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Efficient removal of Cd(II), Cu(II), Ni(II) and Pb(II) by polyamine-polyurea polymer modified with 2,4-dihydroxybenzaldehyde from synthetic and real wastewaters

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ABSTRACT

The present study reports a synthesis of novel polymeric sorbent of polyamine-polyurea polymer modified with 2,4-dihydroxybenzaldehyde (DMPPP) and analysing of its adsorption efficiency towards some metal ions including Cd(II), Cu(II), Ni(II) and Pb(II). The effect of variation in solution pH, adsorbent dose, initial metal ion concentration, contact time and temperature on the adsorption mechanism was studied. Adsorption of the metal ions was obtained maximum at pH of 6.0 and was reached to equilibrium in contact time of 120 min. The compliance of adsorption equilibrium data with Langmuir and Freundlich isotherm models were investigated and Langmuir model was found to be in better harmony with correlation coefficient values of over 0.99 for all metal ions. The maximum adsorption capacity (q_e) of DMPPP for Cd(II), Cu(II), Ni(II) and Pb(II) ions were found to be 105.3, 117.6, 137.0, 144.9 mg g^{-1}, respectively. The kinetics of heavy metal ions were assessed by pseudo-first-order, pseudo-second-order and intraparticle diffusion models. It is discerned that the kinetic mechanisms of the heavy metal ion adsorption on DMPPP were better expressed by the pseudo-second order kinetic model. Results obtained from thermodynamic studies were interpreted the process as endothermic with the positive values of ΔH, as spontaneous with the negative values of ΔG and as having an increased randomness with the positive values of ΔS. Desorption of Cd(II), Cu(II), Ni(II) and Pb(II) ions using 20 mL of 0.5 M HNO_3 solutions was found to be quantitative (≥90%). The developed adsorption technique using novel sorbent was also successfully applied to real wastewater to remove Cd(II), Cu(II), Ni(II) and Pb(II) ions.

Keywords: Chelating resin; Polymer; Adsorption; Removal; Heavy metal; Wastewater

1. Introduction

Water is of vital for all the living organisms on the earth, for human in particular, but only 0.01% of the amount of freshwater contains the salutary anions and cations that are appropriate to consume as nutrient for humans [1,2]. It is regrettable that the freshwater is being contaminated by the human activities in a majority [2].

Heavy metals are one of the pollutants that have considerable attention owing to increased amounts of metals in water. Heavy metals are deleterious to living organisms in water environment with a number of features; it is not biologically possible to degrade heavy metals, so accumulation occurs in living organisms [3]. There are numerous negative effects of heavy metals on human health as it is to the aquatic environment, and metals can cause various diseases depending on their concentration. Cadmium (Cd) and lead (Pb) may induce cancer, bone damage, lung, kidney and liver disorders, insomnia, dizziness, nausea, headache, rapid, respiration, coughing, dermatitis, chronic asthma over definite limits [4–7], despite this particular concentrations of some metals (Cu, Fe, Mn, Ni and Zn) serve as nutrients for organisms [2,8].

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The treatment of heavy metal polluted water is a serious environmental problem therefore a large number of methods has been developed and applied. These methods can be listed as electrocoagulation and chemical precipitation [9], extraction [10], flotation [11], ion-exchange [12], membrane separation [13], electrochemical deposition [14], biosorption [15] and adsorption [16]. It is very important to select the method which will be applied for the removal of heavy metals. Cost-effectiveness of the method is decisive factors. Some distinguishing features such as inexpensive investment costs, easy operating process, recovery option of metals and more than once usage of adsorbents makes adsorption preferred among the other methods [1,17].

Adsorbent is a primarily identifier that determines the efficiency of adsorption process. Fully convincing adsorbent is expected to be cheap, easily available, regenerable, reusable and to have high adsorption capacity. Production of the polymeric adsorbent has been started nearly 50 years ago, but researchers have continued to study for synthesis of sorbent material having the desired excellent properties [18]. For example, Zhu et al. [19] have used hyper-crosslinked polymeric adsorbents for pyridine adsorption, Xiao et al. [20] have synthesized a polymeric adsorbent with high microporous surface area and studied its theophylline adsorb properties, again Xiao et al. [21] have worked with four different polymeric adsorbent for phenol adsorption in another study. A polymeric adsorbent was used for reactive dye adsorption by Blanco et al. [22]. Adsorption of heavy metals using polymeric resins has been widely used in many applications due to high adsorption capacity [23]. For example, Sambaza et al. [24] have used polymeric nanocomposite adsorbents, Liu et al. [25] have used two different chelating adsorbents for chromium(VI) adsorption, Liu et al. [26] have synthesized covalently crosslinked nanocomposite hydrogel and used it for Cu(II), Cd(II), Ni(II), Zn(II), Pb(II) adsorption, Hayati et al. [27] have prepared dendrimer functionalized carbon nanotubes and examined adsorption capacities for Ni^{2+}, Zn^{2+}, As^{3+}, Co^{2+} ions, Zhang et al. [28] have studied with 5-aminopyridine-2-tetrazole-functionalized polystyrene resin to adsorb Cu(II), Pb(II) and Hg(II) ions in recent studies.

It has been reported that polymeric resins display notable sorption capacity owing to amino groups, which act as a crosslinking agent [29]. Previously we synthesized polyamine-polyurea polymer (PPP) contains a large amount of amine groups and used for adsorption of Cr(VI). Modification of PPP with pyromellitic dianhydride was caused to strengthen the chelating ability of the polymer with metal ions [30,31]. The obtained high adsorption capacities for some metal ions have been incentive for new modification of PPP with other ligands containing donor atoms such as oxygen.

This study reports a synthesis of novel sorbent produced by modification of PPP with 2,4-dihydroxybenzaldehyde and the obtained polymer was characterized by elemental analysis and infrared spectroscopy. Adsorption ability of the polymer for Cd(II), Cu(II), Ni(II) and Pb(II) ions was investigated batchwise. A large number of batch experiments were carried out for defining the effects of parameters such as solution pH, adsorbent dose, initial metal ion concentration, contact time and temperature on adsorption process. Adsorption kinetic, equilibrium and thermodynamic of each metal ions were investigated. Additionally, the developed adsorption method based on the usage of novel sorbent was applied to real wastewater.

2. Experimental studies

2.1. Materials

The stock solutions of Cd(II), Cu(II), Ni(II) and Pb(II) ions at 1,000 mg L^{-1} used in the adsorption studies were prepared by taking the essential amount of $CdCl_2 \cdot H_2O$ (catalogue no. 1.02011.0100), $CuCl_2 \cdot 2H_2O$ (CAS 10125-13-0), $NiCl_2$ (CAS 7718-54-9) and $PbCl_2$ (CAS 7758-95-4) salts (Merck KGaA, Darmstadt, Germany), respectively. Stock solutions were stored in pre-washed plastic bottles.

Polyethylenimine (PEI; CAS 25987-06-8) used for the syntheses of polymer was purchased from BASF (Ludwigshafen, Germany) and the other chemicals such as 2,4-dihydroxy benzaldehyde (DHBA) (CAS 95-01-2), ethanol (CAS 64-17-5), diethyl ether (CAS 60-29-7), nitric acid (CAS 7697-37-2) and hydrochloric acid (catalogue no. 100317) solutions were purchased from Merck KGaA (Darmstadt, Germany).

2.2. Instruments

An atomic absorption spectrometer (Shimadzu AA-6200, Shimadzu Corporation, Kyoto, Japan), for the determination of concentration of Cd(II), Cu(II), Ni(II) and Pb(II) ions, an oven (Nuve FN 400, Turkey), a digital pH meter (WTW pH 720), a temperature-controlled orbital shaker (KS4000i, IKA-Werke GmbH, Germany), and an overhead mechanical stirrer (Yellowline by IKA, Germany) were used in the study.

2.3. Preparation of polymer DMPPP

Polyamine-polyurea polymer (PPP) was synthesized according to the literature [30,31]. In order to modify PPP with 2,4-dihydroxybenzaldehyde, 70 g of the polymer and 70 g (0,51 mol) of DHBA was added in 100 mL of ethanol and then, the obtained suspension was stirred within 4 h at 50°C. The resulting modified polymer was washed with distilled water until reaching neutral pH value. Then, it was washed with alcohol and ether. The obtained product of polyamine polyurea polymer modified with 2,4-dihydroxybenzaldehyde (DMPPP) was kept in the oven at 40°C for 24 h and then used throughout the experiment. The synthesis reaction is given in Fig. 1.

2.4. Experimental procedure

The adsorption of Cd(II), Cu(II), Ni(II) and Pb(II) ions onto DMPPP were studied by batch technique. Individual solutions of Cd(II), Cu(II), Ni(II) and Pb(II) were prepared by diluting of their stock solution at 1,000 mg L^{-1}. The experimental studies were accomplished as following: The different amounts of polymer were added into 50 mL of pH-adjusted working solutions then shaken at 200 rpm and different temperatures for varying time intervals.

The suspensions were percolated through filter paper and the concentration of the metals in the filtrates was measured using flame atomic absorption spectrometer (FAAS). The metal ions adsorbed per unit amount of the polymer were calculated using Eq. (1).

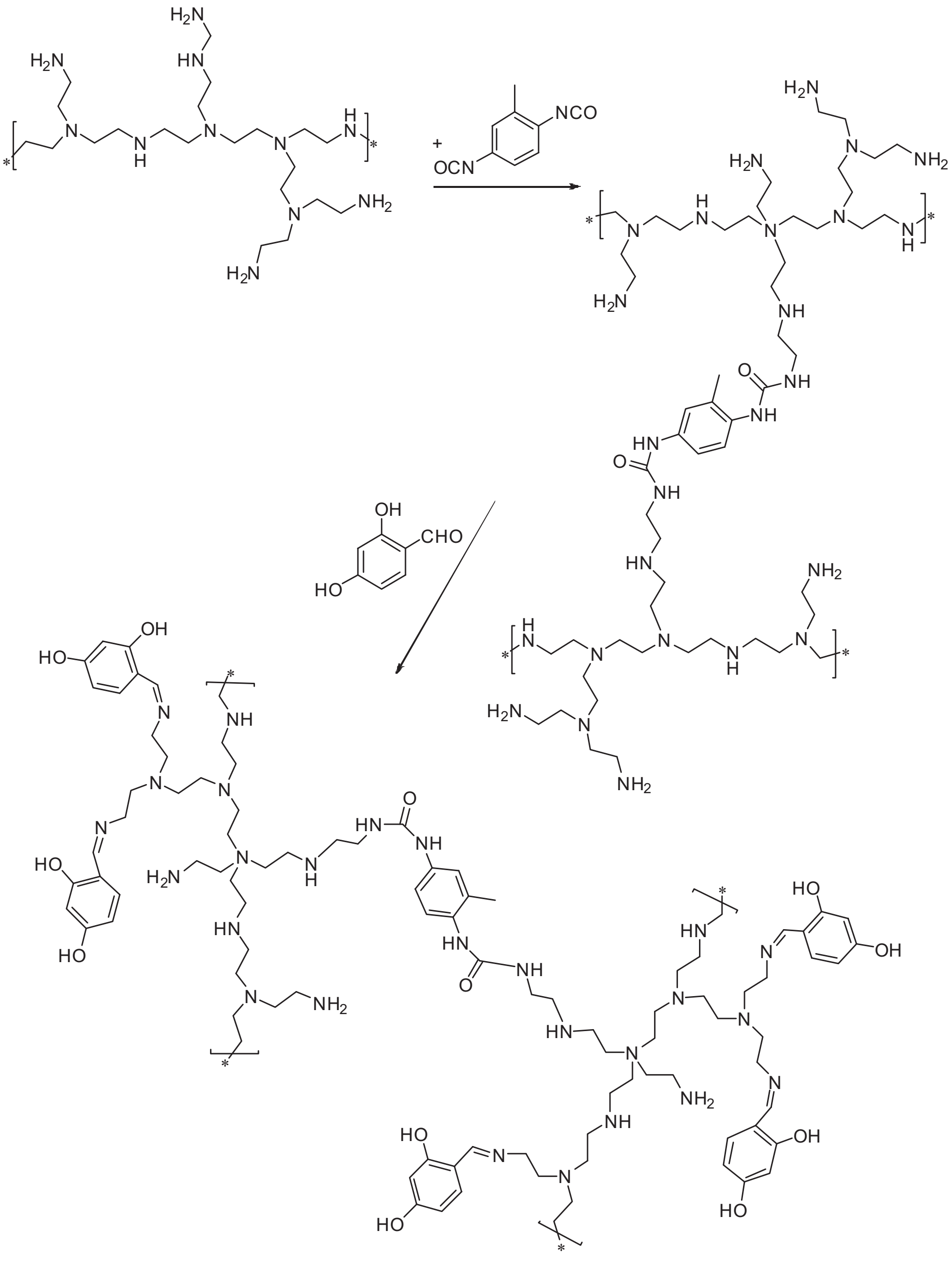

Fig. 1. Synthesis scheme of polyamine-polyurea polymer and its modification with 2,4-dihydroxybenzaldehyde.

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{1}$$

where q_e (mg g^{-1}) is the amount of metal ions adsorbed onto the polymer unit, C_0 (mg L^{-1}) is the initial concentration of metal ions, C_e (mg L^{-1}) is the concentration of metal ions in equilibrium in the liquid phase, V (L) is volume of the adsorbent and m (g) is the amount of the DMPPP.

3. Results and discussion

3.1. Characterization of the polymers

According to elemental analysis results (Table 1), the unsaturated hydrocarbon structure in the system was increased after attachment of dihydroxybenzaldehyde to the PPP polymer structure. This increase in unsaturation caused an increase in the carbon content from 53.25% to 55.80% along with the decrease from 7.58% to 7.26% in hydrogen content, which is the determinant of saturated structure. In the same way, the absence of nitrogen in the

Table 1
Elemental analysis results

Polymer	C%	H%	N%
PPP	53.25	7.58	21.10
DMPPP	55.80	7.26	19.64

content of DHBA that added to the system will cause a decrease in the structure of the % N content. Therefore, a decline from 21.10% to 19.64% has been observed in the nitrogen content.

The chemical structure of the prepared polymer was also confirmed by Fourier transform infrared (FTIR) spectroscopic investigation. In the FTIR spectrum of DMPPP, the stretching of 2,4-dihydroxybenzaldehyde group occurred at 3,372 cm^{-1}, N–H stretching of the secondary NH groups appeared at 3,297 cm^{-1}. The C–H stretching of the aromatic groups was seen as a weak band at 3,060 cm^{-1}. The aliphatic C–H stretching bands formed the main skeleton of the polymer chain were determined in the range of 2,924–2,834 cm^{-1}. The stretching vibrations belong to the C=O functional groups forming the urea group of the polymer appeared at 1,643 cm^{-1} and the stretching vibrations belong to the Schiff bases formed by the addition of the aldehyde derivative have emerged at 1,599 cm^{-1}. Aromatic C=C stretching of the aromatic rings may be due to isocyanates and aldehydes in the polymer structure were recorded at 1,529 cm^{-1}. On the other hand, C–C stretching of aliphatic chains has emerged at 1,450–1,423 cm^{-1} range and N–H deformation bands were remained below them. The moderate peak appeared at 1,227 cm^{-1} can be attributed as the deformation of the carbon oxygen nitrogen (O=C-N) amide bond [32]. These findings show that the 2,4-dihydroxybenzaldehyde was covalently bonded to polyamine polymer.

3.2. Effect of pH

In order to determine the appropriate pH for the adsorption of Cd(II), Cu(II), Ni(II) and Pb(II) from aqueous solutions, 50 mL of their individual solutions at the concentration of 50 mg L^{-1} and pH in the range of 1.0 to 6.0 were suspended with 0.050 g of DMPPP and then the suspensions were stirred for 120 min.

As can be seen from the results (Fig. 2(a)), the small amount of adsorption was observed at the pH value of 1.0 and also 2.0. The amounts of adsorbed metals rapidly increased by increasing the pH value from 2.0 to 4.0, but then the adsorbed quantities have not changed significantly with the rise of pH from 4.0 to 5.0. Because of the insignificant difference of adsorbed ion amounts between pH 5.0 and 6.0 for all metal ions, the pH value of 6.0 was used for the next operations.

The surface of DMPPP includes functional groups such as amine and phenolic hydroxyl groups. The uptake of metal ions from aqueous solution occurred by chelation of the metal ions with these groups. At acidic conditions, amine groups was protonated to form $–NH_3^+$ and weak hydrogen bond occurred between phenolic hydroxyl group and H^+. Hence, adsorption of the metal ions was hindered. By increasing the pH, the electron pair of donor atoms in these functional groups can be used for the chelation of the metal ions. According to Pearson acid-base concept, HSAB, hard and moderate metals can form a complex with hard and moderate ligands [33]. The metal ions such as Cd(II), Cu(II), Ni(II) and Pb(II) can form a complex with both amine and hydroxyl groups. Hence, multidentate complex may occur between DMPPP and the metal ions.

3.3. Effect of contact time

The working solutions (50 mL) containing 50 mg L^{-1} of Cd(II), Cu(II), Ni(II) and Pb(II) ions were suspended with 0.050 g of DMPPP for sequence of time from 5 to 240 min to define the optimal contact time. As shown in Fig. 2(b), the amounts of adsorbed metal ions on DMPPP have increased by increasing the contact time till 120 min but after 120 min it was not seen to change significantly. Therefore, the contact time has been applied as 120 min for the rest of the study.

3.4. Effect of the DMPPP amount

The effect of DMPPP amount on the adsorption of Cd(II), Cu(II), Ni(II) and Pb(II) ions from solutions having initial concentration of 50 mg L^{-1} was investigated with the changing amount of DMPPP between 0.020 and 0.075 g at optimal pH and contact time. Fig. 2(c) was generated using the obtained data , where the adsorbed amount of metal ions was decreasing with increasing amounts of DMPPP. This decrement was expressed with the inverse relationship between the dose of adsorbent and the amount of metal ion which adsorbed by per unit of adsorbent [34,35]. In addition, the diffusion path lengthens due to the agglomeration and aggregation in adsorption regions and the decrease in the total adsorbent surface area may explain the reduction of adsorbed metal ion amount [36].

3.5. Effect of initial metal concentration

The solutions including initial concentrations of Cd(II), Cu(II), Ni(II) and Pb(II) ions ranging from 50 to 300 mg L^{-1} were stirred with 0.050 g dose of DMPPP at appropriate conditions to examine the effect of the initial metal ion concentration on adsorption, the obtained results shown in Fig. 2(d). The adsorbed amounts of Cd(II), Cu(II), Ni(II) and Pb(II) ions on DMPPP have observed to increase depending on the increasing initial metal ion concentration initially but after equilibrium was achieved the amounts of adsorbed ions have reached a constant value. The adsorption has increased with increased concentration because the initial concentration is an important driving force for adsorbing onto the solid phase from the liquid phase of metal ions. On the other hand, the observed equilibrium state at higher concentrations is an expression of the saturation in active binding zones of polymer [37,38].

3.6. Influence of temperature and thermodynamic parameters

The temperature effect on the adsorption of Cd(II), Cu(II), Ni(II) and Pb(II) ions by DMPPP was searched at the concentration of 100 mg L^{-1} and the temperature range of 298 and 328 K. It was found that the adsorption of Cd(II), Cu(II), Ni(II) and Pb(II) ions onto DMPPP increased by increasing the temperature. Adsorption of Cd(II), Cu(II), Ni(II) and Pb(II) ions by DMPPP was 70.9, 70.8, 73.5 and 74.9 mg g^{-1} at 298 K, respectively, and they increased to 75.5, 80.5, 78.1 and 77.8, mg g^{-1} by increasing the temperature to 328 K, respectively. These findings indicate that the processes have endothermic nature.

Thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (ΔH) and the entropy change (ΔS) were also calculated for the adsorption of Cd(II), Cu(II), Ni(II) and

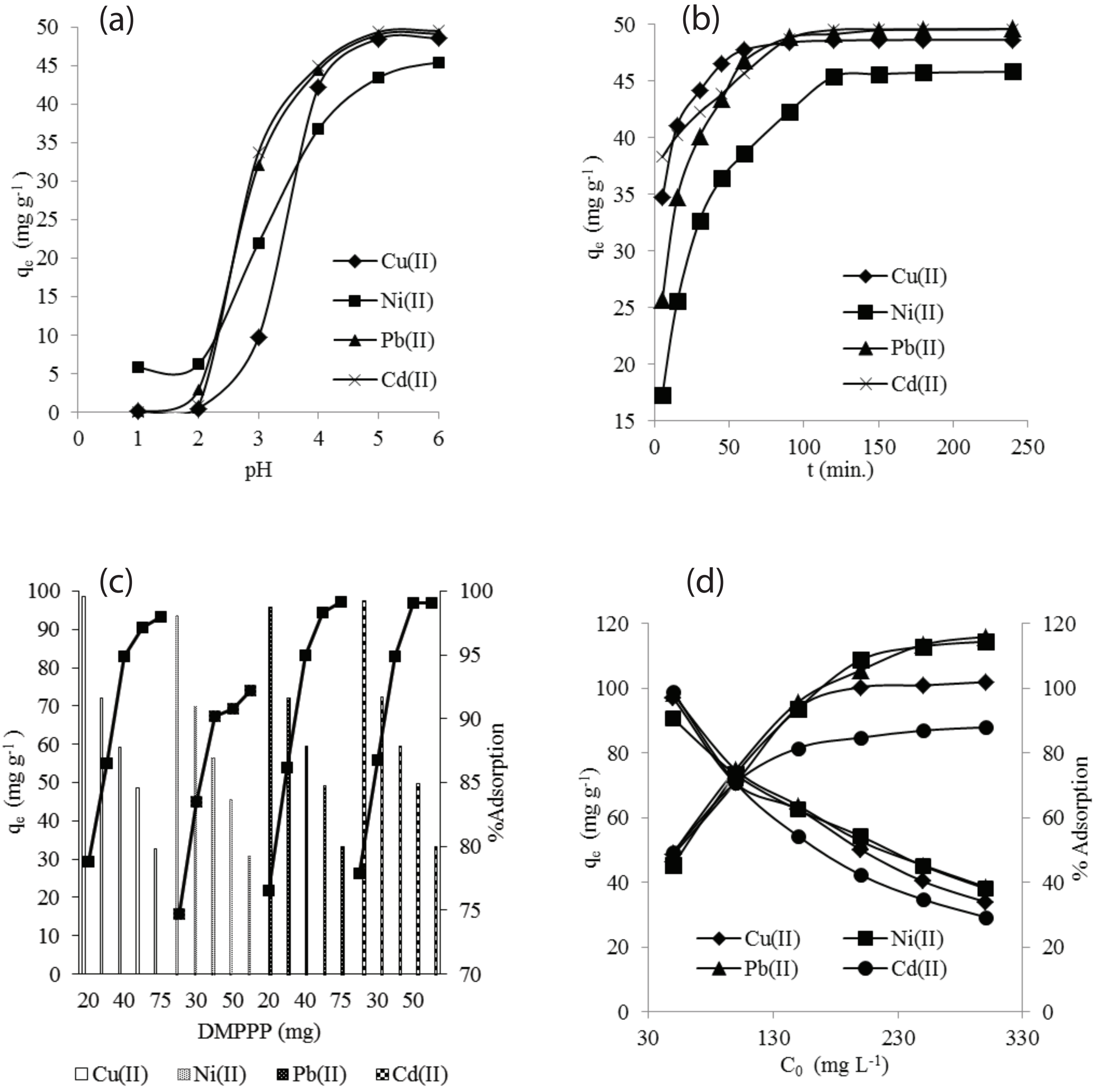

Fig. 2. Effect of various factors on the adsorption of Cd(II), Cu(II), Ni(II) and Pb(II) ions. (a) Ph (experimental conditions: initial ion concentration: 50 mg/L, adsorbent dose: 0.05 g/50 mL, agitation speed: 200 rpm, temperature: 298 K, contact time: 120 min); (b) contact time (experimental conditions: initial ion concentration: 50 mg/L, adsorbent dose: 0.05 g/50 mL, agitation speed: 200 rpm, pH: 6.0, temperature: 298 K); (c) DMPPP dose (experimental conditions: initial ion concentration: 50 mg/L, agitation speed: 200 rpm, pH: 6.0, temperature: 298 K, contact time: 120 min); (d) initial metal ion concentration (experimental conditions: adsorbent dose: 0.05 g/50 mL, agitation speed: 200 rpm, pH: 6.0, temperature: 298 K, contact time: 120 min).

Pb(II) ions onto DMPPP. Eq. (2) was used to calculate the change of Gibbs free energy [39].

$$\Delta G = -RT\ln K_d \qquad (2)$$

The K_d is the distribution constant and was calculated by the ratio of the adsorbate concentration adsorbed on per unit mass of the adsorbent (C_{ads}, mg L^{-1}) to adsorbate concentration remaining in solution (C_e, mg L^{-1}) [31].

Gibbs free energy equation includes two thermodynamic functions, named the enthalpy change (ΔH) and the entropy change (ΔS). Therefore, Eq. (2) can be written as Eq. (3) [39] and Eq. (5) can be derived by equalizing as shown in Eq. (4).

$$\Delta G = \Delta H - T\Delta S \qquad (3)$$

$$\Delta H - T\Delta S = -RT\ln K_d \qquad (4)$$

$$\text{In}K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (5)$$

The values of ΔH and ΔS calculated from the slope and the intercept of the plot drawn between ln$K$ vs. 1/T are given in Table 2. The positive values of ΔH indicate that the processes have endothermic nature. The positive values of the entropy change introduce the increasing randomness in liquid and solid interface during adsorption processes. In addition, the negative value of the Gibbs free energy change is an indication that the adsorption occurs spontaneously [40].

3.7. Adsorption isotherms

The adsorption isotherm data of Cd(II), Cu(II), Ni(II) and Pb(II) ions on to DMPPP were applied to the Langmuir and Freundlich isotherm models.

Linearized expressions of the Langmuir and Freundlich equations are given as Eq. (6) and Eq. (7), respectively.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{1}{q_{\max}} C_e \tag{6}$$

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \tag{7}$$

where q_e is absorbed metal ions by per unit mass of the DMPPP, C_e is the concentration of metal ions in liquid medium in the equilibrium, K_L is Langmiur constant, $q_{\max}$ is the maximum adsorption capacity [41]. K_f and n represent Freundich constant and the adsorption density, respectively, [42].

The constants of Langmuir ($q_{\max}$, K_L) and Freundlich (n, K_f) were calculated from the slope and the intercept of the linear plots of C_e/q_e vs. C_e and lnC_e vs. lnq_e, respectively. The values of constants ($q_{\max}$, K_L and n, K_f) are displayed in Table 3.

The regression coefficient (r^2) values of Langmuir isotherm model were found to be higher compared with Freundlich model. The adsorption of each ions on DMPPP was better expressed with Langmuir isotherm model, it has been also proved by the accordance with the value calculated by Langmuir isotherm equation of experimental data [43]. Fig. 3 also clearly shows that the experimental data for each metal is consistent with the Langmuir isotherm data.

The maximum adsorption capacity of DMPPP for Cd(II), Cu(II), Ni(II) and Pb(II) ions was calculated to be 105.3, 117.6, 137.0 and 144.9 mg g^{-1}, respectively. In order to investigate the effect of modification of PPP with 2,4-dihydroxybenzaldehyde, the adsorption of Cd(II), Cu(II), Ni(II) and Pb(II) ions was also studied using bare polyamine-polyurea polymer. The adsorption capacity of the PPP for Cd(II), Cu(II), Ni(II) and Pb(II) ions was found to be 24.4, 18.7, 46.1 and 29.9 mg g^{-1}, respectively. From these results, DMPPP showed a capacity for the metal ions adsorption at least three times larger than that of PPP. These results showed that adsorption capacity of the PPP was clearly increased by its modification with 2,4-dihydroxybenzaldehyde.

The maximum adsorption capacities of different adsorbents previously reported in the literature are given in Table 4 in order to compare with the capacity of DMPPP produced in this study. The capacities of graphene oxide/polyamidoamine dendrimers and soy protein hollow microspheres are higher than DMPPP and the prepared polymer in this study also has higher metal uptake capacity than the other adsorbents. Hence, DMPPP can be accepted among the adsorbents having high adsorption capacities [10,44–49].

Table 2
Thermodynamic parameters for Cd(II), Cu(II), Ni(II) and Pb(II) adsorption on the DMPPP (experimental conditions: initial ion concentration: 100 mg/L, adsorbent dose: 0.05 g/50 mL, agitation speed: 200 rpm, pH 6.0, contact time: 120 min)

	T (K)	Cd(II)	Cu(II)	Ni(II)	Pb(II)
ΔG (kJ mol^{-1})	298	−2.21	−2.19	−2.52	−2.70
	308	−2.45	−2.65	−2.80	−2.94
	318	−2.74	−3.24	−3.13	−3.15
	328	−3.06	−3.87	−3.46	−3.41
ΔH (kJ mol^{-1})[a]		6.28	14.56	6.83	4.27
ΔS (kJ mol^{-1})[a]		28.42	56.06	31.33	23.64

[a]Measured between 298 and 328 K.

Table 3
Parameters of Langmuir and Freundlich isotherms at different dosage of DMPPP for Cd(II), Cu(II), Ni(II) and Pb(II) adsorption (experimental conditions: agitation speed: 200 rpm, pH: 6.0, Temperature: 298 K, contact time: 120 min)

	Dosage (mg 50 mL^{-1})	Langmuir constants			Freundlich constants		
		$q_{\max}$ (mg g^{-1})	K_L (L mg^{-1})	r^2	K_f (mg g^{-1})	n	r^2
Cd(II)	40	105.3	0.182	0.9992	53.1	7.8	0.9836
	50	89.3	0.214	0.9989	52.9	10.3	0.9918
	75	76.3	0.184	0.9984	36.8	7.2	0.9878
Cu(II)	40	117.6	0.167	0.9986	51.8	6.3	0.9634
	50	105.3	0.144	0.9969	45.4	3.2	0.9531
	75	80.0	0.245	0.9963	33.8	5.6	0.9627
Ni(II)	40	137.0	0.085	0.9981	39.7	4.2	0.9766
	50	128.2	0.081	0.9973	30.8	3.8	0.9821
	75	98.0	0.061	0.9902	20.2	3.3	0.9691
Pb(II)	40	144.9	0.097	0.9967	48.9	4.8	0.9897
	50	120.5	0.100	0.9941	48.9	6.1	0.9750
	75	87.7	0.152	0.9971	37.4	6.1	0.9756

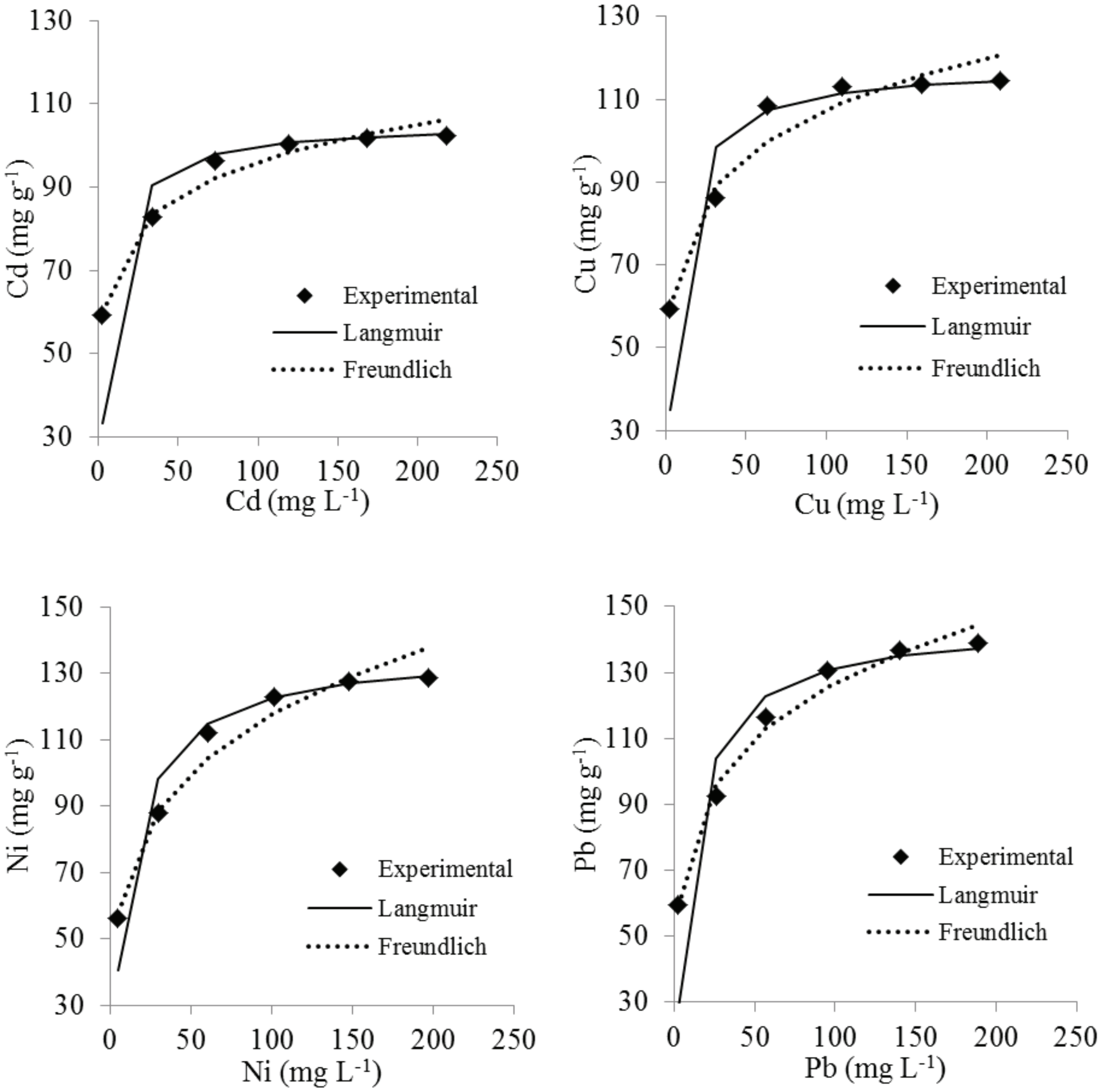

Fig. 3. The compatibility comparison charts of isotherms for Cd(II), Cu(II), Ni(II) and Pb(II) ions (experimental conditions: adsorbent dose: 0.05 g/50 ml, agitation speed: 200 rpm, pH: 6.0, temperature: 298 K, contact time: 120 min).

3.8. Adsorption kinetics

The adsorption kinetics of Cd(II), Cu(II), Ni(II) and Pb(II) ions with DMPPP were studied by the pseudo-first- [50] and the pseudo-second-order [51] kinetic models and their adsorption mechanism was investigated by intraparticle diffusion model [52]. The equations belong to the kinetic models are as follows:

Pseudo-first order: $\ln(q_e - q_t) = \ln q_e = k_1 t$ (8)

Pseudo-second order: $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ (9)

Intraparticle diffusion: $q_e = K_{\text{id}} t^{1/2} + C$ (10)

where t is the time (min), q_e is the amount of adsorbed ions in equilibrium (mg g^{-1}), q_t is the amount of adsorbed ions at the time t (mg g^{-1}), k_1 is the kinetic constant of pseudo-first order (min^{-1}) and k_2 is the kinetic constant of pseudo-second order (g mg^{-1} min^{-1}). c is the intercept point and k_{id} is the diffusion constant (mg g^{-1}min$^{-1/2}$) for intraparticle diffusion model.

As can be seen in Table 5, the $q_{\text{theoretic}}$ values of the second-order kinetic model and the values of q_{empiric} are much closer to each other compared with $q_{\text{theoretic}}$ value of the first-order kinetic model. As supported in the r^2 value, the adsorption kinetics of Cd(II), Cu(II), Ni(II) and Pb(II) ions with DMPPP was found to be quite compatible with second-order kinetic model [53].

The results of the applications to the intraparticle diffusion model are also presented in Table 5. The increase in the value of k_{id} means the strengthened adsorption by the strengthening bond between the adsorbent and adsorbate.

Table 4
The comparison of maximum adsorption capacities of various adsorbents for Cd(II), Cu(II), Ni(II) and Pb(II) ions

Adsorbents	Adsorption capacity								
	Cd(II)	Cu(II) (mg g^{-1})	Ni(II)	Pb(II)	C_0 (mg L^{-1})	pH	m (mg)	V (mL)	Ref.
Carboxyl functionalized MNPs	45.7	44.8	–	74.6	10	6	20	20	[10]
Modified silica particles	55.5	35.7	–	19.6	–	6	10	10	[34]
GO/PAMAM dendrimers	253.8	68.7	–	568.2	800	4.5	100	–	[35]
Synthesized azide cancrinite	45.5	–	38.5	52.6	–	5/6	500	50	[36]
(G-ZnO) composites	–	37.4	–	23.4	10	6	20	20	[38]
Xylan-rich hemicelluloses-based hydrogel	495.0	–	–	859.0	200	5.5/6.5	10	50	[39]
Soy protein hollow microspheres	120.8	115.0	177.1	235.6	200	4.5/5	–	–	[37]
DMPPP	105.3	117.6	137.0	144.9	50	6	40	50	This study

Table 5
Parameters of pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models for Cd(II), Cu(II), Ni(II) and Pb(II) adsorption onto DMPPP (experimental conditions: adsorbent dose: 0.05 g/50 mL, agitation speed: 200 rpm, pH: 6.0, Temperature: 298 K)

	C_0 (mg L^{-1})	$q_{e(\text{exp})}$ (mg g^{-1})	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
			$k_1 \times 10^2$ (min^{-1})	$q_{e(\text{cal})}$ (mg g^{-1})	r^2	$k_2 \times 10^2$ (g mg^{-1} min^{-1})	$q_{e(\text{cal})}$ (mg g^{-1})	r^2	k_{id} (mg g^{-1} min$^{-1/2}$)	c (mg g^{-1})	r^2
Cd(II)	50	49.58	4.5	26.3	0.9615	0.41	51.0	0.9992	1.1	36.4	0.9444
	100	71.9	2.9	20.4	0.9814	0.38	73.0	0.9997	1.3	56.1	0.9483
	150	82.6	2.5	20.5	0.9895	0.33	84.0	0.9996	1.4	65.3	0.9656
Cu(II)	50	45.2	2.9	12.4	0.9668	0.76	49.5	0.9999	1.1	36.8	0.7465
	100	53.9	2.5	18.6	0.9914	0.35	72.5	0.9998	1.5	54.3	0.8648
	150	60.4	2.7	22	0.9927	0.20	95.2	0.9998	1.3	78.8	0.9259
Ni(II)	50	45.83	3.4	40.2	0.9771	0.15	49.5	0.9983	2.5	16.8	0.9056
	100	74.92	2.9	39.3	0.9824	0.17	77.5	0.9985	2.4	45.4	0.9567
	150	95.54	2.8	51.4	0.9862	0.12	99.0	0.9979	3.3	55.1	0.9637
Pb(II)	50	49.61	3.5	25.5	0.9920	0.28	51.8	0.9995	2.0	27.3	0.8249
	100	76.5	3.0	36.0	0.9643	0.20	78.7	0.9988	2.1	51.3	0.9692
	150	96.6	2.8	28.2	0.9863	0.25	98.0	0.9994	1.9	74.0	0.9626

The plots q_t vs. $t^{1/2}$ have reflected the two-step mechanism for Cd(II), Cu(II), Ni(II) and Pb(II) ions adsorption onto DMPPP. The external surface adsorption and intraparticle diffusion considered to occur at first and second steps, respectively. It was observed that none of the curves have passed through the origin. So, the intraparticle diffusion is not singly limiting factor on the adsorption kinetics of the metal ions. The adsorption kinetics were controlled by external surface adsorption jointly with intraparticle diffusion [52,54,55].

3.9. Desorption of Cd(II), Cu(II), Ni(II) and Pb(II) ions from DMPPP

Desorption experiments were carried out using 20 mL of 0.5 M HNO_3 solutions after simultaneous adsorption of Cd(II), Cu(II), Ni(II) and Pb(II) ions. These experiments were performed three cycles using same adsorbent. In all cycle, the adsorption and desorption percent were found to be quantitative (≥90%). These results demonstrate the usefulness of the DMPPP for the repeated application.

3.10. Removal of Cd(II), Cu(II), Ni(II) and Pb(II) ions from real wastewaters

The developed adsorption process was tested for the removal of Cd(II), Cu(II), Ni(II) and Pb(II) ions from real wastewater supplied from two automotive factories (Turkey). The characterization of wastewater samples was given below. The pH of the wastewaters 1 and 2 was found to be 4.35 and 6.02, respectively. Suspended solid matter (mg L^{-1}) and chemical oxygen demand (mg L^{-1}) was 10 and 42 for wastewater 1 and 77 and 650 for wastewater 2, respectively. The conductivity (µS) of the wastewaters 1 and 2 was found to be 1,188 and 1,355, respectively. The level of Ni (II) ions (mg L^{-1}) in wastewaters 1 and 2 was found to be 35.50 and 28.25, respectively, and the level of Pb(II), Cd(II) and Cu(II) was found to be below detection limits of flame atomic absorption spectrometer which were calculated to be 0.052, 0.015 and 0.029 for Pb(II), Cd(II) and Cu(II), respectively. Hence, these metal ions were spiked to the wastewater to be 25.0 mg L^{-1} and then, adsorption experiments were performed.

After filtration of the water samples and pH adjustment, 0.05 g of the polymer was added to the water samples (50 mL) and then, the obtained suspension was shaken at optimal contact time of 120 min. After determination of the metal ions levels in the filtrates, the percent removal was calculated. Removal of Cd(II), Cu(II), Ni(II) and Pb(II) ions was achieved to be 82.0%, 97.5%, 84.6% and 87.2% for wastewater 1, and 93.0%, 98.0%, 89.0% and 86.0% for wastewater 2, respectively. It can be concluded that the prepared polymeric adsorbent of polyamine-polyurea polymer modified with 2,4-dihydroxybenzaldehyde was highly efficient for simultaneous removal of Cd(II), Cu(II), Ni(II) and Pb(II) ions from real wastewater supplied from automotive factories.

4. Conclusion

The present study reveals that new modified polyamine-polyurea polymer can be effectively used as a material for removing heavy metal ions from aqueous solution. As can be seen from the results of experimental studies, the maximum adsorptions of heavy metals were obtained at solution pH of 6.0 and adsorption equilibrium was reached in contact time of 120 min. Isotherm and kinetic mechanisms of heavy metal adsorption on DMPPP were seen to be identified by the Langmuir and the pseudo-second-order models, respectively. Results obtained from thermodynamic studies interpreted the process as endothermic with the positive values of ΔH, as spontaneous with the negative values of ΔG and as having an increased randomness with the positive values of ΔS. Finally, a successful synthesis and an efficient removal were carried out with DMPPP having the highest adsorption capacity for Cd(II), Cu(II), Ni(II) and Pb(II) ions between polyamine polymers. It is clear that DMPPP can be used as an adsorbent to remove heavy metals from wastewater.

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