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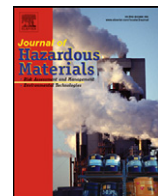
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The study of adsorption characteristics Cu^{2+} and Pb^{2+} ions onto PHEMA and P(MMA-HEMA) surfaces from aqueous single solution

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ABSTRACT

The adsorption characteristics of Cu^{2+} and Pb^{2+} ions onto poly(2-hydroxyethyl methacrylate) (PHEMA) and copolymer 2-hydroxyethyl methacrylate with monomer methyl methacrylate (P(MMA-HEMA)) adsorbent surfaces from aqueous single solution were investigated with respect to the changes in the pH of solution, adsorbent composition (changes in the weight percentage of MMA copolymerized with HEMA monomer), contact time and the temperature in the individual aqueous solutions. The linear correlation coefficients of Langmuir and Freundlich isotherms were obtained. The results revealed that the Langmuir isotherm fitted the experimental results better than the Freundlich isotherm. Using the Langmuir model equation, the monolayer adsorption capacity of PHEMA surface was found to be 0.840 and 3.037 mg/g for Cu^{2+} and Pb^{2+} ions and adsorption capacity of (P(MMA-HEMA)) was found to be 31.153 and 31.447 mg/g for Cu^{2+} and Pb^{2+} ions, respectively. Changes in the standard Gibbs free energy (ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) show that the adsorption of mentioned ions onto PHEMA and P(MMA-HEMA) are spontaneous and exothermic at 293–323 K.

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1. Introduction

The discharge of toxic heavy metal ions into the environment is a serious pollution problem affecting water quality. Major sources of water pollution with heavy metals are plating plants, mining, metal finishing, welding and alloys manufacturing [1]. Several methods have been applied during many years for the elimination of these metal ions present in the industrial wastewaters. The traditional methods commonly used for removal of heavy metal ions from aqueous solution include ion-exchange [2], solvent extraction, chemical precipitation [3], nano-filtration [4], reverse osmosis [5] and adsorption [6–8].

Precipitation methods are particularly reliable but require high installation cost (large settling tanks for the precipitation) and usually a further treatment is also needed, in order to meet the law requirements. Adsorption, which is a more sophisticated technique, has the advantage of allowing the recovery of metallic ions, though is sometimes more expensive than the other techniques. Studies on the treatment of effluents containing heavy metals have revealed the adsorption to be a highly effective technique for the removal of heavy metals from wastewater. Additionally, adsorp-

tion is a more economic process, simple to design and easy to operate [9]. Copper ions are of particular interest because of its toxicity and widespread presence in the industrial applications, e.g. electrical, electro-plating, metal finishing and paint industries. The toxicity of copper may cause itching and dermatitis, keratinization of the hands, and the soles of the feet [10]. Therefore, the concentration of this ion must be reduced to the levels satisfying environmental regulations for various bodies of water. Lead ions are one of the major environmental pollutants. It is mainly discharged from exhaust gases of automobiles to environment [11]. Moreover, it diffuses to the water and environment through effluents from lead smelters, battery manufacturers, paper and pulp industries and ammunition industries [11]. In recent years, various adsorbents have been used for removal of Cu^{2+} and Pb^{2+} ions from aqueous solutions. However, new adsorbents which are locally available, and have high adsorption capacity are still needed [12,13]. Several authors have reported studies on various adsorbents. A number of adsorbent materials such as activated carbon derived from fertilizer waste [14], tea factory waste [15], kaolinite [16], phenolated wood resin [17], modification of cellulose [18], and bagasse fly ash [19], zeolites [20] and modified jute [21] has used in heavy metal removal from wastewaters. The obvious advantage of adsorption method is the lower costs involved. Hence, it is a need to search for more economical and effective adsorbents [22].

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Hydrogels that are cross-linked hydrophilic polymers have been widely used in application field from agriculture to controlled delivery systems [23], adsorption of protein in medicine application [24] and removal of some ions from aqueous solution for environmental application and wastewater [25,26]. Among the potential adsorbents for removal of heavy metal ions such as Cu^{2+} and Pb^{2+} ions aqueous, polymeric adsorbents with high surface area and pore structure have proved to be the promising candidates [27,28]. Yun Tian showed that synthetic polycationic P(DMAEMA/HMEA) were capable of removal more than 99.5% of the nitrate ions from aqueous solutions [29]. Salih et al. has been illustrated that for the effective removal of heavy metals ions poly(EGDMA/HEMA) can be used [30]. Polymers which can selectively adsorb metal ions should consist of two monomer groups, each having a different role. One group forms a complex with the target (adsorption part) and the other allows the polymers to stretch and shrink reversibly in response to environmental change (the responsive part). Generally, 2-hydroxyethyl methacrylate is chosen as the responsive monomer. Polymers with the interpenetration network structure were also studied to investigate adsorption of heavy metal ions [31,32].

There are various possible interaction effects between different species in solution and the surface depending on the adsorption mechanism. Factors that affect the preferences for an adsorbate may be related to the characteristics of the binding sites (e.g. functional groups, structure, surface properties, etc.), the properties of the adsorbate (e.g. concentration, ionic size, ionic weight, ionic charge, molecular structure, ionic nature or standard redox potential, etc.) and solution specifications (e.g. pH, ionic strength, etc.) [33–35].

The goal of the present work is to investigate the adsorption potential of PHEMA and P(MMA-HEMA) surfaces for removal of Cu^{2+} and Pb^{2+} ions in the individual aqueous solutions. Firstly (PHEMA and P(MMA-HEMA)) surfaces were synthesized and then effect of pH, HEMA/MMA ratio, contact time and temperature on the adsorption capacity of PHEMA and P(MMA-HEMA) surfaces were studied. The Langmuir and Freundlich isotherm models were used to describe equilibrium data. The adsorption mechanisms of Cu^{2+} and Pb^{2+} ions from aqueous solution onto PHEMA and P(MMA-HEMA) surfaces were also evaluated in terms of thermodynamics.

2. Experimental

2.1. Characterization of adsorbent

The materials used in the experiments were as follows: the MMA and HEMA from Sigma Company were used as monomers to prepare the polymers in the presence of ammonium peroxy disulfate (APS), and sodium disulfite (SDS) as initiator, ethylene glycol dimethacrylate (EGDMA) as cross-link agent (all from Merck Company). For synthesis of poly(HEMA) 99.5% (w/w) HEMA as monomer and 0.5% percent weight EGDMA as cross-link agent, APS and SDS as initiators were used. Also for synthesis of poly(MMA-HEMA), the weight percentage of MMA and HEMA monomers was changed. Surfaces with (1%MMA-HEMA), (2%MMA-HEMA), (3%MMA-HEMA), (4%MMA-HEMA) and (5%MMA-HEMA), were prepared. The amount of EGDMA was fixed at 0.5%, then APS and SDS used as initiators for all surfaces. Then all surfaces are dried at 105°C for 24 h. Also all surfaces were washed with distilled water several times to remove dust and other water-soluble impurities. The same process for preparation of the surfaces was reported frequently [36–39]. P(HEMA) and P(MMA-HEMA) were used as similar disk-shaped sheets of 1 g of weight. Here after in all experiments, the amount of adsorbents refer to the above expressed. It is notable that, PHEMA has neutral surface charge, but P(MMA-HEMA) has negative charge, because MMA is a polar monomer containing carboxylate group [36,40].

2.2. Adsorption procedure

In this section, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$ were used from Merck Company. Sodium dihydrogen phosphate, phosphoric acid, ammonium acetate, acetic acid, ammonium chloride and ammonia were used to prepare different basic and acidic buffer solution. All components were purchased from Merck Company with purity more than 99.99%. Quality assurance of analytical measurements was performed in this study. Lead and copper atomic spectroscopy standard solution of $1000\text{ mg/L} \pm 0.3\%$ were used for measurements. Calibration curves between 10 and 50 mg/L were prepared and detection limit were found as 1 mg/L. Precision of the parallel measurements were as $\pm 3\%$ SD. Initial solutions with different concentration of Cu^{2+} and Pb^{2+} ions were prepared by proper dilution from 1000 mg/L standards. All the adsorption processes were carried out in 100 mL of ion containing solutions. To determine the amount of ions adsorbed onto the surfaces, the difference between the initial and the equilibrium ion concentration by atomic absorbance spectrophotometry AAS (Perkin-Elmer AAnalyst 700) was measured ($\pm 0.01\%$). The concentrations of the adsorbed ions onto surfaces were determined through a calibration curve for the known ions concentration in the individual aqueous solution. The surfaces (PHEMA and P(MMA-HEMA)) were treated by ion solution individually and contents in the sample solution were shaken for the desired contact time in an electrical thermostatic shaker at 110 rpm for all experiments. The adsorption percentage of metal ion was calculated as follows:

$$\text{Adsorption (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and final metal ion concentrations, respectively. The experiments were repeated at 293, 303, 313 and 323 K. In this work, the contact time was varied from 10 to 160 min; the pH of the solution from 2 to 10, and the initial metal concentration from 10, 20, 30, 40 and 50 mg/L. In all of the experiments double distilled deionized water (Milli-Q treated) was used and pH-meter (M-12) from HORIBA Company for controlling the pH of the solution (± 0.01) was applied.

3. Results and discussion

3.1. Effect of contact time

In order to optimize contact time for the adsorption, PHEMA and P(1%MMA-HEMA) surfaces were prepared. The surfaces were treated by Cu^{2+} and Pb^{2+} ions solutions with 10 mg/L of concentration, in pH 6 and $T = 303 \pm 1\text{ K}$. The concentration of adsorbed ions on the surfaces was analyzed by AAS. Fig. 1 shows the amount of Cu^{2+} and Pb^{2+} ions adsorbed as a function of contact time. It

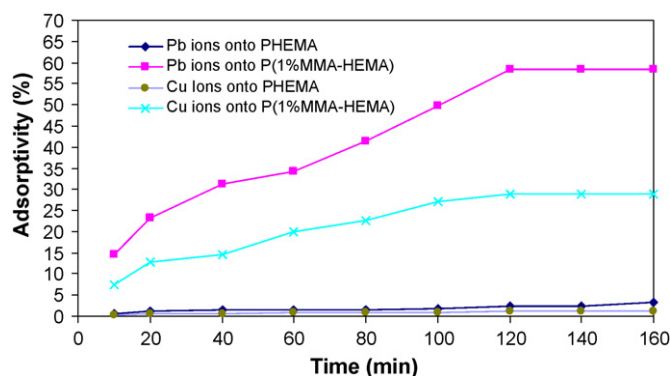


Fig. 1. Effect of contact time on the adsorption Cu^{2+} and Pb^{2+} ions onto PHEMA and P(1%MMA-HEMA) surfaces (metal ions concentration, 10 mg/L; pH 6; $T = 303 \pm 1\text{ K}$).

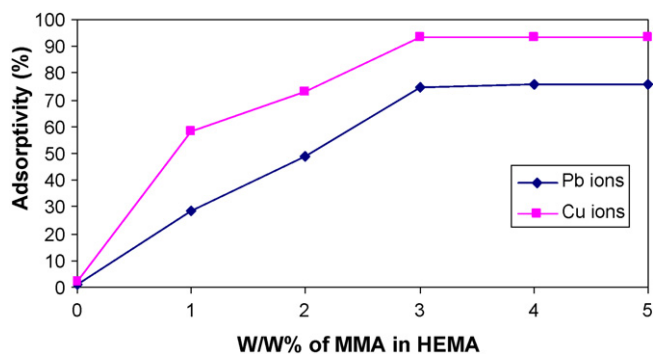


Fig. 2. Effect of adsorbent composition on the adsorption of Cu^{2+} and Pb^{2+} ions (metal ions concentration, 10 mg/L; pH 6; $T = 303 \pm 1$ K and contact time = 120 min).

can be seen that the amounts of Cu^{2+} and Pb^{2+} ions adsorbed onto P(1%MMA-HEMA) are more than the amounts were adsorbed by PHEMA surface, since both metal ions have positive charge and P(1%MMA-HEMA) has negative surface charge, this result may be expected. It seems that attractive interaction has the main role in the adsorption process, since PHEMA has a neutral surface [36,40]. Also, with increasing the contact time to 120 min, the percentage of adsorption increased. Giving time more than 120 min, the amount of adsorbed ions remained unchanged. So, this duration was chosen as the optimum contact time for all further experiments. The same equilibrium times have been reported in several earlier works which related to the adsorption of Cu^{2+} and Pb^{2+} ions on various adsorbents [41,42].

3.2. Effect of adsorbent composition

When the ions in solution contact another phase (solid, liquid, or a gas) which is immiscible, the ions tend to accumulate at the interface of two phases. This tendency has a great effect on various natural and technological processes. Adsorption of ions takes place almost instantaneously when a solid surface comes into contact with most aqueous solutions [43]. Adsorbent composition plays an important role in the adsorption process. The effect of adsorbent composition on the adsorption percentage of Cu^{2+} and Pb^{2+} ions is shown in Fig. 2. In this section, PHEMA, P(1%MMA-HEMA), P(2%MMA-HEMA), P(3%MMA-HEMA), P(4%MMA-HEMA) and P(5%MMA-HEMA) surfaces were prepared and treated by the solutions containing Cu^{2+} and Pb^{2+} ions of concentration 10 mg/L, pH 6 and $T = 303 \pm 1$ K, and the contact time was 120 min. For preparing the solutions, fresh double-distilled deionized water was used. When the MMA weight percentage was increased from 1 to 3, the adsorption percentage raised from 1.07 to 28.8% for Cu^{2+} and from 2.31 to 58.3% for Pb^{2+} ions. The increase in the adsorption percentage with the change of adsorbent composition is due to the increase of the active sites on the adsorbent which makes penetration of the metal ions to the adsorbing site much easier. Also, attractive interaction increases between ions and adsorbent surface. The adsorption percentage of both metal ions at 3% (w/w) of MMA is almost at its highest level (for Cu^{2+} 74.5% adsorption percentage and Pb^{2+} 93.5% adsorption percentage ions) and with further increasing of MMA, it remains constant.

The main reason for this trend may be that the surfaces are fully covered and saturated [44]. Therefore, the amount of P(3%MMA-HEMA) was chosen for further adsorption experiments.

3.3. Effect of pH solution on adsorption

The pH of solution is one of the most important variables affecting metal ions adsorption. This is partly because hydrogen ions

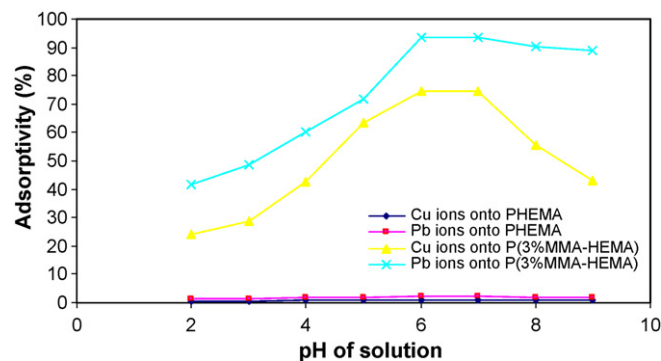


Fig. 3. Effect of pH solution on Cu^{2+} and Pb^{2+} ions adsorption onto PHEMA and P(3%MMA-HEMA) surfaces (metal ions concentration, 10 mg/L; $T = 303 \pm 1$ K and contact time = 120 min).

themselves are strongly competing with metal ions. Fig. 3 shows the effect of pH on the adsorption of Cu^{2+} and Pb^{2+} ions onto PHEMA and P(3%MMA-HEMA) surfaces. In this section, the concentration of each ion was chosen to be 10 mg/L and $T = 303 \pm 1$ K. Also, buffer solutions were used in all experimental sections in order to keep the pH of the solutions constant [45]. Sodium phosphate buffer (0.1 mol/L) was prepared by adding an appropriate amount of phosphoric acid to sodium dihydrogen phosphate solution to make a solution with pH 2. Ammonium acetate buffers (0.1 mol/L) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to result in solutions with pH 4–6. Ammonium chloride buffer solutions (0.1 mol/L) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to result in solutions of pH 7–9 [45]. The adsorption percentage was found to increase from 0.52 to 23.9% for Cu^{2+} onto PHEMA and P(3%MMA-HEMA) surfaces and 1.45 to 41.5% for Pb^{2+} onto PHEMA and P(3%MMA-HEMA) surfaces, when pH was increased from 2 to 9 respectively. At low pH values, the poor adsorption may be explained due to electrostatic attraction occurring between P(3%MMA-HEMA) surface and metal ions, since P(3%MMA-HEMA) surface has a negative charge and ions have a positive charge. With the increase of pH solution, the amount of adsorption increased up to pH 6–7 which shows the maximum amount of adsorption for both surfaces. In all solutions, there has been competitive adsorption among hydronium ions (H_3O^+) and Cu^{2+} and Pb^{2+} ions. At low pH values, hydronium ions are adsorbed more than other ions, since hydronium ions have a high concentration and more tendencies to be adsorbed [47,48]. With increasing the pH, hydronium ion concentration is reduced and results in other ions being better and more adsorbed [46–48]. A considerable increase in the adsorption was observed at pH 6–7 and the maximum amount of Cu^{2+} and Pb^{2+} ions adsorption was observed at these pH values. At higher pH

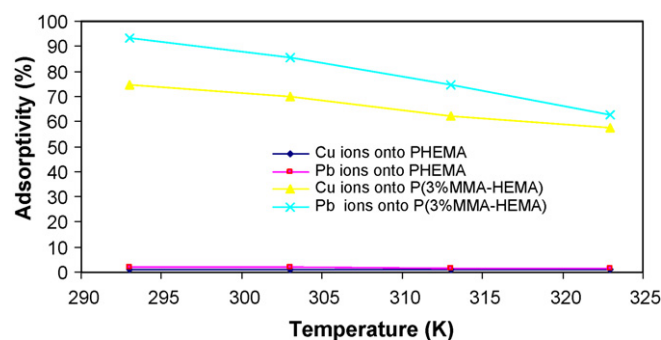


Fig. 4. Effect of temperature on Cu^{2+} and Pb^{2+} ions adsorption onto PHEMA and P(3%MMA-HEMA) surfaces (metal ions concentration, 10 mg/L; pH 6; and contact time = 120 min).

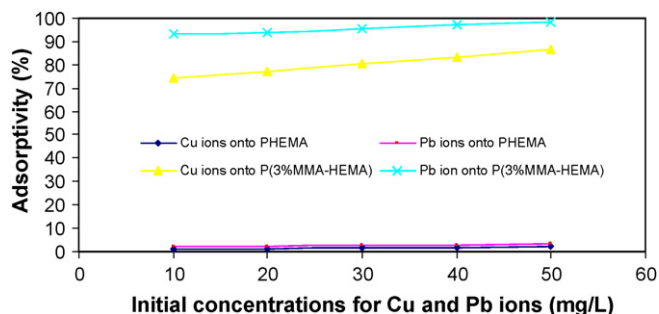


Fig. 5. Effect of initial Cu²⁺ and Pb²⁺ ions concentration on the adsorption onto PHEMA and P(3%MMA-HEMA) surfaces (pH 6; T=303 ± 1 K and contact time = 120 min).

values, metal precipitation took place and the adsorbent was deteriorated with the accumulation of metal ions onto surfaces [46]. Therefore, pH 6 was selected as the optimum pH for further studies. Similar results were reported by several earlier workers for metal ions adsorption on different adsorbents [47,48].

The results for PHEMA surface are similar to P(3%MMA-HEMA) surface, but PHEMA surface is neutral and other variable interaction such as hydrophobicity surface has effect on the adsorption [49].

3.4. Effect of temperature on the adsorption

Temperature has a pronounced effect on the adsorption capacity of adsorbents. Fig. 4 shows the representative plots of isotherm adsorption percentages of Cu²⁺ and Pb²⁺ ions onto PHEMA and P(3%MMA-HEMA) surfaces against different temperature ranging from 293 to 323 K. In this section, concentration of both ions was 10 mg/L, pH 6 and contact time was 120 min. It was found that with increasing the temperature the adsorption of both ions onto surfaces decreased. A decrease in the adsorption of both ions with the rise in temperature may be explained by being more active adsorbing sites at low temperature [50]. When the temperature was increased from 293 to 323 K, the adsorption percentage decreased from 1.06 to 0.78% for Cu²⁺ ions and 2.31 to 1.45% for Pb²⁺ ions onto PHEMA surface, 74.5–57.64% for Cu²⁺ ions and 93.5–62.78% for Pb²⁺ ions onto P(3%MMA-HEMA) surface at the equilibrium time. Also an increase in temperature results in mobility of the ions being increased and a decrease in the retarding forces acting on the adsorption ions [50]. This result may also confirm the exothermic nature of both ions adsorption onto PHEMA and P(3%MMA-HEMA) surfaces. So, 293 K was chosen as the solution temperature. Similar trends have been observed for the adsorption of other heavy metal ions [51].

3.5. Effect of initial Cu²⁺ and Pb²⁺ ions concentration on the adsorption

The adsorption of both Cu²⁺ and Pb²⁺ ions were carried out at different initial concentrations ranging from 10, 20, 30, 40 and

Table 2

Parameters of Langmuir adsorption isotherm for Cu²⁺ and Pb²⁺ ions onto surfaces.

Surfaces	q _m (mg/g)	K _L (L/mg)
Cu ions onto PHEMA	0.840	0.011
Pb ions onto PHEMA	3.037	0.007
Cu ions onto P(3%MMA-HEMA)	31.153	0.075
Pb ions onto P(3%MMA-HEMA)	31.447	0.341

Concentration of each ion is 10, 20, 30, 40 and 50 mg/L, pH 6 and T = 293 ± 1 K, contact time is 120 min.

50 mg/L at pH 6, at 293 K with 120 min of contact time. As shown in Fig. 5, when the initial concentrations of both ions (Cu²⁺ and Pb²⁺) increased from 10 to 50 mg/L, the adsorption increased (1.06–2.05% for Cu²⁺ and 2.31–3.19% for Pb²⁺ onto PHEMA surface respectively; 74.5–86.33% for Cu²⁺ and 93.5–98.1% for Pb²⁺ onto P(3%MMA-HEMA) surface respectively). The results may be explained by the fact that, at the defined pH, the surface of adsorbent would be also surrounded by hydronium ions which enhance ions interactions with binding sites of the adsorbent by greater attractive forces. As the initial concentrations were increased, the adsorption percentage increased. Note that, the maximum adsorption percentage for Pb²⁺ ions onto P(3%MMA-HEMA) surface is achieved.

3.6. Equilibrium point adsorption

Equilibrium data can be analyzed using commonly known adsorption isotherms, which provide the basis for the design of adsorption systems. The most widely used isotherm equation for modeling of the adsorption data is the Langmuir equation, which is valid for monolayer adsorption onto a surface with a finite number of identical sites and is given by Eq. (2).

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (2)$$

where K_L is the adsorption equilibrium constant including the affinity of binding sites (L/mg), q_m is the maximum adsorption capacity (mg/g), C_e the equilibrium metal ion concentration in the solution (mg/L), and q_e is the amount of adsorbed ion at equilibrium point (mg/g). It represents a practical limiting adsorption capacity when the surface is fully covered with ions. q_m and K_L can be determined from the linear plot of Eq. (2). This equation can be written as follows [52,53]:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \frac{1}{C_e} \quad (3)$$

The Freundlich model is an empirical equation based on adsorption onto a heterogeneous surface. The Freundlich model in linear form is [54]:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

where K_f and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively [24]. Linear plots of 1/q_e versus 1/C_e and ln q_e versus ln C_e, were drawn and

Table 1 Comparison between the Langmuir and Freundlich isotherm.

Surfaces	Langmuir isotherm		Freundlich isotherm	
	Equation ^a	R ²	Equation ^b	R ²
Cu ions onto PHEMA	Y = 105.39X – 1.1901	0.9997	Y = 1.4078X – 5.5459	0.9915
Pb ions onto PHEMA	Y = 45.601X – 0.3293	0.9997	Y = 1.2143X – 4.268	0.9977
Cu ions onto P(3%MMA-HEMA)	Y = 0.4276X – 0.0321	0.9969	Y = 1.5966X + 0.437	0.9744
Pb ions onto P(3%MMA-HEMA)	Y = 0.0932X – 0.0318	0.9958	Y = 1.8397X + 0.9855	0.9997

Concentration of each ion is 10, 20, 30, 40 and 50 mg/L, pH 6 and T = 293 ± 1 K, contact time is 120 min.

^a Y = 1/q_e, X = C_e (Eq. (3)).

^b Y = ln q_e, X = ln C_e (Eq. (4)).

Table 3
Thermodynamic parameters of Cu²⁺ and Pb²⁺ ions adsorption onto surfaces.

Surfaces	ΔH^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)	ΔG_{293}^0 (kJ mol ⁻¹)	ΔG_{303}^0 (kJ mol ⁻¹)	ΔG_{313}^0 (kJ mol ⁻¹)	ΔG_{323}^0 (kJ mol ⁻¹)
Cu ions onto PHEMA	-8.036	-65.09	-11.05	-116.69	-12.34	-12.99
Pb ions onto PHEMA	-12.799	-74.74	-34.73	-35.45	-36.19	-36.94
Cu ions onto P(3%MMA-HEMA)	-20.672	-61.55	-38.70	-39.32	-39.94	-40.55
Pb ions onto P(3%MMA-HEMA)	-56.400	-17.08	-61.40	-61.58	-61.75	-61.92

Concentration of each ion is 10, 20, 30, 40 and 50 mg/L, pH 6 and $T=293 \pm 1$ K, contact time is 120 min.

are summarized in Tables 1 and 2. Eqs. (3) and (4) are plotted by the fitting equations of Langmuir and Freundlich isotherms and correlation coefficients for PHEMA and P(3%MMA-HEMA) are summarized in Table 1. Using the values of the intercepts and slopes, values of q_m and K_L . In this section, adsorption of Cu²⁺ and Pb²⁺ ions onto PHEMA and P(3%MMA-HEMA) surfaces at 293 K were used.

It can be seen from Table 1, that the Langmuir isotherm yields a better fit than the Freundlich isotherm by comparing the results of the correlation coefficient (R^2) values at different concentrations for both ions; the correlation coefficient were found to be 0.9997 and 0.9997 for Cu²⁺ and Pb²⁺ ions onto PHEMA surface respectively and 0.9969 and 0.9958 for Cu²⁺ and Pb²⁺ ions onto P(3%MMA-HEMA) surface respectively. The main reason for this trend is the electrostatic interaction between adsorbent molecules (polymeric surfaces) and adsorbate (heavy metal ions). When electrostatic interaction between P(3%MMA-HEMA) with negative surface charge and ions with positive charge exists, the Langmuir isotherms does not result as well as when other interactions exist between adsorbent and adsorbate [55]. Also the hydrophobic interaction exists between PHEMA surface and heavy metal ions [56].

The values of Langmuir adsorption isotherm parameters are indicated in Table 2. The values for maximum adsorption capacity (q_m) were found to be 0.840 and 3.037 mg/g for Cu²⁺ and Pb²⁺ ions onto PHEMA surface respectively. The amounts of q_m were found to be 31.153 and 31.447 mg/g for Cu²⁺ and Pb²⁺ ions onto P(3%MMA-HEMA) surface respectively. The values K_L value were found as 0.011 and 0.007 L/mg for Cu²⁺ and Pb²⁺ ions onto PHEMA surface respectively and 0.075 and 0.341 L/mg for Cu²⁺ and Pb²⁺ ions onto P(3%MMA-HEMA) surface.

3.7. Thermodynamic parameters of adsorption

The thermodynamic parameters of the adsorption, i.e. the standard enthalpy change, ΔH^0 , the Gibbs free energy change, ΔG^0 and the standard entropy change, ΔS^0 were calculated using Eqs. (5–7) [56,57]:

$$\Delta G^0 = -RT \ln K_0 \quad (5)$$

$$K_0 = \frac{q_e}{C_e} \quad (6)$$

$$\ln K_0 = -\frac{\Delta H^0}{R} \frac{1}{T} + \frac{\Delta S^0}{R} \quad (7)$$

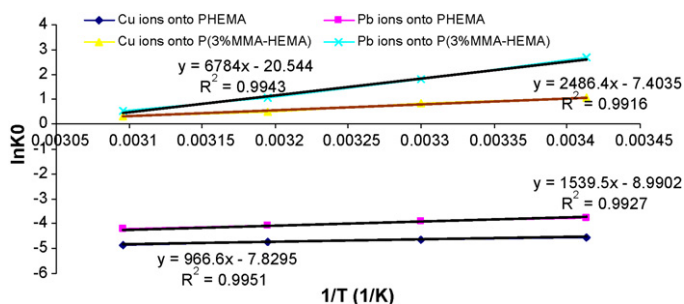


Fig. 6. In K_0 versus $1/T$ plot (concentration of each ion is 10, 20, 30, 40 and 50 mg/L, pH 6 and $T=293 \pm 1$ K, contact time is 120 min).

where T is temperature in Kelvin and R is the universal gas constant (8.314 J mol⁻¹ K⁻¹). The thermodynamic equilibrium constant was determined by Eq. (6) at different temperatures and then was used to derive the values of ΔH^0 and ΔS^0 [58].

Furthermore, ΔS^0 and ΔG^0 changes should be considered to determine whether the process is spontaneous. The Gibbs free energy change indicates if the adsorption process is spontaneous and higher negative value reflects a more energetically favorable adsorption [59]. The results of experiments are indicated in Fig. 6 and summarized in Table 3.

The equilibrium constants obtained from Langmuir isotherm at 293, 303, 313 and 323 K were used to determine the Gibbs free energy changes. Table 3 shows the thermodynamic parameters values for the adsorption of Cu²⁺ and Pb²⁺ ions onto the surfaces.

The standard enthalpy changes were determined -8.036, -12.799 kJ mol⁻¹ for Cu²⁺ and Pb²⁺ ions onto PHEMA surface respectively, -20.672, -56.40 kJ mol⁻¹ for Cu²⁺ and Pb²⁺ ions onto P(3%MMA-HEMA) surface respectively (Fig. 6). Also the standard entropy changes were determined -65.09, -74.74 J mol⁻¹ K⁻¹ for Cu²⁺ and Pb²⁺ ions onto PHEMA surface respectively, -61.55, -17.08 J mol⁻¹ K⁻¹ for Cu²⁺ and Pb²⁺ ions onto P(3%MMA-HEMA) surface respectively from Fig. 6. The negative values obtained for standard enthalpy change in this study indicates that the adsorption of both ions by PHEMA and P(3%MMA-HEMA) surfaces is exothermic, which is evidence by the decrease observed in the adsorption of both ions with increasing the temperature. A negative change in ΔG^0 reveals that the adsorption reaction is spontaneous [60,61]. The standard entropy change was found to have negative values for those processes. It mirrors a decrease in the randomness at solid–solution interface during the adsorption of Cu²⁺ and Pb²⁺ ions onto PHEMA and P(3%MMA-HEMA) surfaces. The results are similar to previous literatures [62–65].

4. Conclusions

Adsorption of Cu²⁺ and Pb²⁺ ions from aqueous solutions onto PHEMA and P(MMA-HEMA) at different conditions such as contact time, pH, adsorbate composition, and temperature, were studied to investigate optimum values of the mentioned parameters for removal of the metal ions by the different surfaces. It is shown that the changes in the variables affect the adsorption process and changes the obtained values of the amounts of ions adsorbed. It was found that pH 6 is the best pH to have the maximum adsorption amount, also the best contact time was found to be 120 min and the optimum temperature is 303 K. For optimum condition, it is illustrated that P(MMA-HEMA) surface adsorbs the metal ions much better than PHEMA and seems to be a better adsorbent for removal of both ions off the aqueous single solutions. The adsorption percentage has its maximum value when 3% (w/w) of MMA was used as copolymer (74.5% for Cu²⁺ and 98.1% for Pb²⁺, initial concentration each of ions is 10 mg/mL). The Langmuir and Freundlich isotherms for Cu²⁺ and Pb²⁺ ions onto the polymeric surfaces were studied. It is illustrated that Langmuir isotherm fit the experimental data better than the other isotherm. The negative value of the standard Gibbs free energy change revealed that the adsorption procedure is a spontaneous process. The change in standard entropy was found

to have negative values for the processes. It shows a decrease in the randomness at solid–solution surface during the adsorption of Cu^{2+} and Pb^{2+} ions onto PHEMA and P(3%MMA-HEMA) surfaces. Also a negative value for the standard enthalpy change obtained in this research, indicates that the adsorption of both ions onto PHEMA and P(3%MMA-HEMA) surfaces is exothermic, which is evidenced from the decrease in the adsorption of both ions with increasing the temperature.

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