



Preparation and characterization of hydroquinone based polyoxalate and its application in the removal of heavy metals from water

Diya Alsafadi^{a,*}, Bassam A. Sweileh^b and Fawwaz I. Khalili^b

^a Scientific Research Center, Royal Scientific Society, Amman 11941, Jordan

* Corresponding author e-mail: Diya.safadi@rss.jo

^b Department of Chemistry, The University of Jordan, Amman 11942, Jordan

ABSTRACT

Hydroquinone based polyoxalate was synthesized from oxalyl chloride and hydroquinone. The polymer was characterized with FTIR, ¹H-NMR, ¹³C-NMR, PXRD, SEM and thermal analysis. The chelation behaviour of the polymer towards Pb(II), Cd(II), and Hg(II) in aqueous solutions was studied by batch technique as a function of contact time and pH. The polymer showed high metal uptake toward Pb(II) and Cd(II) and moderate metal uptake toward Hg(II). The adsorption capacity was not affected by the pH of solution. The adsorption data were fitted with second order kinetic model and the isotherms models of Langmuir and Freundlich. Thermodynamics measurements showed that sorption process was spontaneous. Furthermore, the chelating polymer was loaded with metal ions using fixed bed column. For regenerating the loaded polymer, different eluting agents include HNO₃, H₂SO₄, and EDTA was investigated. The highest recovery of metal ions was achieved using HNO₃, indicating that desorption process was governed by the solubility factor and cation exchange mechanism.

Indexing terms/Keywords

Heavy metals; chelating polymer; adsorption; polyoxalate; isotherm models; desorption.

Academic Discipline And Sub-Disciplines

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1. INTRODUCTION

Excessive release of toxic heavy metals into the environment has posed a great problems worldwide [1]. Unlike organic biodegradable pollutants, heavy metals are stable and cannot be degraded into harmless end products [2]. Furthermore, heavy metals can easily enter the food chain and cause progressive toxic effects with gradual accumulation in living organisms over their lifespan. Lead, mercury and cadmium are examples of such heavy metals that have been classified as priority pollutants by the United States Environmental Protection Agency (USEPA) [3].

Many methods have been evaluated for their ability to remove heavy metals from environment resources particularly, from the waste-water streams. The traditional methods such as chemical precipitation and ultrafiltration did not provide sufficient metals contaminant removal to meet water standards limits [4]. In an alternative approach advance adsorption methods using synthetic chelating polymers [5-8] or clays minerals [9] have been intensively investigated for their high selectivity and efficiency and cost effectiveness.

The backbone of chelating polymers composed active functional groups capable for coordinating with different metal ions. These functional groups usually contain electron donor atoms (Lewis base) such as N, O and S that can coordinate with most of the toxic heavy metals (Lewis acid) [10]. Several criteria are important in the design of chelating polymers include specific and fast metal uptake, high mechanical strength and ability for reusability [11].

Polyoxalates are an interesting class of polymers with two adjacent carbonyl groups in their repeating unit, and these carbonyl groups may act as good ligands for metal complexing. Moreover, polyoxalates have unique properties such as, biodegradability and high mechanical strength [12]. Polyoxalates have been investigated for use in certain applications, include drug delivery [13-14], and water treatment for the removal of heavy metal ions [15]. The synthesis of polyoxalates involve polycondensation of either oxalyl chloride, oxalic acid or oxalic esters with diols. Recently, Polyoxalates have been synthesized from bio-renewable diols via oxalate metathesis polymerization [16].

The chelating behavior of aliphatic polyoxalate (Poly 2,2-dimethyl-1,3-propylene oxalate) toward heavy metals was reported by Abu-Awwad et al [17]. The polymer showed high metal-ion uptake capacity towards Pb(II) and moderate to low capacity towards Cd(II) and Hg(II) ions. In our effort to increase the metal-ion uptake capacity herein, we describe the synthesis and characterization of an aromatic polyoxalate, poly(1,4-phenylene oxalate) (PPO). The sorption properties of PPO toward Pb(II), Cd(II), and Hg(II) ions was examined and compared with the results obtained from the aliphatic counterpart. A real water sample contaminated with heavy metals was also studied in order to provide evidence for the applicability of the prepared polymer in wastewater treatment.

2. EXPERIMENTAL

2.1. Materials

Oxalyl chloride, sodium sulfate, potassium carbonate and 4-dimethyl-aminopyridine (4-DMAP) were purchased from Acros. Acetic acid, nitric acid, sulfuric acid, hydrochloric acid and ethylenediamine tetra acetate–disodium salt (EDTA) were supplied from Scharlau. Sodium acetate and sodium perchlorate were purchased from Sigma. Hydroquinone and pyridine were purchased from GPR. For the adsorption studies, Pb(II), Hg(II), and Cd(II) metal ions were prepared directly from their standard solutions (Standard of Pb(II), Hg(II), and Cd(II), 1000 ppm, Merck A.G., Germany). Other reagents were purchased as analytical grade.

2.2. Preparation of Poly(1,4-phenylene oxalate)

PPO was synthesized using single phase organic solvent polymerization [17] with some modifications. The procedure involved dissolving of hydroquinone (0.10 mol), pyridine (0.3 mol) and a catalytic amount of 4-dimethylaminopyridine (4-DMAP) in 100 mL of chloroform. To this solution (0.10 mol) oxalyl chloride in (100 mL) chloroform was added drop wise with stirring.

The reaction mixture was left under stirring for 1 hour at 5 °C, then the ice/water bath was removed and the mixture was left at 25 °C with stirring for 24 h. After that, 100 mL of chloroform was added to the mixture and the reaction was quenched with 100 mL distilled water. The mixture was transferred to a separatory funnel, shaken well and left until an effective separation of the two layers was observed. The organic layer was separated, acidified with aqueous HCl solution (8 % v/v, 100 mL) and washed with water and with potassium carbonate solution (10% wt/v) until a neutral washing was obtained. The remaining organic layer was dried over anhydrous sodium sulfate and filtered in 250 mL-round bottomed flask. The solvent was completely evaporated under vacuum at 60 °C. An off-white polymer powder was collected and dried overnight in a vacuum oven at 60 °C. For metal adsorption experiments, the obtained polymer was grained and sieved between 40-60 mesh particle sizes.

2.3. Polymer characterization

The infrared spectrum of the PPO polymer was recorded with a Nicolet Impact 400 FTIR-Spectrophotometer (4000-500 cm^{-1}). The ^1H - and ^{13}C -NMR spectra of the polymer were recorded on a Bruker avance DPX 300 Spectrometer. The thermal gravimetric analysis (TGA) of the polymer was studied with NETZCH STA 409 PG/PC Thermal Analyzer. The shape and surface morphology of the polymer was examined with a SUPER SCAN SSX Series (Shimadzu SEM) scanning electron microscope. The crystallinity testing of the polymer was performed with X-ray powdered diffraction (Shimadzu PXRD-6000). The inherent viscosity of the solution of the polyoxalate polymer was measured with a dilution Ubbelohde glass capillary viscometer in a thermostated water bath at 25 °C.



2.4. Adsorption kinetics

The effect of contact time on the rate of metal-ion uptake was studied using batch equilibrium technique by the following manner. A 100 mg $\pm$ 0.1 mg of the dried polymer was suspended in 25 mL of acetate-acetic acid buffer pH 5.0 for two h. To this mixture, 25.0 mL of metal ions solution (300 ppm Pb(II), Hg(II), and Cd(II)) were added. After being shaken for a definite period of time at 25 °C, the mixture was filtered and the amount of metal ion remaining in the filtrate was determined with optical emission inductively coupled plasma spectrometer (Shimadzu ICPS-7510). The adsorption capacity (q) of metal ions was calculated as follows:

$$q = (C_0 - C_{eq})V/m \quad (1)$$

Where V is the volume of aqueous solution, C_0 and C_{eq} are the concentrations of initial and residual metal ions, respectively and m is the mass of the polymer.

In order to examine the controlling mechanism of adsorption process such as mass transfer and chemical reaction, the kinetic data were modeled using first and second order kinetic models. The first-order kinetic equation and second order kinetic equation are expressed as Eq. (2) and Eq. (3), respectively.

$$\text{Log } (q_e - q_t) = \text{Log } q_e - K_1 t / 2.303 \quad (3)$$

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (2)$$

Where q_e is the amount of metal ion adsorbed at equilibrium (mg metal /g polymer); q_t is the amount of metal adsorbed (mg metal ion/g polymer) at time t ; t is the time in hours (h); K_1 and K_2 are the rate constants of first and second order kinetic equations (g polymer/ mg metal.h), respectively.

The general expression for the distribution coefficient K_d was calculated using the following equation:

$$K_d = \frac{\text{Metal ion adsorbed on the polymer (mg)}}{\text{Metal ion remain in the solution (mg)}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of polymer (g)}} \quad (4)$$

For evaluating the effect of pH on the adsorption process similar experiments were performed using different buffer solutions of pH 4.0, 5.0 and 6.0 at fixed contact time of 24 h.

2.5. Adsorption isotherms studies

Adsorption isotherms for Pb(II), Cd(II), and Hg(II) ions were carried out by taking a mass of 100 mg $\pm$ 0.1 mg of the polymer, swelled latter with 25 mL of sodium acetate-acetic acid buffer, pH 5.0 for two h. 25.0 mL of metal solutions with concentration ranging from (10-150) ppm for each metal were added. The mixtures were shaken for 24 h at different temperatures (25 °C, 35 °C and 45 °C). The adsorption isotherms were also studied using similar conditions but under different pH values of 4 and 6.

The adsorption behavior of metal ions onto polymer surface was described using the linearized Langmuir isotherm Eq. (5) and Freundlich isotherm Eq. (6) plots [19].

$$1/q = (1/(q_m K_L)) 1/c + 1/q_m \quad (5)$$

$$\log q = \log K_F + 1/n \log c \quad (6)$$

Where c is the equilibrium concentration of the metal ion in solution (mg/L), q the equilibrium adsorption capacity (mg/g), q_m the monolayer saturated adsorption capacity (mg/g) and K_L , K_F , n are the constants.

In order to understand the possible adsorption mechanism involved in the removal process, thermodynamic functions for the system, including changes in Gibbs free energy (ΔG^*), changes in enthalpy of adsorption (ΔH^*) and changes in entropy of adsorption (ΔS^*), were calculated using Eq. (7) and Eq. (8) [20].

$$\ln K_d = \Delta S^*/R - \Delta H^*/RT \quad (7)$$

Where K_d is the equilibrium constant, R is the universal gas constant and T is the temperature in Kelvin.

The change in Gibbs free energy (ΔG^*) was calculated using the following equation:

$$\Delta G^* = \Delta H^* - T \Delta S^* \quad (8)$$

2.6. Metal ion-uptake by the polymer using fixed bed column

Glass column with 150 mm length and 10 mm inner diameter was used in this experiment. The column was packed with $0.5 \text{ g} \pm 0.0001 \text{ g}$ of dried polymer. 50 mL acetate-buffer, pH 5.0 was added and the polymer allowed swelling for 24 h. The acetate buffer was then followed at a flow rate of 1.0 mL/min. A sample 50.0 mL containing 1000 ppm Pb(II), was then passed through the column at the same flow rate (1.0 mL/min). The eluate was collected in a 50 mL volumetric flask, and the concentration of the metal ion was determined by ICPS. The same experimental conditions were used for the determination of Cd(II) and Hg(II) ions uptake, where the sample which passed through the column was 1000 ppm for both Cd(II) and Hg(II).

2.7. Desorption Studies

In order to determine the reusability of the polymer, consecutive adsorption–desorption steps were performed. The desorption of the Pb(II), Cd(II), and Hg(II) ions, were carried under column condition, where the polymer was loaded with each metal ion as described in previous section. 50 mL of three eluting agents, 1 N HNO₃, 1 N H₂SO₄, and 0.5 N EDTA were used for polymer recovery from adsorbed metal ion, keeping the flow rate for elution at 1 mL/min. The metal ion in the eluate was collected and the concentration was determined with ICP. The percentage recovery of each metal ion was calculated with Eq. (9).

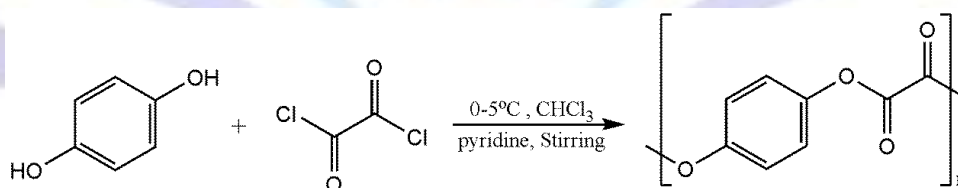
$$\% \text{ Recovery} = \frac{\text{Amount of metal ions in the elution agent}}{\text{Amount of metal ions adsorbed on the polymer}} \quad (9)$$

3. RESULTS AND DISCUSSION

3.1. Polymer synthesis

The synthesis of PPO was performed by polycondensation of oxalyl chloride and hydroquinone, the reaction was catalyzed with pyridine as given in Scheme 1.

An off-white powder with 85% yield was obtained. The synthesized polymer was insoluble in most common organic solvents such as chloroform, dimethyl formamide (DMF), tetrahydrofuran (THF) 1,4-dioxane and showed good solubility only in dimethyl sulfoxide (DMSO).



Scheme 1. Preparation of PPO.

3.2. Polymer characterization

3.2.1. FTIR spectrum of the polymer

PPO was analyzed with FTIR spectroscopy (Figure 1). The FTIR spectrum of the polymer exhibits characteristic absorption bands for the major bonds involved in the polymer. The results of the IR analysis (NaCl disc) showed two strong absorption bands due to the stretching vibration of the carbonyl group (C=O) of the oxalate function at 1708 cm^{-1} and at 1757 cm^{-1} , and due to the (C-O-C) at 1137 , 1179 and 1229 cm^{-1} . The IR spectrum also showed broad band at about 3252 cm^{-1} , this band was assigned to the terminal aromatic hydroxyl groups of the oligomers that formed.

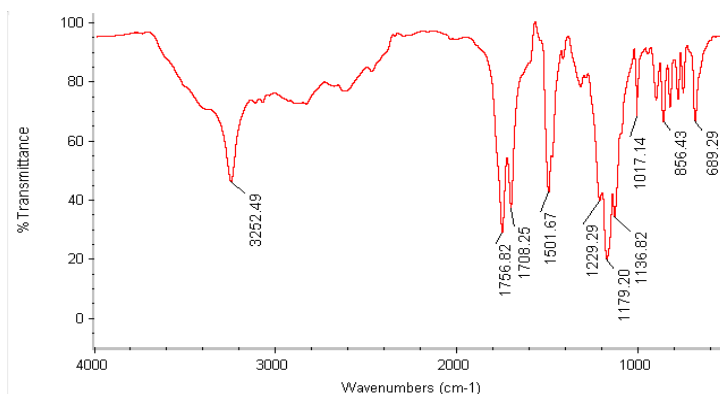


Figure 1. IR spectrum of PPO.

3.2.2. NMR spectra

PPO structure was also confirmed with NMR spectroscopy. The protons of the aromatic ring of hydroquinone unit were observed as singlet at $\delta = 7.4$ ppm. In addition to this peak, two other small aromatic peaks were also observed in the ^1H -NMR spectrum; the first was observed at $\delta = 7.1$ ppm which was attributed to the ring protons in ortho position to a terminal hydroxyl group of phenol. The second peak was observed at $\delta = 6.8$ which was attributed to the ring protons in meta position to a terminal hydroxyl group of phenol. The proton of a phenolic hydroxyl group was observed at $\delta = 3.4$ ppm. The appearance of these small signals in the ^1H -NMR spectrum of PPO indicates that the terminal phenolic units of the end group are detectable. The small sizes of these signals indicate that the product obtained is the oligomer rather than the mature polymer. The ^1H -NMR spectrum is shown in Figure 2.

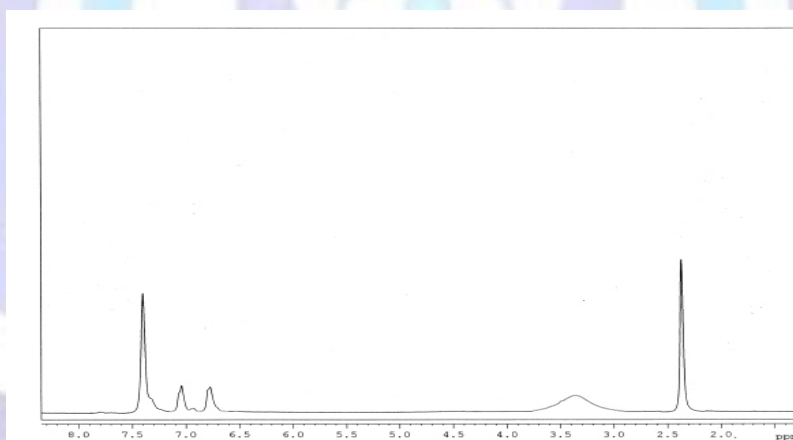


Figure 2. ^1H -NMR spectrum of PPO

The ^{13}C -NMR spectrum of the polymer is presented in Figure 3. The signal of the carbonyl carbon atoms of the oxalate unit appeared at 156.2 ppm. The carbon atoms of the aromatic ring of hydroquinone unit were observed at 122.5 ppm and 148.5 ppm. The signal that appeared at 122.5 ppm was attributed to aromatic methine carbon atoms, and the aromatic quaternary carbon that is directly bonded to oxygen observed at 148.5 ppm. In addition to these peaks, other signals were also observed at 116.2, 123.2, 142.7, and 155.7 ppm which were attributed to the terminal phenolic end .

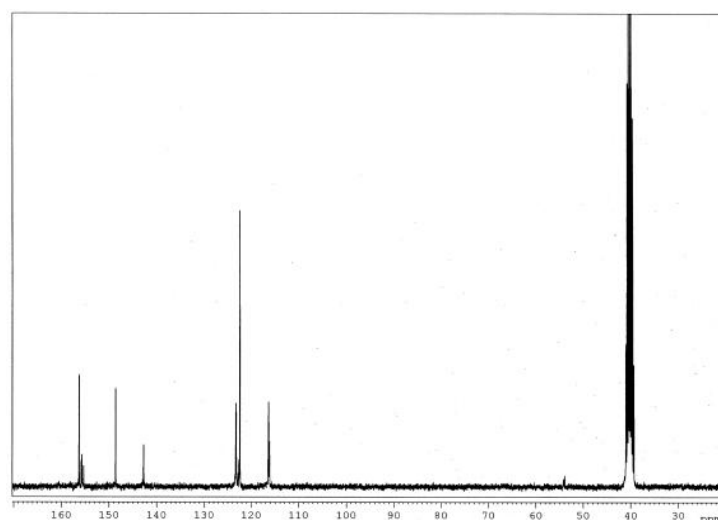


Figure 3. ^{13}C -NMR spectrum of PPO.

3.2.3 Thermal analysis

To examine the thermal degradation behavior of the polymer, thermogravimetric analysis (TGA) was conducted under dry nitrogen atmosphere. The TGA curve of the polymer displayed almost one stage characteristics with a slow loss of mass starting from 77 °C to 168 °C and a relatively fast loss between 193 °C to about 380 °C (Figure 4). A similar thermal decomposition analysis of polyoxalate has been previously reported by Thibeault et al [21]. The TGA data of polyoxalates were explained by the decarboxylation of the oxalate groups, and the formation of polyenes and CO_2 .

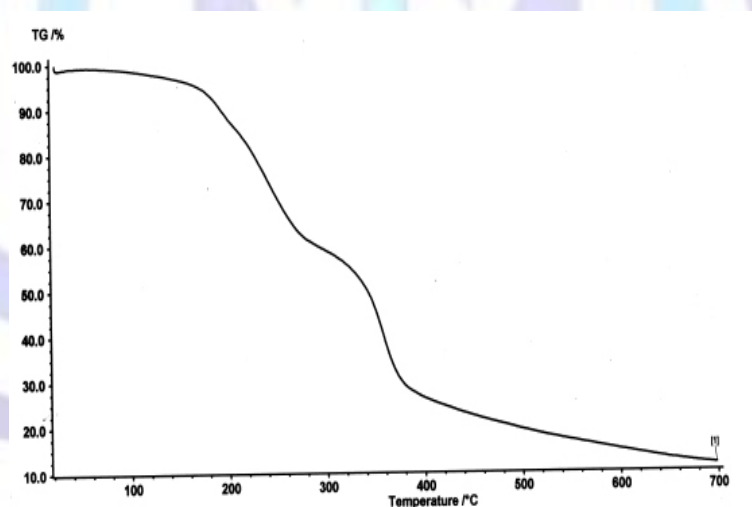


Figure 4. TGA curve for PPO.

3.2.4. Scanning electron microscopy and X-ray diffraction analysis

The surface feature of PPO was examined through scanning electron microscopy (SEM) (Figure 5). It is clearly seen that there are abundant pores distributed on the polymer surface. The existence of these pores would provide convenient diffusion channels for metal ions into the polymer core. These pores would play an important role when the polymer used for metal uptake from aqueous solution.

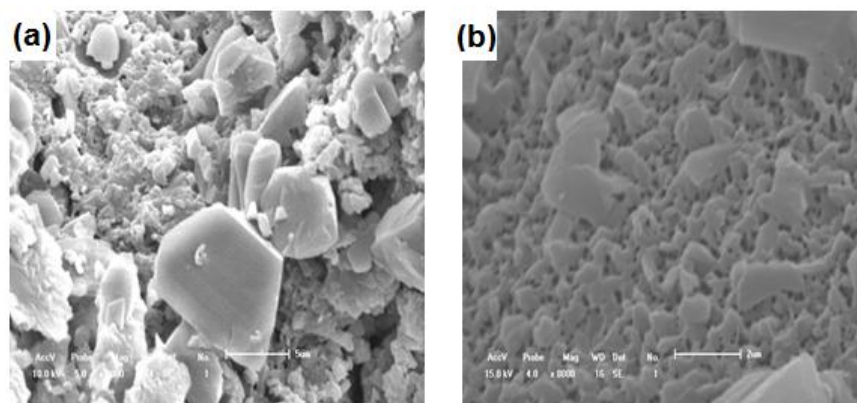


Figure 5. SEM images of PPO (a) magnification = 3000 time and (b) magnification = 8000 time.

The powder X-ray diffraction (PXRD) pattern of the synthesized polymer is depicted in Figure 6. The diffraction pattern showed that the PPO is found to be more amorphous in nature; this implies that the polymer structure has a relatively low regular packed crystal system within its molecules. The amorphous structure could be arisen from the existence of aromatic bulky group which enhance the irregularity between the polymer molecules.

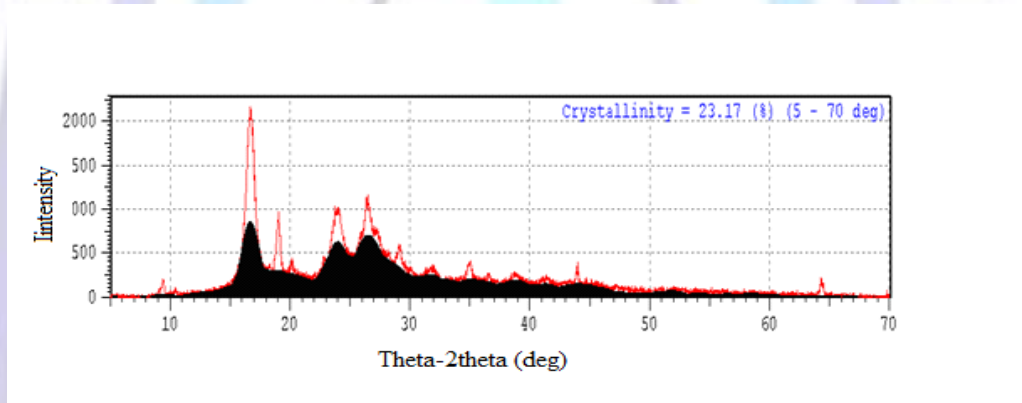


Figure 6. PXRD pattern of PPO. The percent of crystallinity (red) equal 23% and the percent amorphous (black) equal 77%.

3.2.5. Viscosity measurements

The inherent viscosity of the polymer was determined from the viscosity measurements of diluted polymer solutions (0.5 g/dl) in dimethyl sulfoxide (DMSO), at 25 °C using Ubbelohde glass capillary viscometer. The polymer had inherent viscosity of 0.14 dl/g. From this value, the polymer prepared had a low to moderate inherent viscosity, which means that the polymer with a low to moderate molecular mass was produced.

3.3. Adsorption properties

3.3.1. Effect of pH

The effect of pH on the uptake of Pb(II), Cd(II) and Hg(II) by PPO was studied using batch procedure at pH range (4 – 6) for a fixed contact time of 24 h at 25 °C (Figure 7). The results in Figure 7 show that the changing of pH has no effect on the sorption capacity profile of the polymer. This could be related to the fact that the polymer has no ionizable functional groups. Figure 7 also indicates that the selectivity of PPO is high toward Pb(II) and Cd(II) and moderate uptake towards Hg (II).

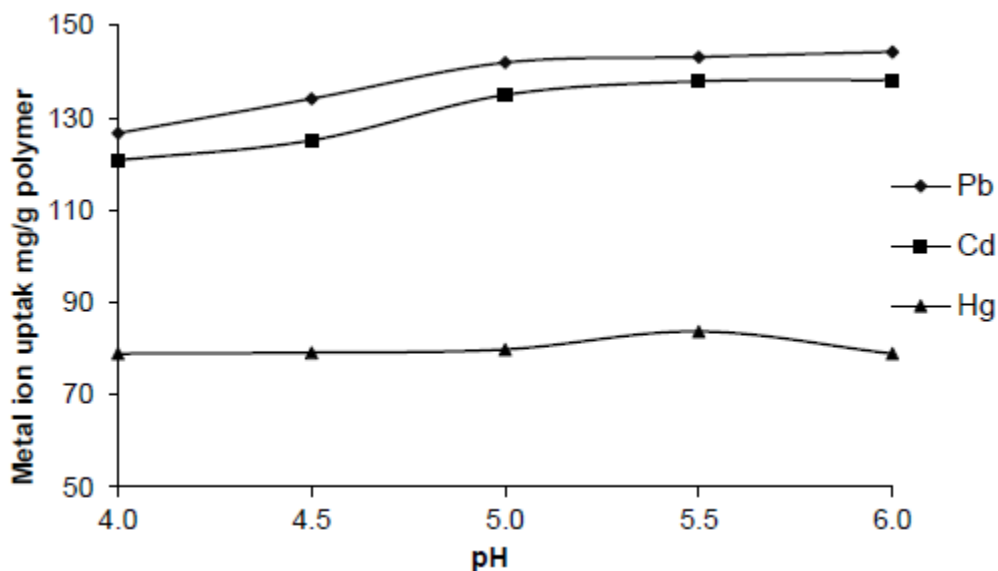


Figure 7. Metal uptake at different pHs.

To confirm this selectivity, the distribution coefficient of metal ions (K_d) between the polymer phase and the aqueous phase was calculated at pH ranging from 4 – 6 (Figure 8). As expected the distribution ratio of the metal ions follows the order $Pb(II) > Cd(II) > Hg(II)$. Interestingly, Figure 8 shows that there is no linear correlation between the pH values and the logarithm of distribution coefficients (Log K_d) which implies that the adsorption process is beyond the ion exchange behaviour or to the lack of acidic/basic functional groups [22].

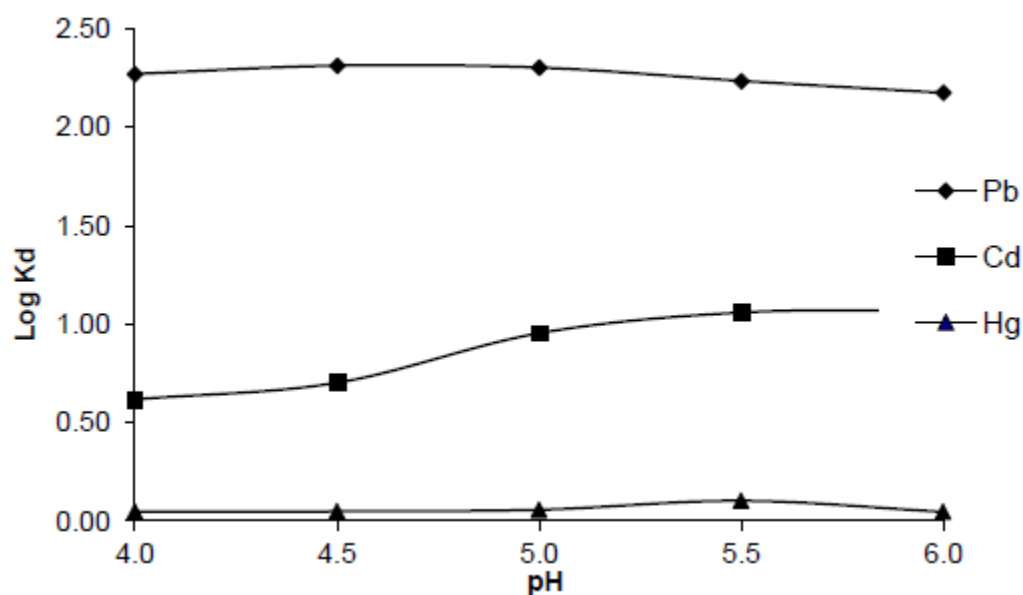


Figure 8. Relation between Log K_d versus pHs.

3.3.2. Adsorption kinetics

The rate of metal ion uptake by the PPO was evaluated at different time intervals and the results are presented in Figure 9. The time profile of metal ions adsorption showed high sorption rate during the first 15 minutes with percent uptake for $Pb(II)$, $Cd(II)$ and $Hg(II)$ 98.33%, 88.97% and 48.12%, respectively. Furthermore, the uptake for all metal ions increase with time until complete saturation (plateau) was obtained after 12 hours of contact time. The fast metal ion uptake could



be attributed to the porous structure of the polymer which accelerates the metal ion diffusion toward polymer active groups.

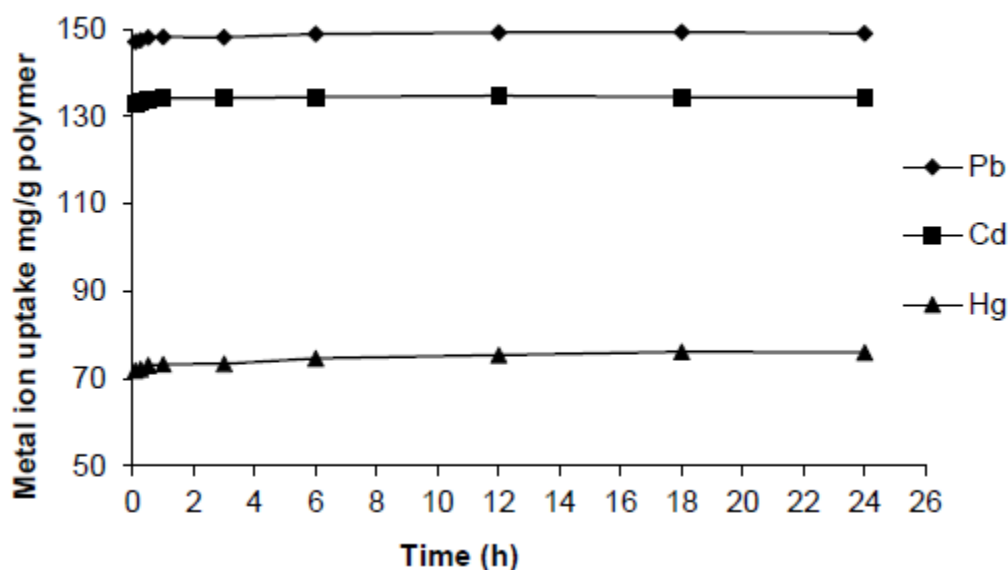


Figure 9. Metal uptake as a function of contact time, at pH 5 and initial concentration of 300 ppm.

The first and second order models (Eq. (2) and Eq. (3)) were used to fit the experimental data of adsorption kinetics. For the first order model the amount of metal ion adsorbed at equilibrium (q_e) and the rate constant (K_1) were calculated from the slope and intercept for the plots of t vs. $\log(q_e - q_t)$ (Figure 10). For the second order model, the values of q_e and K_2 at different concentrations were calculated from the slope and intercept of the plots of t vs. t/q_t (Figure 11). The obtained values are presented in Table 1.

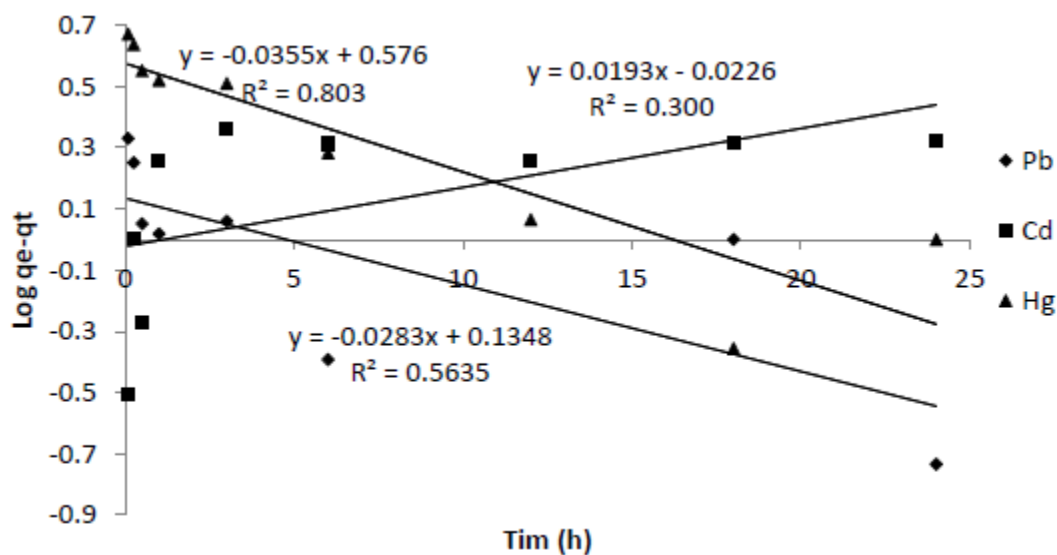


Figure 10. Plot of first-order kinetic model.

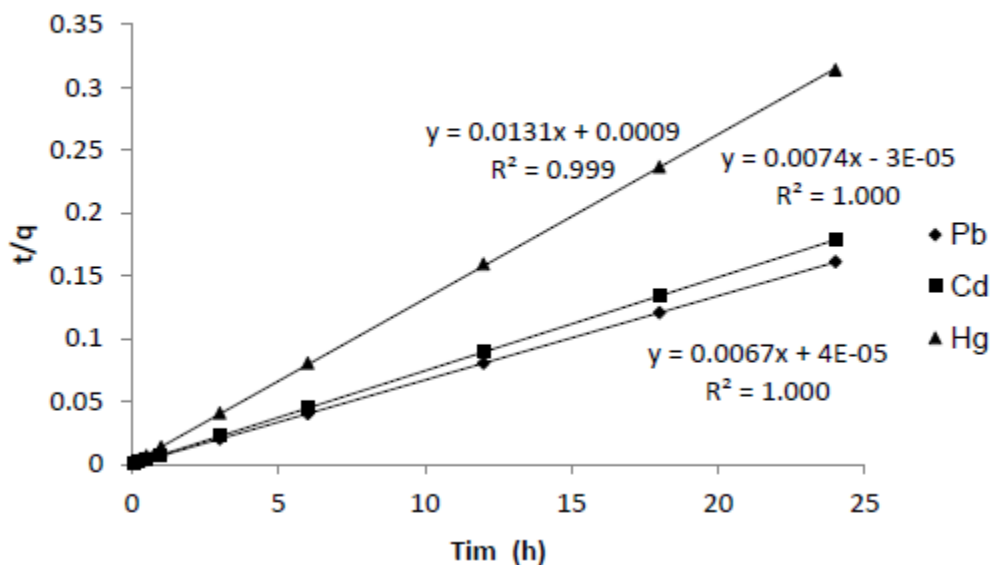


Figure 11. Plot of second-order kinetic model.

Table 1 First order and second order adsorption rate parameters

Metal	First order kinetic model				Second order kinetic model		
	q_e (exp) mg g^{-1}	q_e (cal) mg g^{-1}	$K_1 \text{ h}^{-1}$	R_1	q_e (cal) mg g^{-1}	$K_2 \text{ g mg}^{-1} \text{ h}^{-1}$	R_2
Pb(II)	149.30	1.36	0.04	0.564	149.25	1.12	0.999
Cd (II)	133.33	1.05	0.05	0.300	135.13	1.83	1.000
Hg(II)	57.80	3.77	0.08	0.804	76.33	0.19	1.000

From the values of correlation coefficients R_1 and R_2 in Table 1, we can predict that the adsorption kinetics followed a second order kinetic model for all the selected metals, while the first-order kinetic model fits poorly the experimental data. Furthermore, the experimental q_e values were very close to the calculated q_e from second order kinetic. These results indicate that the rate-limiting step of the adsorption process is the chemical adsorption [23].

Adsorption isotherms .3.3.3

The adsorption isotherms were determined for Pb(II), Cd(II), and Hg(II) in the range of concentrations from 10-150 mg/L at pH 5.0 and different temperatures (25° C, 35° C and 45° C). The results of the adsorption isotherm were analyzed using the linearized adsorption isotherm of Langmuir and Freundlich .The isotherm data for the investigated heavy metal ions are summarized in Table 2.

**Table 2. Langmuir and Freundlich isotherm parameters for Pb(II), Cd(II), and Hg(II) with PPO.**

T (°C)	Metal ion	Langmuir equation parameters			Freundlich equation parameters		
		q_m (mg/g)	K_L (L/g)	R_1	K_F	n	R_2
25	Pb(II)	*	*	0.932	2.40	0.60	0.970
	Cd(II)	133.33	5.74×10^{-3}	0.998	0.76	1.03	0.994
	Hg(II)	57.80	0.03	0.992	2.89	1.62	0.928
35	Pb(II)	*	*	0.990	3.67	0.71	0.990
	Cd(II)	128.21	7.87×10^{-3}	0.964	1.03	1.11	0.988
	Hg(II)	28.33	0.089	0.972	2.39	1.61	0.995
45	Pb(II)	*	*	0.990	0.18	0.50	0.969
	Cd(II)	123.46	3.86×10^{-3}	0.957	0.88	1.14	0.954
	Hg(II)	31.35	0.056	0.950	1.91	1.42	0.929
*High affinity of Pb(II) ion toward the polymer was observed, so no significant amount of Pb(II) remained in the solution after adsorption, intercept of plot of $1/q$ and $1/c$ was negative. R_1 and R_2 are the correlation coefficient of Langmuir and Freundlich isothermal adsorption plots							

According to Table 2 the equilibrium adsorption (q_m) of the polymer towards metal ions fall in the order: Pb(II) > Cd(II) > Hg(II). This sequence could be attributed to the stability of complexes that formed between the donor atom (oxygen) in polymer active groups and the type of metal ions. The stability of metal complexes can be explained by the hard and soft acids and bases (HSAB) theory, in which hard acids tend to associate with hard bases, and soft acids with soft bases [24]. Based on HSAB theory, Pb(II) and Cd(II) (relatively hard acids) have high tendency to make strong complexes with hard donor atom like oxygen. On the other hand, Hg(II) is a very soft metal and its coordination chemistry favour the liner arrangement with ligands and this could decrease the possibility of forming stable chelate ring with polymer active sites.

The correlation coefficient (R^2) is a mathematical expression which reveals the favorability of the adsorption process. Since R^2 values (Langmuir) listed in Table 2 are very close to 1, the adsorption of all metal ions onto PPO followed well the Langmuir isotherm equation. The high fitness of Langmuir isotherm gives indication for homogeneous monolayer coverage of PPO active sites by the metal ions.

A comparative study for PPO with previously reported resins was established, the data was expressed in terms of adsorption capacity as shown in Table 3.

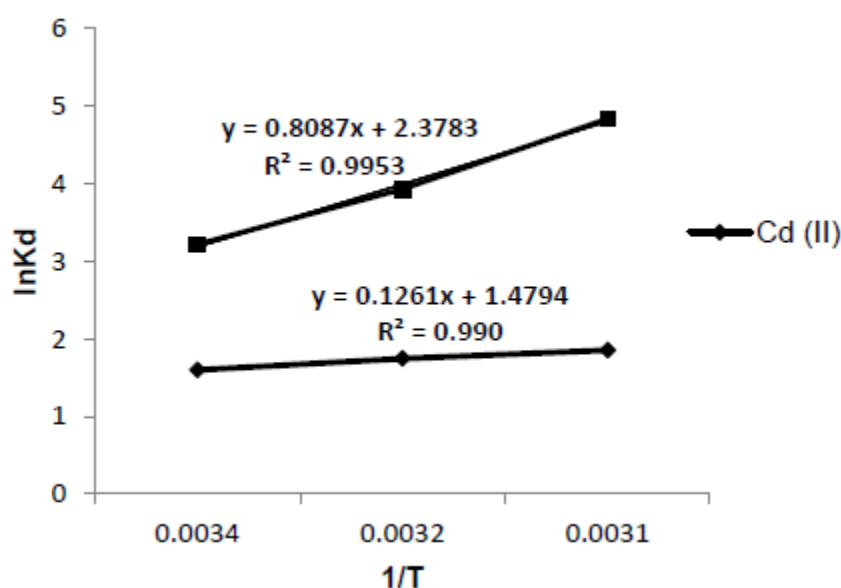
**Table 3. Adsorption capacities for Pb(II), Cd(II), and Hg(II) onto PPO and various adsorbents reported in the previous literatures.**

Chelating Polymer	(Adsorption capacity (mg/g))		
	Pb(II)	Cd(II)	Hg(II)
Cross-linked magnetic chitosan-phenylthiourea [25]	-	120.3	134.4
Bis[2-(2 benzothiazolylthioethyl)sulphoxide] [26]	76.7	40.3	270.8
Silica-supported dithiocarbamate [27]	82.9	40.5	80.2
Polysiloxane resins modified by bisglycidyl calix[4]arene [28]	62.1	-	80.0
[Polyamine chelating resins with sulfide group [29]	207.0	56.2	421.3
Polystyrene chelating resin with imidazolylazo benzene functional group having azo group [30]	51.8	15.7	22.1
Polystyrene supported dithiocarbamates [31]	4.1	2.3	6.0
Poly(2,2-dimethyl-1,3-propylene oxalate) [17]	-	38.6	44.8
PHQ	-	133.3	57.8

The results presented in Table 3 reveals that, PPO has a good advantage in adsorption of Cd(II) more than the previously reported resins. Compared with aliphatic polyoxalate [16] in Table 3, the adsorption capacities of PPO for Cd(II) and Hg(II) are higher. The high potential of PPO for uptake of heavy metals can be explained by the presence of phenyl group in the polymer structure which enhance the chelating interaction between the the donor atom (oxygen) and metal ions. A similar effect of the aromatic group has been previously reported in aromatic polyamides [32]. The authors reported that the presence of an aromatic group in the chelating polymer structure improves the chemical stability and binding ability of the polymer to metal ions.

3.3.4. Thermodynamics of Adsorption on polymer

For further exploration the adsorption mechanism of heavy metals onto PPO, the thermodynamic functions for the system, including changes in Gibbs free energy (ΔG^*), change in enthalpy of adsorption (ΔH^*) and changes in entropy (ΔS^*) were calculated. The values of enthalpy (ΔH^*) and entropy (ΔS^*) were obtained from the slopes and intercept of $\ln K_d$ vs. $1/T$ plots as shown in Fig. 12. Changes in Gibbs free energy ($\Delta G^* = -RT \ln K_d$) were calculated from the $\ln K_d$ values.

**Figure 12. Plots of $\ln K_d$ Vs $1/T$ for Cd(II), and Hg(II) metal ions at different temperatures.**

**Table 4. Thermodynamic parameters for adsorption of metals ion on PPO at 298 K.**

Metal ion	ΔH^* (J/mol)	ΔS^* (J/mol.K)	ΔG^* (KJ/mol)
Cd (II)	1.03	12.03	-3.58
Hg (II)	6.58	19.34	-5.76

Table 4, shows that the adsorption of metal ions on PPO is a favorable process indicated by the negative value of ΔG^* . The positive ΔH^* values reflect the endothermic nature of the adsorption process. Also, the positive values of ΔS^* could be related to the increase of randomness, when the hydrated water molecules, that bounded to the polymer and the metal ions were replaced upon adsorption.

3.3.5. Metal ion-uptake by the polymer using fixed bed column technique

The applicability of PPO in the removing of heavy metals was investigated using fixed bed column. The solution of metal ions was passed through adsorbing column that contains PPO at flow rate of 1 mL/min. The percent uptake for Pb(II), Cd(II) and Hg(II) was 46.0 %, 45.8 % and 35.6 %, respectively. It can be seen that the order of metal ion uptake using column technique was similar to that of batch experiment; Pb(II) > Cd(II) > Hg(II). However, the values of metal ions uptake in column experiment were lower than those obtained in batch experiments. This could be related to the short contact time, which was not enough for achieving the complete saturation of metal ions on polymer surface.

3.4. Desorption study

To be useful in metal ion recycling processes, chelated metal ions should be easily desorbed under suitable conditions. Desorption experiments were performed using three eluting agents 1N HNO₃, 1N H₂SO₄ and 0.5 N EDTA keeping the flow rate of elution at 1 mL/min. The eluate was collected and the results are expressed as percent recovery as shown in Table 5.

Table 5. Percent recovery for metal ions using different eluting agents.

Eluting agent	% Recovery Pb	% Recovery Cd	% Recovery Hg
1N HNO ₃	69.8	77.9	72.7
1N H ₂ SO ₄	12.4	46.8	46.3
0.5N EDTA	25.8	66.4	65.1

Depending on the values of % recovery in Table 5, the following trends were observed for the eluting agents: 1N HNO₃ > 0.5N EDTA > 1N H₂SO₄ for all metal ions.

The chelating strengths of the eluting agents toward different metal ions are not in agreement with the adsorption and stability constants reported for the complexation of the metal ions and used ligands which follow this order EDTA²⁻ > SO₄²⁻ > NO₃⁻ [33]. The results of the desorption process indicate that the elution of metal ions from the polymer is governed by the solubility factor.

Chelation properties of the polymer in a real sample .3.5

A real sample was also employed in order to check the capability of metal uptake by the polymer for environmental application. A sample containing 30 ppm Pb(II) was brought from HOPPECKE batteries factory. The same procedure of metal uptake was performed on this sample keeping the exposed time at 24 h. the percentage uptake was found about 95% .The removal of Pb(II) from real wastewater sample was efficient, and it can be said that nearly complete adsorption was achieved ,which confirm the applicability of PPO in waste water treatment.

4. CONCLUSION

In this work we present the preparation of poly(1,4-phenylene oxalate) (PPO) as the chelating polymer for the removal of heavy metals from aqueous solutions. The structure of the polymer was clearly confirmed by spectral analysis. From the SEM images and XRD analysis, the polymer was found to be very amorphous and porous in nature.

The kinetic study showed that the adsorption of heavy metals on PPO follows second order kinetics model. PPO showed an excellent adsorption capacity toward Pb(II) and Cd(II) compared to the previous prepared chelating polymer in the literatures include the aliphatic polyoxalate (Poly 2,2-dimethyl-1,3-propylene oxalate). The order of adsorption capacity of metal ions onto PPO was Pb(II) > Cd(II) > Hg(II), this order was explained by the stability of complexes that formed between polymer active groups and the metal ions.

Adsorption isotherms confirmed that the adsorption followed Langmuir monolayer adsorption. The thermodynamic parameters for the adsorption process were calculated. The positive values of ΔH^* and ΔS^* and negative value of ΔG^* indicating that the metals adsorption process is endothermic and spontaneous. The regeneration study shows that PPO



can be reused with high desorption percentage of metal ions. The investigation on real wastewater sample has also revealed PPO can be utilized to remove heavy metal ions, especially, lead from the aquatic environment.

All these findings indicate the applicability of PPO for the separation and recovery of heavy metal ions from wastewater.

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