Synthesis, Characterization and Kinetic Studies of Chelate Polymer Derived from 3-Nonyl Benzene and its Use for the Removal of Some Heavy Metals from Aqueous Solutions

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Abstract

A new chelate polymer (2-5-hydroxy-3-methyl-2- (3-nonyl benzene) imino) methyl) benzyl) 4-6-dimethyphenol] (K4) was prepared by using the condensation reaction method and identified by several techniques, including FT-IR, NMR, and atomic absorption spectroscopy, as well as TG-DTA thermal analysis. The kinetic equilibrium for the sorption of lead and cadmium ions on the chelate polymer surface was also investigated. The results showed that the sorption of both ions followed the pseudo-first-order and pseudo-second-order kinetic equilibrium. The rate constant values of pseudo-first-order reaction were equal to 0.062 and 0.057 min^{-1} , while the values of pseudo-second-order were 0.0103 and 0.053 $L.mg^{-1}$ $min^{-1)}$ for the sorption of Pb (II) and Cd (II) on chelate polymer, respectively. Thermodynamic parameters were also investigated and the sorption values for Pb^{+2} were achieved at 25 ^{o}C, ΔG = 0.436 KJ/mole, ΔH = 10.55 KJ/mole, and ΔS= 0.08 KJ/mole, , whereas those for Cd^{+2} were 25 ^{o}C , ΔG = -2.345 KJ/mole, ΔH = 4.378 KJ/mole, and ΔS= 0.09 KJ/mole. The results showed that the sorption process was spontaneous and endothermic in nature for the sorption of each of Pb^{+2} and Cd^{+2} on polymer surface.

Keywords: chelate polymer, heavy metals, adsorption, kinetics, thermodynamics parameters.

تحضير وتشخيص ودراسة حركية للبوليمر المخلبي المشتق من الكيل بنزين واستخدامه لإزالة بعض العناصر الثقيلة من محاليلها المائية

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الخلاصه

خُضِر بوليمر مخلبي جديد (2-5-hydroxy-3-methyl-2- (3-non-yl benzene)

imino) methyl) benzyl)4-6-dimethyphenol] (k4) عن طريق تفاعل بلمره التكثيف والذي

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شُخِص بعدة تقنيات منها مطيافية الاشعة تحت الحمراء ومطيافية الرنين النووي المغناطيسي والتحليل الحراري التفاضلي. تمت دراسة الاتزان الحركي لعملية الامتزاز لأيونات المعادن الثقيلة على سطح الراتنج المحضر. اظهرت نتائج الاتزان الحركي ان عملية الامتزاز تتبع المرتبة الكاذبة الاولى والمرتبة الكاذبة الثانية, وان ثابت الاتزان لعملية الامتزاز هو (0.062 min^{-1}) دقيقة لامتزاز ايون الرصاص (II) Pb و (0.057 min^{-1}) دقيقة لامتزاز ايون الكادميوم (II) Cd وعُين ثابت الاتزان الحركي للمرتبة الثانية الكاذبة والتي كانت 0.0103 ($L.mg^{-1}$ min^{-1}) لامتزاز عنصر الرصاص و (0.053 L.mg^{-1}.min^{-1}) لامتزاز عنصر الكادميوم على سطح البوليمر المخلبي. تم التحقق من الدوال الثرموديناميكية مثل $\Delta G, \Delta H,$ and ΔS واظهرت النتائج ان عملية الامتزاز هي عملية تلقائية ماصة للحرارة في طبيعة امتزاز كل من Pb^{+2} and Cd^{+2} عل سطح البوليمر. لهذا السبب يمكن اعتبار راتنج البوليمر المخلبي كسطح امتزاز جيد في تطبيقات معالجة مياه الصرف الصحي.

Introduction

Human life is facing serious environmental issues due to globalization and rapid technological development. The heavy metals presence in wastewater and industrial effluent is a major concern of environmental pollution [1]. Heavy metals represent serious threats to human being and can cause severe health effects such as cancer, organ damage, nervous system damage, and in extreme cases, death [2].

Low concentration of heavy metals is highly toxic, therefore, removal of these metal ions from wastewater is essential and it attracts the attention of extensive research. Several methods and effective technologies such as chemical precipitation, ion exchange, adsorption, and membrane filtration have been used to remove heavy metals from contaminated water [3-4].

Chelating polymers have been focused on recently as adsorbents in water pollution treatment [5-7]. The synthetic polymer resins such as styrene-divinylbenzene copolymers, polyacrylate, and poly (glycidyl methacrylate-iminodiacetic acid) were used in ion exchange and gained considerable attention [8-9]. The chelating resin modified with a cross-linker N,N′-methylene basic arylamide was used for the removal of Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+} and Mn^{2+} ions from aqueous solutions [10-14].

Recently, numerous approaches have been discovered to develop low-priced and more effective technologies for water purification. Alkyl benzene compounds are important organic compounds in organic chemistry and have been used as raw materials for the preparation of many organic derivatives, such as organic acids which include benzoic acid, phthalic and anhydride, which are used in the manufacture of plastics and polyunsaturated resins [15].

The main purpose of this work is to synthesize a chelate polymer by the copolymerization method. Depending on the ability of this chelate polymer, it is used for the adsorption of metal ions. The determination of the equilibrium kinetics of the adsorption of the metal ions-chelating polymer is the other aim of this study. The choice of these polymers mainly depends on their ability to chelate and/or adsorb metal ions.

Experimental details

All materials mentioned in the synthetic process, such as 3-nonyl benzene, Mwt = 204.35 g/mole, purity 96 %; dichloromethane, Mwt = 84.93 g/mole, purity for HPLC ≥99.8%; NaOH, Mwt = 40 g/mole, purity ≥98% (acidimetric), pellets (anhydrous); HCl Mwt = 36.5 g/mole, ACS reagent, 37%; KOH, Mwt = 56.106 g/mole, ACS reagent, ≥85%, pellets; Pb (NO$_3$)$_2$, Mwt = 331.2 g/mol, ACS reagent, ≥99.0%; Cd (NO$_3$)$_2$, Mwt = 308 .49 g/mole, purity 98%; and aluminum chloride, Mwt = 133.34 g/mole, reagent grade, 98%, were of reagent grade and used as received from the supplier (Chemically pure, Shanghai Chemical Reagent Co. Ltd., Shanghai, China) without further treatments.

Preparation of chloromethyl-4-(3-nonyl benzene) compound [K1]

K1 compound was prepared from the reaction of dichloromethane (0.86 g , 0.01 mol) with 3-nonyl benzene (3g, 0.01 mol) and anhydrous aluminum chloride by stirring the reaction mixture under reflux until the white precipitation formed. Then, it was filtrated and dried to give 52% yield. The melting point was measured and showed a value of 163-165 $^{\circ}$ C.

Preparation of 4-(3-nonyl phenyl) methanamine compound [K2]

The compound k2was prepared by mixing aluminum chloride (6.64 g, 0.01 mol) , 3-nonyl benzene

(3 g, 0.01) and potassium hydroxide (0.56 g, 0.01 mol) in 20 ml distilled water. The reaction mixture was put under reflux in oil bath for 5 h , then the mixture was cooled until a brown precipitate was formed. The yield was filtrated and dried to obtain a percentage weight of 56%, with a melting point of 180-182 ^{o}C.

Preparation of Schiff base 2-(4-(3-nonyl benzyl)imino)methyl)phenol compound [K3]

K3 compound was prepared by mixing 0.3g, 0.002 mol, of K2 with 0.002 mol of benzaldehyde in ethanol solvent in a round bottom flask, followed by reflux for 5h at 80 ^{o}C until the precipitate was formed. The precipitate was filtrated and dried, giving a percentage weight of 71% at a melting point of 202-204 ^{o}C.

The structural formulae, nomenclature, melting points (m.p ^{o}C), colors, and percentage yields for the synthesized imine compounds are given in Table-1.

Table 1- Physical properties of the prepared compounds [K1-K3]

No	Formula	Melting points. ^{o}C	Yield	Color
K1	$C_{16}H_{25}C$	163-165	52%	White
K2	$C_{16}H_{27}N$	180-182	56%	Brown
K3	$C_{23}H_{31}NO$	202-204	71%	White
K4	$(C_{30}H_{36}NO_2)n$	266-268	68%	Brown

Preparation of chelating resin [K4]

The chelate polymer [K4] was prepared by adding 1.5 g of k3 compound to 25 ml formaldehyde. Then 7g of phenol was added to the mixture. The pH of the mixture was adjusted between 9 and 10.5 by 10 % NaOH. The reaction mixture was refluxed for 5 h until the brown gelatin formed. Then, the solvent was evaporated and the product was dried in an oven at 120 ^{o}C for 2 hours. The polymer was then crushed and washed with deionized water to remove unreacted compounds and re-dried for analysis.

Kinetic study

The effects of contact time and initial concentrations of Pb^{+2} and Cd^{+2} ion solutions on the sorption of the chelate polymer were studied using two series bottles, labeled from 1- 10, at fixed temperature. A volume of 25 ml of each ion solution was added to a single bottle containing 0.1g of chelate polymer.

Effect of temperature

The two stock solutions (1000 ppm) of each metal ion were prepared by dissolving 1.6 g of lead nitrate in 1 L of distilled water and 2.1 g cadmium nitrate in 1 L of distilled water. A series of appropriate dilutions of different concentrations (5 to 50 ppm) were prepared to each ion from the stock solutions. To each concentration, 0.1g of adsorbent polymer was added, then shacked for 2 h in thermostatic water bath at the required temperature and left to stand for 2 h. The solutions were centrifuged for 10 min at 7000 rpm, then the ions were measured by atomic absorption spectroscopy. The amount of adsorbed dye was calculated according to the following equation [16]:

$$q_e = \frac{(C_i - C_e)V}{m} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where, q_e = amount of ion adsorbed (mg/g), C_i = initial concentration of adsorbed (mg/L), C_e= the concentration at equilibrium time (mg/L), m = mass of adsorbent (g) and V=volume of ion solution (ml).

Results and Discussion

A number of compounds derived from 3-nonyl benzene to prepare the chelate polymer are shown in scheme 1 below, which shows the prepared compounds K1-K4 [17].
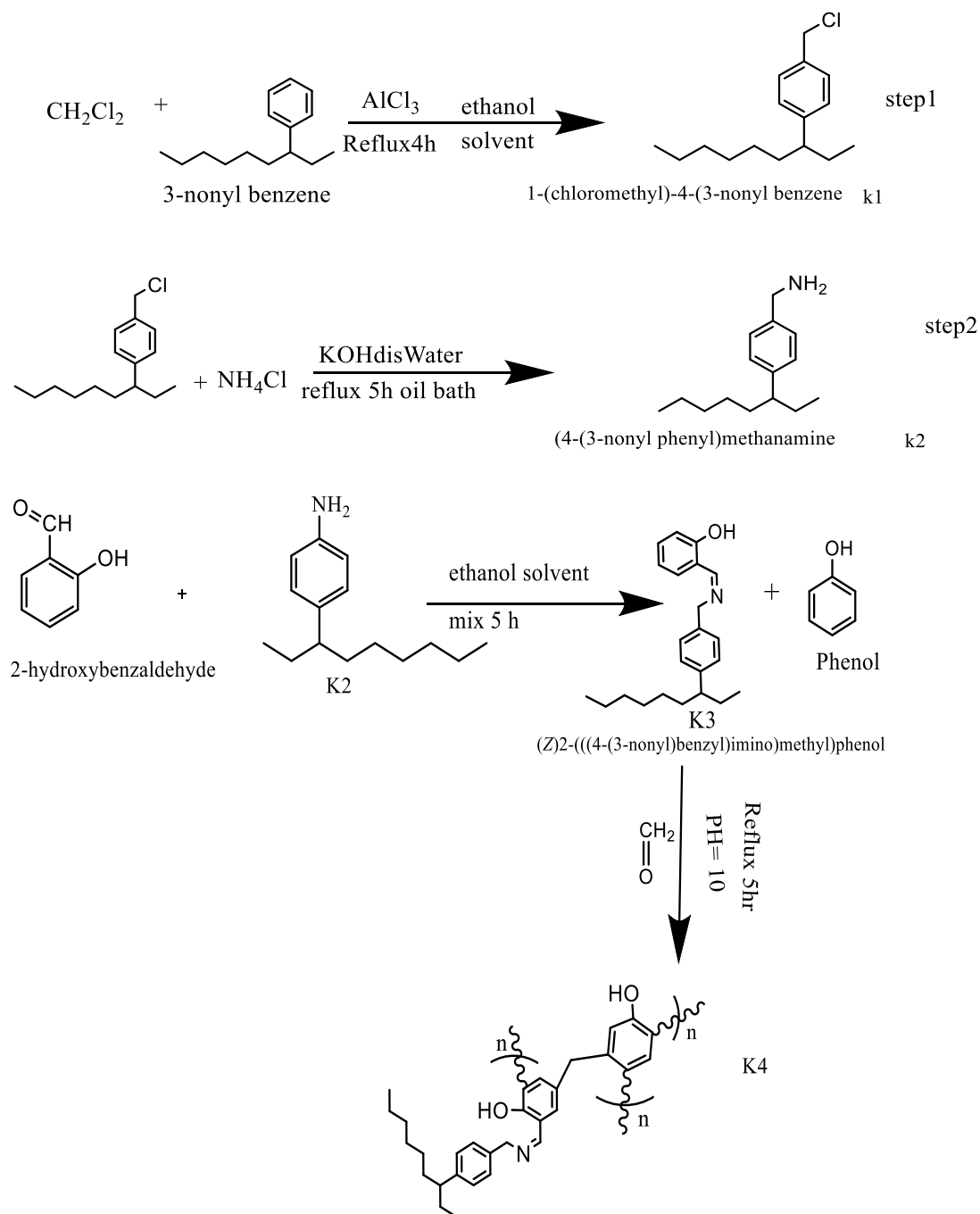
(*Z*)-4-(2-hydroxy-3,5-dimethylbenzyl)-2-methyl-6-(((4-(3-nonyl)benzyl)imino)methyl)phenol

Scheme 1- Scheme illustrates the chemical reactions for the preparation process of compounds K1-K4.

FT-IR analysis of compound K1]

Figure-1 shows the appearance of the stretching absorption bands of the characteristic groups of the resulting K1 (Ar-H) at 3071 cm^{-1}, in addition to a stretching band at 2913 cm^{-1} due to aliphatic (C-H) with the stretching absorption at 1566.7cm^{-1} due to (C=C) [18].
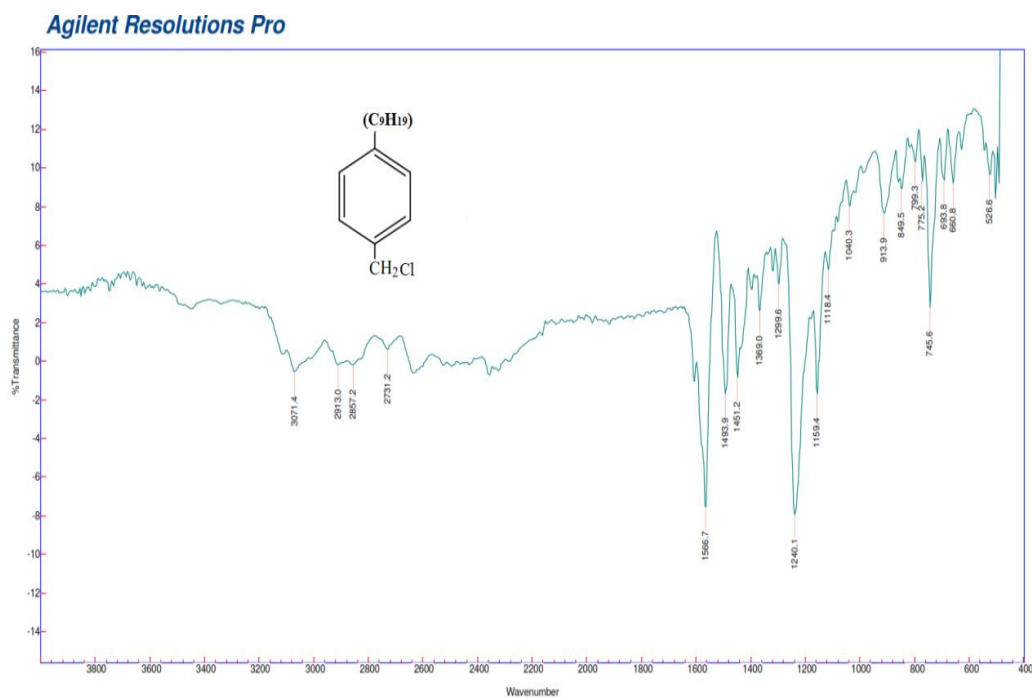
Figure 1- FT-IR spectrum of compound K1

Figure- 2 shows the ^{1}H- NMR spectrum of K1. The singlet peak in 4.2 ppm belongs to the protons of CH_2Cl group, whereas the multiple peaks at 6.29-7.32 ppm indicate the protons of aromatic ringlet (Ar-H) and the other multiple singlet refers to the protons 2.08-2.29 ppm of the Ar-$(CH_2)_8$ group [19].

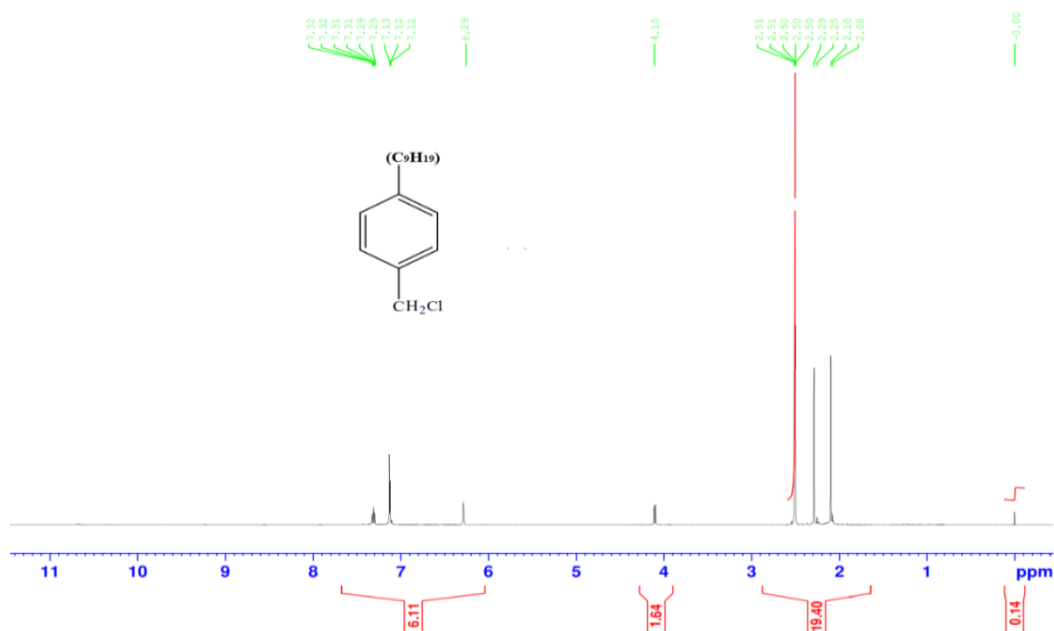**Figure 2-**^{1} H- NMR spectrum of compound K1

^{1}H-NMR spectrum of K2

The ^{1}H-NMR spectrum of the compound K2 in dimethyl sulfoxide solvent is illustrated in Figure-3, which shows chemical schiff δ(ppm), triplet in 0.92 ppm (3H, CH_3), multiple in 7.87 ppm (NH_2), singlet in 5.01 ppm (CH_2 -NH_2), singlet in 7.01-7.12 ppm (Ar), and multiple in 2.1- 2.28 ppm (($CH_2)_8$) [19].
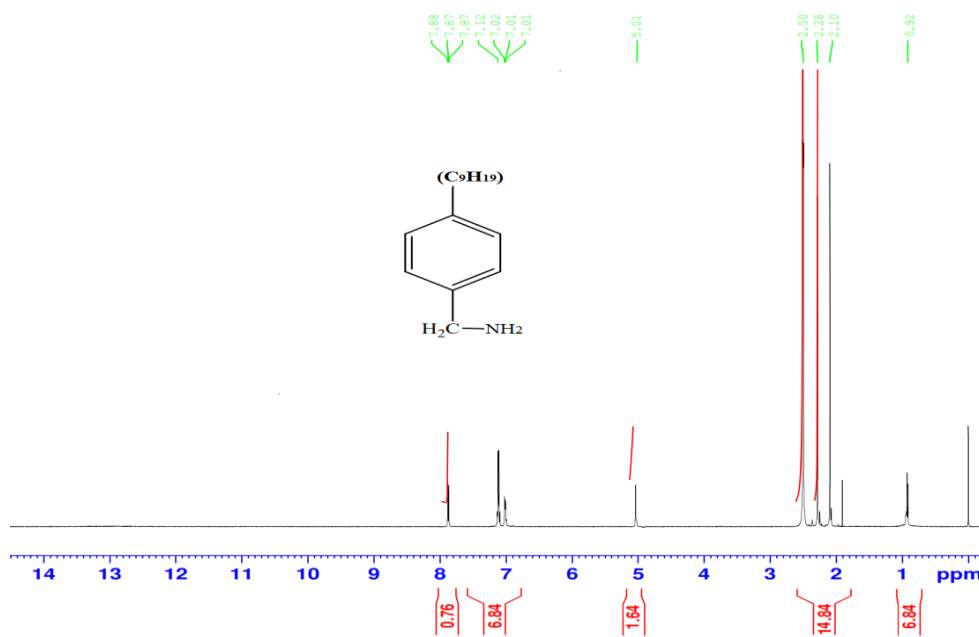.

Figure 3- ^{1} H- NMR spectrum of compound K2

IR-spectrum of K3

The FT-IR spectrum shows the disappearance of the stretching absorption for NH_2 group, which might be due to the formation of isomethene group (N=C-H). The stretching absorption bands of the characteristic groups of (OH) appear at the range 3452 cm^{-1}, whereas the stretching absorption bands appearing at the range 3075 cm^{-1} are due to the (C-H) stretching of the aromatic bond [20-21].
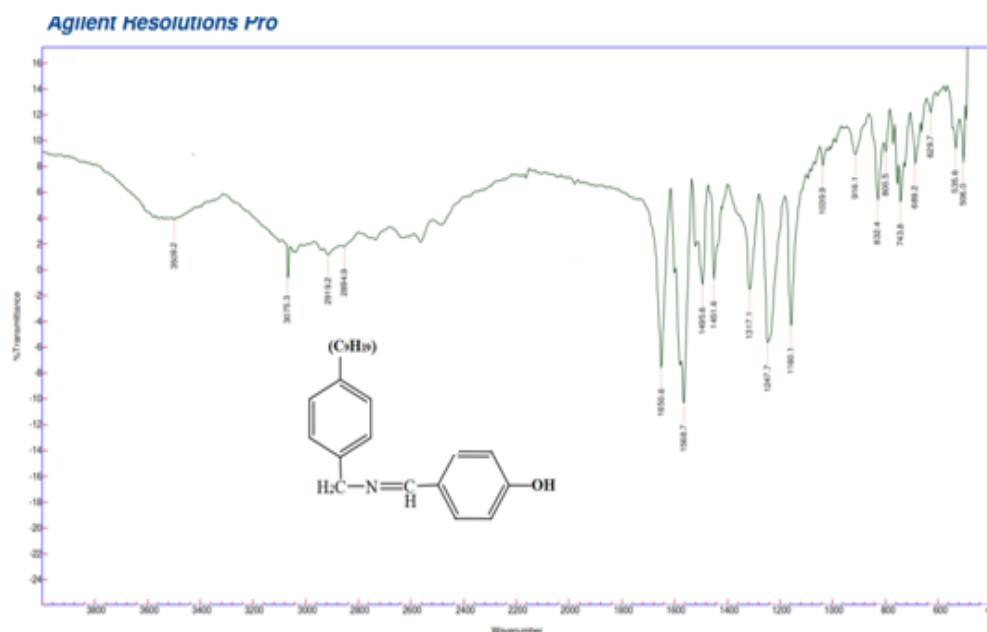

Figure 4- FT-IR spectrum of compound K3

The ^{1}H-NMR spectrum of compound K3 in DMSO-d^6 solvent is demonstrated in Figure-5, which shows chemical schiff, δ(ppm), singlet in 9.74 ppm (OH), single in 8.97 ppm (CH =N), multiple in 7.07-7.59 ppm (Ar), singlet in 0.96 ppm (CH$_3$), and multiple in 1.2- 1.74 ppm (Ar-CH$_2$)$_8$ [21].
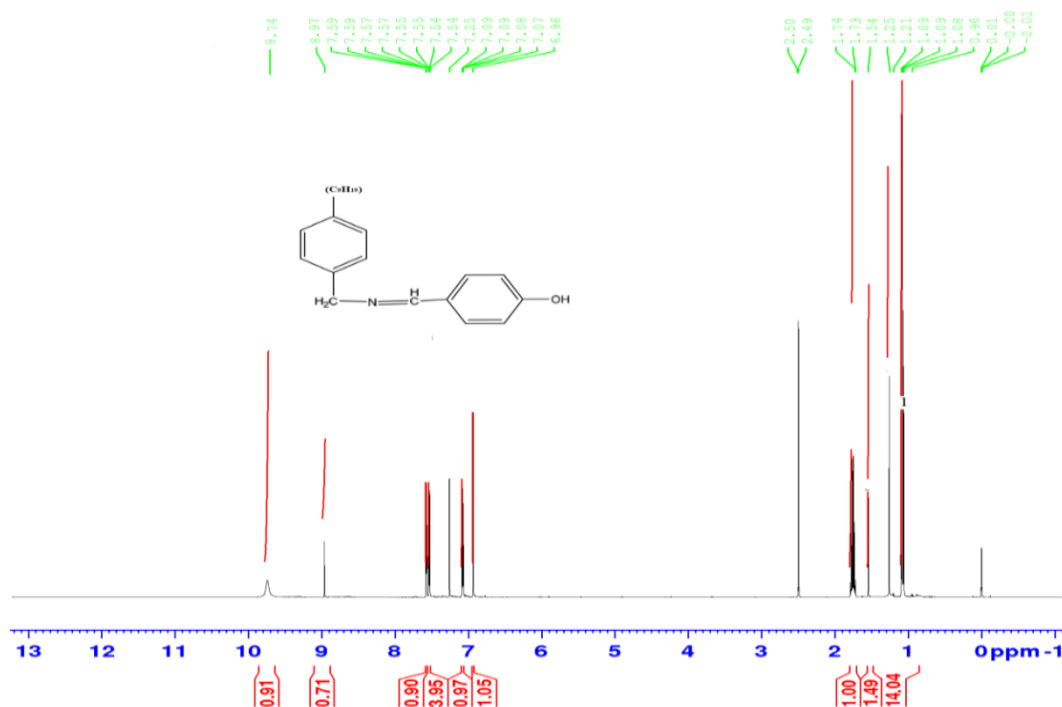
Figure 5- [1] H- NMR spectrum of compound K3

Thermal analysis

According to the results, the chelate polymer resin can produce a promising adsorbent material for wastewater treatment applications. Thermal analysis (DTG, TG) of the prepared polymer, as illustrated in Figure-6, exhibited three stages of distinct weight loss between 90 and 900 ^{o}C. The first stage is at a range of 90 – 380 ^{o}C with 20.12% weight loss. This stage can be attributed to the degradation of the main backbone of the polymer, beside the loss of the adsorbed and bound water. The second and third stages are detected in the temperature ranges of 400- 500 ^{o}C with 16.26 % weight loss and 600-900 ^{o}C with 17.22 % weight loss. These stages are namely due to the continuing degradation of the main and branched chains of the polymer backbone [22].
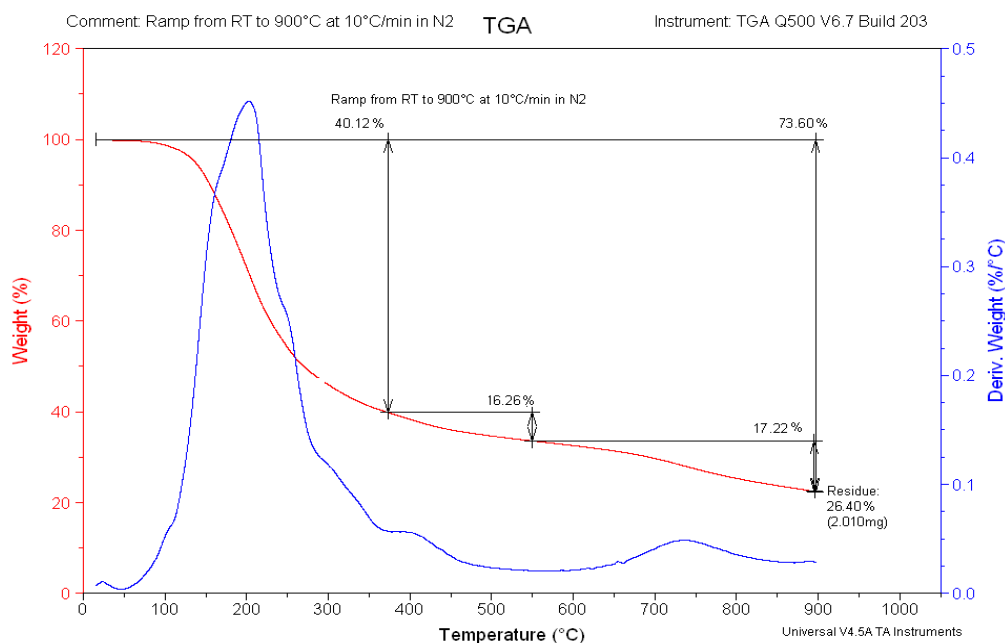

Figure 6- The thermal symmetry curve (DTG, TGA) for polymer K4.

Effects of contact time

The effects of contact time and ion concentration were studied on the removal of Pb^{+2} and Cd^{+2} ions by chelate polymer from aqueous solution. A plot between the amount of adsorption (mg/g) and interval time is shown in Figure-7. The solution concentration of 50 mg/ L of each ion conducts with 0.1 g of the polymer adsorbent at the same volume. It was observed that the adsorption of each ion on the surface of the polymer was rapid in the initial stages, proceeding to up to the first 40 minutes of contact time, at all initial ion concentrations studied. Afterwards, the adsorption efficiency reached equilibrium and stabilized at a maximum value.
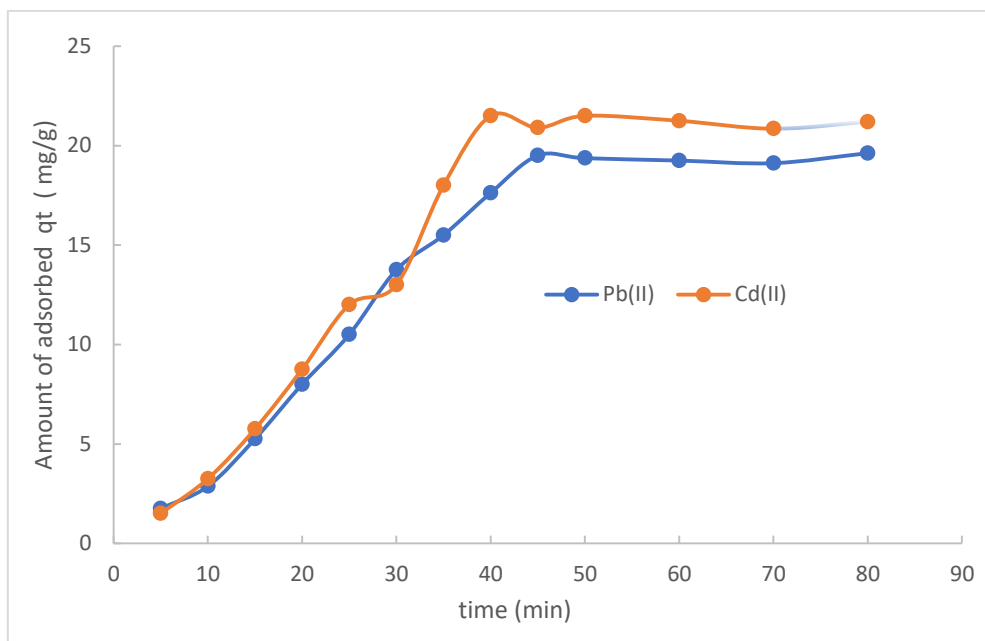
Figure7- Effects of contact time for the adsorption of 50 mg/L Pb^{+2} and 50 mg/L Cd^{+2} on 0.1g chelate polymer (K4) at 25 ^{o}C.

Kinetic studies

The importance of the kinetic study is that it provides evidence for the mechanisms of chemical processes. The kinetic equilibrium study can describe the rate of retention or release of a solute from an aqueous environment to a solid-phase interface at a given adsorbents. In the present study, the adsorption kinetics of Pb^{+2} and Cd^{+2} onto the polymer adsorbent were investigated with two kinetic models, namely the Lagergren pseudo—first—order and pseudo—second—order models [23]. Lagergren rate equation is one of the most widely used adsorption rate equations for the adsorption of solute from a liquid solution. The pseud first order kinetic model can be expressed by the following equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \ \dots\dots\dots\dots\dots\dots\dots\dots\dots. (2)$$

where q_t is the amount of ion adsorbed in mg g^{-1} at time (t), q_e is the maximum adsorption capacity, and k is the first-order rate constant (min^{-1}). The plot versus time (t) gives a slope that is equal to - k1/2.303 and an intercept that is equal to ($\log q_e$) to determine the adsorption capacity and adsorption rate constants for Pb^{+2} (Figure-8) and Cd^{+2} (Figure-9) on the resin. The second–order kinetics of adsorption was analyzed by using larger equation, expressed as [24].

$$\frac{dq}{dt} = k_{2(q_e - q_t)}2 \ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(3)$$

Equation (3) was arranged to obtain following equation:

$$\frac{d(q_e - q_t)}{(q_e - q_t)2} = -k_2 \ dt \ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(4)$$

When applying the conditions of integration, i.e. t = 0 then qt = 0, the ions are not adsorbed on the adsorbent surface at time equal to zero, but after a period of time, the ions are adsorbed at t=t and q_t=q_t . The integrated form of equation (3) becomes [25]:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t$$ ....(5)

Equation (4) can be rearranged to obtain a linear equation form of [24]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$ ....(6)

where k_2 is the rate constant of second order in mg g^{-1} min $^{-1}$ and q_e is the equilibrium adsorption capacity in mg /g. The values of q_e and k_2 are obtained from the slope and intercept, respectively, when (t/qt) is plotted against time (t). Figures-10 and 11 show the plot between (t/qt) and time (t) to determine the adsorption capacity and adsorption rate constants for the adsorption of Pb^{+2} and Cd $^{+2}$, respectively, on chelate polymer. The kinetic adsorption results of both ions show that the best correlation for the system, which is provided by the pseudo-first order model from the start of adsorption until 40 minutes of contact time, might be due to the availability of more empty sites on the surface of the adsorbent and the high concentration of the adsorbate. After the 40 minutes, the data were best fit to pseudo-second-order kinetic, according to the correlation factors. This might be due to the occupation of all sites of the adsorbent surface and that the adsorption reached to equilibrium. The results of kinetics parameters are listed in Table-2,
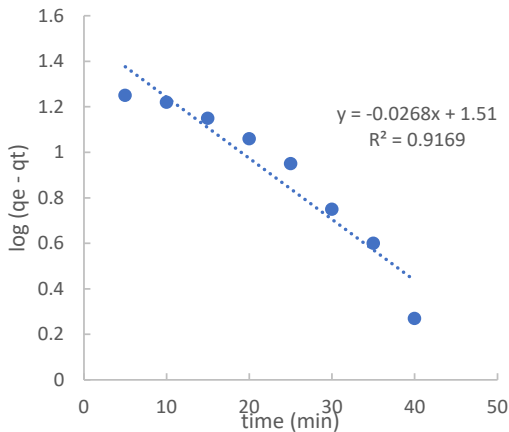

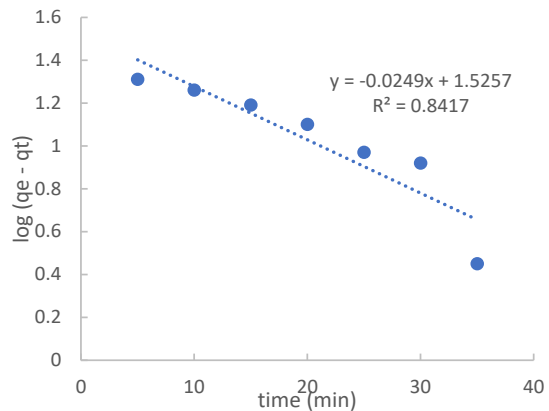Fig (8) : pseudo -First order kinetic plot for the sorption of Pb+2 on polymer at 25 oC

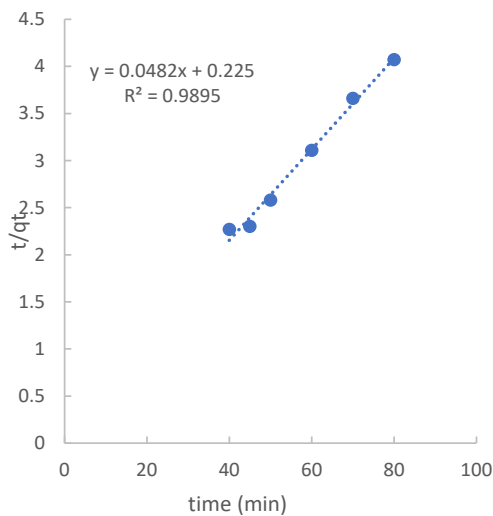Fig (9) : pseudo -First order kinetic plot for the sorption ef Cd+2 on polymer at 25 oC

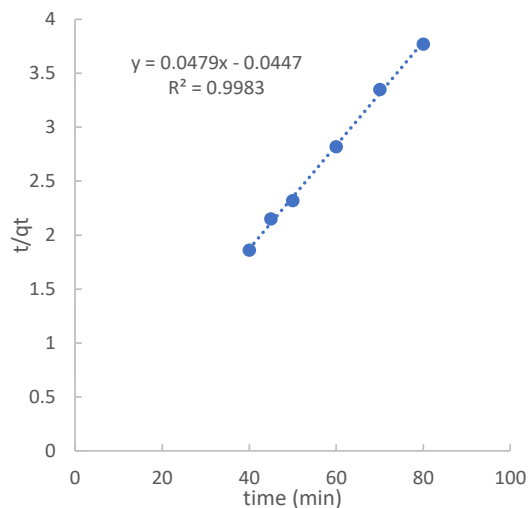Fig (10): Pseudo -Second Order kinetic plot for the sorption of Pb +2 on polymer at 25 0C

Fig (11) : pseudo second order kinetic plot for the sorption ef Cd+2 on polymer at 25 oC

Table 2- Kinetic parameters for sorption of 50 mg/L Pb^{+2} and 50 mg//L Cd^{+2} on 0.1 g chelate polymer (K4) as adsorbent at 25 ^{o}C.

Adsorbents		Pb^{+2}	Cd^{+2}
1st order	R^2	0.9169	0.8417
	K (min^{-1})	0.062	0.057
	q_{max} (mg/g)	32.35	33.55
2nd order	R^2	0.9895	0.9983
	K_2(L.mg^{-1}.min^{-1})	0.0103	0.051
	q_e (mg/g)	20.74	20.84
Experimental	q_e (mg/g)	19.5	21.5

Effects of Temperature

The nature of the adsorption process of Pb^{+2} and Cd^{+2} on polymer surface was studied by the estimation of thermodynamics parameters, including Gibbs free energy, enthalpy, and entropy, which are the most important characteristic of adsorption mechanisms. The value of (ΔH) can be estimated from the plot of the maximum amount of adsorption (lnXm) versus a reciprocal temperature (1/T) according to Vant Hoff- Arrhenius equation [26]:

$$\ln x_m = \frac{-\Delta H}{RT} + Constant \qquad \text{............... (7)}$$

where Xm is the maximum amount of adsorption (mg/g) , ΔH is the enthalpy of the reaction (KJ/mol), R is gas constant (8.313 J/mol.K), and T is the temperature (kelvin). The value of Gibbs free energy (ΔG) can be determined by the following Equations [27]:

$$\Delta G = -RT \ln \frac{Q_e}{C_e} \qquad \text{..................... (8)}$$

where Qe is the maximum amount of adsorption (mg/g) and Ce is concentration at equilibrium (mg/L). The entropy can be evaluated by Gibbs equation at equilibrium:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad \text{.................... (10)}$$

The results show that the adsorption of both of Pb (II) and Cd (II) on the chelate polymer gradually increased by increasing the temperature from 298 to 328 K, as shown in Figures-1 and 13. The maximum amount of sorption of each of Pb^{+2} and Cd^{+2} at different temperatures were calculated, as demonstrated in Figures-14 and 15. The enthalpy for the sorption of both Pb^{+2} and Cd^{+2} on a chelate polymer surface were determined by plotting the maximum amount of adsorption against reciprocal temperature, according to equation (7), which has a slop that indicates - ΔH/R. Positive values of ΔH (10.55 KJ/mol for the sorption of Pb ion and 4.73 KJ/mol for the sorption of Cd ion) were gained, which approved that the adsorption process of Pb and Cd ions over the surface of the polymer was feasible. It could be suggested that endothermic evolution might occur by increasing the Pb $^{+2}$ and Cd $^{+2}$ solutions temperature on the exterior boundary layer and, therefore, improving the inner pores of the applied adsorbent [28-29]. Gibbs free energy for the sorption of Pb and Cd ions on the polymer at different temperatures was investigated using equation (8). The results showed that, by increasing the temperature, the negative values of ΔG were gradually increased from 0.436 to -1.45 kJ/mol for the sorption of Pb ion and from -2.34 to -5.01 KJ/mol for the sorption of Cd ion. These results indicate that the adsorption of both of Pb^{+2} and Cd^{+2} on the chelate polymer is a spontaneous and reasonable process in nature [30-31]. The positive estimations of ΔS confirmed the increased randomness over the liquid–solid interface during the adsorption process of Pb^{+2} and Cd^{+2} over the surface of the chelate polymer, which is similar to the results described in the literature [32].
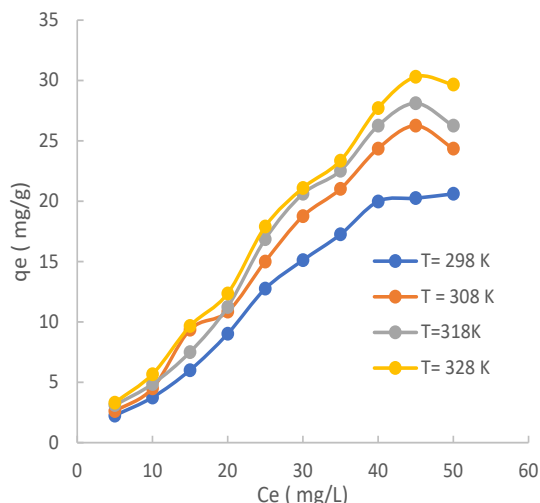
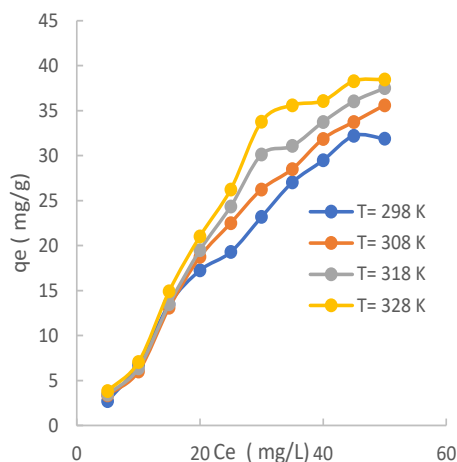Fig. (12)Effect of temperature on adsorption of Pb^{+2} on to polymer

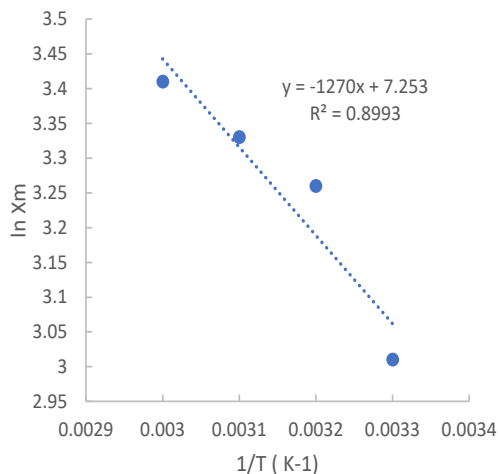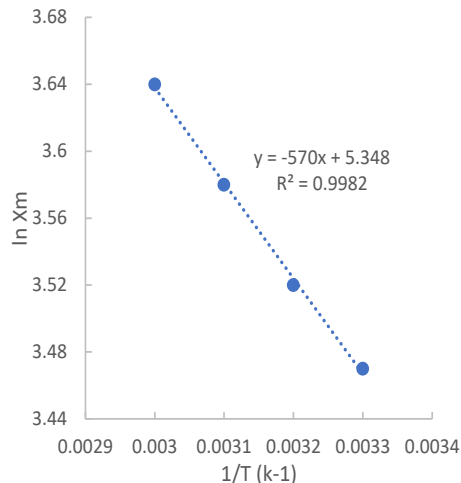Fig. (13): Effect of temperature on adsorption of Cd^{+2} on to polymer

Fig. (14): Plot of lnXm against reciprocal temperature for Pb^{2+} sorption on polymer.

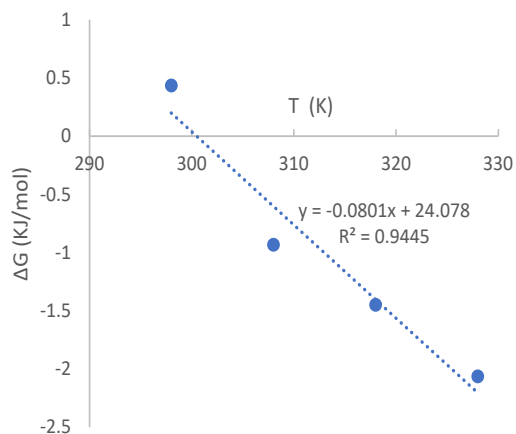(15): Plot of lnXm against reciprocal tFig. emperature for Cd^{2+} sorption on polymer.

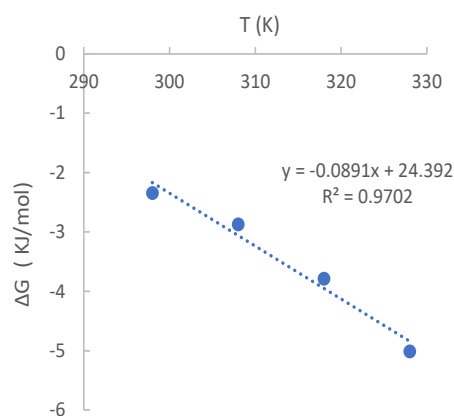Fig. (16): Plot of ΔG against temperature for Pb^{2+} sorption on polymer.

Fig. (17): Plot of ΔG against temperature for Cd^{2+} sorption on polymer.

The values of calculated thermodynamic parameters at different temperatures for the adsorption of Pb^{+2} and Cd^{+2} by using chelate polymer are listed in Table 3.

Table 3- Values of thermodynamic parameters for the sorption of 50 mg/L Pb^{+2} and 50 mg/L Cd^{+2} on 0.1g chelate polymer (K4) at different temperatures.

Ions	Temperature (k)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mol)
Pb^{+2}	298	0.436	10.557	0.08
	308	-0.934		
	318	-1.45		
	328	-2.063		
Cd^{+2}	298	-2.345	4.738	0.09
	308	-2.87		
	318	-3.787		
	328	-5.01		

Conclusions

A new chelate polymer resin was prepared by using the condensation polymerization method. It was derived from 3- nonyl benzene and characterized by FT-IR spectroscopy, ^{1}H- NMR spectroscopy and TG-DTA thermal analysis. The product resin was used for Pb^{+2} and Cd^{+2} ions from aqueous solutions. The kinetic equilibrium reaction for the sorption of each ion was investigated. The results showed that the sorption of both of ions followed the pseudo first order and pseudo second order models.

Thermodynamic parameters, such as ΔG, ΔH, and ΔS were also investigated and the results showed that the sorption process is spontaneous and endothermic in nature for the sorption of each of Pb^{+2} and Cd^{+2} on the polymer surface.

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