{2+}$ can also cause various disorders in bones and lungs in the human body as well as other heavy metals and it reduces bacterial and viral resistance [2]. Pb$^{2+}$ is another highly toxic ion, which its exposure can produce a wide variety of substantial health effects for both adults and children. The presence of this ion can increase blood pressure, fertility problems, nervous disorders, muscle, and joint pains, and loss of memory in adults [3].

The presence of heavy metals ions in water sources may cause serious dangers in the environment and the health of mankind. Therefore, the elimination of heavy metal ions from the environment has been under the spotlight in recent years as an important subject of environmental chemistry [4].
The attraction of heavy metal ions such as Pb\(^{2+}\) and Cd\(^{2+}\) to alive beings create serious disordering in their metabolic process and shows some unusual happens [5].

To prevention of heavy metal ions pollution, different processes such as adsorption, chemical precipitation, coagulation, flocculation, electrodialysis, membrane filtration, ion exchange, etc. are applied [6-10].

Most of these techniques have some disadvantages such as expensive processes, producing toxic residues, and being energy/space consuming [11]. Among all existed techniques, using inexpensive adsorbents for the removal of toxic metal ions can be a cost-effective method [12].

Several inorganic and organic adsorbents such as zeolites, montmorillonite, clay minerals, trivalent and tetravalent metal phosphates, biosorbents, activated carbon, polymer-based adsorbent, polymer-inorganic hybrid adsorbents and so on. Among them, the polymer-based or polymeric adsorbents such as polyaniline (PANI), polyethyleneimine (PEI), polypyrrole (Ppy) and their composites have received considerable attention due to their potential applications in adsorbing various heavy metal ions, their facility for preparation and operation, appropriate stability, and relatively inexpensive [13]. Application of polyamidoamine–cyclodextrin in adsorption of heavy metal ions was introduced by Li and coworkers. In this manner, several effective factors on the performance of polymeric adsorbent were studied and their results showed that polyamidoamine–cyclodextrin has high potential in adsorption of harmful ions [14]. A Pyromellitic acid dianhydride/ N-(3-(trimethoxysilyl) propyl ethylene diamine (PMDA/TMSPEDA) hybrid polymeric nanocomposite was synthesized and applied by Alsohaimi and coworkers. They showed that this new adsorbent exhibited adequate behavior at heavy metal ions adsorption [15]. Also, polyampholyte hydrogel with applicable in sorption of heavy metal ions was synthesized by Zhou and coworkers. This adsorbent was tested and its performance in adsorption of selected heavy metal ions was evaluated [16].

According to scientific sources can be found that preparing and application of new polymeric adsorbents in removing heavy metal ions field were rarely reported. Therefore, in continuation of our previous works for the development of the novel adsorbents [17, 18], in this study, a new polymeric adsorbent with the base of the acrylate family was proposed. FTIR analysis showed that the 2-hydroxyethyl methacrylate - acrylic acid (AA) - 1,4-butanediol dimethacrylate (HEMA-AA-BDDMA) polymer was successfully synthesized. Activities of the synthesized adsorbent to removing of Pb\(^{2+}\) and Cd\(^{2+}\) ions were investigated at different conditions. Furthermore, the influence of different parameters such as pH, metal ion
concentrations, temperature, contact time, the mass of polymer, and the stirring speed was also examined. Finally, the isothermal process and kinetic studies on new adsorbent were studied with several proposed models.

2. Experimental

2.1. General

Reagents used in this study such as 2-hydroxyethyl methacrylate, 1,4-butane diol dimethacrylate, acrylic acid, AIBN, THF, Cd(NO$_3$)$_2$, Pb(NO$_3$)$_2$ and organic materials like HCl and NaOH were purchased from Merck with ultra-pure grade. Co (Germany). The material in this study was used as purchased with no further purification. Deionized water was used to make aqueous solutions of metal salts. Stock solutions of Pb$^{2+}$ (500 mg/L) and Cd$^{2+}$ (500 mg/L) were prepared by dissolution 0.0799 g of Pb(NO$_3$)$_2$ and 0.1374 g of Cd(NO$_3$)$_2$.4H$_2$O in deionized water, respectively, and also these solutions were diluted for preparing other solutions with different concentrations.

2.2. Measurements

Atomic absorption spectrometry (AAS- analytical jenanov AA400, fitted with lead and cadmium hollow cathode lamp, Germany) was used to detection of heavy metal ions. The related wavelengths for lead and cadmium in this spectroscopy were respectively 283.3 and 228.8. A digital pH meter (Metrohm 827, Switzerland) was applied for pH measurements and the pH results for each ion was adjusted with 0.1 NaOH or HCl standard solutions purchased from Merck. A horizontal bench shaker is used to be sure of proper exposure (Heidolph PROMAX 2020, Germany). The identification of chemical functional groups was performed by Fourier transform infrared spectroscopy (FT-IR- Nexus-670- Thermo Nicolet, USA). To study the crystal structure and morphology of the particles, X-ray diffraction (X pert Philips-Netherland). Scanning electron microscopy (SEM- MIRA3 TESCAN, Czech Republic) were utilized. Thermogravimetric Analysis (TGA) of the polymer was determined with a LENSES STA PT-1000 calorimeter (Germany) at a heating rate of 10°C/min up to 600°C under N$_2$ atmosphere.

2.3. Preparation of polymeric adsorbent

To synthesize the adsorbent polymer, 1 g (0.014 mol) acrylic acid and 1.822 g (0.014 mol) 2-hydroxyethyl methacrylate with 1.584 g (0.007 mol) 1,4-butane diol dimethacrylate as a crosslinker agent at a molar ratio of 1: 1: 0.5 in THF as solvent was degassed in the presence of Ar for 20 min and then AIBN as a primer added to the solvent. The obtained was then refluxed for 24 hours at the Ar atmosphere. With the termination of the polymerization process, due to the formation of the polymer, the product network is removed from the
solution. The obtained solution was filtrated and washed several times with THF for 24 hours and dried in a vacuum oven at 50 °C. Schematic of the synthesis process shown in scheme 1.

The swelling index (x) of the synthesized polymer was investigated and calculated using equation 1. Therefore, 0.5 g of HEMA-AA-BDDMA polymer was completely dried and dispersed in deionized water. It was then dried again after a certain time and the swollen polymer was weighed. The achieved results exhibit that the adsorption of water can be referred to as the polymer textural properties and functional groups, which are responsible for improvement or depreciation of hydrophilicity.

\[ x(\%) = \frac{M_s - M_d}{M_s} \times 100 \]  

(1)

Where \(M_s\) and \(M_d\) are the mass of swollen and dry polymer, respectively.

2.4. Adsorption investigations

Adsorption experiments were conducted with dispersing 10 mg of synthesized polymer in 10 ml of Cd\(^{2+}\) and Pb\(^{2+}\) solutions in a 50 ml beaker. Standard solutions were diluted to reach the solutions for experimenting. The aforementioned system was then stirred 200 rpm in ambient temperature. When the adsorption process was completed, the solutions were filtered and the concentration of the considered metal ions was measured by atomic absorption spectrometry. The obtained results were used to calculate the removal percent of metal ions in equation 2:

\[ \text{heavy metal ions removal (\%) } = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \]  

(2)

Where \(C_0\) and \(C_e\) are initial and equilibrium concentrations of metal ions, respectively.

2.5. Key adsorption parameters investigation

10 ml of solutions contained metal ions were utilized for investigation of pH effect on adsorption of Pb\(^{2+}\) and Cd\(^{2+}\), which their concentration was about 10mg/L. in this study, pH was adjusted in the range of 2-6 using HCl 0.1 N or NaOH 0.1 N and the solutions were stirred for 90 min after the addition of a certain amount of HEMA-AA-BDDMA polymer. The solutions were filtered with Whatman 42 paper when the adsorption process was completed and supernatant solutions were measured using atomic absorption spectrometry. The obtained results were the average value of four times the repetition of an experiment.
The adsorption experiments were performed in the time range of 10-180 min for the initial concentration of toxic metal ions (10 mg/L) in pH, 6. The optimum amount of added polymer to the solutions was 10 mg in a 50 ml beaker. The considered solutions were stirred at room temperature. A similar procedure with the previous section was utilized for the measurement of the adsorbed metal ions.

Different amount of adsorbent was used in this experiment for 10 ml of metal ion solutions with a concentration of 10 mg/L in pH = 6 for 90 min at room temperature. The samples were filtered and analyzed with atomic absorption spectrometry.

The influence of metal ion's initial concentration on the adsorption behavior of HEMA-AA-BDDMA polymer was also investigated. Various concentrations of metal ion solutions with constant volume (10 ml) were prepared (5-45 mg/L) and adsorption behavior of HEMA-AA-BDDMA polymer (10 mg) in pH = 6 was measured with atomic absorption spectrometer after stirring in room temperature for 90 min and filtration.

To study the effect of stirring speed on adsorption, 10 ml of metal ion solutions with a concentration of 10 mg/L with a certain amount of HEMA-AA-BDDMA polymer was stirred in pH = 6 at room temperature with various speeds of stirring (100-300 rpm) for 90 min. The obtained samples were analyzed according to the procedure described in previous sections using atomic absorption spectrometry.

The investigation of temperature effect on adsorption behavior was performed about the solutions with certain concentrations and volume in the temperature range of 10-40 degrees centigrade. It should be noticed that 10 mg of HEMA-AA-BDDMA polymer in pH = 6 was used during the temperature optimization for 90 min of contact time as an optimum time of adsorption. The obtained samples were analyzed with AAS after filtration.

2.6. Recycling and frequent application of the adsorbent

The desorption of metal ions from the surface of HEMA-AA-BDDMA polymer was established using a 0.2 M HCl solution. HCl solution contained polymer particles was stirred for 30 min until reaching equilibrium and the samples were analyzed using AAS. Desorption ration ($D$) of metal ions was calculated using equation 3:

$$D(\%) = \frac{C_d V_d}{(C_0 - C_e) V} \times 100$$  \hspace{1cm} (3)

Where $V$ is the solution volume, $C_d$ is the concentration of metal ions in the desorbed solution based on mg/L, and $V_d$ is the volume of desorbed solutions. The collected polymer from the
desorption process was washed with deionized water and dried for further use. This process was repeated 15 times.

2.7. **Equilibrium isotherms and kinetic studies**

Investigation of the isotherms was performed in the presence of 0.01 g HEMA-AA-BDDMA polymer in the solutions contained various concentrations of metal ions in pH, 6 for 90 min and their measurement with AAS. Equation 4 was used to measure the adsorbed metal ion \((q_e)\) by HEMA-AA-BDDMA polymer:

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]  

(4)

Where \(q_e\) is the adsorbed amount of metal ions based on mg/g, \(V\) is the solution volume (L), and \(m\) is the mass of the adsorbent. To investigate the kinetics of the adsorption process, the samples were isolated according to the aforementioned procedure and analyzed with AAS. The amounts of the adsorbed metal ions were calculated in the times, \(t\) and \(q_t\) using equation 5:

\[
q_t = \frac{(C_0 - C_t)V}{m}
\]

(5)

Where \(C_t\) is the concentration of metal ions in the solution after spending the time.

3. **Results and discussion**

3.1. **Synthesis and characterization of polymeric adsorbent**

The polymeric adsorbent was synthesized using radical polymerization. In the first step, two radicals are created from the AIBN. In the second step, radicals are transferred from the initiator molecules to the carbon-carbon double bonds of HEMA, AA, and BDDMA. Because BDDMA has two carbon-carbon double bonds, it can crosslink two polymeric chains. The structure of the targeted copolymer was schematically presented in scheme 2. From this Figure can be observed that the synthesized adsorbent has so many active ion-exchange sites that can be activated to the removal of heavy metal ions from aqueous solution. Microstructures of polymeric adsorbent were investigated by SEM images and have been shown in two different magnifications in Figure 1A, B. Monodispersity and spherical morphology of the particles has been clearly shown in these figures and diameters of particles were about 100 nanometers. XRD patterns of the prepared polymer have been shown in Figure 1C. There is only a moderate peak in 2\(\theta\)= 20, which is attributed to the amorphous
nature of the polymer. The diffusion of water molecules and metal ions from amorphous regions is very easier than crystalline structures. This is an important principle for the polymeric adsorbent.

The swelling behavior of the polymeric adsorbent was studied and obtained results were shown in Figure 1D. These results showed that the values of the swelling index of the synthesized polymer are acceptable for its application in the removal of heavy metal ions. Characteristic functional groups of the synthesized polymer and their ability in the attraction of metal ions were studied by FTIR analysis and obtained data was presented in Figure 2A. In this Figure, the FTIR spectrums of pure adsorbent, adsorbent-Pb$^{+2}$ and adsorbent-Cd$^{+2}$ have been exhibited. From the spectrum of the pure polymer can be seen that some remarkable peaks such as stretching bands of C=O (1635 cm$^{-1}$) related to carbonyls of esters groups, aliphatic C-H (2850-3000 cm$^{-1}$), and O-H (3400-3600 cm$^{-1}$) are observed. The methyl groups show a weak band at 1380 cm$^{-1}$ and a medium band at 1260 cm$^{-1}$. Comparing the position of these bands determined that the presence of metal ions is effective on the mentioned chemical bonds. For clarifying this reason, the FTIR spectrum between 1380 to 2200 cm$^{-1}$ was zoomed. From this Figure can be obtained that after adsorption of metal ions on the surface of the adsorbent, the peaks existed in 1635 cm$^{-1}$ and 1473 cm$^{-1}$ were sharpened and shifted to 1625 cm$^{-1}$ and 1465 cm$^{-1}$ respectively, which indicates that the strong bonds between polymer and metal ions were undoubtedly formed [19].

TGA and DTG thermo-grams for the synthesized polymer can be observed in Figure 2B. From this Figure can be found that the samples exhibited relatively a high degradation temperature and had various peaks that each one is representative for a specific kind of structural decomposition. In the polymer, the initial weight loss at a temperature of 150$^\circ$C is related to the loss of moisture of the polymer. The second weight loss at the temperature of 250$^\circ$C was attributed to the formation of acid anhydride from the carboxyl groups with a loss of water. The last step was the representative for the degradation of crosslinking agents.

3.2. Investigation of key parameters on adsorption of Pb$^{+2}$ and Cd$^{+2}$ ions

The most important parameters of adsorption such as pH, content time, the dosage of adsorbent, concentration of metal ions, temperature and agitating speed were tested that the results are as follows:

3.2.1. Sorption of Pb$^{+2}$ and Cd$^{+2}$ as a Function of pH
pH in aqueous solution plays an essential role in the adsorption phenomenon of heavy metal ions. In this study, the influence of pH in the range of 2 – 6 on adsorption of heavy metal ions was investigated, because metal ions can form hydroxide compounds in pH levels higher than 6 [20]. According to FTIR data, carboxyl groups of the synthesized polymer have a poor acidic property and their degree of protonation in acidic pH is moderate. Then it is obvious that there are no strong bonds between functional groups on polymer macromolecules and metal ions. This analysis was performed and results were presented in Figure 3. At first, a glance can be seen that increasing the amount of pH is an important factor in the adsorption of metal ions. In this Figure, the adsorption level in pH = 2, is about 0, while by increasing pH to 6, the adsorption of both metal ions does increase and in pH, 5-6 a constant state can be easily observed. The highest amount of adsorption for Pb\(^{2+}\) and Cd\(^{2+}\) in pH, 6 was 96.59% and 97.75 %, respectively. The reason for this observation can be attributed to the decreasing of hydrogen ions concentration is considered to range of pH and reducing the competition between H\(^{+}\), Pb\(^{2+}\) and Cd\(^{2+}\) ions in the formation of chemical bonds with functional groups of polymer adsorbent.

**3.2.2. Effect of Contact Time on Adsorption**

Another important factor in the adsorption of metal ions on solid surfaces of adsorbent is contact time. This factor was exactly studied on the efficiency of adsorbent in the time range between 0 to 180 min and obtained results were presented in Figure 4. From this Figure can be seen that in the initial moments of contact time, rapid adsorption for metal ions was observed and then the adsorption rate decreases gradually. The adsorption reaches the equilibrium in about 60-80 min. These observations could be explained by this fact that the adsorption values for metal ions increase with increasing the contact time, but the polymer chains aggregate with spending the time and the fraction of accessible sites for metal ions begin to decrease. Consequently, the penetration of metal ions into the polymer active sites is limited and the adsorption process reaches to equilibrium condition [21].

**3.2.3. Effect of Adsorbent Dosage**

The amount of polymer adsorbent has an important factor on the adsorption of Pb\(^{2+}\) and Cd\(^{2+}\) from aqueous solutions. The results are shown in figure 5. The obtained results demonstrated that the adsorption performance of the synthesized polymer increases gradually by increasing the amount of polymer. This result is expected because the increasing concentration of adsorbent provides more surface area and subsequently, more active sites for adsorption of metal ions [22].
3.2.4. Effect of Metal Ion Concentration

The adsorption rate is a function of metal ion concentration and this can be regarded as an important factor, the related results are demonstrated in Figure 6. Generally, these results demonstrated that increase metal ion concentration to about 15mg/L was lead to constant value adsorption and this can be attributed to the saturation of active sites of synthesized polymer in high heavy metal ions concentrations. For a better understanding of this argument can attention to networked structures of the polymer in Scheme. 2.

3.2.5. Effect of Temperature on metal ions Adsorption

To investigate the influence of temperature on the adsorption process, solutions with the concentration of 10 mg/L were prepared in different temperatures (10-45 °C) in pH, 6. The obtained results are shown in Figure 7 and these results indicate that increasing temperature improves the adsorption of heavy metal ions. It can be stated that the adsorption process in this study is endothermic.

3.2.6. Effect of stirring speed on metal ions Adsorption

Effect of speeds of stirring (100-300 rpm) on heavy metal ions adsorption at constant volume and concentration were studied and results were presented in Figure 8. As shown in this Figure, increasing stirring speed leads to an increase in heavy metal ions adsorption. The highest rate of adsorption was observed at the speed of about 200 rpm and it was 94.26% and 94.95% respectively for Pb^{2+} and Cd^{2+}. It can be claimed that increasing stirring speed may increase the probability of collisions between adsorbent particles and metal ions and decrease the thickness of barrier film.

3.3. Desorption and frequent use of newly synthesized adsorbent

Recyclability is an important factor for many adsorbents and most of them possess high adsorption capacities as well as good desorption properties. The property of desorption is a valuable option from an economic point of view. As seen in Figure 9, the desorption process of metal ions from the synthesized polymer is a function of time and this process reaches equilibrium after 30 min and desorption ratio of Pb^{2+} and Cd^{2+} is respectively 95.48% and 93.52%. The reusability of adsorbent with consecutive cycles of adsorption/desorption (15 times) was studied in present work and as shown in Figure 10, there is no significant loss in adsorption capacity of metal ions was observed during these experiments.

3.4. Calculation of equilibrium distribution coefficients (K_d) of new adsorbent
Distribution coefficient \( K_d \) can be regarded as a criterion for the affinity of polymer adsorbent to metal ions following equation 6 [23]:

\[
K_d = \frac{\text{amount of metal ion in the adsorbent \times V}}{\text{amount of metal ion in solution \times m}}
\]  

(6)

Where \( V \) is the solution volume based on ml and \( m \) is the mass of adsorbent based on (g). The values of \( K_d \) are listed in Table 1 for \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \). According to this obtained result, high values of \( K_d \) exhibits that the concentration of metal ions in the solid phase is high and this means that a high amount of adsorbent is present in the solid phase. This indicates a high capacity of adsorption by the polymer.

### 3.5. Modeling of Adsorption isothermal data of new adsorbent

Numerous mathematical models have been applied to describe the experimental data of adsorbents in isothermal conditions. In this section, several models such as Langmuir [24], Freundlich [25], Temkin [26] and Dubinin & Radushkevin [27] were selected.

#### 3.5.1. Langmuir Isotherm

Langmuir's model is widely used in several adsorption processes concerning heavy metal ions. Langmuir's model can be expressed by equation 7 [24]:

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \left( \frac{1}{q_m} \right) C_e
\]  

(7)

Where \( C_e \) is the equilibrium concentration (mg/L), \( q_e \) is the amount of adsorbed metal ions in the equilibrium state (mg/g), \( q_m \) is the highest capacity of adsorbent (mg/g), and \( K_L \) is the Langmuir's constant, which is adsorption dependent. The plot of Langmuir adsorption isotherm for this work was shown in Figure 11. The slope and the ordinate can be respectively regarded as \( K_L \) and \( q_m \) for \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \). The results of these calculations have presented in Table 2. It should be mentioned that the best consistency for both of the cations was achieved with Langmuir's model. The separation factor of the Langmuir model can be calculated with equation 8:

\[
R_L = \frac{1}{1 + K_L C_0}
\]  

(8)
Where \( C_0 \) is the initial concentration of metal ion (mg/L) and \( K_L \) is the Langmuir's constant (L/mg). Figure 12 shows the results of the separation factor, which is depended on the concentration of metal ions. The values of \( R_L \) determine the kind of isotherm, which can be reversible \((R_L = 0)\), favorable \((0 < R_L < 1)\), linear \((R_L = 1)\), and/or unfavorable \((R_L > 1)\). These values were calculated for metal ions to be lower than 1, which indicates that synthesized polymer has favorable adsorption.

### 3.5.2. Freundlich Isotherm

Another selected model for adsorption of heavy metal ions is the Freundlich model. The related model indicates heterogeneity in the surface of the adsorbent and can be presented by equation 9:

\[
\log q_e = \frac{1}{n} \log C_e + \log K_F
\]  

(9)

Where \( K_F \) and \( l/n \) are the experimental constants for the Freundlich equation, which indicate respectively the relative capacity of adsorption and adsorption intensity. Applying this model to experimental data was done and results were exhibited in Figure 13. The Freundlich equation constants can be calculated from the slope and the ordinate of this line. Values of \( K_F \) and \( n \) for \( Pb^{2+} \) and \( Cd^{2+} \) ions can be obtained and have been presented in Table 2. As seen in the previous section, the best fit was observed for Langmuir’s model compared with Freundlich isotherm.

### 3.5.3. Temkin Isotherm

The Temkin model was selected for obtaining related interaction parameters between adsorbent and metal ions. The linear form can be expressed as equation 10:

\[
q_e = B_T \ln A_T + B_T \ln C_e
\]  

(10)

In the above equation, \( B_T \) is the difference between adsorption energies (kJ/mol) and \( A_T \) is Temkin constant (L/g), which is related to maximum energy \[28\]. Temkin model was applied on experimental data and their results have been presented in Figure 14 and also slope and ordinate of obtained lines were reported in Table 2. According to these data, the value of \( A_T \)
for Cd\textsuperscript{2+} is higher than Pb\textsuperscript{2+}, which is attributed to the influence of the ion exchange process during polymer-metal interactions, which is higher for Cd\textsuperscript{2+} compared with Pb\textsuperscript{2+}.

### 3.5.4. Dubinin & Radushkevich Isotherm

The Dubinin & Radushkevich model for approximation adsorption free energy (E) for heavy metal ions adsorption was studied. The supporting linear equation for this model can be expressed as equation 11 [29]:

\[
\ln C_{ads} = \ln X_m - \beta S^2
\]  

(11)

Where \( C_{ads}, X_m, \beta, \) and \( S \) are the number of heavy metal ions adsorbed in the mass unit of polymer (mol/g), maximum adsorption capacity (mol/g), constant of adsorption energy (mol\textsuperscript{2}/kJ\textsuperscript{2}), and Polanyi's potential respectively. The parameter of \( S \) from the above equation can be obtained from equation 12:

\[
S = RT \ln \left( 1 + \frac{1}{C_e} \right)
\]  

(12)

Where \( R \) is the global constant of gasses (kJ/mol) and \( T \) is the absolute temperature. Using slope and the ordinate of the curve, \( \ln C_{ads} vs S^2, \beta, \) and \( X_m \) can respectively be obtained. The experimental results are indicated in Figure 15.

The straight lines obtained were useful in calculating the D–R isotherm constants, which are given in Table 2. Adsorption energy can also be calculated through equation 13:

\[
E = \frac{1}{\sqrt{-2\beta}}
\]  

(13)

Free energy for the adsorption of Pb\textsuperscript{2+} and Cd\textsuperscript{2+} was 1.58 kJ/mol and 2.24 kJ/mol, respectively and these values are lower than 8 kJ/mol and it can be dedicated that the physical adsorption is predominant in this study.

### 3.6. Kinetic study of new adsorbent

It was found that the adsorption process can be effective in the removal of different contaminants from aqueous solutions. The kinetic predictions of closed equilibriums are considerable for designing adsorption systems.
3.6.1. Pseudo-first order model

The model of pseudo-first-order equation for investigation of the kinetic study of heavy metal ions adsorption was selected and its linear form can be expressed as the equation 14 [30]:

$$\log(q_e - q_t) - \frac{K_1}{2.303}t$$  

(14)

Where $q_e$ is the adsorbed metal ions in the equilibrium state (mg/g), $q_t$ is the adsorbed metal ions in time, $t$, and $K_1$ is the rate constant for pseudo-first-order equation ($1/min$). The slope of the curve, log ($q_e$-$q_t$) against $t$ was shown in Figure 16. The values of $K_1$ parameters for target ions were obtained and reported in Table 3. The values of $R^2$ are relatively low and the calculated $q_e$ has a good agreement with the experimental values.

3.6.2. Pseudo-second order model

Ho and McKay in 2000 proposed a second-order equation for adsorption systems contained bivalent metal ions [31], which was based on the amount of adsorbed material on the adsorbent. The linear form of the equation can be expressed as equation 15:

$$\frac{1}{q_t} = \frac{1}{K_2q_e^2} + \frac{1}{q_e}t$$  

(15)

In this equation, $k_2$ is the second-order rate constant and $q_t$ is the amount metal ions adsorbed in the time, $t$. Kinetic constants of pseudo-second-order equation ($K_2$ and $q_e$) can be plotted in the curves, $t/q_t$ vs. $t$ (Figure 17). The kinetic investigations for adsorption of Pb$^{2+}$ and Cd$^{2+}$ from aqueous solutions have a good consistency with pseudo-second-order equations proposed by ho (Table 3).

High amounts of $R^2$ and their good adaptation with $q_e$ and related experimental data confirm that the mechanism of adsorption using new adsorbent polymer follows pseudo-second-order.

3.6.3. Investigation of Intra-particle diffusion kinetic

This model is often used to investigate the determining step in the adsorption process and first presented by Vir and Moris (equation 16) [32]:

$$q_t = k_{pi}t^{1/2} + C_i$$  

(16)
Where $k_{pi}$ is intra-particle diffusion constant (mg/g min$^{1/2}$) and $C_i$ is another constant for the thickness of the barrier layer (mg/g). They can be obtained respectively from the slope and ordinate of the curve, $q_t$ vs. $t^{1/2}$ and obtained results showed in Figure 18.

As can be seen, this curve is multi-lines for Pb$^{2+}$ and Cd$^{2+}$, which indicates that the adsorption process is governed by more than one step. Based on these curves, the adsorption process of these two metal ions is comprised of two steps. Therefore, the intra-particle kinetic model isn't the sole and determining step during the reaction [33]. The first sharp section of the curve shows the diffusion of metal ions to the internal surface of adsorbent (liquid film diffusion). The second part of the curve is responsible for the diffusion of metal ions into the pores of adsorbent (intra-particle diffusion), the slowest and determining step in the rate of reaction [34]. The obtained results of this model have been listed in Table 3. Based on these results, for both metal ions, $K_{pl}$ is higher than $K_{p2}$, the concentration of metal ions present in the solution decreases rapidly.

3.6.4. The validity of kinetic models

To find the best model for the description of Pb$^{2+}$ and Cd$^{2+}$ adsorption mechanism on the surface of the synthesized polymer, the percent of normal standard deviation (SD %) was used by the equation 17 [35]:

$$SD(\%) = 100 \times \left\{ \frac{\sum (q_{e,exp} - q_{e,calc})^2}{N - 1} \right\}^{1/2}$$

Where $q_{e,exp}$ is the equilibrium adsorption capacity (mg/g), $q_{e,calc}$ is the calculated adsorption capacity (mg/g), and $N$ is the points of data. Based on the results of Table 3, the values of obtained SD for the pseudo-first-order kinetic model are higher than those obtained for the pseudo-second-order model. Furthermore, higher values for $R^2$ in the pseudo-second-order model indicate that this model is the most appropriate equation for the description of adsorption kinetics of Pb$^{2+}$ and Cd$^{2+}$ using synthesized polymer. Consequently, the total rate of adsorption process is controlled by chemical adsorption, including covalent forces originated by sharing or exchange electrons between the adsorbent and the adsorbed material [36].

3.7. Thermodynamic adsorption study
Free energy and enthalpy are the important factors, which should be determined during an adsorption process and any other unexpected event. These parameters are the actual criterion for adsorption processes. The adsorption capacity depends on these thermodynamic parameters. The calculation of the adsorption thermodynamics using Wanthof method can be performed by the equations 18 – 20:

\[ K_c = \frac{C_A}{C_S} \]  

\[ \Delta G^0 = -RT \ln K_c \]  

\[ \ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \left( \frac{1}{T} \right) \]  

In above equations, \( K_c \) is equilibrium constant, \( C_A \) is the concentration of the adsorbed metal ions on the surface of adsorbent at equilibrium state (mol/L), \( C_s \) is the concentration of metal ions present in the solution at equilibrium state (mol/L), \( \Delta G^0 \) is representative of standard free energy (kJ/mol). \( \Delta S^0 \) and \( \Delta H^0 \) are respectively the standard entropy (kJ/mol) and enthalpy (kJ/mol) [37]. To calculate the related parameters, the slope and the ordinate of the Vant hoof graph are required and drawing \( \ln K_c \) vs. \( 1/T \) could obtain these values (Figure 19).

Increasing the values, \( T \) may decrease the value of \( K \) [38, 39]. The calculated values for the aforementioned thermodynamical parameters are given in Table 4. The positive numbers for \( \Delta H \) demonstrate that the adsorption process is endothermic and the possibility of strong bonding between metal ions and adsorbent exists. The obtained data also show that the adsorption process is temperature-sensitive.

The positive values of entropy indicate the tendency of adsorbent to the material being adsorbed and some structural variations in these species. These values are evidence that the reaction is being proceeded toward the increasing chaos. The temperature and \( \Delta G^0 \) have an inversed relationship with each other and the reaction tends to be performed spontaneously with increasing temperature.

### 4. Conclusion

A newly synthesized polymer adsorbent was introduced and its application in heavy metal ions investigated. Adsorption of Pb\(^{2+}\) and Cd\(^{2+}\) by synthesized polymer is found to be
effective in the pH range of 2–6. By increasing the adsorbent dose from 0.5 to 3.0 g/L, the removal percentage of heavy metal ions increased. The removal percentage increased with time up to 60–80 min and after this time it remains constant. The Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherms equilibrium data have been applied on experimental data and the characteristic parameters for each isotherm and related correlation coefficients have been determined. The Excellent fits were shown within the following isotherms order: Langmuir > Freundlich > Temkin > Dubinin–Radushkevich, based on its correlation coefficient values. The adsorption energy from the Dubinin–Radushkevich isotherm was found at 1.58 and 2.24 kJ/mol for Pb²⁺ and Cd²⁺, respectively. For investigating the adsorption mechanism, three simplified kinetic models, pseudo-first-order, pseudo-second-order, and intra-particle diffusion, were tested. The pseudo-second-order kinetic model fits very well with the dynamical adsorption behavior of Pb²⁺ and Cd²⁺ ions based on the highest R2 values. According to the results, the HEMA-AA-BDDMA polymer is a reusable polymer that has a good potential for adsorption of metal ions up to 15 cycles by maintaining performance. Using this polymer for the removal of toxic metal ions has approximately high efficiency and this is a simple, green, and clean technology method and maybe can provide a strategic approach to remove heavy metal ions from industrial sewage. It can also be used for separating Pb²⁺ and Cd²⁺ ions in separation columns because of its high adsorption and desorption properties.

References


Dr. Vahabodin Goodarzi is affiliated to the Applied Biotechnology Research Center, Baqiyatallah University of Medical Sciences, Iran. He is currently providing services as Assistant Professor has authored and co-authored multiple peer-reviewed scientific papers and presented works at many national and international conferences. Dr. Vahabodin Goodarzi's contributions have acclaimed recognition from honorable subject experts around the world. He is actively associated with different societies and academies. Dr. Vahabodin Goodarzi's academic career is decorated with several reputed awards and funding. Dr. Vahabodin Goodarzi's research interests include Medical Science.

Reza Abdolahi studied for a bachelor's degree in applied chemistry at Urmia University during 2012-2016. After completing the undergraduate course, he was studying for a master's degree at Urmia University for two years, when he finally received my degree in analytical chemistry in 2018. During these two years, he studied the synthesis of some polymeric adsorbents and their effect on the removal of heavy metals from water. In recent work, he
synthesized a novel polymeric adsorbent based on 2-hydroxyethyl methacrylate and tested its efficiency in the removal of Pb\(^{2+}\) and Cd\(^{2+}\).

Dr. Mohammad Hadi Baghersad is an assistant professor at the Applied Biotechnology research center, Baqiyatallah University of Medical Sciences. He researched the synthesis of novel organic compounds and polymers. Still, the applicable and useful ones are further in his interest, such as molecularly imprinted and ion absorbent polymers, biodegradable and – compatible polymers, polymer grafted – nanoparticles, and organic molecules such as pharmaceuticals, potentially drugs, plasticizers and so on.

List of captions:

Scheme captions:

Scheme 1 Synthesis process of copolymer

Scheme 2 Structure of synthesized polymer

Figure captions:

Figure 1. SEM images of polymer (A) scale = 1 μm, (B) scale = 2 μm, (C) XRD patterns of the synthesized polymers and (D) Swelling index of the polymer

Figure 2. (A) FT-IR spectra of polymer before and after complexation with Pb(II) and Cd(II). (b) Expanded FT-IR spectrum and (B) TGA/differential thermograms of the polymers

Figure 3. Effect of pH value on metal ions adsorption onto polymer ([Pb\(^{2+}\)] = 10 mg/L, [Cd\(^{2+}\)] = 10 mg/L, adsorbent dose = 1 g/L, contact time = 90 min).

Figure 4. Effect of contact time on the adsorption of heavy metal onto polymer ([Pb\(^{2+}\)] = 10 mg/L, [Cd\(^{2+}\)] = 10 mg/L, adsorbent dose = 1 g/L, pH = 6).

Figure 5. Effect of adsorbent dose on metal ions adsorption by polymer ([Pb\(^{2+}\)] = 10 mg/L, [Cd\(^{2+}\)] = 10 mg/L, contact time = 90 min, pH = 6).

Figure 6. Effect of concentration of metal ion on metal ions adsorption by polymer (adsorbent dose = 1 g/L, contact time = 90 min, pH = 6)

Figure 7. Effect of temperature on metal ions adsorption by polymer ([Pb\(^{2+}\)] = 10 mg/L, [Cd\(^{2+}\)] = 10 mg/L, adsorbent dose = 1 g/L, contact time = 90 min, pH = 6)

Figure 8. Effect of agitating speed on adsorption of heavy metal ions ([Pb\(^{2+}\)] = 10 mg/L, [Cd\(^{2+}\)] = 10 mg/L, adsorbent dose = 1 g/L, contact time = 90 min, pH = 6).

Figure 9. Desorption of metal ions from polymer-metal ions complex by 0.5M HCl solution
Figure 10. Removal of metal ions after repeated adsorption-desorption operations at 25°C ([Pb$^{2+}$] = 10 mg/L, [Cd$^{2+}$] = 10 mg/L, adsorption time 90 min, pH = 6, adsorbent dose = 1 g/L).

Figure 11. Langmuir isotherms for Pb(II) and Cd(II) adsorption onto polymer (pH = 6, time = 90 min, resin dose = 1 g/L).

Figure 12. Separation factor (RL) profile for biosorption of Pb(II) and Cd(II) as function of concentration of metal ion (pH = 6, time = 90 min, resin dose = 1 g/L).

Figure 13. Freundlich isotherms for Pb(II) and Cd(II) adsorption (pH = 6, time = 90 min, resin dose = 1 g/L).

Figure 14. Temkin isotherms for adsorption of Pb(II) and Cd(II) (pH = 6, time = 90 min, resin dose = 1 g/L). and (C).

Figure 15. Dubinin–Radushkevich isotherms for adsorption of Pb(II) and Cd(II) (pH = 6, time = 90 min, resin dose = 1 g/L).

Figure 16. Pseudo-first-order plot for Pb(II) and Cd(II) adsorption (pH = 6, concentration of metal ions = 10 mg/L, resin dose = 1 g/L).

Figure 17. Pseudo-Second-order plot for Pb(II) and Cd(II) adsorption (pH = 6, concentration of metal ions = 10 mg/L, resin dose = 1 g/L).

Figure 18. intra-particle diffusion plot for Pb(II) and Cd(II) adsorption (pH = 6, concentration of metal ions = 10 mg/L, resin dose = 1 g/L).

Figure 19. The plot of log $K_C$ against 1/T for the adsorption of Pb(II) and Cd(II) metal ions onto the polymer.

Table captions:

Table 1 Distribution coefficient, $k_d$, of toxic metal ions adsorption by the polymer.

Table 2 Isotherm parameters for the adsorption of Pb(II) and Cd(II) ions onto the polymer.

Table 3 Kinetic parameters for the adsorption of Pb$^{2+}$ and Cd$^{2+}$ ion onto the polymer.

Table 4 Thermodynamic data for Pb$^{2+}$ and Cd$^{2+}$ adsorption onto the polymer.
Scheme 1

Scheme 2
Figure 1.
Figure 4

Figure 5

Figure 6

Figure 7
### Table 1

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### Table 3

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