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Adsorption of Cu(II), Ni(II) and Pb(II) ions onto polyamine-polyurea polymer modified with pyromellitic dianhydride: kinetic, isotherm and thermodynamic studies

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ABSTRACT

In this study, a polyamine-polyurea polymer modified with pyromellitic dianhydride was used for batch adsorption of Cu(II), Ni(II), and Pb(II) ions to examine the effects of parameters such as pH, contact time, amount of adsorbent, temperature, and initial concentration of heavy metals. The optimum pH value was found to be 6.0 and the contact time required to reach equilibrium was 120 min. Adsorption kinetics, thermodynamics and equilibrium were analysed. The adsorptions of the metal ions were found to comply with the Langmuir isotherm equation and the pseudo-second-order kinetic model. The maximum monolayer adsorption capacity of the modified polymer for Cu(II), Ni(II), and Pb(II) ions was found to be 73.5, 81.3, and 109.9 mg g^{-1}, respectively. Adsorption mechanism studies of the intraparticle diffusion model showed that surface sorption and intraparticle diffusion contribute to the rate-limiting step. Thermodynamic parameters showed the adsorption processes for all metals with the polymer have an endothermic, irreversible and spontaneous nature.

Keywords: Heavy metals; Adsorption; Polyamine-polyurea polymer; Modification; Pyromellitic dianhydride; Isotherms; Kinetics; Thermodynamics

1. Introduction

The discharge of wastewater involving heavy metals is a growing environmental problem [1]. The aquatic environment is polluted not only from industrial discharge and residential dwellings; groundwater infiltration is also an additional cause of heavy metal pollution [2]. Some heavy metals (Cd, Zn, Hg, Pb, Ni, Cr, Cu, As, etc.) have been the focus of more attention because of their high toxicity potential, even if the potential is small [3]. Moreover, the non-biodegradable nature of heavy metals causes an increase of their concentration in the food chain [4]. These metals, which are toxic even in low concentrations and are non-biodegradable, must be removed from wastewater [5] because heavy metal pollution of the food chain and drinking water has been linked to various health problems.

There are numerous methods such as chemical oxidation [6], membrane separation [7], electrochemical

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coagulation, precipitation [8], ion exchange [9], biological treatment [10] and adsorption [11,12] that have been applied to resolve heavy metals from water. Amongst these techniques, the fact that it can be applied in low concentrations makes adsorption preferable for the removal of heavy metals. Adsorption is an effective and simple method, but the effectiveness of the method substantially depends on the choice of adsorbent [13].

There are a wide variety of adsorbent types including activated carbon, agricultural waste and zeolite employed for removal of various pollutants such as colouring agents, metal ions and organic molecules. The agricultural wastes such as soybean hulls and pine cone are cheap and easily available, but their adsorption capacities are very low [14,15]. The efforts to increase the efficiency of adsorption mean that researchers have aimed to create a new material that has high complexation potential with heavy metals [16]. The superiorities of chelating polymers to adsorb heavy metals are their ease of use and the fact that they can be repeatedly used, along their high adsorption capacity and selectivity [13,17]. In the literature, there are numerous reports where chelating polymers have been used to remove and recover heavy metal ions from wastewater [18–22]. Adsorption of some metal ions using polyamine-polyurea resin has been reported in the literature [23]. To increase the adsorption capacity of the polyamine-polyurea polymer, it was modified with pyromellitic dianhydride (PMDA) and used to remove Cd(II) ions from aqueous solutions [24]. The good adsorption performance of the resin for Cd(II) ions prompted us to investigate the adsorption of other metal ions such as Cu(II), Ni(II), and Pb(II).

In the present study, the adsorption of Cu(II), Ni(II), and Pb(II) ions onto the PMDA-modified polyamine-polyurea polymer from an aqueous solution was investigated. The efficacies of experimental conditions such as pH, contact time, amount of adsorbent, initial concentration of heavy metals and temperature were analysed. The Langmuir and Freundlich equations were used to investigate the suitability of the equilibrium isotherms. Adsorption kinetics were compared with the first- and second-order kinetic models and evaluated using an intraparticle diffusion model. The thermodynamics of Cu(II), Ni(II), and Pb(II) adsorption were also performed.

2. Experimental

2.1. Chemicals

Metal salts such as $CuCl_2.2H_2O$, $NiCl_2$, and $PbCl_2$ were used as sources of metal ions; all the working solutions were prepared by diluting the stock solution (1,000 mg L^{-1}). Polyethyleneimine (Lupasol FG) was bought from BASF (Ludwigshafen, Germany). PMDA was used as a modifying agent. PMDA and the other chemicals including toluene diisocyanate (TDI), dimethylformamide (DMF), ethanol, and diethyl ether were used in the synthesis of the polymer. Acid solutions were obtained from Merck KGaA (Darmstadt, Germany). All chemicals used in the experiments were of analytical purity.

The modified polymer, PMPPP, was synthesised and characterised in a previous study. Briefly, PPP was prepared by polymerisation of TDI and polyethyleneimine in DMF. Then, PPP was modified with PMDA in DMF by mechanical stirring at 50˚C. The obtained material was neutralised with dilute NaOH solution [24].

2.2. Instruments

The concentration of the Cu(II), Ni(II), and Pb(II) ions was determined by an atomic absorption spectrometer (Shimadzu AA-6200, Shimadzu Corporation, Kyoto, Japan). An oven (Nüve FN 400, Turkey), which is capable of heating up to 250˚C, was used for the drying of the polymer. In all phases of the study, pH measurements and adjustments were performed with a digital pH meter (WTW pH 720). A temperature-controlled orbital shaker (KS4000i, IKA-Werke GmbH, Germany) was used for the adsorption studies performed using the batch method. An overhead mechanical stirrer (Yellowline by IKA, Germany) was used for the synthesis of the polymer.

2.3. Analytical procedure

The adsorption of Cu(II), Ni(II), and Pb(II) ions by PMPPP was studied using the batch method. Working solutions were obtained by dilution from the stock solution. A solution volume of 50 mL was used in all adsorption experiments. After pH adjustment of the working solutions with 0.1 M HCl or NaOH solutions, different amounts of the polymer were added over the solutions in stoppered Erlenmeyer flask and they were stirred on an orbital shaker at 200 rpm during predetermined time intervals and at different temperatures.

Metal concentration in the filtrate was measured using AAS and the amount of metal ions adsorbed per unit amount of adsorbent was calculated by Eq. (1):

$$q_t = \frac{(C_0 - C_t).V}{m} \tag{1}$$

where q_t is the metal uptake in milligrams per gram of polymer, C_0 and C_t are the initial and residual concentrations (at time t) of metal in the solution in milligrams per litre, respectively, V is the volume of the metal solution in litres and m is the amount of added polymer in grams. Eq. (2) was used to calculate the percentage of metal removal [25].

$$\text{Adsorption } (\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{2}$$

where C_0 and C_t are the initial concentration and the concentration at time t, respectively [26].

Competitive adsorption of Cu(II), Ni(II), and Pb(II) was carried out with binary and ternary solutions including 200 mg L^{-1} concentrations of each metal ion at pH 6.0. These solutions were stirred for 120 min at 200 rpm by adding 0.05 g of PMPPP. The adsorbed quantities were calculated after measuring their equilibrium concentration in filtrate.

Desorption of Cu(II), Ni(II), and Pb(II) from PMPPP was performed after their adsorption from individual solutions at 300 mg L^{-1} by 50 mg of PMPPP. The adsorbed metal ions were desorbed by 25 mL of 0.01, 0.1, and 0.5 M HNO_3. The adsorbed and desorbed concentrations of the metal ions were measured using AAS. Eq. (3) was used to calculate the percentage of desorption [27].

$$\text{Desorption } (\%) = \frac{\text{Desorbed metal ion amount}}{\text{Adsorbed metal ion amount}} \times 100 \tag{3}$$

3. Results and discussion

3.1. Effect of pH

The experimental studies were performed in the pH range of 1.0–6.0 for the purpose of determining the optimum pH value of Cu(II), Ni(II), and Pb(II) solutions (50 mg L^{-1}) in a volume of 50 mL. Then, 0.05 g of PMPPP was added and stirred for 120 min at 298 K. As can be seen in Fig. 1, the amount of adsorbed ions is very low at pH 1.0 and 2.0, rapidly increasing with the release of the pH from 2.0 to 4.0. After a pH of 4.0, small increases were observed for these metals' adsorption by increasing the pH value to 5.0. Their adsorption was essentially unchanged by increasing the pH to 6.0. The adsorption of the metal ions was not studied at higher pH values than 6.0 due to possible precipitation of them. So, the optimal pH value for adsorption of Cu(II), Ni(II), and Pb(II) was selected to be 6.0 in subsequent studies.

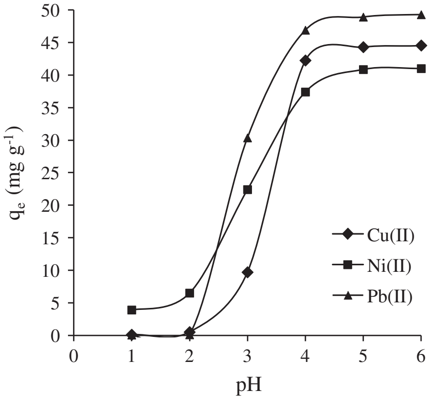

Fig. 1. Effect of pH on the adsorption of Cu(II), Ni(II), and Pb(II) ions onto PMPPP.

The low adsorption capacity at a low pH is explained as follows. Functional groups of the polymer are protonated at an acidic pH due to the competition that occurs between protons and heavy metals for the active binding sites of the polymer; attachment of the heavy metal ions to the polymer surface is prevented or reduced. As a result of the increased pH, protonation and competition in binding sites disappear through the functional groups that become free; heavy metals may be attached to the polymer surface. Therefore, by increasing the solution's pH, the heavy metal adsorption capacity of the polymers increased [28]. Similar findings have been shared in the literature by other researchers. In one of these studies, at low pH values, positively charged metal ions were being electrostatically pushed by the positively charged adsorbent surface and this resulted in an inhibition of the metal ion adsorption [29].

3.2. Effect of contact time

During the experiment, 0.05 g of PMPPP was added to 50 mL solutions that contained 50 mg L^{-1} initial concentrations of Cu(II), Ni(II), and Pb(II) ions and stirred for time periods ranging from 5 to 240 min in order to determine the appropriate contact time. The data of adsorbed metal ions per unit adsorbent with time for different initial concentrations of metal ions are shown in Fig. 2. The results show that the uptake was faster at the start-up phase of contact (the first 40 min) and continued up to 120 min with declining speed. Previously, congener results have been reported that explain the rapid uptake onset as due to the larger surface area and easy accessibility to the active site [1,30]. The system was considered to have reached equilibrium at 120 min because of the

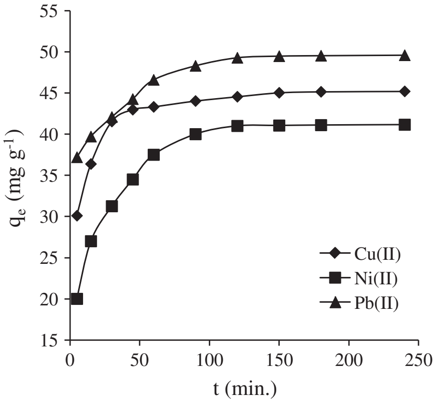

Fig. 2. Effect of contact time on the adsorption of Cu(II), Ni(II), and Pb(II) ions onto PMPPP.

negligible increase in heavy metal uptake between 120 and 240 min.

3.3. Effect of adsorbent dosage

Amounts ranging between 0.02 and 0.075 g of PMPPP were added to solutions including 50 mg L^{-1} of Cu(II), Ni(II), and Pb(II) ions. The solution was mixed for 120 min at pH 6.0 with the intention of examining the effect of adsorbent dosage on adsorption. As can be seen from Fig. 3, the increase in the polymer amount resulted in an increase in the adsorption percentage, but a decrease of the heavy metal content absorbed per unit mass of the PMPPP [31]. This decrease can be explained by the following mathematical expression.

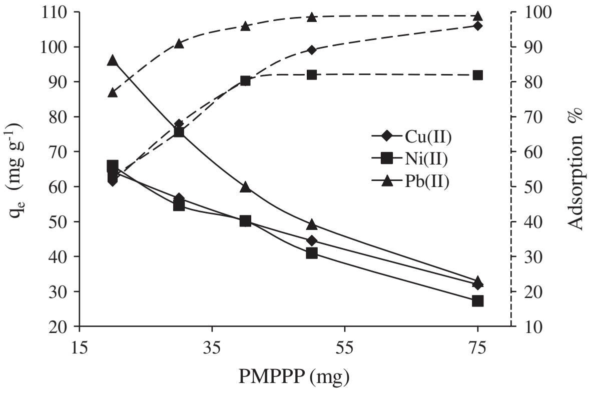

Fig. 3. Effect of PMPPP dose on the adsorption of Cu(II), Ni(II), and Pb(II) ions.

$$q_e = \frac{\%\ \text{Ads}.C_0.V}{100\ m} \tag{4}$$

Starting from the mathematical expression, there is an inverse relationship between q_e and m. Namely, for fixed percentage adsorption, the adsorbed heavy metal ion amount per unit mass of PMPPP (q_e) will decrease with an increase in PMPPP amount (m) because C_0 (initial metal concentration) and V (the volume of metal solution) are constant [32,33]. As shown in Fig. 3, the adsorption percentages of Ni(II) and Pb(II) did not change after the 50 mg dosage and so the optimum PMPPP dosages were found to be 50 mg for Ni (II) and Pb(II) ions. For Cu(II) ions, there was a small increase in the percentage of adsorption when increasing the PMPPP mass from 50 to 75 mg. So, the optimal PMPPP dosage was found to be 75 mg for Cu(II) ions.

3.4. Effect of initial concentration of metal ions

The effect of initial Cu(II), Ni(II), and Pb(II) concentrations on the metal adsorption with PMPPP is shown in Fig. 4. The metal solutions in varying concentrations from 50 to 300 mg L^{-1} were stirred with 0.05 g of PMPPP and under previously determined appropriate conditions. The amount of adsorbed metal ions was seen to increase depending on the initial concentration until equilibration was reached. The equilibrium state visible in Fig. 4 was caused by the saturation of the active binding sites of the polymer [12,34].

3.5. Equilibrium isotherms

The Langmuir model is the most simple and logically theoretical model for adsorption. This model is

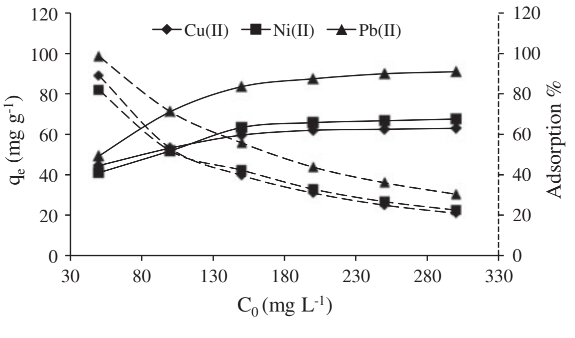

Fig. 4. Effect of initial metal ion concentration on the adsorption.

based on several assumptions, including adsorption cannot go beyond monolayer coating, all adsorption sites are equivalent and the surface is perfectly smooth at the microscopic level [35]. The linear form of the Langmuir equation is given as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L\ q_{max}} + \frac{1}{q_{max}} C_e \tag{5}$$

where q_e is adsorbed heavy metal ion amount per unit mass of PMPPP in mg per gram, C_e is the concentration of metal ions in solution at equilibrium in mg per litre, q_{max} is the maximum adsorption capacity of PMPPP and K_L is the Langmuir constant used to define relevance between the adsorbent and adsorbate. From the plots between (C_e/q_e) and C_e, the slope $(1/q_{max})$ and the intercept $(1/K_L q_{max})$ can be calculated [36].

The located adsorption areas on the surface of an adsorbent are characterised as heterogeneous areas that are formed by different kinds of adsorbing sites by the Freundlich isotherm. The linearised Freundlich equation can be written as follows [37]:

$$\log q_e = \log K_F + (1/n) \log C_e \tag{6}$$

where q_e is the adsorbed heavy metal ion amount per unit mass of PMPPP in mg per gram, C_e is the concentration of metal ions in solution at equilibrium in mg per litre, K_F and n are the constants of the isotherm related to the binding energy and intensity, respectively [38]. From the plots between (log q_e) and C_e, the slope (n) and the intercept (K_F) can be calculated (Fig. 5).

It can be observed from Table 1 that for all the metal ions, the regression coefficients of the Langmuir isotherm were greater than those of the Freundlich isotherm's, demonstrating that the equilibrium adsorption isotherm can be very well represented by the Langmuir isotherm with the maximal adsorption capacities being 73.5, 81.3 and 109.9 mg g^{-1} for Cu(II), Ni(II), and Pb(II) ions, respectively. The q_{max} values calculated according to the experiment's results obtained using 0.05 g of unmodified PPP were found to be 18.7, 46.1, and 29.9 mg g^{-1} for Cu(II), Ni(II), and Pb(II) ions, respectively. These results show that a modification of PPP with PMDA improved the adsorption capacity of the polymer. The comparisons of the maximum adsorption capacity of metal ions using various polymer adsorbents are listed in Table 2 [3,22,27,29,30,39–41].

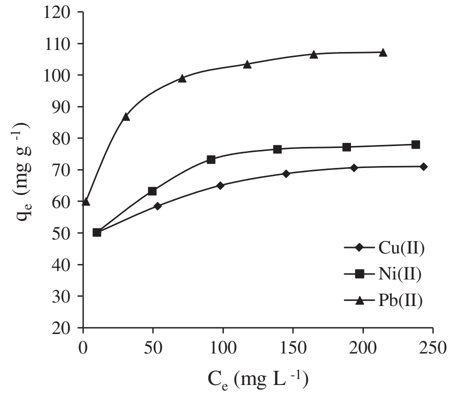

Fig. 5. Adsorption isotherms of Cu(II), Ni(II), and Pb(II) ions onto PMPPP.

3.6. Adsorption kinetics

The adsorption rate mechanisms of metal ions on PMPPP were evaluated by pseudo-first-order and pseudo-second-order kinetic models with the intraparticle diffusion model.

The pseudo-first-order equation is known as the Lagergren equation and is often used to describe the first-order reactions [42]. The Lagergren equation is expressed by Eq. (7):

$$\ln\,(q_e - q_t) = \ln q_e = k_1 t \tag{7}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of metal ions adsorbed by per unit mass of the PMPPP equilibrium and at time t (min), respectively, k_1 is the adsorption rate constant (min^{-1}) and computed from the slope of the straight line between ln (q_e−q_t) vs. t [43,44].

The pseudo-second-order model is used to measure the adsorption capacity of the solid phase and to describe the chemisorption mechanism as a speed control step [45]. The pseudo-second-order equation is given below:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of the second-order kinetic model, the q_e and k_2 values were calculated using the plot of t/q_t vs. t [45]. The results of the pseudo-first-order and second-order models are given in Table 3. The values of $q_{e,teo}$ from the pseudo-second-order kinetic equation were seen to fit the experimental data [39,46].

Table 1
Parameters of Langmuir and Freundlich isotherms at different dosages of PMPPP for Cu(II), Ni(II), and Pb(II) adsorption

		Langmuir constants			Freundlich constants		
	Dosage (mg 50 m L^{-1})	$q_{\max}$ (mg g^{-1})	K_L (L mg^{-1})	r^2	K_f (mg g^{-1})	n	r^2
Cu(II)	40	73.5	0.103	0.9985	38.1	8.7	0.9841
	50	64.5	0.165	0.9992	37.6	10.3	0.9791
	75	49.5	0.151	0.9980	29.6	11.0	0.9667
Ni(II)	40	81.3	1.059	0.9991	36.3	6.8	0.9733
	50	70.9	0.091	0.9981	28.6	6.1	0.9605
	75	56.5	0.675	0.9973	17.0	4.6	0.9798
Pb(II)	40	109.9	0.181	0.9991	55.5	7.8	0.9908
	50	92.6	0.187	0.9987	50.8	8.9	0.9900
	75	70.9	0.225	0.9990	36.1	7.6	0.9926

Table 2
The comparison of maximum adsorption capacity of metal ions using various polymer adsorbents

	Adsorption capacity			Conditions				
Adsorbents	Cu(II) (mg g^{-1})	Ni(II)	Pb(II)	C_0 (mg L^{-1})	m (mg)	pH	V (mL)	Refs.
SMA beads	17.5	13.9	–	200	500	6.7	20	[3]
Pendant chlorobenzylidene rings	–	–	274.6	300	40	10	10	[22]
Semi-IPN cryogels	40.7	9.3	–	1[a]	10	4.7	20	[27]
Cellulose nanocrystals	–	–	27.9	300	1,000[b]	5.5	150	[29]
Succinic cellulose nanocrystals	–	–	367.6	300	1,000[b]	5.5	150	[29]
Sodic cellulose nanocrystals	–	–	465.1	300	1,000[b]	5.5	150	[29]
Fe_3O_4/cyclodextrin polymer	–	13.2	64.5	300	120	5.5	10	[39]
Modified γ-Al_2O_3 with DNPH	–	–	100.0	50	50	5.0	50	[40]
Silica nanohollow sphere	–	8.4	26.9	100	15	4.5	5	[41]
Amino-functionalised silica gel	–	25.9	54.4	100	15	4.5	5	[41]
Amino-functionalised silica nanohollow sphere	–	31.3	96.8	100	15	4.5	5	[41]
PMPPP	73.5	81.3	109.9	50	50	6.0	50	This study

[a] mmol L^{-1}.
[b] 1 g L^{-1}.

3.7. Adsorption mechanism

Adsorption can occur in a multi-step process, including film diffusion, intraparticle diffusion and sorption onto interior sites [47]. The quantitative method used to detect the control mechanism is the square root analysis of contact time and can be explained by the following equation:

$$q_t = k_{\mathrm{id}} t^{1/2} + c \qquad (9)$$

where k_{id} is the diffusion coefficient (mg g^{-1} $min^{-1/2}$) and c is the intercept. The data of the intraparticle diffusion model, which are calculated from the plot of q_t vs. $t^{1/2}$, are given in Table 3.

The obtained parameters of Cu(II), Ni(II), and Pb (II) ions such as diffusion coefficient correlation coefficients and c parameters are listed in Table 3. The c parameters revealed that all linear lines did not pass through the origin, showing intraparticle diffusion is not the only rate-limiting factor. Surface sorption and intraparticle diffusion contribute to the rate-limiting step [45,47,48].

3.8. Effect of temperature and thermodynamic study

All the experiments with Cu(II), Ni(II), and Pb(II) were conducted in the temperature range of 298–328 K. This temperature interval was selected for practical reasons and the obtained data were also

Table 3
Parameters of pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models for Cu(II), Ni(II), and Pb(II) adsorption onto PMPPP

	Pseudo-first-order					Pseudo-second-order			Intraparticle diffusion		
	C_0 (mg L^{-1})	$q_{e,exp}$ (mg g^{-1})	$k_1 \times 10^2$ (min^{-1})	$q_{e,cal}$ (mg g^{-1})	r^2	$k_2 \times 10^2$ (g mg^{-1} min^{-1})	$q_{e,cal}$ (mg g^{-1})	r^2	k_{id} (mg g^{-1} $min^{-1/2}$)	c (mg g^{-1})	r^2
Cu(II)	50	45.2	2.9	12.4	0.9668	0.65	45.9	0.9999	1.13	32.4	0.7341
	100	53.9	2.5	18.6	0.9914	0.34	55.2	0.9996	1.58	35.3	0.8712
	150	60.4	2.7	22.0	0.9927	0.31	61.7	0.9997	1.86	38.8	0.8392
Ni(II)	50	41.2	3.7	27.8	0.9797	0.25	43.5	0.9990	1.82	20.2	0.8746
	100	52.3	3.0	24.4	0.9864	0.29	54.1	0.9996	1.64	32.8	0.9137
	150	64.4	2.3	18.8	0.9765	0.32	65.8	0.9997	1.88	42.5	0.8340
Pb(II)	50	49.6	3.2	18.3	0.9905	0.43	50.8	0.9995	1.16	35.8	0.9296
	100	72.6	2.6	27.5	0.9843	0.24	74.1	0.9991	1.84	50.0	0.9606
	150	84.6	2.5	18.8	0.9961	0.36	85.5	0.9997	1.35	68.1	0.9525

enough for the evaluation of the thermodynamic parameters of metal ions. The amount of adsorbed metal ions on PMPPP was found to increase with increasing temperatures, for Cu(II), Ni(II), and Pb(II) ions (Fig. 6). The direct proportion between temperature and the amount of adsorbed metal ions verified that the processes were endothermic. This situation may be due to the need for greater energy consumption to overcome the pushing force between positively charged cations and the polymer surface. This has been associated with positive values of enthalpy (ΔH°), as reported earlier by Da'na and Sayari [49].

Gibbs free energy change (ΔG°) is a measure of chemical affinity and calculated with Eq. (10):

$$\Delta G^\circ = -RT \ln K \tag{10}$$

where K is the apparent equilibrium constant for the process and can be derived from:

$$K = \frac{C_{\text{ads}}}{C_{\text{e}}} \tag{11}$$

where C_{ads} (mg L^{-1}) is the adsorbate concentration adsorbed on unit mass of PMPPP and C_{e} (mg L^{-1}) is the adsorbate concentration remaining in the solution [50].

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{12}$$

The enthalpy changes (ΔH°) and entropy changes (ΔS°) for the adsorption process for all the metal ions were obtained from the plots of ln$K$ drawn against $1/T$. The calculated thermodynamic data are collected in Table 4.

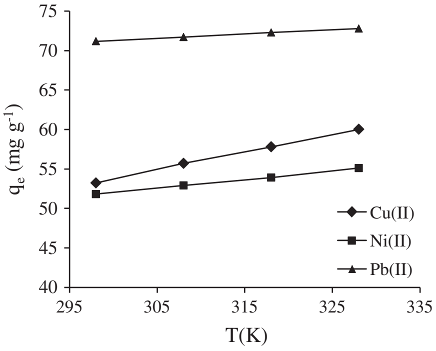

Fig. 6. The temperature-dependent change in the adsorbed amount of Cu(II), Ni(II), and Pb(II) ions by PMPPP.

Table 4
Thermodynamic parameters for Cu(II), Ni(II), and Pb(II) adsorption on the PMPPP

	T (K)	Cu(II)	Ni(II)	Pb(II)
ΔG° (kj mol^{-1})	298	−0.32	−0.18	−2.24
	308	−0.59	−0.30	−2.38
	318	−0.83	−0.41	−2.53
	328	−1.11	−0.56	−2.68
ΔH° (kj mol^{-1})[a]		7.46	3.56	2.17
ΔS° (kj mol^{-1})[a]		26.09	12.52	14.78

[a]Measured between 298 and 328 K.

Positive entropy values are signs of the increasing irregularity at the interface of the solid-phase solution during the adsorption process and also indicate that the reaction is irreversible [51]. Negative values of Gibbs free energy change indicate the adsorption is spontaneous [52].

3.9. Competitive adsorption of Cu(II), Ni(II), and Pb(II)

In order to examine the competitive adsorption of Cu(II), Ni(II), and Pb(II) metals, binary and ternary solutions including 200 mg L^{-1} of each metal ions were used. The adsorption percentages calculated from the measurement results are given in Table 5. As seen from the data, the adsorption of metal ions decreased in the binary and ternary metal solutions compared to the single metal solution. This decrease can be explained by the competition between different metal ions in the binding sites of PMPPP. The metal ion having a high affinity to PMPPP can be easily adsorbed, whilst low affinity metal ions remain in the solution [39]. The affinity of PMPPP for binary ions was determined as Cu(II) > Ni(II), Ni(II) > Pb(II), and Cu(II)) > Pb(II). From the ternary solution, the affinity order of the metal ions was found to be as Cu(II) > Ni (II) ≈ Pb(II) onto PMPPP based on the percentage removal of the metals. In Liu et al. the coordination

Table 5
Percentages of single, binary, and ternary adsorption of metal ions on PMPPP

	Adsorption (%)		
Composition of the solution	Cu(II)	Ni(II)	Pb(II)
Single metal Ion	31.0	32.9	43.8
Cu(II) + Ni(II)	28.5	20.8	–
Cu(II) + Pb(II)	27.5	–	20.5
Ni(II) + Pb(II)	–	26.0	22.0
Cu(II) + Ni(II) + Pb(II)	22.0	18.5	18.0

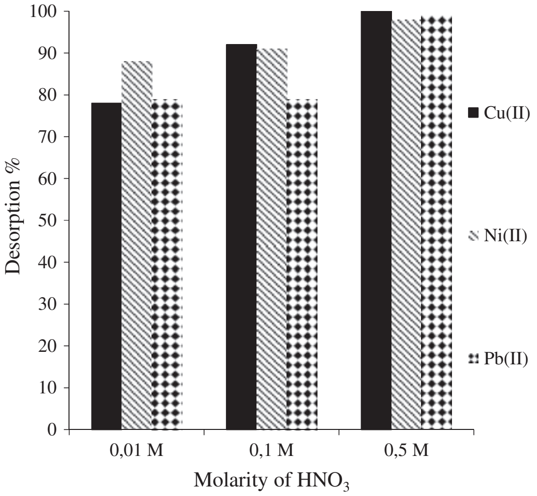

Fig. 7. The desorption percentage of metal ions depended on acid molarity.

geometry has been reported as an important factor for the determination of the adsorption selectivity for heavy metal ions [53].

3.10. Regeneration of PMPPP

The regeneration is very important for practical application of the sorbents. With the purpose of examining the regeneration ability of PMPPP, desorption of Cu(II), Ni(II), and Pb(II) from PMPPP was performed after their adsorption from individual solutions at 300 mg L^{-1} with 50 mg of PMPPP. The adsorbed metal ions were desorbed by 25 mL of 0.01, 0.1, and 0.5 M HNO_3. The calculated desorption percentages of metal ions by changing molarities of HNO_3 are illustrated in Fig. 7. The increasing desorption percentages were obtained by increasing the molarity of the HNO_3 solution. Quantitative desorption yield (≥95%) was obtained using 0.5 M of HNO_3 for Cu(II), Ni(II), and Pb(II) ions. The regenerability of PMPPP is another good property of the adsorbent [27,39,54].

4. Conclusion

The adsorption attitude of PMPPP was investigated with Cu(II), Ni(II), and Pb(II) ions and the amount of adsorbed metal ions on PMPPP was found to increase by increasing pH, contact time and temperature. Adsorption processes of Cu(II), Ni(II), and Pb(II) ions onto PMPPP were observed to be compatible with the Langmuir isotherm. The maximum adsorption capacity values were calculated as 73.5, 81.3, and 109.9 mg g^{-1} for Cu(II), Ni(II), and Pb(II) ions, respectively. The kinetic mechanisms of the ions were obtained to fit the pseudo-second-order kinetic model. The positive ΔH and ΔS values indicated the endothermic and irreversible nature of the adsorption, respectively. Negative values of Gibbs free energy change showed that the adsorption was spontaneous. According to the obtained results, it can be said that PMPPP is an effective and practical adsorbent for removing heavy metals from an aqueous medium.

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