



Removal of Hazardous Metal Ions by Newly Synthesized Polymers Bearing Thiourea Groups

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Two new polymers were synthesized from the reaction of adipoyl isothiocyanate with aromatic amines, poly[N-(4'-aminophenyl)amino]-carbonothioyl-N'-thioformylhexanediamide] and poly[N-(4'-aminobiphenyl-4-yl)amino]carbonothioyl-N'-thioformylhexanediamide]. The synthesized polymers were characterized by FTIR, ^1H and ^{13}C NMR. They proved to be effective sorbent materials for the removal of some hazardous metal ions (Cu^{2+} , Cd^{2+} , Zn^{2+} and Co^{2+}) from aqueous solutions. The study included the effect of different conditions on the adsorption efficiency such as contact time, initial metal ion concentration, pH and temperature of the solution. The adsorption isotherms could be fitted well Langmuir and Freundlich adsorption isotherms. Thermodynamic values of ΔH° and ΔS° revealed that the adsorption process was endothermic and accompanied by randomness at the solid-liquid interface. However, ΔG° values indicate that the adsorption process was a spontaneous, feasible process in most of the cases.

Keywords: Thiourea, Adipoyl chloride, Aromatic amines, Adsorption, Thermodynamic parameters.

INTRODUCTION

Large amounts of metal contaminated wastewaters are produced by various industries. The wastewater contains hazardous soluble metal ions such as Cu^{2+} , Cd^{2+} , Zn^{2+} , Co^{2+} and Pb^{2+} , causing a great damage to health and the environment. Therefore, the wastewater should be treated prior to discharge into rivers and lakes [1]. Numerous approaches have been used for treatment such as, chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation-flocculation, flotation and electrochemical methods [2,3]. A potentially low cost sorbents such as chitosan, zeolite, clay, sea weed, *etc.* were tried for heavy metal removal [4].

Chitosan and water insoluble cross-linked chitosan beads were investigated as sorbents for Cu(II) ions [5]. A modified crosslinked polyacrylamides with various functional groups were used for the removal of Cu(II), Cd(II) and Pb(II) ions at different pHs. Moreover, it was found that the metal ions removal capacities were mainly depend on the variation of chemical structure of the modified crosslinked polyacrylamide [6]. Poly-(1-vinylimidazole) with a trimethoxysilyl group at one side grafted onto nanoparticles (Mag-Im18) was synthesized and some metal ions removal efficiency was determined [7]. A concentrated heavy metal ions were removed from aqueous solutions by poly(N,N'-dipropionitrileacrylamide) enriched with amidoxime groups. The study included the removal of UO_2^{2+} , Pb^{2+} , Cu^{2+} and Co^{2+} ions [8]. A selective removal of

hazardous heavy metal ions from industrial wastewater and replaced by those non-hazardous ions using an ion exchange technique were also successively carried out [9].

An efficient complexing membrane consists of poly(ethyleneimine) in poly(vinyl alcohol) matrix was used to remove Pb^{2+} , Cd^{2+} and Cu^{2+} ions from aqueous solutions having removal efficiency of 96-99.5 % [10]. The removal of four metal ions of Ag^+ , Cu^{2+} , Fe^{2+} and Pb^{2+} by poly(acrylonitrile) nanofiber mats was evaluated at various conditions, *viz.* pH, initial concentration of metal ion solution and contact time [11]. The magnetic nanoparticles Fe_3O_4 modified with certain polymers proved to have an excellent ability to remove some heavy metal ions from aqueous solutions. Furthermore, it can be used as a reusable adsorbent with easy conditions [12]. Novel polymeric adsorbents having amide, azomethine, pyridyl and thiourea binding centers were tested for the removal of Cd^{2+} and Pb^{2+} ions from different aqueous solutions, the study showed that adsorption-desorption process was a reversible process [13]. A hyper-crosslinked resin that chemically modified with thiourea was synthesized and examined as an efficient material for the removal of Pb^{2+} , Cu^{2+} and Cd^{2+} from aqueous solutions [14].

In this work, we intended to synthesize two multifunctional polymers and study their adsorption capacities under various conditions towards some heavy metal ions (Cu^{2+} , Cd^{2+} , Zn^{2+} and Co^{2+}). The synthesized polymers were derived from the reaction of adipoyl dichloride with diamines.

EXPERIMENTAL

Adipoyl dichloride, ammonium thiocyanate, 1,4-phenylene diamine, 4,4'-biphenyl diamine and acetone were purchased from Sigma-Aldrich company and used without any further purification. Melting points were determined in open capillary tubes on SMP30 melting point (Stuttgart, Germany) without correction. Fourier transform infrared (FT-IR) spectra were recorded in the range of (4000-600 cm^{-1}) by Shimadzu model FTIR-8400S, using an ATR kit (Japan). ^1H and ^{13}C NMR were measured by Bruker spectrometer model ultra-shield at 300 MHz and 100 MHz, respectively. Deuterated dimethyl sulphoxide ($\text{DMSO-}d_6$) was used as solvent and tetramethylsilane (TMS) as internal standard, the chemical shifts were recorded in ppm. Atomic absorption analysis was performed by Phoenix-986 AA (Cyprus).

Synthesis of polymers: Adipoyl dichloride (0.10 mol, 1.83 g) was dissolved in acetone (25 mL) and the resulted solution was added dropwise to a cooled solution (0-5 $^{\circ}\text{C}$) of ammonium thiocyanate (0.20 mol, 1.52 g) in acetone (50 mL). The reactants were stirred for additional 2 h and the formed precipitate (NH_4Cl) was removed by filtration. The filtrate was treated with the solution of 1,4-phenylene diamine (0.10 mol, 1.08 g) to get polymer **P1** and when treated with 4,4'-phenylene diamine (0.10 mol, 1.84 g) in 50 mL acetone 50 mL, polymer **P2** was formed. The amine solution was added drop-wise with continuous stirring at room temperature. The resultant mixture was left to stir overnight and the formed polymeric precipitate was separated by filtration and washed with hot acetone.

Poly[N-(4'-aminophenyl)amino]carbonothioyl]-N'-thioformylhexanediamide (P1): Yield 72 %, m.p. 300-309 $^{\circ}\text{C}$; FT-IR (ν_{max} , cm^{-1}): 3163 (N-H), 3078 (C-H, arom.), 2945, 2850 (C-H, aliph.), 1689 (C=O, amide), 1606, 1518 (C=C, arom.), 1155, 1246 (br.) (C=S). ^1H NMR ($\text{DMSO-}d_6$), (δ ppm): 1.4-2.05 (8H, m, CH_2), 7.49-7.89 (4H, 2d, arom.), 11.50 (2H, s, CONH), 12.50 (2H, s, ph-NH). ^{13}C NMR ($\text{DMSO-}d_6$): (δ ppm), 23.72-35.98 (4C, $(\text{CH}_2)_4$), 118.98-137.32 (6C, arom.), 175.19 (1C, C=O), 178.69 (1C, C=S).

Poly[N-(4'-aminobiphenyl-4-yl)amino]carbonothioyl]-N'-thioformylhexanediamide (P2): Yield 71 %, m.p. 280-288 $^{\circ}\text{C}$; FT-IR (ν_{max} , cm^{-1}): 3165 (N-H), 3061 (C-H, arom.), 2956, 2860 (C-H, aliph.), 1687 (C=O, amide), 1599, 1521 (C=C, arom.), 1151, 1247 (br.) (C=S). ^1H NMR ($\text{DMSO-}d_6$), (δ ppm): 1.70-2.20 (8H, m, CH_2), 6.80-8.10 (8H, m, arom.), 11.50 (2H, s, CONH), 12.60 (2H, s, ph-NH). ^{13}C NMR ($\text{DMSO-}d_6$): 23.72-35.47 (4C, $(\text{CH}_2)_4$), 96.66-137.40 (12C, arom.), 177.10 (1C, C=O), 197.17 (1C, C=S).

Removal studies of metal ions: The adsorption properties of the synthesized polymers (**P1** and **P2**) were examined by using aqueous solutions of four heavy metals (Cu^{2+} , Cd^{2+} , Zn^{2+} and Co^{2+}). The procedure starts by suspending 50 mg of polymer in solution of the metal ions (10 mL of 2 mg/L) and the resulted mixture was left to stir continuously for the different periods (1, 3, 5, 10, 20, 30 and 180 min). The solid material was separated by filtration and the concentration of the metal ion residue was measured by flame atomic absorption spectrometry.

RESULTS AND DISCUSSION

Two new polymers (**P1** and **P2**) containing thiourea group in their backbone were synthesized from the reaction of adipoyl dichloride with ammonium thiocyanate, followed by condensation with either phenylene diamine to furnish polymer (**P1**) or *p*-diphenylene diamine to produce polymer (**P2**). The reaction includes two steps, the first one is a nucleophilic attached with thiocyanate anion on the carbon of adipoyl carbonyl group leading to the formation of adipoyl diisothiocyanate. The later is a monomer with two similar functional groups, was subjected to a condensation reaction with aromatic diamine monomers *via* step polymerization mechanism [15]. The reaction steps and the suggested mechanism are depicted in **Scheme-I**.

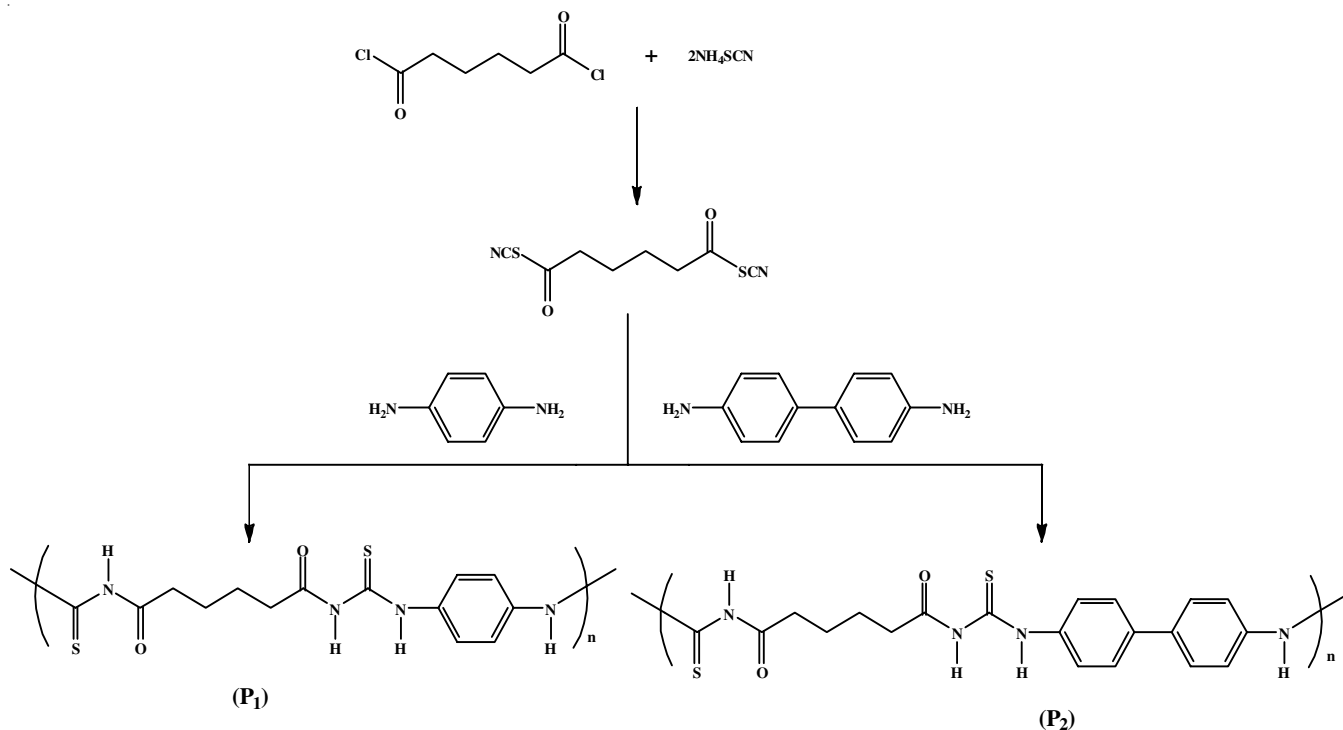
An analogue condensation reactions were to synthesize polymers and compounds having thiourea moiety in their structure were reported previously, but in the presence of some solid-liquid phase transfer catalyst such as PEG-400 or PEG-600 [16,17]. However, the conditions used in synthesizing polymers (**P1** and **P2**) were based on the procedures reported to prepare thiourea derivatives from the reaction of acid chlorides with different secondary amines [18-21].

IR and NMR spectra: The FT-IR and NMR spectra of the synthesized polymers (**P1** and **P2**) confirmed their suggested structure. The main bands in FT-IR spectra of polymer **P1** appeared at 3163 cm^{-1} for N-H, 3078 cm^{-1} for C-H (arom.), 2945 and 2850 cm^{-1} for C-H (aliph.), 1689 cm^{-1} for (C=O, amide), 1606, 1518 cm^{-1} for (C=C, arom.) and 1155, 1246 cm^{-1} for (C=S) group. This was associated with absence of adipoyl carbonyl band which usually appears at 1790 cm^{-1} .

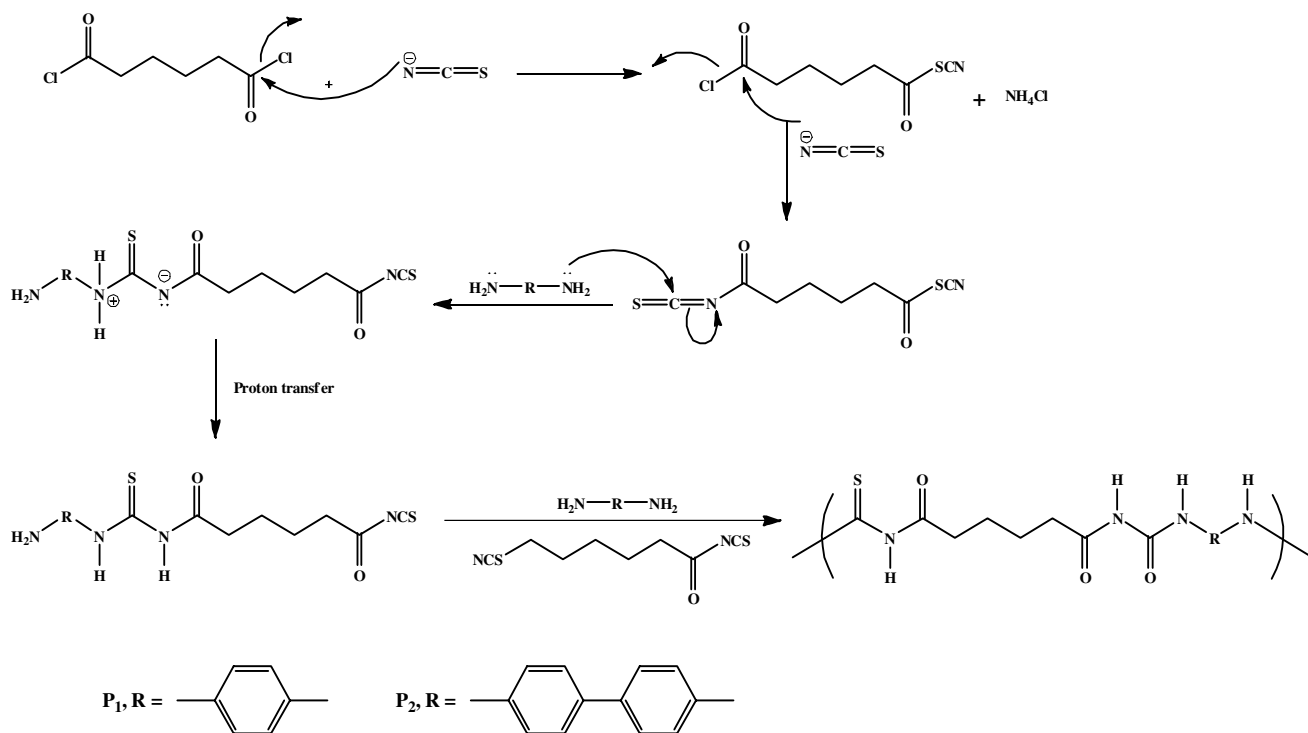
^1H NMR spectrum of polymer **P1** demonstrated various signals, which confirmed the proposed structure, A multiplet signal at δ 1.40-2.05 ppm were assigned to eight protons of aliphatic chain $(\text{CH}_2)_4$ and two doublets at δ 7.49-7.89 ppm were assigned to four aromatic protons. Two signals appeared at δ 11.50 ppm, 2H for (CONH) and at δ 12.50 ppm, 2H for (ph-NH). These two signals were disappeared on the addition of D_2O , This was due to the proton exchange at N atoms. This result provides an additional conformation to N-H proton positions in the polymer structure. ^{13}C NMR analysis showed that the chemical shift of aliphatic carbons $(\text{CH}_2)_4$ appeared in the range of δ 23.72-34.98 ppm, six aromatic carbons at δ 118.98-137.32 ppm. Finally, carbonyl and thiocarbonyl carbons appeared at 175.19 and 178.69 ppm, respectively.

The FTIR spectrum of polymer **P2**, exhibited a characteristic band at 3165 cm^{-1} for N-H stretching vibration and for aromatic C-H at 3061 cm^{-1} . Two bands at the usual position of C-H aliphatic stretching vibrations (2956 and 2860 cm^{-1}). The carbonyl (C=O, amide) and thiocarbonyl (C=S) bands appeared at (1687 cm^{-1}) and (1151, 1247 cm^{-1}), respectively.

The ^1H NMR spectrum of polymer **P2** showed a multiplet signal between δ 1.70 - 2.20 ppm, 8H assigned for protons of aliphatic chain $(\text{CH}_2)_4$. The aromatic protons of two rings appeared as multiplet signal in the range of 6.80-8.10 ppm, 8H, two signals at δ 11.50 ppm, 2H for (CONH) and at δ 12.60 ppm, 2H for (ph-NH), These signals were disappeared from the spectrum on the addition of D_2O due to proton exchange on N-atoms. This gives a profound support to the position of N-H in the



Mechanism



Scheme-I: Schematic representation and the suggested mechanism for the synthesis of polymer **P1** and **P2**

structure of polymer **P2**. ^{13}C NMR spectrum of polymer **P2** exhibited chemical shift at the range δ 23.72–35.47 ppm due to four carbons of aliphatic chain $(\text{CH}_2)_4$ and a signal at δ 96.66–137.40 ppm assigned to 12 carbons of the two aromatic rings. The last two signals at δ 177.10 ppm and δ 197.17 ppm were assigned for carbons of $(\text{C}=\text{O})$ and $(\text{C}=\text{S})$, respectively. Moreover, it is interesting to mention that important bands in FT-IR

spectra of polymers **P1** and **P2** and the signals in their ^1H , ^{13}C NMR were compatible with those reported for similar compounds and polymers [16–21].

Effect of contact time: A set of experiments was carried out to determine the optimum contact time to reach the equilibrium between studied metal ions and synthesized polymers. The removal efficiency was conducted using initial metal ion

concentration of 2 mg/L at 25 °C and 50 mg of polymer at 7 different intervals (1, 3, 5, 10, 20, 30 and 180 min). The removal efficiency (R %) was calculated from eqn. 1:

$$R (\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where C_i is the initial concentration of the metal ions, C_e is the concentration at equilibrium. The optimum contact time (at maximum R %) for the four metal ions with their corresponding polymer are recorded in Table-1.

Metal ion	Polymer P1		Polymer P2	
	Time (min)	R (%)	Time (min)	R (%)
Cu^{2+}	5	55.65	20	97.45
Cd^{2+}	3	36.10	3	62.90
Zn^{2+}	3	49.50	3	70.35
Co^{2+}	3	47.40	5	13.95

Effect of pH: The effect of pH of the metal ion solutions on the adsorption of studied metal ions on the synthesized polymers was examined in a pH range 4, 6, 8, and 10. The removal metal efficiencies (R %) were plotted against pH (Figs. 1 and 2). The results showed that the percentage removal efficiencies of all the metal ions (except Cu^{2+}) start to increase at pH above 6 then developed to high value at pH 10. However, the removal of Cu^{2+} was almost completed at pH from 4 to 10. The most expected explanation for the remarkable increases in the adsorption of the metal ions at above 6 is the decreases in the competition between the protons (H^+) available in the solution and the metal ions due to the decrease of acidity of the solution. Moreover, the value of pH is remarkably related to the surface charge of polymer, ionization of metal and speciation of metal in adsorption operation [22,23]. Therefore, increase of pH of the metal ion solution increases the accessibility of metal ions to the binding sites of polymers under study. This creates a favourable polymer surface charge ready to adsorb the metal ions.

Effect of initial metal ion concentration: A series of experiments concerning the effects of initial metal ion concentration (2, 4, 6, 8, and 10 mg/L) on the removal efficiencies of the used polymers (P1 and P2) were carried out at 0.05 g polymer, pH 10 at 25 °C. The suspension of polymer and metal ion

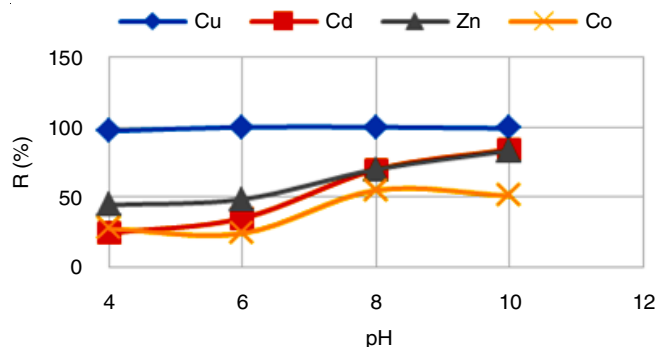


Fig. 1. Effect of the pH of solution on metal ions removal by polymer 1

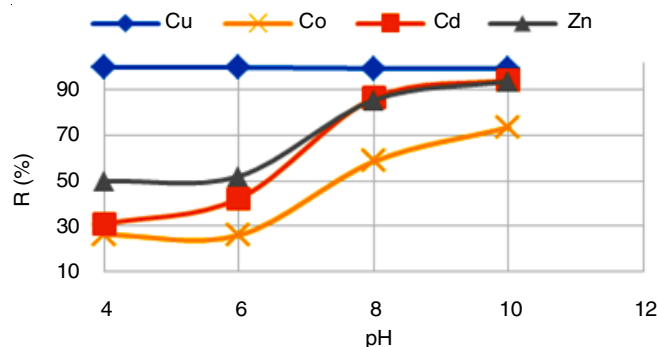


Fig. 2. Effect of the pH of solution on metal ions removal by polymer 2

solution was stirred for the intervals (contact time) as listed in Table-1. The adsorption capacity (q_e) was determined according to eqn. 2:

$$q_e = (C_i - C_e) \times \frac{V}{W} \quad (2)$$

where, C_i is the initial concentration of metal ion (mg/L), C_e is the concentration of metal ion at equilibrium (mg/L), V is the total volume of solution (L) and W is the polymer weight (g). The results (Figs. 3 and 4) revealed that an increase in the adsorption capacities of two polymers took place as a function of increases in initial metal ion concentration. The cause of such increases might be due to the increase in the driving force for mass transfer from the aqueous phase to solid, this led to increase the occupation of vacant adsorbing centers per unit mass at the surface of examined polymers [23,24].

Effect of temperature: A study was carried out to examine the adsorption performance of polymers (P1 and P2) towards the four metal ions studied at different temperatures (20, 30,

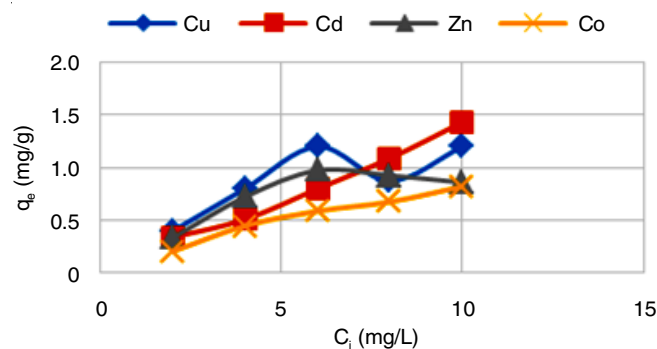


Fig. 3. Effect of initial metal ion concentration onto metal ions removal by polymer 1

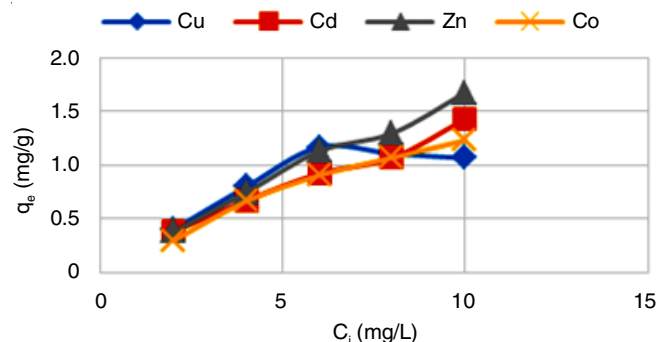


Fig. 4. Effect of initial metal ion concentration onto metal ions removal by polymer 2

40, 50 and 60 °C). The initial metal concentration was (2 mg/L), polymer weight (0.05 g), pH 10 and optimum contact time for each metal ion with corresponding polymer as mentioned in Table-1. In case of polymer **P1** (Fig. 5), the results indicated a significant improvement of the removal efficiency for Cd²⁺ and limited improvement for Co²⁺ ion with increasing temperature of the solutions. It has no negative impact on the removal efficiency in case for Cu²⁺ and Zn²⁺. For the polymer **P2** (Fig. 6), the results showed an increase of the removal efficiency of Cd²⁺ and Zn²⁺ ions with the increase of temperature. In addition, the results also confirmed that no effect on the total removal of Cu²⁺ and medium removal of Co²⁺ with increase temperature of the solutions [25].

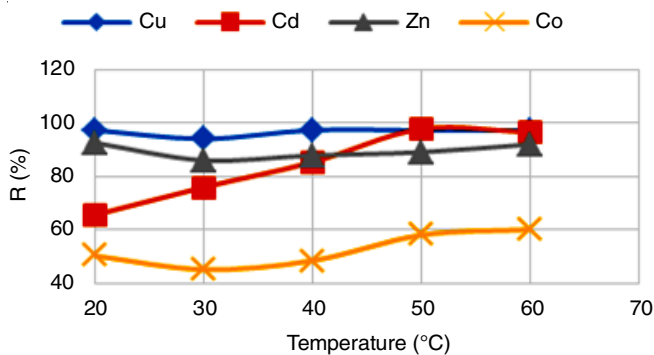


Fig. 5. Effect of the temperature of solution on metal ions removal by polymer 1

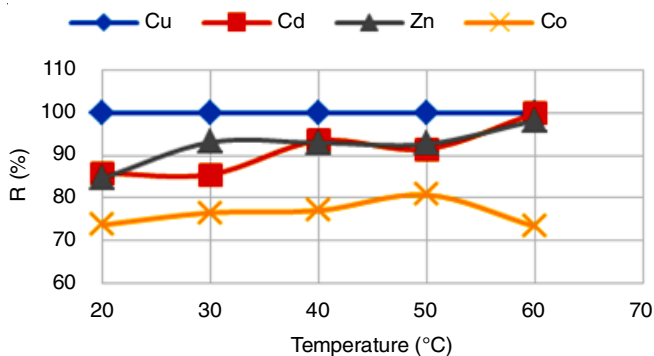


Fig. 6. Effect of the temperature of solution on metal ions removal by polymer 2

Langmuir isotherm: This model proposes that a maximum adsorption is closely related to a saturated monolayer of the soluble material molecules on the surface of the adsorbent, with constant energy of the adsorbent surface, therefore no trans migration of the adsorbed species at the surface [26]. The linear relationship form of this model is represented in eqn. 3:

$$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{1}{Q_o C_e} \quad (3)$$

where C_e is the concentration of adsorbed species on equilibrium (mg/L) at 25 °C and b represent a constant linked to the affinity between adsorbent and adsorbate species. Q_o is the Langmuir constant attached to adsorption capacity. The conclusion of Langmuir model is represented by a constant called dimensionless separation factor (R_L) [27], which is calculated from eqn. 4:

$$R_L = \frac{1}{1 + bC_o} \quad (4)$$

where C_o is the initial concentration (mg/L) of the solution, and b represents the Langmuir constant (L/mg). The values of Langmuir constants, Q_o (mg/g), b (L/mg) and R² were extracted from the plot of C_e/q_e versus C_e at 25 °C and are listed in Table-2. In this study, the calculated values of R_L for the systems of the four ion solutions and the two polymers (**P1** and **P2**) were between (0-1) (Table-3), suggesting a favourable nature of adsorption processes [28].

Adsorbent	Parameters	Cu ²⁺	Cd ²⁺	Zn ²⁺	Co ²⁺
P1	Q _o	0.791	0.791	1.502	2.103
	b	12.639	6.479	27.966	1.621
	R ²	0.993	0.9994	0.977	0.909
P2	Q _o	1.197	1.463	2.005	1.927
	b	29.512	1.720	3.076	0.282
	R ²	0.989	0.907	0.976	0.918

Freundlich isotherm: This model is suitable for treatment of heterogeneous systems. Moreover, the presence of various active groups on the surface of adsorbent in addition to the existing of different interaction between adsorbate and adsorbent will rise the heterogeneous character. The model is an empirical equation based on the hypothesis assumes that adsorption centers are dispersed exponentially relative to the heat of adsorption. The model assumes that occupation takes place first on the strong adsorption sites and as the binding site occupation increased the strength will decrease [28]. Eqn. 5 represents the Freundlich linear model.

$$\log Q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (5)$$

where K_F represents Freundlich constant that related to the maximum adsorption capacity, while n is the Freundlich

C _i (mg/L)	Cu ²⁺		Cd ²⁺		Zn ²⁺		Co ²⁺	
	P1	P2	P1	P2	P1	P2	P1	P2
2	0.0140	0.0043	0.640	0.231	0.084	0.151	0.742	0.494
4	0.0079	0.0021	0.471	0.130	0.044	0.082	0.590	0.328
6	0.0047	0.0014	0.372	0.091	0.029	0.056	0.489	0.246
8	0.0035	0.0010	0.308	0.070	0.022	0.042	0.418	0.196
10	0.0028	0.0008	0.263	0.056	0.018	0.034	0.395	0.395

exponent constant and its value describes the nature of the process. The values of these constants (K_f and n) are determined from plotting of $\log Q_e$ against $\log C_e$. In Freundlich treatment operations, if the value of $1/n$ is less than 1, it reflects a favourable nature of the adsorption process and the smaller values of $1/n$ recommend a good adsorption mechanism associated with stronger bonding between adsorbate and adsorbent [29]. The resulted values of n lies between 1.38 and 50 for the carried experiments (Table-4), suggested a physical and chemical adsorption [30].

TABLE-4
FREUNDLICH ISOTHERM CONSTANTS FOR THE
REMOVAL OF METAL IONS BY POLYMERS (P1 AND P2)

Adsorbent	Parameters	Cu ²⁺	Cd ²⁺	Zn ²⁺	Co ²⁺
P1	n	50	1.68	4.25	1.38
	K _f	0.88	0.58	0.67	0.24
	R ²	0.0335	0.8217	0.4489	0.9313
P2	n	8.63	7.5	10.9	7.9
	K _f	0.5	1.5	1.23	0.90
	R ²	0.0554	0.7382	0.2958	0.8949

The calculated values of R^2 for all experiments in this study (Tables 2 and 4) revealed that the Langmuir treatment is more applicable than Freundlich model. This conclusion is based on the degree of best fit of adsorption isotherms of the studied metal ions with synthesized polymers. It reflects the fitness of the experimental data with Langmuir model more than with Freundlich model. Moreover, the results suggest the homogeneity of adsorption centers with most probable monolayer coverage of polymer surface with studied metal ions (Cu²⁺, Cd²⁺, Zn²⁺ and Co²⁺). Finally, the results revealed that all adsorption centers on the polymer surface are similar in term of energy [31].

Thermodynamic studies: Various thermodynamic parameters, such as Gibbs free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) of the adsorption process provide vital information which help describes the process [32,33]. In present study, the mentioned parameters were calculated at a temperature range (293-333 K) by applying eqn. 6:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

where R represents the universal gas constant (8.314 J/mol K), T is the temperature of the solution (K) and K_d is the distribution coefficient. The latter is calculated from eqn. 7:

$$K_d = \frac{C_{Ac}}{C_e} \quad (7)$$

where C_{Ac} (mg/L) is the metal ion concentration of solution that adsorbed at the polymer surface at equilibrium, while C_e (mg/L) is the concentration of metal ion solution at equilibrium. The values of ΔH° and ΔG° for the adsorption processes in this study were determined from the slope and the intercept respectively of the plots between $\ln K_d$ against $1/T$. Moreover, eqn. 8 was used to calculate the values of ΔS° , for these processes.

$$\Delta G^\circ = -RT \ln K_d \quad (8)$$

The calculated thermodynamic parameters for adsorption of the four metal ions on polymers **P1** and **P2** are tabulated in Table-5.

The positive values of ΔH° refer to the endothermic nature of all adsorption processes in this study, while the positive values of ΔG° for all experiments indicated the affinity of used two polymers for metal ions (Cu²⁺, Cd²⁺, Zn²⁺ and Co²⁺) because of the increased randomness at the interface between polymer-metal ion solution phases [34], while the negative values of (ΔG°) for these systems, except the adsorption of Co²⁺ on polymer **P1** at 30 and 40 °C, pointed out the spontaneous nature and the feasibility of these processes [35].

Conclusion

Two multifunctional polymers were synthesized from adipoyl dichlorides. They proved to be efficient in removing a representative hazardous metal ions from aqueous solution by adsorption, especially above pH 6. The efficiency of these polymers might be due to their chemical structure that posses various electron donating groups. The removal of Cu²⁺ by these two polymers was significant under all the conditions used in this study, which reflected the strong affinity between Cu²⁺ ions and the surfaces of two polymers. This may be due to the compatibility between the size of metal ion and the active sites on the polymers surface, which enhance the chemical and physical interaction between the metal ions and the synthesized polymers.

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REFERENCES

1. F.A. Nasr, H.S. Doma, H. Abdel-Halim and S.A. El-Shafai, *Environmentalist*, **27**, 275 (2007); <https://doi.org/10.1007/s10669-007-9004-0>.
2. F. Fu and Q. Wang, *J. Environ. Manage.*, **92**, 407 (2011); <https://doi.org/10.1016/j.jenvman.2010.11.011>.

TABLE-5
THERMODYNAMIC PARAMETERS VALUES FOR THE REMOVAL OF METAL IONS BY POLYMERS (P1 AND P2)

Adsorbent	Metal ion	ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)				
				293 K	303 K	313 K	323 K	333 K
P1	Cu ²⁺	0.087	0.69	-8.8	-7.0	-9.5	-9.6	-10.0
	Cd ²⁺	0.95	3.31	-1.5	-2.9	-4.6	-10.3	-9.3
	Zn ²⁺	0.069	0.28	-1.6	-4.6	-5.1	-5.6	-6.8
	Co ²⁺	0.151	0.49	-0.02	0.49	0.16	-0.87	-1.1
P2	Cu ²⁺	-0.48	-0.86	-18.5	-7.4	-19.7	-20.4	-8.6
	Cd ²⁺	0.27	1.10	-3.4	-3.4	-4.9	-3.9	-7.0
	Zn ²⁺	0.52	2.06	-5.8	-5.7	-8.2	-8.3	-11.7
	Co ²⁺	0.14	0.61	-2.9	-3.0	-2.5	-3.3	-5.0

3. M.A. Barakat, *Arab. J. Chem.*, **4**, 361 (2011); <https://doi.org/10.1016/j.arabjc.2010.07.019>.
4. S.E. Bailey, T.J. Olin, R.M. Bricka and D.D. Adrian, *Water Res.*, **33**, 2469 (1999); [https://doi.org/10.1016/S0043-1354\(98\)00475-8](https://doi.org/10.1016/S0043-1354(98)00475-8).
5. W.S.W. Ngah, C.S. Endud and R. Mayanar, *React. Funct. Polym.*, **50**, 181 (2002); [https://doi.org/10.1016/S1381-5148\(01\)00113-4](https://doi.org/10.1016/S1381-5148(01)00113-4).
6. H. Kasgoz, S. Ozgumus and M. Orbay, *Polymer*, **44**, 1785 (2003); [https://doi.org/10.1016/S0032-3861\(03\)00033-8](https://doi.org/10.1016/S0032-3861(03)00033-8).
7. M. Takafuji, S. Ide, H. Ihara and Z. Xu, *Chem. Mater.*, **16**, 1977 (2004); <https://doi.org/10.1021/cm030334y>.
8. P.A. Kavakli and O. Guven, *J. Appl. Polym. Sci.*, **93**, 1705 (2004); <https://doi.org/10.1002/app.20616>.
9. A. Dabrowski, Z. Hubicki, P. Podkoscielny and E. Robens, *Chemosphere*, **56**, 91 (2004); <https://doi.org/10.1016/j.chemosphere.2004.03.006>.
10. H. Bessbousse, T. Rhlalou, J.-F. Verchere and L. Lebrun, *J. Membr. Sci.*, **307**, 249 (2008); <https://doi.org/10.1016/j.memsci.2007.09.027>.
11. P. Kampalananonwat and P. Supaphol, *ACS Appl. Mater. Interfaces*, **2**, 3619 (2010); <https://doi.org/10.1021/am1008024>.
12. F. Ge, M.-M. Li, H. Ye and B.-X. Zhao, *J. Hazard. Mater.*, **211-212**, 366 (2012); <https://doi.org/10.1016/j.jhazmat.2011.12.013>.
13. S.D. Kirupha, A. Murugesan, T. Vidhyadevi, P. Baskaralingam, S. Sivanesan and L. Ravikumar, *Sep. Sci. Technol.*, **48**, 254 (2012); <https://doi.org/10.1080/01496395.2012.681745>.
14. Z. Yang, X. Huang, X. Yao and H. Ji, *J. Appl. Polym. Sci.*, **135**, 45568 (2018); <https://doi.org/10.1002/app.45568>.
15. G. Odian, Principles of Polymerization, John Wiley & Sons, Inc., Hoboken, New Jersey, edn 4 (2004).
16. X.P. Mao, J.F. Huang and Z.F. Duan, *Chin. Chem. Lett.*, **16**, 609 (2005).
17. Y.-M. Zhang, T.-B. Wei and L.-M. Gao, *Indian J. Chem.*, **39B**, 700 (2000).
18. H. Arslan, N. Duran, G. Borekci, C.K. Ozer and C. Akbay, *Molecules*, **14**, 519 (2009); <https://doi.org/10.3390/molecules14010519>.
19. C.K. Özer, H. Arslan, D. van Derveer and N. Külc, *Molecules*, **14**, 655 (2009); <https://doi.org/10.3390/molecules14020655>.
20. G. Binzet, G. Kavak, N. Külc, S. Ozbey, U. Flörke and H. Arslan, *J. Chem.*, **Article ID 536562** (2013); <https://doi.org/10.1155/2013/536562>.
21. M. Sivadhayanithy, L. Ravikumar and T. Ramachandran, *J. Chil. Chem. Soc.*, **52**, 1230 (2007); <https://doi.org/10.4067/S0717-97072007000300007>.
22. N. Ünl and M. Ersoz, *J. Hazard. Mater.*, **136**, 272 (2006); <https://doi.org/10.1016/j.jhazmat.2005.12.013>.
23. M. Anis, S. Hayder and A.J. Bari, *Environ. Eng. Manage. J.*, **12**, 2117 (2013).
24. Z. Melichova and L. Hromada, *Pol. J. Environ. Stud.*, **22**, 457 (2013).
25. A. Ahmadi, S. Heidarzadeh, A.R. Mokhtari, E. Darezereshki and H.A. Harouni, *J. Geochem. Explor.*, **147**, 151 (2014); <https://doi.org/10.1016/j.gexplo.2014.10.005>.
26. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918); <https://doi.org/10.1021/ja02242a004>.
27. T.W. Weber and R.K. Chakravorti, *AIChE J.*, **20**, 228 (1974); <https://doi.org/10.1002/aic.690200204>.
28. K.R. Hall, L.C. Eagleton, A. Acrivos and T. Vermeulen, *Ind. Eng. Chem. Fundam.*, **5**, 212 (1966); <https://doi.org/10.1021/i160018a011>.
29. M. Hosseini, S.F. Mertens, M. Ghorbani and M.R. Arshadi, *Mater. Chem. Phys.*, **78**, 800 (2003); [https://doi.org/10.1016/S0254-0584\(02\)00390-5](https://doi.org/10.1016/S0254-0584(02)00390-5).
30. A. El Nemr, *Chem. Ecol.*, **23**, 409 (2007); <https://doi.org/10.1080/02757540701653350>.
31. C. Erkey, Supercritical Fluids and Organometallic Compounds: From Recovery of Trace Metals to Synthesis of Nanostructured Materials, Elsevier, Amsterdam, edn 1 (2011).
32. X. Liu and D.-J. Lee, *Bioresour. Technol.*, **160**, 24 (2014); <https://doi.org/10.1016/j.biortech.2013.12.053>.
33. J. He, S. Hong, L. Zhang, F. Gan and Y.-S. Ho, *Fresen. Environ. Bull.*, **19**, 2651 (2010).
34. O. Yavuz, Y. Altunkaynak and F. Guzel, *Water Res.*, **37**, 948 (2003); [https://doi.org/10.1016/S0043-1354\(02\)00409-8](https://doi.org/10.1016/S0043-1354(02)00409-8).
35. Y.-X. Chen and G.-Y. Wang, *Colloids Surf. A Physicochem. Eng. Asp.*, **289**, 75 (2006); <https://doi.org/10.1016/j.colsurfa.2006.04.008>.