Synthesis, Characterization of Poly(1,4–cyclohexanedimethylene oxalate) and the Study of its Metal Uptake Behavior Towards Pb(II), Zn(II), and Cd(II) Ions

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Summary: Poly(1,4–cyclohexanedimethylene oxalate) was synthesized from oxalyl chloride and cis/trans–1,4–cyclohexandimethanol. The polymer was characterized by viscosity, FT–IR, NMR, elemental analysis, DSC, TGA, and SEM. The metal uptake behavior of the polymer towards Pb(II), Zn(II) and Cd(II) ions was studied by batch technique as a function of pH, temperature, concentration, contact time and by column technique. Their uptake increases slightly with pH reaching maximum at 6.00. The order of adsorption capacity was: Pb(II) > Cd(II) > Zn(II). The uptake of the polymer shows fittings to both Langmuir's and Freundlich equations. ΔG° , ΔH° and ΔS° were determined for Pb(II). The metal-unbound polymer was regenerated by treating the metal-sorbed polymer with 1.0 M HNO₃ > 1.0 M HCl >0.01 M EDTA.

Keywords: 1,4–Cyclohexandimethanol, Polyoxalate, Condensation Polymerization, Metal Ions Uptake, Adsorption.

Introduction

Pollution by heavy metals presents serious problems for human health and life. The disposal of heavy metals results from several actions like chemical manufacturing, mining, extractive metallurgy, coating, painting and other industries. Those metals bring about a harmful effect on fauna and flora of lakes and streams [1, 2]. Consequently, Pb(II), Zn(II) and Cd(II) cause environmental pollution, threats to human health and ecosystems [3]. It has been reported that polymers containing appropriate donor groups remove metal ions from aqueous solutions [4], and the uptake is generally affected by factors such as the chemical structure of the donor groups, physicochemical properties, and the porosity of the polymer matrix. Therefore, there are substantial differences in the selectivity and stability towards certain metal ions [5].

The majority of polymers used for metal uptake purposes have been hydrophobic materials [6]. However, the type and number of functional groups in the polymer backbone and their accessibility in taking metal ions are prime factors in the uptake efficiency. It has been found that polymers with functional groups containing oxygen, nitrogen, phosphorus, and sulfur are capable of coordination with different metal ions [6]. Polymers capable of metal adsorption have wide range of applications in various fields [7], such as: selective determination of metal ions, preconcentration of trace elements from aqueous solutions by sorption on polymers [8], water treatment [9], and antidotes for some types of metal ion poisoning [10].

Polyoxalates is a class of polymers characterized by having two adjacent carbonyl groups in the structural repeating unit which can be represented by the general formula R-OCOCOOor Ar—OCOCOO— where R and Ar are aliphatic and aromatic alkane chains, respectively. It has been demonstrated that polyoxalates having a relatively high average molecular mass exhibit satisfactory mechanical properties and are appropriate for practical use [11]. The synthesis of some polyoxalates based on diphenols and diols and the effect of some experimental parameters on the polymerization reaction was described in the literature [12, 13]. The polymerization kinetics of oxalyl chloride with 4,4'-isopropylidinediphenol (bisphenol A, BPA) in the presence of pyridine was studied and found that the molecular mass of the polymer was independent of reaction rate [14, 15]. The thermal resistance of poly(bisphenol A oxalate) was the highest in the aromatic diol-oxalic acid polyester series, incomparable to that of polycarbonates [16, 17]. Many efforts have been made to study the adsorption capacity and selectivity of polymers uptake towards various metal ions [4, 5, 9, 11, 14, 18, 19, 20-24]. Table-1 shows the adsorption capacity reported in the literature for some resins toward Pb(II), Zn(II), and Cd(II) ions.

Polymer	Metal ion	Uptake mmol/g polymer	Reference
Polysiloxane Resins Modified by Bisglycidyl Calix[4]arene	Pb(II)	0.30	Li et al., (2004) [15]
Doludinhonulamina regin	Pb(II)	0.092	El Mostanha at al. (2005) [17]
r oryurphenylanime resin	Zn(II)	0.56	En Wiostaphia et al., (2003)
Bis(benzeimidazole) resin supported on epoxide	Zn(II)	1.30	Shu, et al., (2006) [18]
Dely/himkenel A evalute)	Pb(II)	0.548	Al Homidi et al. (2008) [19]
Poly(Disphenoi A oxarate)	Zn(II)	0.426	AI-Haimui et al., (2008)
Poly(2-octadecylbutanedioic acid)	Pb(II)	1.70	Laurino (2008) [20]
Delyamine sheleting using with fulfide group	Pb(II)	1.00	Bongium et al. (2005) [7]
Foryamme cherating resins with Sunide group	Cd(II)	0.50	Kongjun et al., (2005)
Madified cilies col	Pb(II)	0.09	Mahmoud and Al-Saadi, (2005)
Mounieu sinca gei	Cd(II)	0.45	[16]
Acrylonitrile copolymer	Pb(II)	0.10	Godjevargova et al., (2001) ^[2]
Silica and standard instant	Pb(II)	1.27	
Silica gei etnyieneimine	Cd(II)	1.02	Arakaki et al., (2006)
Polystyrene chelating resin with imidazolylazobenzene functional	Pb(II)	0.25	D-11
group having azo group	Cd(II)	0.14	Reddy and Reddy (2003) (3)
Delveturene summerted Dithiosonhometer	Pb(II)	0.02	McClain and Heich (2004)[13]
r orystyrene-supported Ditmocarbamates	Cd(II)	0.02	MicCiani and Hsien (2004) ¹²³
m-Phenylene Diglycine chelating resin	Zn(II)	1.27	Gregor et al., (1952) [21]

Table-1: Adsorption capacity of some resins toward Pb(II), Zn(II), and Cd(II) ions.

Throughout the course of preparation of this manuscript, we found out that the same polymer was prepared and published before we do. However, a closer look at those works, we found that the polymer did not receive full characterization. In some reports, the polymer, synthesized in the form of nanoparticles for delivery of bioactive agents, was characterized by NMR [25], the polymer nanoparticles as new biodegradable and non-inflammatory drug delivery systems was characterized by gel permeation chromatography (GPC) and NMR [26]. The high molecular weight biodegradable polyoxalates were characterized by GPC and DSC, while the hydrolytic degradation kinetics and the degradation products were characterized by NMR and GPC [27-29]. In another study, the morphology of valsartan-loaded polyoxalate microspheres was developed by varying the polyoxalate molecular weight, surfactant content, and initial drug loading rate and the morphology of the valsartan loaded polyoxalate microspheres was evaluated by scanning electron microscopy (SEM) and the hydrolysis kinetics of polyoxalates were investigated, but nothing was mentioned about characterization of the unloaded polymer [30]. Therefore, the aim of this work was to synthesize, characterize poly(cis/trans-1,4-cyclohexane dimethylene oxalate) and to study its uptake towards Cd(II), Pb(II) and Zn(II) ions as a function of shaking time, concentration, pH, and temperature. The data are analyzed by Langmuir and Freundlich adsorption models, and their linearized forms. This work is an extension to previous works done in our laboratories on the uptake properties of oxalate polymers toward some transition metals [22, 31].

Experimental

Instrumentation

The inherent viscosity of the polymer solution in chloroform (Concentration 0.5 g/dL) was measured with dilution Ubbelohde glass capillary

viscometer (Rheotek, Poulten Selfe & Lee Ltd.) in a water bath at 30.0°C for approximately 10 minutes before measuring the viscosity.

The infrared spectrum of the polymer was recorded from 400–4000 cm⁻¹ using a ThermoNicolet NEXUS 670 FT–IR spectrophotometer using thin films prepared by casting chloroform solution of the polymer over NaCl plates. Single beam spectra were obtained after averaging 48 scans to reduce the noise with a resolution of 4 cm⁻¹. The IR spectra of three metal-sorbed polymer samples with Pb(II), Zn(II), and Cd(II) ions were also recorded and their bands compared to the pure polymer.

Elemental analysis was conducted with a EuroEA 3000 Single Elemental Analyzer (EuroVector) using 2,5–bis(5–tert-butyl-2benzoxazolyl)thiophene (BBOT) as the standard.

The ¹H and ¹³C-NMR spectra of the polymer in CDCl₃ were recorded with a Bruker Avance DPX 300 Spectrometer at 300 MHz chemical shift (δ 's) for ¹H and of 75 MHz for¹³C in ppm.

The glass-transition temperature (T_g) of the polymer was studied with a Netzsch 204 F 1 differential scanning calorimeter on 10 mg sample under dry nitrogen atmosphere. The sample was first heated from room temperature to 150°C and maintained for 2 minutes before rapid quenching.

Thermal stability of the polymer was studied by thermogravimetric analysis with a NETZCH STA 409 PG/PC Thermal Analyzer at a heating rate of 10° C/min and N₂ gas purging at a rate of 50 mL/min.

The shape and surface morphology of the polymer was examined with a Shimadzu-SEM

SUPER SCAN SSX Series equipped with a FEI–SEM–Field Emission Gun.

The concentrations of metal ions in aqueous solutions were determined with Varian Spectra AA–250 plus atomic absorption spectrometer (AAS) by taking the average value of 3 readings with % RSD less than 3. Samples of the polymer in solution were shaken using Memmert type WB22 shaker thermostated water bath (Schwabach). The pH was measured using METROHM 605 pH–meter.

Materials

The chemicals used were commercially available analytical grade reagents and used as received: oxalyl chloride, 4-dimethylaminopyridine cis/trans-1,4-cyclohexanedimethanol (4–DMAP), (CHDM) from Acros (Geel, Belgium); cadmium(II) nitrate tetrahydrate and zinc(II) nitrate hexahydrate from BDH (Poole, England); pyridine from Riedelde Haën (Seelze, Germany); nitric acid (60% w/w), hydrochloric acid (32%) w/w). and ethylenediaminetetraacetate-disodium salt (EDTA) from Scharlau (Barcelona. Spain). sodium perchlorate from Sigma-Aldrich (St. Louis, Mo, USA), lead(II) nitrate from Panreac (Barcelona, Spain); anhydrous chloroform from VWR (Souchez, France) and tetrahydrofuran (THF) from (Sds, Carlo Erba Reactifs, Cedex, France) and used as received. Dried THF was used.

Polymer synthesis

cis/trans-1,4-Cyclohexanedimethanol

(14.42 g, 0.10 mol), pyridine (23.73 g, 0.30 mol) and 4-DMAP catalyst were dissolved in THF (100 mL) at 0-5°C. A solution of oxalyl chloride (12.69 g, 0.10 mol) in THF (110 mL) was added drop wise with stirring for 1 h and at room temperature for 24 h, and then THF was evaporated under reduced pressure. A white solid was obtained and dissolved in 1000 mL chloroform, washed with distilled water (2 x 800 mL), (5 % v/v) HCl solution (1 x 800 mL), and finally with fresh distilled water (3 x 800 mL). The chloroform layer was separated, dried over anhydrous sodium sulfate and added drop wise to methanol (800 mL). The precipitated polymer was filtered and dried over night at 60° C under vacuum (yield = 86 %). The polymer was obtained as a white powder which was sieved to a particle size between 40-60 mesh and used for metal uptake experiments.

Preparation of Metals Stock Solutions

Stock solutions (1000.0 mg/L) of the three metal ions were prepared by dissolving specified

masses of the metal salts of lead(II) nitrate, zinc(II) nitrate hexahydrate, and cadmium(II) nitrate tetrahydrate, in 0.1 M NaClO₄ adjusted to the desired pH. Different concentrations (20.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0 and 100.0 mg/L) were prepared using 0.10 M NaClO₄ and adjusted with 0.10 M HClO₄ to achieve the desired pH values of 4.00, 5.00 and 6.00

Water regain (α)

Water regain was performed as described in our earlier publication [31].

Sorption of Metal Ions on the Surface of the Polymer (Batch Experiments)

Metal uptake of the polymer with each metal ion was studied using the batch equilibrium technique. The polymer (100 mg \pm 0.10 mg) was swollen with 50.0 mL of buffer solution for 2 h in an Erlenmeyer flask (100 mL). A known concentration of metal ion solution was added to the flask, and mechanically shaken. After the specified period of time at 25°C, the swollen polymer was filtered out and concentration of metal ion remaining in the filtrate was determined with atomic absorption spectrometry (AAS).

Rate of metal ion uptake

To determine equilibrium time for metal uptake, 100 mg \pm 0.10 mg of the polymer, was stirred with 25.0 mL of acetate–acetic acid buffer (pH = 5) for 2 h. Then 25.0 mL of metal ion solution containing 300 ppm was added and the resulting mixture was mechanically shaken for the specified contact times (from 5 minutes to 24 h) at 25°C. The metal–bound polymer was filtered out and the amount of the metal ion remaining in the filtrate was determined with AAS.

• Amount of metal ion uptake by the polymer (q) was calculated by the following expression.

$$q = (C_o - C_{eq})V/m$$
(1)

C_o: initial metal ion concentration (ppm).

C_t: the residual concentration of the metal ion at any time t.

C_e: the residual concentration of the metal ion at equilibrium.

V: volume of solution (mL)

m: mass of polymer (g)

• The percentage of metal ion uptake by the polymer is equal to

Metal ion uptake (%) =
$$[(C_o - C_t) / C_o] \ge 100\%$$
 (2)

The distribution coefficient (K_d) was calculated using equation (3)

$$K_{d} = \frac{\text{metal ion on the polymer (mg)} \times \text{volume of the solution (L)}}{\text{metal ion in solution (mg)} \times \text{mass of the polymer (g)}}$$
(3)

pH effect on metal-ion uptake

Similar experiments were carried out in buffer solutions of pH (4, 5 and 6) for 24 h to determine the effect of pH.

Adsorption isotherms studies

The adsorption of Pb(II), Zn(II), and Cd(II) ions was done by taking a known mass of the polymer (100 mg \pm 0.1 mg), swollen with 25 mL of sodium acetate-acetic acid buffer of pH 5 for 2 h. Then 50.0 mL of solutions of concentrations ranging from (20-100) ppm for each metal were added and shaken for 24 h at different temperatures (25, 35, 45°C). Adsorption isotherms were studied using the same conditions but under different pH values of 4, 5 and 6. ΔG° , ΔH° , and ΔS° are thermodynamic functions that relate to the conditions of the experiment. The values of ΔH° and ΔS° were calculated from the slope and intercept of the plots of lnK_d versus. 1/T (K). The change in Gibbs free energy (ΔG°) was calculated using the following equation:

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{4}$$

Column experiment

A glass column of 500 mm length and 10 mm inner diameter was used in this work. The column was packed with 1.0000 g dried polymer in 50.0 mL acetate–buffer of pH 5 and allowed to swell for 24 h. The solution was then flowed at a rate of 1.0 mL/min. A 50.0 mL containing Pb(II) of 1.0000 g/L passed through the column at a flow rate of 1.0 mL/min. The eluate was collected in a 100.0 mL flask, and concentration of the metal ion was determined by AAS. The same experimental conditions were used for Zn(II), and Cd(II) ions uptake.

Desorption studies

The desorption of the Pb(II), Zn(II), and Cd(II) ions from column was done using three eluting agents (50.0 mL each); 1.0 M HNO_3 , 1.0 M HCl, and 0.01 M EDTA at a flow rate of 1.0 mL/min. The

eluate was collected in five 10.0 mL portions, and metal concentration was determined by AAS. The percentage of metal recovery was calculated by equation 5:

 $%Recovery = \frac{Amount eluted (mg)}{Total amount adsoerbed by the polymer (mg)} \times 100\%$ (5)

Results and Discussion

Polymer synthesis

Poly(cis/trans-1,4-cyclohexanedimethylene oxalate) was prepared in high yield by polycondensation of stoichiometric amounts of oxalyl chloride and cis/trans-1,4-cyclohexanedimethanol in THF below 5.0° C (Scheme-1). The reaction proceeded according to the route depicted in Scheme-1 by pyridine-catalyzed nucleophilic displacement of the chloride of oxalyl chloride with the alcoholic group of 1,4-cyclohexanedimethanol [32]. The formed polymer was found to be insoluble in many common organic solvents such as THF, DMSO, 1,4-doixane, diethylether and methanol but soluble in chloroform, dichloromethane, and (40:60) phenol: tetrachloroethane solvent mixture.



Scheme-1: Preparation of poly(cis/trans-1,4cyclohexanedimethylene oxalate).

*In this Scheme, only the trans-1,4-cyclohexanedimethanol isomer was used for plotting the scheme

Solution viscosity measurement

The inherent viscosity of the polymer was calculated from viscosity measurement of a dilute polymer solution (Concentration 0.5 g/dL) in (40:60) phenol: tetrachloroethane as a solvent mixture at 30° C. The polymer had an inherent viscosity of 0.26 dL/g, therefore, a polymer with a moderate inherent viscosity (i.e., a moderate molecular mass) was obtained [33].

Infrared spectroscopy

The polymer was analyzed by FTIR spectroscopy. The FTIR spectrum (NaCl disc)

showed an absorption band due to (C=O) stretching of the oxalate groupat 1743 cm⁻¹ and a weak shoulder at 1761 cm⁻¹. The spectrum exhibited another band at 1180 cm⁻¹ due to the (C–O–C) bond. The FTIR spectrum also showed two strong bands at 2859 and 2930 cm⁻¹ assigned to the C-H stretching in the cyclohexanedimethylene unit. The absorption bands owing to the alcoholic groups of CHDM diol was almost absent in the IR spectrum of the polyoxalate polymer. The band due to the carbonyl group of oxalyl chloride which was observed at 1777 cm⁻¹ was shifted to 1743 and 1761 cm⁻¹ in the IR spectrum of the polyoxalate polymer. These IR data, which are typical for the oxalate group, are in accordance to the data reported in the literature [13, 34-36] and are consistent with the structure assigned to the polyoxalate polymer and thus confirm its formation.

In addition to the above FTIR spectrum of the pure polymer, three metal ions-sorbed polymer samples were also recorded; the resulting spectra indicated that no characteristic absorption bands were observed in the FTIR spectra of the metal ion adsorbed polymer and that of pure metal ion freepolymer. This result could have been due to the low concentration of metal ions on the polymer surface and the strong absorptions of the polymer molecules. This result is conformed to the result of another similar investigation already reported in the literature [37].

¹H–NMR spectroscopy

The polymer was analyzed by NMR spectroscopy in order to elucidate its chemical structure and support its preparation. In the ¹H–NMR spectrum of polymer, the terminal methylene protons of cyclohexanedimethylene signal (denoted 1 in the structure below) attached to the oxygen of the oxalate group appeared at $\delta = 4.08$ ppm. The cyclohexylene ring tertiary CH protons denoted 2 showed at $\delta =$ 1.84 ppm, whereas the methylene ring protons denoted 3 in the range $\delta = 1.0-1.7$ ppm. The signal of the alcoholic group of CHDM diol observed at $\delta =$ 3.55 ppm was absent in the polymer spectrum, this indicates that the polycondensation reaction has occurred via this group. The shift in position of the signal from $\delta = 3.47$ ppm in the spectrum of CHDM to $\delta = 4.08$ ppm in the spectrum of the polymer indicate attachment of this terminal methylene group to the oxalate oxygen.

¹³C–NMR spectroscopy

In the present case, the carbon peak of each chemically equivalent carbon neatly appears at a specific chemical shift in the spectrum and is completely separated and distinguished from the peaks of other carbon atoms. This fact made the ¹³C-NMR analysis a clear-cut evidence for the structure of the alternating polymer. The signal of the terminal methylene carbon atoms of cyclohexanedimethylene unit (denoted 1) in the structure below, attached to the oxygen of the oxalate appeared at $\delta = 71.5$ ppm. The signal of the cyclohexylene ring tertiary carbon atoms (denoted 2) appeared at $\delta = 36.7$ ppm, and those of the methylene ring carbon atoms (denoted 3) were observed at $\delta = 28.5$. The carbonyl carbon atom signal of the oxalate group appeared at $\delta = 158$ ppm. The attachment of this carbon (denoted 1) to the oxygen of the oxalate group led to a down field shift that was reflected in the shift in position of the peak from $\delta = 68.6$ ppm in the spectrum of CHDM diol to $\delta = 71.5$ ppm in the spectrum of the polyoxalate polymer. Additionally, the peak of the cyclohexylene ring tertiary carbon atom CH was shifted upfield from δ = 40.6 ppm in CHDM diol to δ = 36.7 ppm in the polymer. These two effects are highly indicative for the formation of the polyoxalate polymer in the present work.

Furthermore, an extra feature in the ¹³C– NMR spectrum of the polyester also worth's mentioning. The carbonyl carbon peak of the oxalate group was observed as a single line in the ¹³C–NMR spectrum of the polymer. The occurrence of a single line peak for the carbonyl carbon atom indicates that this group is present in the polymer chain in the same chemical environment. This means that the CHDM is connected alternately to the oxalate group in the polymer backbone, i.e., the carbonyl carbon atoms of the oxalate unit is always surrounded from both sides with cyclohexanedimethylene unit. The ¹H and ¹³CNMR spectral data for the polymer were assigned to various protons and carbons are presented in Table-2.

Table-2: ¹H–NMR and ¹³C–NMR data for poly(cis/trans–1,4–cyclohexanedimethylene oxalate).



Elemental analysis

The polymer was also analyzed by elemental analysis to investigate the percentage composition of the elements and to confirm its structure. The results are summarized in Table-3 and demonstrate the calculated and the experimentally found percentages for each element in the polymer. Based on these data the calculated formula of the structural repeating unit is $(C_{10}H_{14}O_4)$ while the suggested formula is $(C_{10.36}H_{14.04}O_{4.00})$ i.e., $(C_{10}H_{14}O_4)$. This difference could be attributed to instrumental error, presence of impurities in the sample and presence of polymer chain end groups.

Table-3: Elemental analysis of poly(cis/trans-1,4- cyclohexanedimethylene oxalate).

% Element	% C	% H	% O
Calculated	60.6	7.1	32.3
Experimental	61.5	6.8	31.7

Thermal properties

Thermal properties of the polymer prepared were investigated with DSC and TGA. The polymer showed an unexpectedly high glass transition temperature (T_g) value of 130°C, this value is quite high for such an aliphatic polyoxalate compared to the aromatic polyoxalate poly(bisphenol A oxalate) which showed a Tg value of only 40°C [22]. This implies that poly(CHDM oxalate) has a considerable high degree of rigidity. Principally, this rigidity is due to the existence of stiffening groups, good close packing characteristics or the presence of structural symmetry in the chain. The net effect of these factors is normally reflected in the experimentally observed value of T_g . This fact may be explained by that the structural repeating unit of the polymer molecule contains the planar chair conformation of cyclohexane ring coplanar with the oxalate group and even the upper or lower tetrahedral angle forms of the methylene unit of CHDM which fit to the corresponding planes of next molecule, so they can stack very well and close enough in the crystal lattice (Fig. 1). It may be plausible to consider that the cyclohexylene ring moiety being a ring promotes fixing the upper and lower tetrahedral angle forms of the methylene moieties in space thus rendering them better fittings on each other. These facts would collectively permit very good packing of polymer chains [38].







Structure ¹³C

The thermal stability of the polymer was also evaluated by TGA under a dry nitrogen atmosphere. The TGA thermogram of the polymer (Fig. 2) displayed a slow mass loss starting from 280°C to 320°C and a fast loss between 320°C and 450°C. The fast mass loss may be attributed to decomposition of the polymer backbone. The T_d^{1%} (191.5°C), $T_d^{5\%}$ (255.5°C), $T_d^{10\%}$ (285°C), and $T_d^{50\%}$ (347.5°C) decomposition temperatures, which correspond to the temperatures at which 1, 5, 10, and 50% loss of mass of polymer occurred. The residual mass percentage remaining after heating the polymer to 500°C was quite low (2.92%), the polymer may, therefore, be practically considered thermally completely depolymerizable.



Fig. 1: The structure of poly(cis/trans-1,4cyclohexanedimethylene oxalate) showing stacking of the various planar molecular sections and tetrahedral methylene bonds.

SEM characterizations

SEM micrographs for the synthesized polymer are shown in Fig. 3. The figure shows that a rod like structure with a range of diameters of 15–30 μ m randomly distributed and a rough surface has formed. Small pores with an average size of less than 3 μ m are also located on the rods surface. These pores provide convenient diffusion channels for the adsorbed metal ions into the interior of the polymer. The interior structure of the polymer showed that large gaps and air pockets randomly distributed have been created in the structure of the solid polymer. The spongy structure of the inner rods maximizes the contact surface between the polymer and the solution which would lead to increased metal ion uptake.

TG /%

100



Fig. 2: The TGA thermogram of poly(cis/trans-1,4-cyclohexanedimethylene oxalate). TG% is the mass percentage of the sample remaining after heating to 500°C.

Water and hydrophilic character (α)

The polymer was also analyzed for its water affinity to reveal its hydrophilic character. Water regain experiments were performed to determine the water regain ratio (α) for the polymer. Water regain is usually correlated with the hydrophilic character of the polymer, the higher the water regain the more hydrophilic the polymer is. The water regain value was found to be 0.064 g/g after 2 h, and 0.087 g/g after 24 h of stirring. Based on these values the polymer may be considered slightly hydrophilic. These values are generally comparable to those obtained for poly(2,2–dimethyl–1,3–propylene oxalate)[31] and for poly(bisphenol A oxalate) [22].

Metal ions uptake by polymer

Linear AAS calibration curves were obtained for Pb(II), Zn(II), and Cd(II) ions using a blank sample and a set of standard samples for each metal ion. Two calibration curves were used for each metal ion, one for low equilibrium concentrations and another for high equilibrium concentrations. The sorption of Pb(II), Zn(II), and Cd(II) ions on polymer surface was determined by batch equilibrium technique as a function of contact time at a pH value of 5.0 and as a function of pH at contact time of 24 h. AAS was used to measure the concentration. The adsorption kinetics of metal ions was determined for exposure times from 5 min to 48 h for Pb(II), Zn(II), and Cd(II) at pH= 4.0, 25.0° C, and initial

concentration of 100.0 mg/L for each metal ion. The dependence of metal ion uptake on contact time for the polymer is presented in Fig. 4.

Rate of metal ion uptake by the polymer

The results of adsorption kinetics for Pb(II), Zn(II), and Cd(II) ions by the polymer are shown in Fig. 4. The uptake of all metal ions increase with time until complete saturation is obtained after about 20 h of contact time, high sorption rate is also observed during the first hour with percent uptake of Pb(II) ions reaching 23%. This observed high adsorption rate could be attributed to:

- i. The slight hydrophilicity of carbonyl groups facilitates their interaction with water molecules, due to good water compatibility and high accessibility of the metals to the sorbing groups [8].
- ii. The low degree of polymerization increases the number of functional groups that could exist as end groups of polymer chains [39]. Regarding our polymer the hydroxyl groups may also exist as end groups. These end groups may have a positive effect on the metal sorption process.

The experiments given in Fig. 4 were fitted to pseudo–second–order model kinetics, while correlations for pseudo-first-order model were much lower. In most figures, the correlation coefficients were higher than 0.98. Moreover, the calculated q_e values agreed very well with the experimental data in Table-4. This model is considered more appropriate to represent the kinetic data. This tendency indicates that the rate determining step of these heavy metals is chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate [40].

It was observed that during the first 3 h, 50-55% of the metal ions are taken up by the polymer. The distribution coefficients (K_d), is defined as [41]

$$K_{d} = M_{resin} / M_{solution}$$
(6)

where, M_{resin} and $M_{solution}$ are the concentration of the metal in the resin and the solution. Based on the K_d values (Table-5), the trend found in this study was the following;

$$Pb(II) > Zn(II) > Cd(II)$$
 at $pH = 4.0$ and $25^{\circ}C$



a. Magnification = 4000 time



b. Magnification = 12000 time



c. Magnification = 24000 time



d. Magnification = 50000 time

Fig. 3: SEM images of poly(cis/trans-1,4-cyclohexanedimethylene oxalate).

Metal(II) q_e(mg/g)	Pb(II)	Zn(II)	Cd(II)	
Calculated	33.33	16.95	31.25	
Experimental	31.16	15.89	29.82	

Table-5: Distribution coefficient for Pb(II) ion at 100.0 mg/L for different temperatures and pH values and thermodynamic functions for Pb(II) at 298.15 K.

Н	1/T(1/K)	ln K _d	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS ^o (J/mol.K)
	3.36×10 ⁻³	-0.3206			
1.00	3.25×10 ⁻³	-0.1124	0.752	12.01	41.79
4.00	3.14×10 ⁻³	0.0141	0.755	13.21	41./8
	3.36×10 ⁻³	-0.2523			
5.00	3.25×10 ⁻³	-0.1275	0.614	12.24	20.22
5.00	3.14×10 ⁻³	0.0619	0.044	12.34	39.23
	3.36×10 ⁻³	-0.0227			
6.00	3.25×10 ⁻³	0.0877	0.086	10.91	25.07
	3.14×10 ⁻³	0.2523	0.086	10.81	35.97

Adsorption isotherms of the polymer

The adsorption isotherms of Pb(II), Zn(II) and Cd(II) ions were determined at different pH values (4.00, 5.00 and 6.00) and temperatures (25.0° C, 35.0° C and 45.0° C) in the concentration



Pb(II) uptake









Pseudo-second order sorption kinetics of Pb(II)



Pseudo-second order sorption kinetics of Zn(II)



Fig. 4: Metal ion uptake and pseudo-second order sorption kinetics as a function of contact time, at pH= 4.00, 25.0°C and initial concentration of 100.0 mg/L.

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T(°C)	R ²	qm(mg/g)	K _L (L/mg)	R ²	qm(mg/g)	K _L (L/mg)	R ²	qm(mg/g)	K _L (L/mg)
Pb(II)		pH= 4.0			pH= 5.0			pH= 6.0	
25	0.992	46.341	0.038	0.976	48.224	0.038	0.982	52.040	0.043
35	0.978	47.286	0.051	0.964	30.017	0.237	0.955	44.051	0.078
45	0.975	47.010	0.051	0.983	37.306	0.237	0.990	61.514	0.078
Zn(II)		pH= 4.0			pH= 5.0			pH= 6.0	
25	0.983	19.665	0.025	0.988	34.020	0.011	0.991	32.849	0.011
35	0.987	24.379	0.017	0.987	20.688	0.028	0.977	22.262	0.035
45	0.983	20.902	0.017	0.979	34.965	0.028	0.984	25.055	0.035
Cd(II)		pH= 4.0			pH= 5.0			pH= 6.0	
25	0.988	43.129	0.030	0.995	51.678	0.025	0.992	49.704	0.033
35	0.984	36.988	0.038	0.986	33.257	0.065	0.998	62.203	0.030
45	0.990	44.050	0.038	0.987	32.155	0.065	0.988	45.106	0.030

Table-6a: The R², q_m and K_L, values obtained from the Langmuir plots of Pb(II), Zn(II) and Cd(II).

Table-6b: The R²,K_F and n values obtained from the Freundlich plots of Pb(II), Zn(II) and Cd(II).

T(°C)	\mathbb{R}^2	K _F	n	\mathbb{R}^2	K _F	n	\mathbb{R}^2	$\mathbf{K}_{\mathbf{F}}$	n
Pb(II)		pH= 4.0		pH= 5.0				pH= 6.0	
25	0.999	3.746	1.804	0.994	3.570	1.718	0.994	4.129	1.716
35	0.987	4.570	1.836	0.995	7.175	2.403	0.986	6.018	2.025
45	0.979	5.697	1.979	0.982	6.304	2.009	0.984	4.995	1.678
Zn(II)		pH= 4.0			pH= 5.0			pH= 6.0	
25	0.989	0.959	1.614	0.970	0.734	1.420	0.979	0.623	1.335
35	0.946	0.892	1.560	0.972	1.240	1.726	0.981	1.528	1.727
45	0.908	1.526	1.894	0.927	1.174	1.534	0.994	0.946	1.482
Cd(II)		pH= 4.0			pH= 5.0			pH= 6.0	
25	0.940	2.540	1.659	0.984	2.063	1.444	0.966	2.709	1.539
35	0.998	2.076	1.512	0.952	3.613	1.901	0.978	2.900	1.455
45	0.998	1.562	1.382	0.992	2.824	1.744	0.983	2.613	1.516

Langmuir model was used to estimate maximum adsorption capacity corresponding to the monolayer saturation of the polymer surface:

$$1/q_e = 1/(q_m K_L)$$
. $1/C_e + (1/q_m)$ (linear form II) (7)

Therefore, a plot of $1/q_e$ versus $1/C_e$ gives a line of slope $(1/q_m K_L)$ and an intercept $1/(q_m)$, where K_L is related to the adsorption/desorption energy, and q_m is the maximum saturation adsorption capacity of the polymer surface.

While, the Freundlich model empirical equation (8) is used to estimate the adsorption intensity of the metal towards the polymer:

$$Log q_e = Log K_F + 1/n Log C_e$$
(8)

Plotting of log q_e versus log c_e gives a slope of 1/n and an intercept of logK_F. Freundlich constants n and K_F, are indicative of adsorption intensity and capacity, respectively. A favorable adsorption tends to have Freundlich constant n between 1 and 10. A larger value of n (smaller value of 1/n) implies stronger interaction between the polymer and the heavy metal. A greater value of K_F indicates a higher capacity for adsorption than smaller values [40, 42]. The q_m and K_L values with correlation coefficients (R²) obtained from Langmuir plots are given in Table-6a, and those of K_F, and n parameters with correlation coefficients (R²) obtained from the Freundlich plots are given in Table-6b. The correlation regression coefficient (R^2) has been determined for each isotherm. In general, data were fitted to both Langmuir and Freundlich adsorption isotherms at all temperatures. The values of correlation regression coefficient (\mathbb{R}^2) showed mostly better applicability of Langmuir equation than Freundlich equation. This implies that the homogenous sites of interaction are better to describe the process more than heterogeneous sites of interaction due to the presence of oxalate groups in the polymer.

Effect of temperature on metal uptake

The effect of temperature on the % uptake of metal ions was investigated. The results are obtained by plotting % uptake of Pb(II) ions at different pH versus temperature (Fig. 6) and showed that the adsorption process for Zn(II) and Cd(II) on the surface of the polymer is enthalpy independent and is entropy driven. The change in entropy is caused by the removal of water molecules from the primary and secondary hydration spheres of water-metal complexes [43]. Since Pb(II) ions % uptake increases with temperature nearly at all pH values, the adsorption process is endothermic.

Thermodynamics of adsorption on polymer

To understand the adsorption mechanism of Pb(II) ion, the thermodynamic functions ΔG , ΔH and ΔS of adsorption were calculated using the equations:

$$K_{d} = \frac{q_{e}}{C_{e}}$$
(9)

$$\operatorname{Ln} K_{d} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$
(10)

Where K_d is the distribution constant, R is the gas constant (8.314 J/mol.K) and T is the temperature in Kelvin. The plots of lnK_d versus 1/T (Fig. 7) for each metal ion give a straight line, where the enthalpy ($\Delta H^{\circ}/R$) and entropy ($\Delta S^{\circ}/R$) values are obtained from the slope and intercept. ΔG° was calculated using the following equation:

$$\Delta G^{o} = \Delta H^{o} - T \Delta S^{o} \tag{11}$$

Table-5 presents the distribution coefficients data for Pb(II) ion and the thermodynamic functions of the adsorption process of Pb(II) ion at different temperature and pH values [44].

The higher negative ΔG° values at higher temperature indicate that the adsorption process gets more favorable [42] while the positive ΔH° values

suggest the endothermic nature of metal adsorptions. One possible explanation of this is the well-known fact that heavy metal ions used are well solvated in water. In order for these ions to adsorb, there is some extent denuded of their hydration sheath. This dehydration process of ions requires energy. The removal of water from ions is essentially an endothermic process [45] and the energy of dehydration is greater than the exothermic binding effect of the ions to the surface. The positive ΔS^{o} values indicate an increase in randomness at the solid/solution interface during adsorption process and reflects the affinity of adsorbent for the metals used. The water molecules, which are displaced by the adsorbate species, gain more translational energy than is lost by the adsorbate ions, thus allowing the prevalence of randomness in the system [45]. The adsorption capacity of adsorbent increase at higher temperatures is due to the strong affinity of the adsorbent to the adsorbate.



Fig. 5: Plots of (a) adsorption isotherm of Pb(II), (b) linearized Langmuir(II), (c) linearized Freundlich, (d) linearized Langmuir(III) at pH= 4.00 and 25.0°C.



Fig. 6: Temperature dependence of % uptake of Pb(II) ions at different pH values.



Fig. 7: Plots of ln K_d Vs 1/T for Pb(II), (a) pH= 4.00 (b) pH=5.00 and (c) pH=6.00.

Comparing % uptake, q_m , K_L and K_F values of Pb(II), Zn(II) and Cd(II) ions

Depending on % uptake and comparing the values of q_m , K_L and K_F , the trends observed for adsorption of metal ions on polymer surface were collectively presented in Table-7. The adsorption capacities (q_m) showed that the polymer has high capacity towards Pb(II) and Cd(II) ions and a lower one towards Zn(II) ion. The relative selectivity of the heavy metals and sorption capacity is related to some relevant metal properties. The predicted affinity sequence of the metal ions is based on their ionic radii are Pb(II) 1.20 > Cd(II) 0.97 > Zn(II) 0.74°A.

It is clear that the trend follows the ionic radii. SEM pictures showed the presence of channels and cavities formed by the polymer. These cavities and holes may act as molecular sieves where large molecules or ions inter these channels and become locked there, while small ions like Zn(II) are freely escaped. Small ions have large hydrated radius, which can't fit in the holes, while large ions have smaller hydrated radius that can fit easily.

Comparing the values of q_m of the synthesized polymer to literature values (Table-1) indicate that the q_m values obtained in this work at pH= 4.00 and 25.0°C for the adsorption of metal ions are reasonable as follows:

Metal ion : Pb(II) > Cd(II) > Zn(II)

 $q_{\rm m} \, ({\rm mg/g}) = 31.2 > 29.8 > 15.9$

Table-7: Trends of % uptake of metal ions, q_m , K_L , and K_F to polymer surface at various temperatures and pH values

pH	Parameter		Temperature						
		25°C	35°C	45°C					
	% uptake	Pb(II) > Cd(II) > Zn(II)	Pb(II)>Cd(II)>Zn(II)	Pb(II) > Cd(II) > Zn(II)					
	$\mathbf{q}_{\mathbf{m}}$	Pb(II) > Cd(II) > Zn(II)	Pb(II) > Cd(II) > Zn(II)	Pb(II) > Cd(II) > Zn(II)					
4.0	$\mathbf{K}_{\mathbf{L}}$	Pb(II) > Cd(II) > Zn(II)	Pb(II) > Cd(II) > Zn(II)	Pb(II) > Cd(II) > Zn(II)					
	$\mathbf{K}_{\mathbf{F}}$	Pb(II) > Cd(II) > Zn(II)	Pb(II) > Cd(II) > Zn(II)	Pb(II) > Cd(II) > Zn(II)					
	% uptake	Pb(II) > Cd(II) > Zn(II)	Pb(II) > Cd(II) > Zn(II)	Pb(II) > Cd(II) > Zn(II)					
	qm	Cd(II) > Pb(II) > Zn(II)	Cd(II) > Pb(II) > Zn(II)	Pb(II) > Zn(II) > Cd(II)					
5.0	$\mathbf{K}_{\mathbf{L}}$	Pb(II) > Cd(II) > Zn(II)	Pb(II) > Cd(II) > Zn(II)	Pb(II) > Cd(II) > Zn(II)					
	K _F	Pb(II) > Cd(II) > Zn(II)	Pb(II) > Cd(II) > Zn(II)	Pb(II) > Cd(II) > Zn(II)					
	% uptake	Pb(II) > Cd(II) > Zn(II)	Pb(II) > Cd(II) > Zn(II)	Pb(II) > Cd(II) > Zn(II)					
	qm	Pb(II) > Cd(II) > Zn(II)	Cd(II) > Pb(II) > Zn(II)	Pb(II) > Cd(II) > Zn(II)					
6.0	$\bar{\mathbf{K}}_{\mathbf{L}}$	Pb(II) > Cd(II) > Zn(II)	Pb(II) > Zn(II) > Cd(II)	Pb(II) > Zn(II) > Cd(II)					
	K _F	Pb(II) > Cd(II) > Zn(II)	Pb(II) > Cd(II) > Zn(II)	Pb(II) > Cd(II) > Zn(II)					

Furthermore, a comparison was also made with our previous results. When the present polymer; poly(1,4-cyclohexanedimethylene oxalate), q_m : [Pb(II) 46.3 > Cd(II) 31.1 > Zn(II) 19.66] was compared to those of our previously prepared polymers from the same family in terms of q_m in mg/gm, poly(hydroquinone oxalate) [46] was found to have the values: [Pb(II) 150 > Cd(II) 133.3 > Hg(II) 57.8], poly(1,3-cyclohexylene oxalate) [47] the values: Pb(II) 150 > Zn(II) 66.7 > Cd(II)17.27 and poly(1,4-benzenedimethylene phthalate) [48] the values: [Pb(II) 21.74 > Zn(II) 15.87 > Cd(II)8.0]. Therefore, it can be noticed that poly(1,4cyclohexanedimethylene oxalate) of the present study has moderate q_m values that are greater than poly(1,4benzenedimethylene phthalate) but are smaller than poly(hydroquinone oxalate) and poly(1,3cyclohexylene oxalate). This comparison also indicated that Cd has a higher q_m value than Zn.

Column Experiments

Metal Ion Uptake

Using column experiment, Pb(II), Zn(II) and Cd(II) ions uptake was determined at pH 4.0, 25.0°C, and initial concentration of 1000 mg/L at a flow rate of 1 mL/min. The %uptake was calculated as shown in Table-8 and the uptake capacity of Pb(II) > Cd(II) > Zn(II). This is parallel to the order of the same metal ions in batch experiment, but is lower because complete saturation needs a much longer time. On the other hand, there is no mechanical shaking associated with column experiments, which result in a decrease in the percent of metal ion uptake.

Table-8: Metal ion uptake using column experiment.

Metal Ion	Initial Concn	Final Concn	Loaded Concn	%
(II)	(mg/L)	(mg/L)	(mg/L)	Uptake
Pb	1000	470	530	52.97
Zn	1000	721	279	27.90
Cd	1000	588	412	41.20

Desorption studies

Three eluting agents, 1.0 M HNO₃, 1.0 M HCl and 0.01 M EDTA were used for desorbing metal ions from the polymer, at the same flow rate (1mL/min). The eluent was collected in five-10.0 mL portions; the percent recoveries are presented in

Table-9: Desorption of metal ions from the polymer.

Table-9. The eluting agents seem to react in two different ways: HNO_3 and HCl act as protonexchange agents whereas EDTA acts as a strong competing chelating ligand. Depending on these values, the percent accumulative recoveries (Table-9) were deduced for each eluting agent from the polymer as follows:

$1.0 \text{ M HNO}_{3} > 1.0 \text{ M HCl} > 0.01 \text{ M EDTA}$

The experiments confirmed that maximum metal desorption can be achieved with mineral acids in concentrations of 1.0 M solutions. This could be attributed to cation exchange between the proton and metal sorbed. However, this method is more complex than simple protonation [5, 49, 50].

Conclusions

In the present work, poly(cis/trans-1,4cyclohexanedimethelene oxalate) was prepared, characterized and its metal ion uptake properties were investigated. The sorption properties of the polymer toward Pb(II), Zn(II), and Cd(II) ions were studied under several experimental conditions using batch and column experiments. The effective desorption for the metal ions was studied, and the accumulative recovery of sorption ability was also investigated. The polymer has high percentages of uptake toward Pb(II), Cd(II) and low percentage of uptake toward Zn(II) ions. The order of metal ions uptake follows this order: Pb(II) > Cd(II) > Zn(II) at 25°C in both techniques. The obtained adsorption data showed fitting to Langmuir, and Freundlich adsorption isotherms models with almost similar correlation coefficients. The adsorption of Cd(II) and Zn(II) ions is enthalpy independent, and the process is entropy driven, while it is an endothermic process in case of Pb(II) ion. Desorption of metal ions from the loaded polymer was done with 1.0 M $HNO_3 > 1.0$ M HCl >0.01 M EDTA. Rapid metal uptake, high sorption capacity for Pb(II) and Cd(II) ions and desorption ability make our polymer feasible for removal, recovery, and preconcentration of metal ions and in order to decrease the time of the experiments consumed in the analytical laboratories and for industrial, and environmental applications.

Table-7. Desorp	uon or met	ai ions noi	in the poly	inci.					
Eluting agent		1M HCl			1M HNO ₃			0.01M EDTA	
%Recovery	Pb(II)	Zn(II)	Cd(II)	Pb(II)	Zn(II)	Cd(II)	Pb(II)	Zn(II)	Cd(II)
First portion	69.16%	63.20%	69.05%	84.95%	85.33%	81.05%	54.79%	53.29%	51.67%
second portion	2.69%	2.28%	3.25%	4.06%	2.94%	3.08%	5.99%	5.58%	6.05%
third portion	0.16%	0.28%	0.12%	0.21%	0.16%	0.24%	0.72%	1.63%	0.24%
fourth portion	0.00%	0.00%	0.00%	0.00%	0.00%	0.03%	0.21%	0.23%	0.07%
fifth portion	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.02%
Cumulative	72.02%	65.77%	72.41%	89.22%	88.43%	84.39%	61.71%	60.73%	58.05%

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