

## Synthesis and characterization of poly(pentamethylene-2,6-pyridinedicarboxylate) and the study of its ability to absorb Pb(II), Cd(II) and Zn(II) ions

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### ABSTRACT

Poly(pentamethylenepyridine-2,6-dicarboxylate) is prepared by the stepwise reaction of equal amounts of 2,6-pyridinedicarbonyl dichloride and 1,5-pentanediol using 1,2-dichlorobenzene as an inactive solvent. The resulting homopolymer is characterized using Fourier-transform infrared spectroscopy,  $^1\text{H}$  and  $^{13}\text{C}$ -NMR, inherent viscosity, elemental analysis, thermal analysis, and scanning electron microscopy. Atomic absorption spectroscopy is used to determine metal ion concentrations. Metal uptake of the polymer towards three toxic divalent ions: Pb(II), Zn(II), and Cd(II) in aqueous solutions is tested by batch and column methods. The influence of different variables such as pH, temperature, concentration, and contact time on the sorption process is also taken into consideration. Pseudo-second-order kinetic models fit the metal adsorption process better than pseudo-first-order models. Langmuir, Freundlich, and Dubinin–Radushkevich adsorption isotherms are applied, establishing that the Langmuir isotherm is the best to represent it. The sequence for increasing adsorption capacity is: Pb(II) > Cd(II) > Zn(II). The sorption process of these ions on the polymer is favorable at high temperatures; the enthalpy values show an endothermic process. Furthermore, positive entropy values mean that randomness increases during the adsorption process. Column experiments are used by treating the loaded polymer with 0.1 M  $\text{HNO}_3$  and 0.1 M ethylenediaminetetraacetic acid, leading to a good percent recovery for  $\text{HNO}_3$ .

**Keywords:** Poly(pentamethylenepyridine-2,6-dicarboxylate); Characterization; Kinetics models; Adsorption models; Desorption

## 1. Introduction

### 1.1. Water pollution

Pollution of water with heavy metals is still one of the most momentous environmental problems around the world. Cadmium, lead, and zinc are among the most studied metals that are responsible for this contamination due to their potential risks to humans and other living systems [1]. Many different techniques have been developed to get rid of these toxic ions from polluted water, one of which depends on the use of chelating substances. Metal sorbing polymers that have heteroatoms such as nitrogen, sulfur,

or oxygen are considered important groups of immense diversity polymers that take place in environmental applications [2]. These polymers are frequently formed by the insertion (conjugation) of an active binding group into a polymeric matrix; such binding groups may be a part of structurally repeated units of the polymer main chain or a pendent group [3].

### 1.2. Classification of polymers

Polymers can be classified in a number of ways; the most general one is based on their occurrence in nature, which

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is divided into three subgroups: naturally occurring polymers, semisynthetic polymers, and synthetic polymers [4]. Synthetic polymers are usually prepared by two different routes: addition and condensation. In addition polymerization, polymers with a high molecular weight are made at the beginning in the presence of a high concentration of monomers, and only starting materials and polymers exist in the mixture. While in condensation polymerization, all kinds of species can be found in the reaction pot, and any two of these moieties, from monomers to oligomers, can react to give a bigger molecule, this means that the molecular weight of the polymer increases gradually [5].

### 1.3. Polyesters

The earliest known class of synthetic condensation polymers was polyesters [6,7]. Polyesters can be modified through blending and copolymerization with other functional groups, and this will display limitless ways to tailor the features and architecture of the resulted macromolecules to cover a wide range of applications in industry, economy, agriculture, and the environment [8]. Polyesters have been prepared either by the reaction of diols with dicarboxylic acids or diacid chlorides (direct esterification) or between diols and diesters (transesterification) [9]. In order to design polyester for metal removal purposes, many factors influencing the adsorption of metals on polymers must be investigated, like its chemical structure, physical properties, nature and amount of donor groups, and molecular weight. Furthermore, there will be differentiation in polymer uptake behaviors, their selectivity, stability, adsorption capacity, kinetic behavior, and surface area per gram of polymer [10]. The most effective factor is the polymer's chemical structure. The multi-ester linkages in their backbone are suitable for this task because of their capability to give variation in coordination behavior [11]. Many flexible and rigid carboxylic acids have found widespread use in this field. Pyridine dicarboxylic acids look like a possible rigid ligand that can easily bind to metal ions [12]. Among this group of molecules is pyridine-2,6-dicarboxylic acid (dipicolinic acid, DPA) (Fig. 1).

DPA shows planarity and zigzag chains that result from the 120° angle between the two carbonyl carbons [13]. DPA is also one of the favorable ligands for designing compounds that are pharmacologically active [14,15]. Also, DPA is an attractive complexing agent; it is a multidentate with the probability of oxygen atoms bridging two metal ions, and its chelating efficiency is not only limited to its anionic pattern, whether it exists as a mono- or di-anion, but also extended to its neutral form [16,17]. The synthesis of

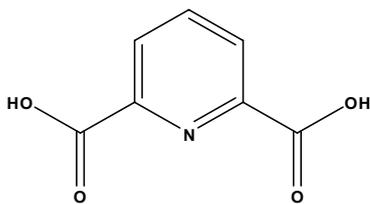


Fig. 1. Pyridine-2,6-dicarboxylic acid (dipicolinic acid).

polymers that contain pyridine rings connected together by ester linkage gave structures that seem to be good candidates for the adsorption of heavy metal ions for wastewater treatment [18].

Polycondensation of 2,6-pyridinedicarbonyl chloride with ethanalamine derivatives has been applied to prepare poly(amide-ester)s, which are considered good metal scavengers. Their sorption toward heavy metals such as Zn(II), Cd(II), Fe(II), Cu(II), Cr(III), Au(III), Os(III), Ir(IV), and Ru(III) was investigated [19]. Roupakias et al. [20] synthesized poly(1,3-propylene pyridine-2,6-dicarboxylate), one of seven polyesters that have been prepared by melt polymerization based on 1,3-propanediol. The metal uptake properties of the polymer were not, however, performed in this work.

Five polyesters based on pyridine-2,6-dicarboxylic acid have been prepared, modified with two thiol derivatives. It was found that these polymers have good resistance against bacterial growth and adhesion [21]. However, a number of polyesters based on oxalyl chloride have been synthesized in our laboratory at The University of Jordan, and adsorption isotherms and kinetics studies were performed at different experimental conditions for various toxic metals. The trend of increasing  $q_m$  for these studies is shown in Table 1.

Coordination polymers have gained great attention over the last two decades because of the potential the versatile modification and functionalization of their physical properties. The pyridine isomer effects on metallo-supramolecular materials, where metal salts are blended with the polymers bearing pyridine coordinative ligands, have been frequently argued based only on steric effects. In the experimental approach,  $ZnCl_2$  was blended with amorphous polyesters uniformly bearing either 4-vinylpyridine or 2-vinylpyridine-type ligands at the side groups. In addition, polyester bearing both ligand types was also used to prepare blends with  $ZnCl_2$ , which enabled a deeper understanding of the pyridine isomer effects on the pyridine-metal coordination [28]. Nevertheless, chelating hyperbranched polyester nanoparticles have become an attractive new material family for developing high-capacity nanoscale chelating agents with highly branched structures and many functional groups in the main chains and end groups that can be used to remove heavy metals from water. Alregeb et al. [29] prepared hyperbranched polyester with a particle size of 180–643 nm and synthesized it using dimethylmalonyl chloride as the difunctional monomer and 1,1,1-tris(4-hydroxyphenyl)ethane as the trifunctional monomer. Batch equilibrium was used to investigate the removal properties of the polyester towards Cd(II) ions. The Cd(II) ion thermodynamics, kinetics, and desorption data were also studied. A hybrid adsorbent based on NaX zeolite, modified with hyperbranched polyester with terminal benzoyl thiocarbamate groups, was synthesized. The sorption activity of a hybrid adsorbent in relation to transition metal ions is investigated on the example of Cu(II) and Co(II) ions. The resulting isotherms were processed in four sorption models: Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin. It is determined that the isotherms of adsorption of the hybrid adsorbent to the ions Cu(II) and Co(II) are most adequately described by the Freundlich model, which confirms the course of

Table 1  
General trend in maximum sorption capacities for seven polyesters

Polymer name	Trend	Optimum pH	$q_{max}$	References
Poly(2,2-dimethyl-1,3-propylene oxalate)	Pb(II) > Hg(II) > Cd(II)	5.0	(* > 44.8 > 38.6) mg·g <sup>-1</sup>	[10]
Poly(bisphenol A oxalate)	Mg(II) > Ni(II) > Pb(II) > Cu(II) > Zn(II) > Cd(II)	5.0	(6.10 > 2.46 > 1.00 > 0.68 > 0.47 > 0.17) mmol·g <sup>-1</sup>	[22]
Poly(1,4-phenylene oxalate)	Pb(II) > Cd(II) > Hg(II)	5.0–5.5	(* > 133.3 > 57.8) mg·g <sup>-1</sup>	[23]
Poly(1,4-cyclohexanedimethylene oxalate)	Pb(II) > Cd(II) > Zn(II)	6.0	(31.2 > 29.8 > 15.9) mg·g <sup>-1</sup>	[24]
Poly(bisphenol A-phthalate) and poly(bisphenol A-succinate)	Pb(II) > Cu(II) > Cd(II)		(72.46 > 52.64 > 28.25) mg·g <sup>-1</sup> poly(bisphenol-phthalate)	
			(62.89 > 32.68 > 14.56) mg·g <sup>-1</sup> poly(bisphenol-succinate)	[25]
Poly(cis,trans-1,4-cyclohexanedimethanol-succinate)	Cd(II) > Cu(II) > Pb(II)	6.0	(61.35 > 49.75 > 43.25) mg·g <sup>-1</sup>	
Poly(1,4-benzenedimethylene phthalate)	Pb(II) > Zn(II) > Cd(II)	6.0	(30.3 > 20.0 > 12.5) mg·g <sup>-1</sup>	[26]
Poly(1,3-cyclohexylene oxalate)	Pb(II) > Zn(II) > Cd(II)	4.0	(14.1 > 9.1 > 3.0) mg·g <sup>-1</sup>	[27]

\*High affinity of Pb(II) ion toward the polymer was observed, so no significant amount of Pb(II) remained in the solution after adsorption

chemisorption on a heterogeneous surface. The maximum sorption capacity and Gibbs energy of the adsorbent for Cu(II) ions are 34.83 g·kg<sup>-1</sup> and -9.66 kJ·mol<sup>-1</sup>, and for Co(II) ions, 18.39 g·kg<sup>-1</sup> and -9.58 kJ·mol<sup>-1</sup> [30]. The objective of this work is to synthesize the new polymer poly(pentamethylene-2,6-pyridine dicarboxylate) (poly(pen-py)) by solution polymerization technique and test its metal uptake behavior and reusability towards some toxic metals, Pb(II), Cd(II), and Zn(II) for possible use as a chelating polymer.

## 2. Methods and materials

### 2.1. Materials

Received chemicals were analytical grade without extra purification as follow: pyridine-2,6-dicarboxylic acid, anhydrous sodium sulphate and sodium perchlorate from Acros Organics (New Jersey, USA), 1,5-pentanediol from Fluka (Buchs, Switzerland), nitric acid, chloroform, extra pure methanol, lead(II) nitrate, glacial acetic acid and ethylenediaminetetraacetic acid disodium salt (EDTA) from Scharlau (Barcelona, Spain), thionyl chloride, *n*-hexane and 1,2-dichlorobenzene from TEDIA (Fairfield, USA), sodium acetate trihydrate and zinc(II)nitrate hexahydrate from LobaChemie (Mumbai, India), cadmium(II) nitrate tetrahydrate from Riedel-de Haën (Seezle, Germany) and sodium hydroxide from JHD (Shantou, China).

### 2.2. Instrumentations

Weighing the samples, pH adjustments of buffer solutions, and mechanical shaking were done by the AW120 analytical balance, Cyberscan 510 pH-meter, and WB22 shaker, respectively. The inherent viscosity of the polymer was measured by a Rheotek Ubbelohde glass capillary viscometer, and the functional groups of the polymer were determined by a Thermo Nicolet 670 Nexus Fourier-Transform Infrared Spectrometer (FTIR) ranging from 400–4,000 cm<sup>-1</sup> with a KBr disk. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were reported using a Bruker 300 MHz Avance DPX 300 spectrometer after dissolving the polymer in deuterated chloroform (CDCl<sub>3</sub>) and using tetramethylsilane (TMS) as a reference. Thermal properties, including thermal stability and thermal transition, were obtained under a dry nitrogen atmosphere using the Netzsch STA 409 PG/PC thermogravimetric analyzer (TGA) and the Netzsch DSC 204 F1 differential scanning calorimeter (DSC), respectively. Different ratios (percentages) of elements from which the polymer was built were determined with the Euro-Vector 3000 elemental analyzer. For metal-polymer adsorption studies, the Varian AA-250 pulse atomic absorption spectrometer was applied. Flame was oxidized with air as an oxidant and acetylene gas as fuel, with different maximum wavelengths: Pb(II) = 261.4 nm, Cd(II) = 326.1 nm, and Zn(II) = 307.6 nm. The crystallinity degree of the polymer was investigated using a Shimadzu 7000-XRD diffractometer. The surface morphology of the polymer has been tested with FEI INSPECT F50 scanning electron microscopy (SEM).

### 2.3. Synthesis of pyridine-2,6-dicarbonyl dichloride (2,6-PDC)

Five grams of pyridine-2,6-dicarboxylic acid (30 mmol) were added to a 50-mL round-bottomed flask containing

10 mL of thionylchloride. The mixture was kept under stirring in an oil bath at 90°C overnight until it became a colorless homogenous solution. The resultant solution was distilled to get rid of excess thionylchloride, and traces of this reagent were removed under reduced pressure. The final product was obtained as white crystals with a melting point of 61°C and an 86% yield.

#### 2.4. Synthesis of poly(pentamethylenepyridine-2,6-dicarboxylate) (poly (pen-py))

To a 100-mL round-bottomed flask containing 10 mL of orthodichlorobenzene, 1,5-pentane diol (10 mmol) was added under stirring at 80°C. After the mixture became almost homogenous, dissolved pyridine-2,6-dicarbonyl dichloride (10 mmol) in 10 mL of orthodichlorobenzene was gradually added under a flow of argon gas. The solution was kept at 80°C until dropwise addition of diacid chloride finished, and then the temperature was raised gradually to 110°C for 2 h to enhance the reaction. To make sure that the last traces of HCl gas were expelled from the reaction, the temperature was increased to 130°C. This solution was kept at this temperature until no change in litmus color was observed. After the reaction mixture was left to cool, dry *n*-hexane was added until no turbidity was noticed in the solution and left to settle. After that, the obtained precipitate was dissolved in 80 mL of chloroform, filtered, and precipitated in methanol. This cycle of chloroform-methanol purification was repeated four times to get the pure polymer. The solid polymer was dried in a vacuum oven at 60°C for 8 h. Poly(pen-py) was obtained as a white fine powder in 58% yield.

#### 2.5. Viscosity of the polymer

An Ubbelohde glass capillary viscometer was used to determine the inherent viscosity of the poly(pen-py) polymer. The measurement of the viscosity of a solution of a concentration of 0.5 g·L<sup>-1</sup> of polymer in chloroform was carried out in a water bath at 25.0°C ± 0.1°C. The solution was allowed to stand for about 20 min to reach the desired temperature. Many runs were made until reproducibility was achieved.

#### 2.6. Preparation of metal ions stock solutions

Three stock solutions (1,000 ppm) with different metal ions (Pb(II), Cd(II), and Zn(II)) were prepared separately by dissolving an appropriate quantity of each metal nitrate salt in an acetate buffer solution having a constant ionic strength of 0.1 M using sodium perchlorate. Three acetate buffers were used for each metal type. Acetate buffer solutions with pH values 4, 5, and 6 were prepared according to the U.S. Pharmacopeia. Working solutions with concentrations ranging from 25–200 ppm were prepared by dilution of the stock solution with acetate buffer.

#### 2.7. Metal uptake by poly(pen-py) using batch method

The batch equilibrium technique was applied to examine the metal uptake behavior of the three metals toward the polymer. A certain volume (25 mL) of buffer solution was

added to a known weight (0.10 mg) of fresh dried polymer, and the mixture was shaken for 2 h at 25°C. An equivalent amount of buffer solution containing a fixed concentration of metal ions was added, and shaking was continued for 24 h at the same temperature. Periodically, a sample was taken, filtered with a 0.45 µm syringe filter, and the residual metal ion concentration in the filtrate was measured by an atomic absorption spectrophotometer.

#### 2.8. Effect of polymer mass

Using different weights of polymer ranging from 0.100 to 0.500 g at 25°C with a metal concentration of 100 ppm, a constant solution volume of 50.0 mL at pH 5.0, and a shaking time of 24 h using the experimental procedure described in Section 2.7 – Metal uptake by poly(pen-py) using batch method.

#### 2.9. Effect of time

A quantity of 100 mg ± 0.1 of poly(pen-py) was swelled in a 25 mL acetate buffer solution for 2 h. Later on, another 25 mL of buffer containing metal (200 ppm) was added to get a final concentration of 100 ppm. This test was carried out under mechanical shaking (120 rpm) at 25°C and pH = 4, 5, and 6. Only the contact time was variable, and it varied from 0.083 to 24 h. After each time interval 0.083, 0.16, 0.25, 0.5, 1, 2, 4, 6, 8, 18, and 24 h, a sample was taken, filtered, and its final metal residual concentration in the filtrate was measured by an atomic absorption spectroscopy (AAS) instrument.

#### 2.10. Effect of pH

Investigation of the influence of the different pH values (4, 5, and 6) on the uptake manner of the three selected metal ions Pb(II), Cd(II), and Zn(II) by the polymer was carried out at 24 h, at 25°C, and at similar conditions as previously mentioned.

#### 2.11. Adsorption isotherm studies

The adsorption equilibrium relationships experiments were carried out at different metal ion concentrations (12.5–100 ppm), different temperatures (25°C, 35°C, and 45°C), different pH values (4, 5, and 6), and at the particular saturation time for each metal.

#### 2.12. Adsorption–desorption studies using column method

A glass column (length 30 cm and inner diameter 1 cm) was well packed with 0.500 g of fresh dried poly(pen-py), swollen with a 30 mL acetate buffer solution of pH 5. After 24 h, the buffer was flowed out of the column at a flow rate of 1 mL 4 min<sup>-1</sup>. A 50 mL of Pb(II) solution of 100 ppm was gradually added to the column and allowed to proceed through it, and the effluent was collected at a flow rate of 1 mL 4 min<sup>-1</sup>. The concentration of Pb(II) ions in the effluent was determined using an AAS instrument. Similar tests were performed for the evaluation of 100 ppm Cd(II) and Zn(II) ions uptake. The loaded polymer with either lead, cadmium,

or zinc ions in the column was then subjected to further investigation in the desorption process. Two eluting agents, 0.1 M nitric acid (HNO<sub>3</sub>) and 0.1 M EDTA, were used. For this test, 50 mL of each eluent was passed through two columns at a flow rate of 1 mL 4 min<sup>-1</sup>, separately. The amount of desorbed metal ions from the polymer was collected in five portions, and their concentration was determined by AAS. The efficiency of the eluting agents was evaluated with the following expression:

$$\% \text{Recovery} = \left( \frac{\text{amount of desorbed metal ions}}{\text{amount of ions adsorbed by the polymer}} \right) \times 100$$

### 2.13. Reusability

1.00 g of fresh-dried polymer was loaded with metal following the procedure described before, except that the contact time was kept constant (24 h). A quantity of 50 mL of 0.1 M nitric acid was added to the loaded polymer, then the mixture was subjected to shaking for 5 h, filtered, and the polymer was washed several times with deionized water until a neutral pH was obtained. The polymer was dried under vacuum at 60°C for 8 h and reused for a second step of metal adsorption. This whole cycle was repeated five times.

## 3. Results and discussion

### 3.1. Synthesis and characterization of poly(pen-py)

Poly(pen-py) polymer is a step-growth polymer that was formed by a stepwise polymerization mechanism by solution polymerization of stoichiometric amounts of 1,5-pentane diol with pyridine-2,6-dicarbonyl chloride in *o*-dichlorobenzene as a non-reactive solvent. The reaction proceeds by nucleophilic substitution of the chloride of acid chloride by the hydroxyl group of diol. Fig. 2 shows the two-step solution reaction scheme for the preparation of the polymer.

The synthesized polymer was purified by precipitation in methanol. The amount of purified polymer obtained was 27.4 g (58% yield). The chemical structure of the prepared polymer was characterized by inherent viscosity, FTIR spectroscopy, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy, elemental analysis, thermal analysis, and surface morphology.

#### 3.1.1. Solution viscosity

In the case of our polymer, the inherent viscosity (a widely known expression of viscosity) was calculated to approximate the molecular weight. The inherent viscosity ( $\eta_{inh}$ ) may be estimated with an Ubbelohde glass capillary viscometer at a constant temperature in a given solvent. The  $\eta_{inh}$  of poly(pen-py) in chloroform solution at 25°C ± 0.1°C was found to be 0.16 d·Lg<sup>-1</sup>. Compared to other prepared polyesters, this value is relatively lower than values obtained by Saleh et al. [31] in their work on a number of polyesters, namely poly(1,6-hexylenepyridine-2,6-dicarboxylate), poly(1,2-ethylenepyridine-2,6-dicarboxylate), and poly(1,4-butylenepyridine-2,6-dicarboxylate), but at the same time it is higher than other values that were obtained by Al-Dweri et al. [25] when they prepared poly(bisphenol-A phthalate) and poly(bisphenol-A succinate). This value is relatively moderate, which reveals that poly(pen-py) prepared generally has a low molecular weight.

boxylate), poly(1,2-ethylenepyridine-2,6-dicarboxylate), and poly(1,4-butylenepyridine-2,6-dicarboxylate), but at the same time it is higher than other values that were obtained by Al-Dweri et al. [25] when they prepared poly(bisphenol-A phthalate) and poly(bisphenol-A succinate). This value is relatively moderate, which reveals that poly(pen-py) prepared generally has a low molecular weight.

#### 3.1.2. Infrared spectroscopy

It was obvious (Fig. 3) that one of the noticeable and strongest IR absorption bands related to the ester carbonyl C=O stretching vibration at 1,741.48 and 1,721.12 cm<sup>-1</sup>. The intense bands at 1,241.79 and 1,145.3 cm<sup>-1</sup> are due to C–O–C stretching. The bands observed in the range of 2,960–2,850 cm<sup>-1</sup> are attributed to alkyl C–H stretching of the aliphatic diol. The band observed at 3,081.89 cm<sup>-1</sup> is due to aromatic C–H stretching. The bands observed at 1,082.99–991.98 cm<sup>-1</sup>, 846.22, 752.70, and 699.51 cm<sup>-1</sup>, and 1,455–1,321 cm<sup>-1</sup> correspond to C–C bending of the pyridine ring, C–H bending of the pyridine ring, and CH<sub>2</sub> bending of the aliphatic diol, respectively. The band observed at 1,582.43 corresponds to C=N, while C–N stretching appeared at 1,239.11. These data confirm the formation of the prospective macromolecule.

#### 3.1.3. Nuclear magnetic resonance spectroscopy (NMR)

##### 3.1.3.1. <sup>1</sup>H-NMR spectrum

There are three types of aliphatic methylene protons in the pentamethylene alkane chain:  $\alpha$ ,  $\beta$ , and  $\gamma$  with respect to ester linkage. The  $\alpha$ -methylene is directly linked to the ester group, the  $\beta$ -methylene group is attached to the  $\alpha$ -methylene group, and the  $\gamma$ -methylene group is, in turn, attached to the  $\beta$ -methylene group. The signals shown in Fig. 4 for  $\alpha$ -,  $\beta$ -,  $\gamma$ -methylene groups are observed as

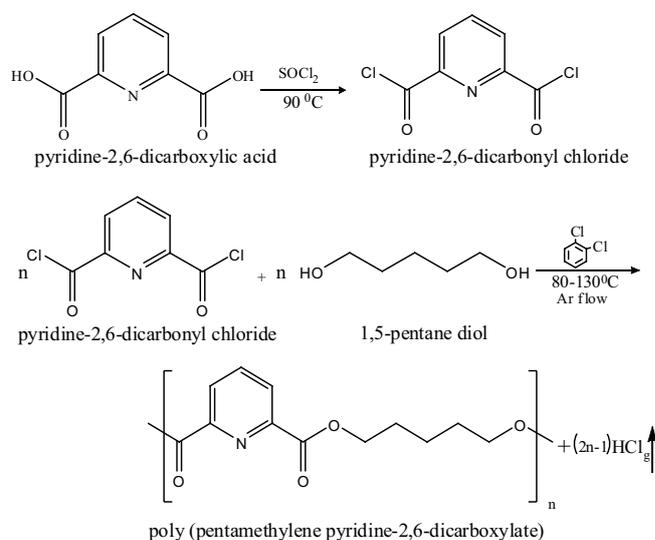


Fig. 2. Synthesis of poly(pentamethylene pyridine-2,6-dicarboxylate).

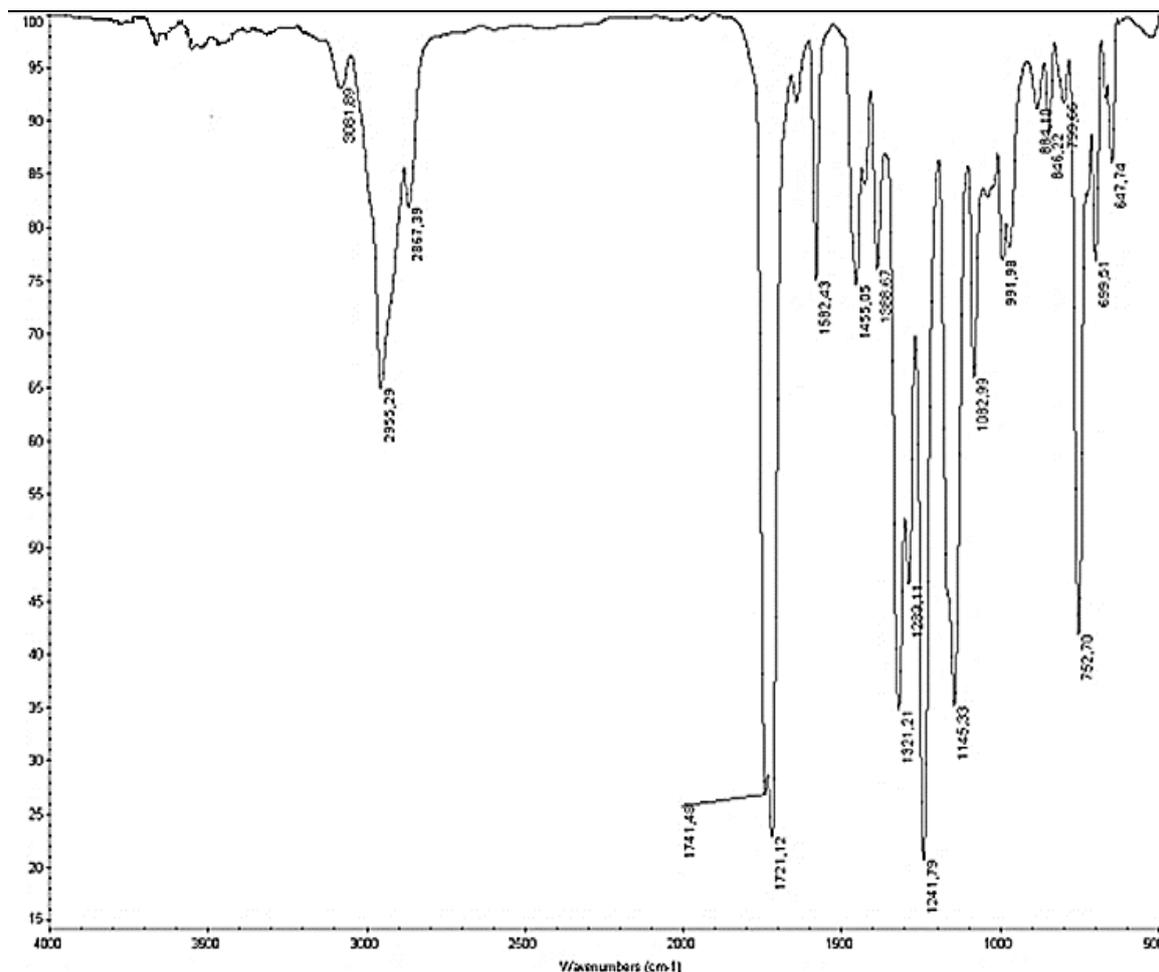


Fig. 3. Infrared spectrum of poly(pentamethylene pyridine-2,6-dicarboxylate).

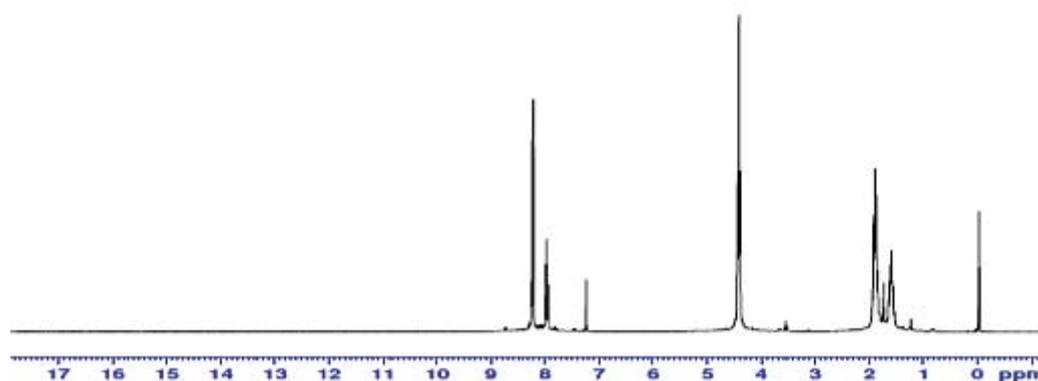


Fig. 4.  $^1\text{H-NMR}$  spectrum of poly(pentamethylene pyridine-2,6-dicarboxylate).

follows: (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 4.40 ppm (t,  $J = 6.8$  Hz, 4H;  $\text{CH}_2$ ), 1.89 ppm (p,  $J = 7.3$  Hz, 4H;  $\text{CH}_2$ ), and 1.59 ppm (p,  $J = 7.1$  Hz, 2H;  $\text{CH}_2$ ), respectively. Regarding pyridine ring protons, the two aromatic protons at meta and para positions to the pyridine-nitrogen atom were observed as 8.23 ppm (d,  $J = 7.8$  Hz, 2H; Ar H) and 7.92 ppm (t,  $J = 7.9$  Hz,  $^1\text{H}$ ; Ar H), correspondingly.

### 3.1.3.2. $^{13}\text{C-NMR}$ spectrum

The  $^{13}\text{C-NMR}$  spectrum exhibits seven characteristic signals. Two signals were related to two meta and one para aromatic carbon atoms in the pyridine ring (Fig. 5). They were observed at  $\delta = 127.9$  ppm and  $\delta = 138.3$  ppm, respectively. The signal with the chemical shift at  $\delta = 148.6$  ppm was attributed to a quaternary aromatic carbon atom bonded to

carbon in C=O. The signal for the carbonyl carbon of the ester group was observed at  $\delta = 164.6$  ppm. The three signals in the aliphatic region were attributed to carbon atoms of the pentane chain at positions  $\alpha$ ,  $\beta$ , and  $\gamma$  with respect to carbonyl carbon, and they appeared at  $\delta = 66.0$  ppm,  $\delta = 28.7$  ppm, and  $\delta = 22.5$  ppm, respectively. The  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectral data are summarized in Table 2.

### 3.1.4. Elemental analysis

The synthesized polymer was analyzed for its elemental content. The results of the analysis showed a satisfactory degree of agreement between the theoretical and practical ratios of elements from which the polymer is constituted. Table 3 reports the elemental analysis results of poly(pen-py).

Referring to Table 3 and to the empirical formula of our polymer ( $\text{C}_{12}\text{H}_{13}\text{NO}_4$ ), it may be concluded that the percentages of elements found match well with what is expected and thus corroborate the identity of our polyester.

### 3.1.5. Thermal analysis

The thermal properties were studied using DSC and TGA instruments under an inert nitrogen atmosphere. The DSC thermogram (Fig. 6) shows a clear downward step representing the  $T_g$  value of poly(pen-py) polymer at  $27.5^\circ\text{C}$ . This value is plausible as it lies between  $55.8^\circ\text{C}$  and  $8.3^\circ\text{C}$ , the corresponding  $T_g$  values of poly(tetramethylene pyridine-2,6-dicarboxylate) and poly(hexamethylene

pyridine-2,6-dicarboxylate), respectively [22]. This  $T_g$  value is considered low, which might be due to the flexibility effect of the aliphatic pentamethylene moiety in the polymer backbone. The TGA thermogram for poly(pen-py) polymer revealed that this polymer has good thermal stability up to  $300^\circ\text{C}$ . A relatively sharp descent in the curve (a single stage) has occurred in the range ( $320^\circ\text{C}$ – $420^\circ\text{C}$ ) due to the mass of the polymer that was lost upon thermal degradation of the polymer chain. The TGA thermogram of the polymer showed the temperatures at which the tested polymer mass lost 1% ( $T_d^1\%$   $323.2^\circ\text{C}$ ), 5% ( $T_d^5\%$   $344.7^\circ\text{C}$ ), 10% ( $T_d^{10\%}$   $356.9^\circ\text{C}$ ), 20% ( $T_d^{20\%}$   $370.6^\circ\text{C}$ ) and 50% ( $T_d^{50\%}$   $393.3^\circ\text{C}$ ). The residual mass at  $500^\circ\text{C}$  equals 11.7%. In some literature, polyesters that have been prepared by other workers show good thermal stability without any degradation until  $300^\circ\text{C}$  [22,25,26]. Our polymer is also within this class of polyesters.

### 3.1.6. X-ray powder diffraction

The diffractogram (Fig. 7) presents several fine and well-defined peaks characteristic of polymer structures,

Table 3  
Elemental analysis data of poly(pen-py) polymer

Element type	% Expected	% Found
N	5.95	6.12
C	61.27	60.87
H	5.57	5.61

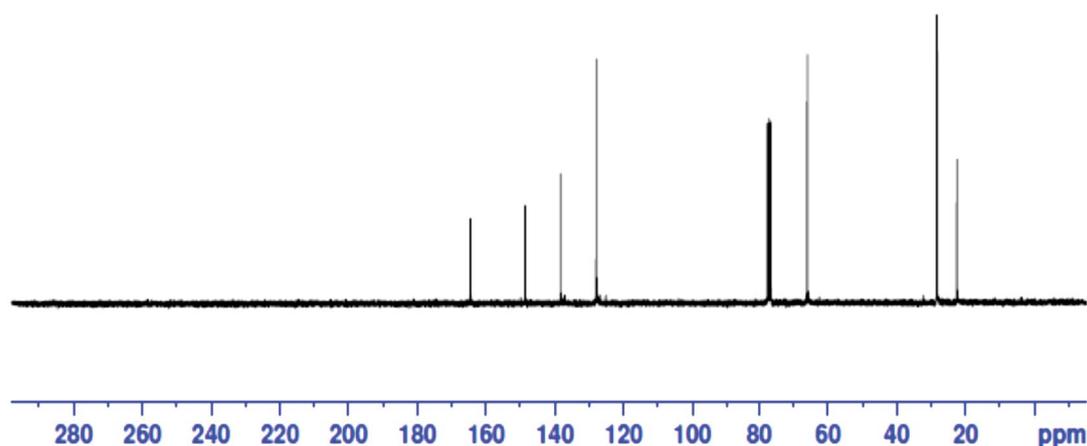


Fig. 5.  $^{13}\text{C-NMR}$  spectrum of poly(pentamethylene pyridine-2,6-dicarboxylate).

Table 2  
 $^1\text{H}$  and  $^{13}\text{C-NMR}$  data for the poly(pentamethylene pyridine-2,6-dicarboxylate)

Polymer structure		1	2	3	4	5	6	7
	$^1\text{H}$	4.4	1.89	1.59	–	–	8.23	7.92
	$^{13}\text{C}$	66.0	28.8	22.7	164.6	148.6	127.9	138.3

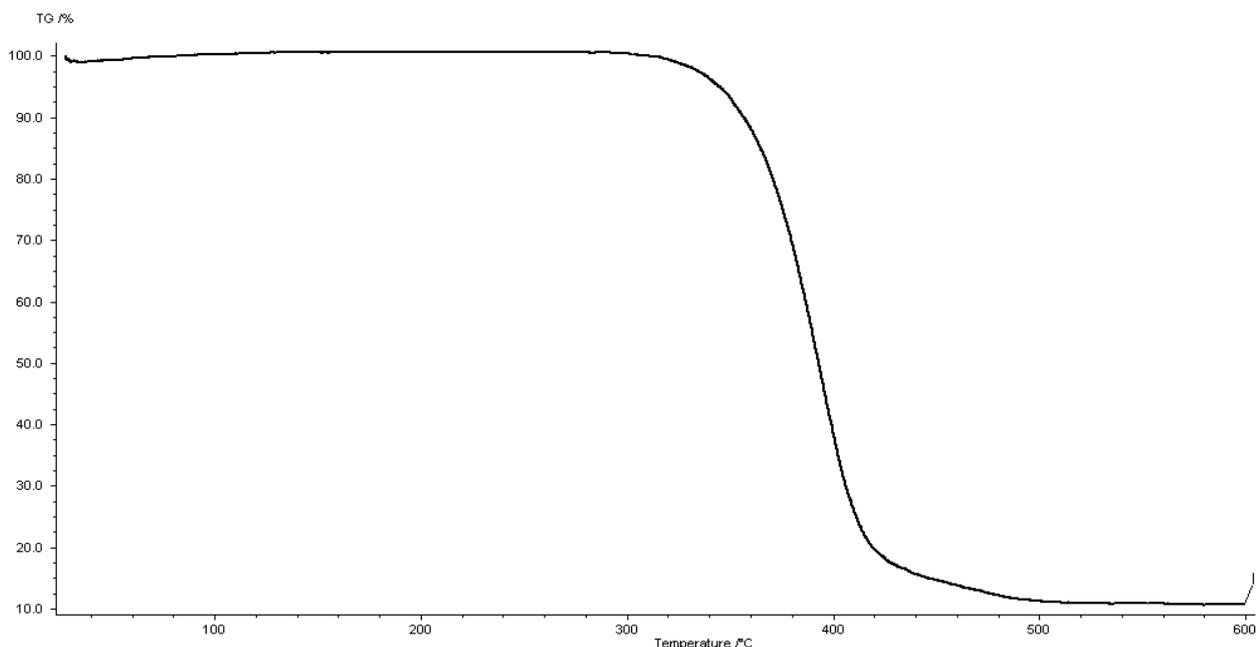


Fig. 6. Thermogravimetric thermogram of poly(pentamethylene pyridine-2,6-dicarboxylate).

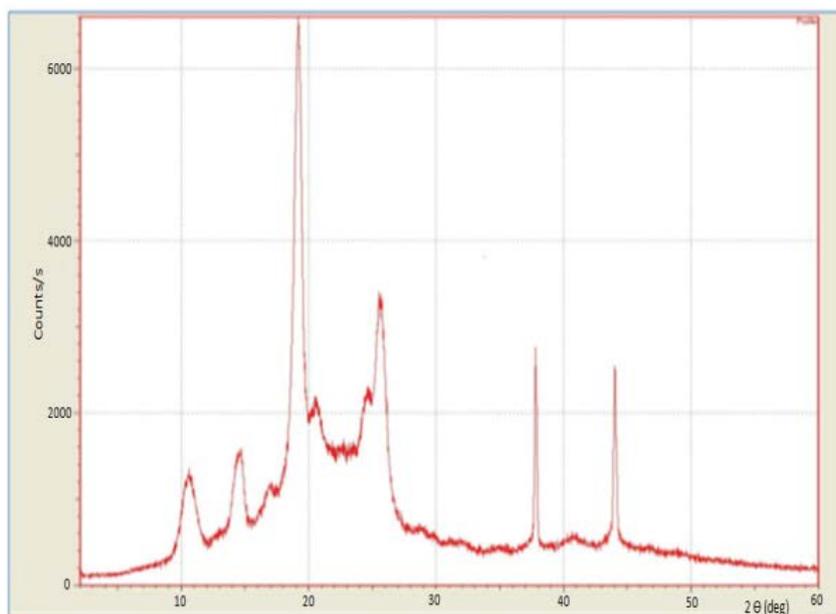


Fig. 7. Diffractogram of poly(pentamethylene pyridine-2,6-dicarboxylate),

corresponding to the presence of a highly organized crystalline structure with a relatively low regular packed crystal system (amorphous region) within its molecules. The diffractogram for our polymer shows intense main peaks at  $2\theta$  of  $19^\circ$  and  $26.5^\circ$ , with several low intensity peaks. These two major peaks are due to graphite-like structure and may have been due to the existence of aromatic groups and the staking of the polymer sheets, as explained by Santos et al. [32] for humic acid.

### 3.1.7. SEM screening

(Fig. 8a) reveals that the polymer has a rough, heterogeneous surface with small pits and less packing. Thus, this surface can provide enough area for metal ions of specific dimensions to be accommodated in the pores and should act as an effective pollutant scavenger. The distribution of these small pores on the rough surface of the polymer took similar forms to flowers that are located on rods with an average size of  $<10\ \mu\text{m}$ . The presence of such pores gives

suitable channels for metal ions to diffuse inside the polymer when the polymer is applied for the sorption of heavy metal ions from polluted water. Interestingly, after metal ions are adsorbed by the polymer, a clear change occurs on the surface features so that a large portion of it became free of holes or voids and is converted to flakes and needle shapes. This is represented in the case of Zn(II)-loaded polymer surfaces in Fig. 8b. Similar observations have also been found for polymers loaded with cadmium and lead ions (Fig. 8c and d). The disappearance of pores on all of these surfaces is clearly noticeable, and this might be due to metal coverage.

### 3.2. Metal uptake properties

#### 3.2.1. Calibration curves

Calibration graphs were built up using acetate buffer as a blank and five standards of concentration (12.5, 25, 50, 75, and 100 ppm) for each metal ion. A straight line with a good  $R^2$  value ( $>0.90$ ) was constructed by plotting standard metal concentrations against the absorbance (Table 4).

#### 3.2.2. Batch method

##### 3.2.2.1. Kinetics studies

The adsorption rate of metal ions on the studied polymer was determined at 25°C, at pH values of 4.0, 5.0, and 6.0, at an initial concentration of 100 ppm, and at different time intervals 0.083–24 h. The same conditions were applied

for the three cations. Generally, in all cases, it was noticed that the metal uptake and time of exposition were proportionally related to each other until a saturation point was reached and a plateau was obtained. In Figs. 9 and 10, it was observed that Pb(II) reached equilibrium more rapidly than Cd(II) and Zn(II). The tabulated data showed better agreement with pseudo-second-order kinetics than with pseudo-first-order kinetics. In contrast to pseudo-first-order kinetics, pseudo-second-order kinetics seemed to be a more suitable one to clarify the kinetics of the studied system where the correlation coefficient ( $R^2$ ) values were greater than 0.99. And the  $q_e$  calculated also coincided very well with the experimental ones (Table 5). This gives an indication about the nature of the rate-controlling step in a given adsorption system, and herein it is stated that this step was chemisorption, in which valence forces were generated by the sharing or exchanging of electrons between adsorbent and adsorbate molecules [33,34].

The pseudo-first-order equation is given as the following expression:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

where  $q_t$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the amount of adsorbate absorbed at time  $t$  (min);  $q_e$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the adsorption capacity at equilibrium;  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant for the pseudo-first-order model. Thus, a plot of  $\ln(q_e - q_t)$  vs.  $t$  should be a straight line with the slope =  $-k_1$  and an intercept =  $\ln q_e$ . If the  $q_e$  values obtained from the intercept do not agree to those obtained experimentally, then the reaction would not be likely to

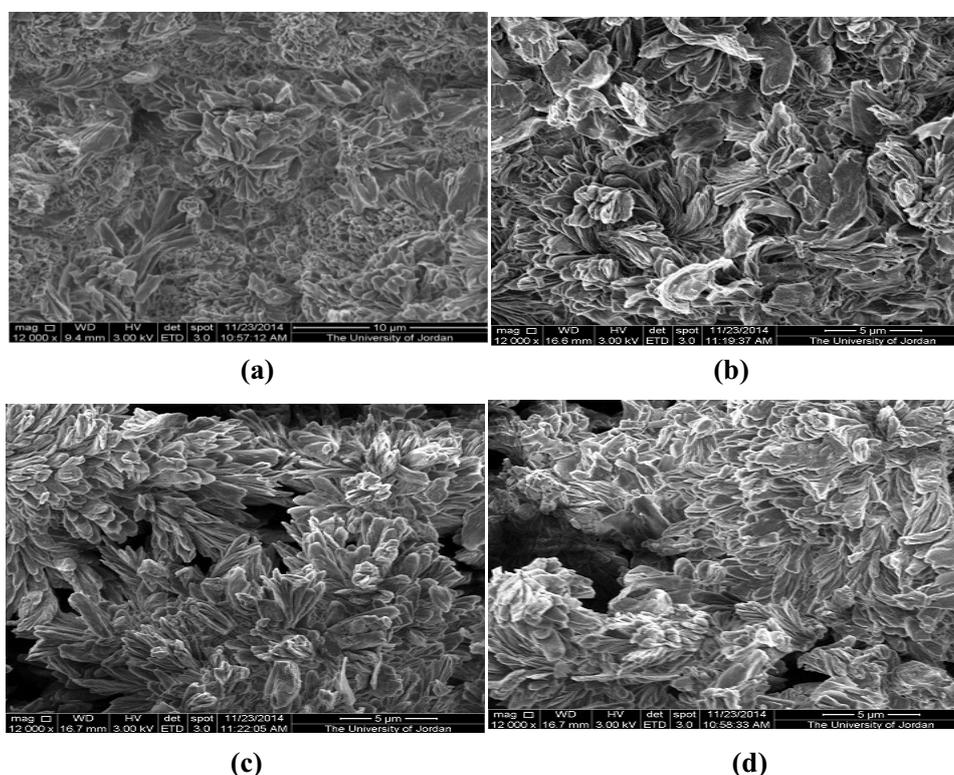


Fig. 8. Surface morphologies of unloaded and loaded poly(pen-py) with different metals Pb(II), Cd(II), and Zn(II) using scanning electron microscopy (magnification = 12,000 times). (a) Pure polymer, (b) polymer-Zn, (c) polymer-Cd and (d) polymer-Pb.

Table 4  
Calibration data for Pb ( $\lambda = 261.4$  nm), Zn ( $\lambda = 307.6$  nm), and Cd ( $\lambda = 326.1$  nm)

Pb(II)		Zn(II)		Cd(II)	
Conc., mg·L <sup>-1</sup>	Absorbance	Conc., mg·L <sup>-1</sup>	Absorbance	Conc., mg·L <sup>-1</sup>	Absorbance
0.00	0.00	0.00	0.00	0.00	0.00
12.50	0.007	12.50	0.001	12.50	0.014
25.00	0.014	25.00	0.003	25.00	0.025
50.00	0.026	50.00	0.005	50.00	0.048
75.00	0.038	75.00	0.008	75.00	0.070
100.00	0.050	100.0	0.010	100.00	0.093

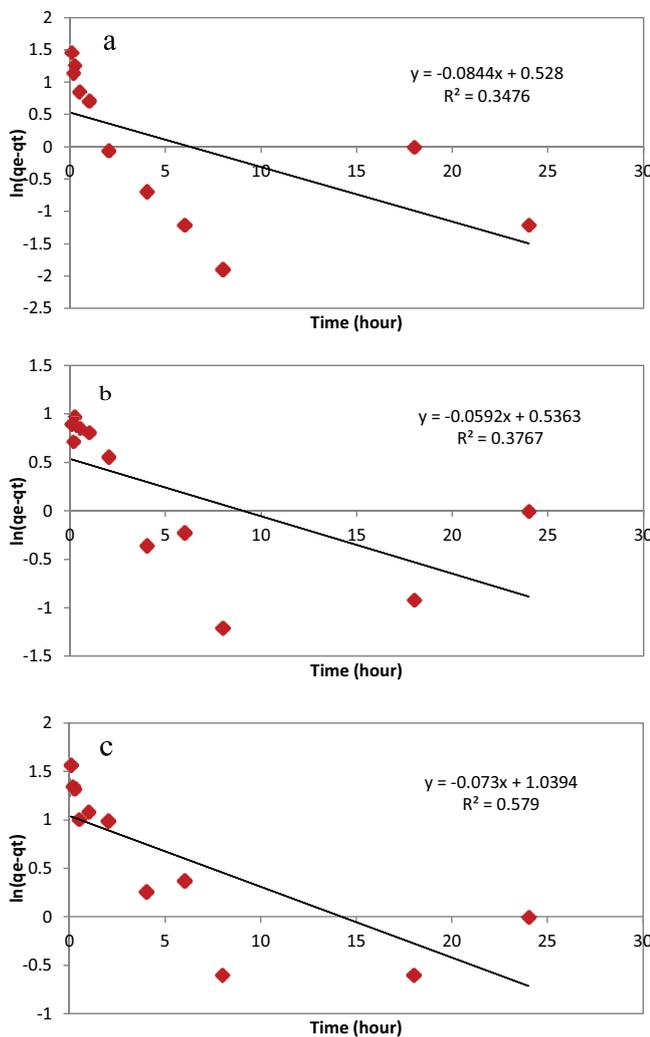


Fig. 9. Pseudo-first-order sorption kinetics of (a) Pb(II), (b) Cd(II), and (c) Zn(II) as a function of contact time.

be a first-order reaction even if the linear plot has a high correlation coefficient (Ho and McKay, 1999).

Adsorption data were also evaluated according to the pseudo-second-order reaction kinetic, which is given as the following expression:

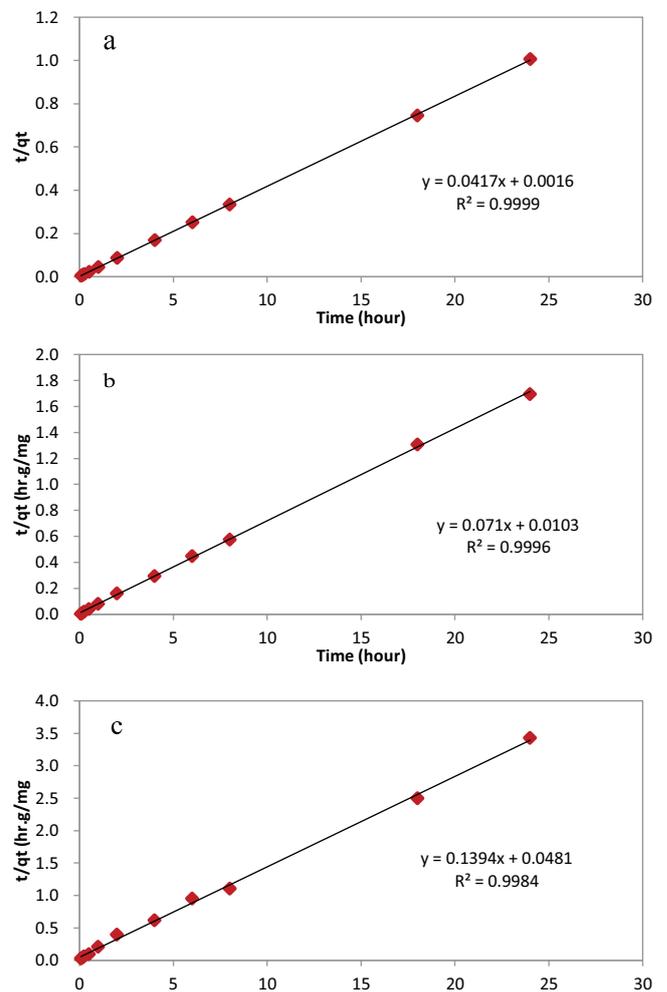


Fig. 10. Pseudo-second-order sorption kinetics of (a) Pb(II), (b) Cd(II), and (c) Zn(II) as a function of contact time.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

The  $k_2$  and  $q_e$  values can be derived from the intercept and the slope of the plot of  $t/q_t$  against  $t$ , respectively. Once more, the value of  $q_e$  obtained from this model should match

Table 5

Calculated and experimental  $q_e$  values based on pseudo-first-order kinetics and pseudo-second-order kinetics at pH = 5.00 and 25°C

Metal ion (II)	Pseudo-first-order kinetics				Pseudo-second-order kinetics			
	$R^2$	$k_1, \text{min}^{-1}$	$q_{e,\text{cal}}$	$q_{e,\text{exp}}$	$R^2$	$k_2, \text{g}(\text{mg}\cdot\text{min})^{-1}$	$q_{e,\text{cal}}$	$q_{e,\text{exp}}$
Pb	0.348	0.084	1.696	24.50	0.999	0.001	23.98	24.50
Cd	0.377	0.059	1.710	14.20	0.999	0.489	14.08	14.20
Zn	0.579	0.073	2.828	6.65	0.998	0.404	7.17	6.65

the experimental value obtained at equilibrium (Ho and McKay, 1999).

### 3.2.2.2. pH effect on metal uptake

This test was carried out at different pH values of 4, 5, and 6 at 25°C with the same procedure that is described in Section 2.4.1. The resultant data are illustrated in Fig. 11.

These results showed that pH changes had no significant effect on the profile of the adsorption capacities for the polymer. This could be explained based on the fact that the poly(pen-py) polymer has non-ionizable functionality, thus the effect of pH on the sorption is low. (Fig. 11) also indicates that the selectivity of the synthesized polymer towards Pb(II) is higher than of Cd(II) and Zn(II).

### 3.2.2.3. Adsorption isotherms studies

Three adsorption isotherm models (Langmuir, Freundlich, and Dubinin–Radushkevich) were utilized to analyze adsorption systems. These experiments were carried out with different experimental parameters: temperatures 25°C, 35°C, and 45°C, pH of the buffer 4, 5, and 6, and the initial concentration of cations 12.5–100 ppm. The linearized patterns of these models were applied. The first isotherm was the Langmuir model, in which the maximum saturation capacity of the polymer outer surface ( $q_{\text{max}}$ ) was estimated using the linearized expression [Eq. (3)].

$$\frac{C_e}{q_e} = \frac{1}{bq_{\text{max}}} + \frac{C_e}{q_{\text{max}}} \quad (3)$$

where  $q_{\text{max}}$  and Langmuir constant  $b$  which is related to adsorption energy, were calculated from the slope and the intercept of the linear graph of  $C_e/q_e$  vs.  $C_e$ , respectively. The second model was the Freundlich isotherm, by which the intensity of adsorption between the selected metals and the surface of the studied polymer was evaluated using its linearized form [Eq. (4)].

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

Freundlich constants ( $n$  and  $K_f$ ) were estimated from a straight line that is generated when  $\log q_e$  is plotted against  $\log C_e$ , where the slope is equal to  $1/n$  and the intercept is equal to  $\log K_f$ . While higher  $K_f$  values mean better adsorption capacities than lower ones,  $n$  values between 1 and 10 reflect the favorability of adsorption, and as  $n$  values

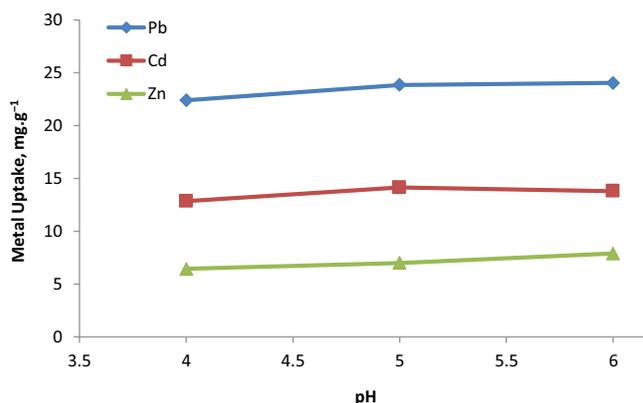


Fig. 11. Metal uptake as a function of pH at 25°C and 24 h, (100 ppm).

increase, the strength of interaction between sorbent and sorbate increases [33]. In general, for both isotherms (Freundlich and Langmuir), the  $R^2$  values were greater than 0.90, but the higher ones were achieved by Langmuir, which means that this model is the best for fitting adsorption data at all pH and temperature values. The applicability of the Langmuir isotherm to our systems implies that the homogeneity of the surface is more favorable than the heterogeneity one to describe the adsorption phenomenon, and this is expected due to the repetition of pyridine-2,6-dicarboxylate units in the polymer backbone [10].

Plots of  $C_e$  vs.  $q_e$  for all adsorption processes for the three cations at various temperature and pH values showed that the isotherms have an L-shape, wherein increments of heavy metal concentrations led to a decrease in the ratio of the ions remained in the filtrate to those captured by the polymer, suggesting that the polymer has a high ability to attract toxic metals at low levels of concentration. This statement is true until a certain concentration is reached; the ratio becomes smaller and smaller, and after a certain increment, the interaction between polymer and solute will become weak due to the empty active points being filled [35].

The third model we were concerned about was the Dubinin–Radushkevich isotherm model. The linearized pattern of it was written as follows:

$$\ln q_e = \ln q_s - \beta_{\text{ad}} \xi^2 \quad (5)$$

Generally, when  $\ln q_e$  was plotted against  $\xi^2$ , a straight line with a good  $R^2$  value ( $>0.90$ ) was obtained. Its slope is equal to  $-\beta_{\text{ad}}$  and its intercept corresponds to  $\ln q_s$ ,  $\beta_{\text{ad}}$  and

$q_s$  reflect the adsorption energy and adsorption capacity, respectively. The  $\beta_{ad}$  value was involved in the calculation of the adsorption mean energy ( $E$ ) as follows:

$$E = (2\beta_{ad})^{-0.5} \quad (6)$$

The determination of whether the adsorption is governed by chemical or physical interactions could be known by using the  $E$  magnitude. In this work, the magnitudes were  $<8 \text{ kJ}\cdot\text{mol}^{-1}$ , and subsequently, the adsorption is expected to have a physical nature.

#### 3.2.2.4. Comparing % uptake, $q_{max}$ , $b$ , $n$ , $K_f$ of Cd(II), Pb(II) and Zn(II)

From Table 6 it was clear that the highest  $q_m$  value was for Pb(II) ions while the lowest one was for Zn(II) ions, which means that the polymer has the highest capacity towards Pb(II) ions but a lower capacity towards Zn(II). This is attributed to the stability of complexes formed between the donor atoms (oxygen and nitrogen) and the metal ions according to the theory of hard and soft acids and bases (HSAB). From this point of view, if oxygen and nitrogen atoms act as active sorption places, then the donor groups are considered hard bases and prefer to interact with hard acids. Actually, Pb(II) ions are borderline acids, but they are closer to being hard, so it will choose oxygen and nitrogen to make a stronger and more stable complex than in the case of Cd(II) ions, which are classified as soft acids [36]. On the other hand, Zn(II) is considered harder than cadmium, but its maximum adsorption capacity is less than that of Cd(II). Herein, it seems that the size of the metal ions plays a crucial role. It was known that the molecular weight and ionic radius of Pb(II) have the largest values among these metals, Zn(II) has the smallest magnitude, and Cd(II) has an intermediate value. It was reported that the higher the ionic radius of the metal to be adsorbed, the smaller the hydration radius, the easier the competition for sorption sites, and thus the greater the accessibility of the metal to the polymer surface [37]. Also, this trend is the same as the electronegativity of these ions. Our findings were compatible with this conclusion.

In this work, the order of metal uptake at 25°C was: Pb(II) > Cd(II) > Zn(II), with maximum adsorption capacities of 30.30, 16.95, and 8.33  $\text{mg}\cdot\text{g}^{-1}$ , at pH = 6, 5, and 4, respectively. It was found in some literature that the  $q_m$  and adsorption trends obtained by other workers were: 53.5 (Pb(II)) > 17.7 (Cd(II)) for poly(cyclohexylenedimethylene phthate) in  $\text{mg}\cdot\text{g}^{-1}$ , at pH = 6.00 [25]. 31.2 (Pb(II)) > 29.8 (Cd(II)) > 15.9 (Zn(II)) for poly(1,4-cyclohexanedimethylene oxalate), in ( $\text{mg}\cdot\text{g}^{-1}$ ) at pH = 6 [24]. The same trend in  $q_m$  values for Pb(II) and Cd(II) ions was also observed by Al-Safadi et al. [23] for poly(hydroquinone oxalate) at pH = 5, and by Abu-Awwad et al. [10] for poly(neopentyl oxalate) polymer at pH = 5. Our results were in good agreement with these trends, and this indicates that poly(pen-py) has reasonable  $q_m$  values.

In our work, the optimum values of  $q_m$  were obtained at 45°C, and this means that as temperature increases, the  $q_m$  magnitudes increase for all metal ions under study, indicating an endothermic process. Comparison data showed that the  $R_L$  values for all metal ions took values between 0 and 1, which implies the favorability of the adsorption processes. Freundlich constants  $n$  and  $K_f$  are also shown in these data. Higher  $K_f$  values mean better adsorption capacities than the lower ones. In the present study,  $n$  values between 1 and 10 imply that adsorption is a favorable process for our systems. A higher value of  $n$  (a smaller value of  $1/n$ ) gives an indication that metal uptake processes are good through the whole applied concentration range; the larger the  $n$ , the stronger the interaction between sorbent and heavy metal.

#### 3.2.2.5. Effect of temperature on metal uptake

The obtained results (Table 7) show that the % uptake increases with increasing temperature at a constant pH value. This was true for all metals at all pH values. This behavior may be attributed to conformational changes due to inter- or intra-molecular interactions that increase the exposure of active sites to the solute ions.

#### 3.2.2.6. Thermodynamics results

For obtaining a clear vision of the prospect mechanism included in the metal uptake process,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  must be estimated. These thermodynamic functions correspond

Table 6  
Langmuir, Freundlich and Dubinin–Radushkevich isotherm parameters for Cd(II), Pb(II), and Zn(II) at pH = 5.00

Metal ion	T (°C)	Langmuir isotherm			Freundlich isotherm			Dubinin–Radushkevich				
		$R^2$	$q_m$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$K_L$ ( $\text{L}\cdot\text{mg}^{-1}$ )	$R_L$	$R^2$	$n$ ( $\text{L}\cdot\text{mg}^{-1}$ )	$K_f$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$R^2$	$\beta$ ( $\text{mol}^2\cdot(\text{kJ}^2)^{-1}$ )	$q_m$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$E$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )
Cd(II)	25	0.992	16.949	0.082	0.1086	0.902	2.217	2.438	0.928	11.470	13.736	0.209
	35	0.997	20.833	0.127	0.0732	0.924	2.457	3.972	0.900	4.923	17.202	0.318
	45	0.993	25.000	0.169	0.0557	0.935	2.688	5.714	0.949	3.144	20.718	0.399
Pb(II)	25	0.995	28.571	0.114	0.0806	0.911	2.178	4.613	0.897	3.145	21.370	0.398
	35	0.990	30.303	0.320	0.0303	0.945	3.115	9.419	0.908	0.668	24.829	0.865
	45	0.990	37.037	0.179	0.0529	0.964	2.232	7.430	0.920	1.649	28.247	0.551
Zn(II)	25	0.995	8.333	0.050	0.1666	0.917	2.169	0.959	0.937	25.130	6.417	0.141
	35	0.993	9.615	0.094	0.0962	0.976	3.257	2.312	0.936	19.280	8.264	0.161
	45	0.999	11.364	0.107	0.0858	0.938	2.907	2.489	0.934	11.160	9.806	0.212

to the change in Gibbs free energy, the change in enthalpy, and the change in entropy, respectively. There are two common equations used to relate these three functions to each other's; the first is Eq. (7):

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

where  $K_d$  is the ratio between the amount of metal ions adsorbed (trapped) by the polymer at equilibrium and that remained in the solution after adsorption; this term is known as the distribution coefficient;  $T$  is the absolute temperature; and  $R$  is the gas constant. The second relationship is Eq. (8):

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

$\Delta H^\circ$  and  $\Delta S^\circ$  can be estimated from a linear plot of  $\ln K_d$  vs.  $1/T$ . While the slope gives  $\Delta H^\circ/R$ , the intercept gives  $\Delta S^\circ/R$ . Their values were then substituted in Eq. (8) to get the  $\Delta G^\circ$  value. Table 7 summarizes the thermodynamic parameters  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  of the three divalent cations at 25°C and different pH values.

Based on the fact that  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  are temperature dependent, plotting  $\ln K_d$  vs.  $1/T$  will give a linear graph with a slope of  $-\Delta H^\circ/R$  and an intercept of  $\Delta S^\circ/R$ . The numerical values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were then substituted in Eq. (8) to get the Gibbs free energy value. The numerical values of Gibbs free energy were found to be between 0.312 and 6.359 kJ·mol<sup>-1</sup>. This gives another good indication about the favorability of the sorption system. The tabulated numbers of  $\Delta G^\circ$  revealed that adsorption of Pb(II) was favorable over Cd(II) and Zn(II), and as temperature rises, the  $\Delta G^\circ$  values decrease, which means that the spontaneity and favorability of the process were better at elevated temperatures due to the presence of ions in dehydrated forms [38].  $\Delta H^\circ$ , with positive values ranging between 12.22 and 31.80 kJ·mol<sup>-1</sup>, indicates the endothermicity of the adsorption of metals on poly(pen-py) surface. This endothermic nature might be attributed to the good solvation behavior of the ions. The ease of the loss of the outer hydration shells of a metal, the faster the adsorption, the lower the needed energy

Table 7  
% uptake and thermodynamic parameters  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  of the three divalent cations at 25°C, and different pH values

Metal ion	pH	% uptake	$\Delta G^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta H^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta S^\circ$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )
Pb(II)	4.00	45.3	-7.087	-16.69	-31.17
	5.00	49.0	-3.922	44.25	164.41
	6.00	50.5	-4.000	77.73	272.98
Cd(II)	4.00	25.3	-3.709	28.99	112.58
	5.00	28.4	-1.417	64.10	219.39
	6.00	26.5	-2.509	25.16	92.58
Zn(II)	4.00	13.8	-0.661	65.36	221.85
	5.00	13.3	1.400	65.18	215.12
	6.00	14.1	0.024	35.22	121.23

for dehydration. In our case, we suppose that the amount of this energy outstrips the exothermicity limits of attachment ions to the surface. In other words, the surrounding area of the ions after sorption will be less aquatic than that in solution, so taking out water molecules from the cations (dehydration) requires energy whose value exceeds that for adsorption by appreciable degrees. Finally, the positive values of entropy show an increasing disturbance at the interface (boundary) between the solid polymer and the aqueous phase of the metal solution. This phenomenon may be due to the replacement of water moieties by the sorbate species during adsorption. Through the replacement process, the quantity of translational energy received (gained) by water molecules is greater than that lost by the sorbate cations, so that the prevalence of disorder throughout the whole system is allowed [39]. Moreover,  $\Delta S^\circ$  values indicate the irreversibility of the removal process.

### 3.2.2.7. Effect of polymer weight on metal uptake

In this test, the varied known amounts of poly(pen-py) were subjected to the same experimental conditions (pH = 5.00, initial concentration of metal cations = 100 ppm, temperature = 25°C, contact time = 24 h, and shaking rate = 120 rpm). Fig. 12 represents the results.

It can be shown that the mass of the polymer was directly proportional to the sorption percent. This relation may be explained based on the fact that as the mass increases, the surface area and subsequently the number of active sites increase [38]. This effect also gives good evidence for poor selectivity towards Zn(II) ions and for high selectivity towards Pb(II) ions. SEM (Fig. 8) for the polymer with higher masses that were loaded with the three ions. It shows aggregates and hubs that covered the entire polymer surface, which reflects high metal adsorption uptake.

## 3.3. Column experiments

### 3.3.1. Metal loading on polymer

The column method was used in order to test metal ion uptake of Pb(II), Cd(II), and Zn(II) by poly(pen-py) at pH 5. For all tested metal ions, the initial concentration of metal solution was 100 ppm, the amount of packed dry polymer in a column was equal to 0.500 g, and the flow rate was

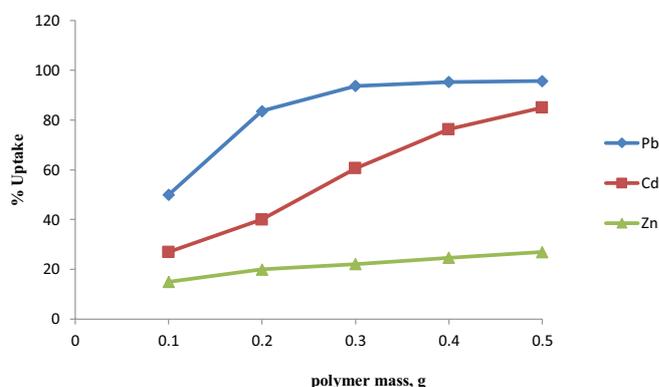


Fig. 12. Polymer mass effect on percent metal-uptake.

1 mL 4 min<sup>-1</sup>. From the data in Table 8, it is clear that loading percentages (capacities) took the following sequence: Pb(II) > Cd(II) > Zn(II). Although this order is in agreement with that obtained by batch experiment, the percentage values of the column method are lower than the percentage values of the batch method, and this might be related to the shaking effect and equilibrium time, where no mechanical shaking was performed and the time required to get the complete saturation was not reached, subsequently a lower percent of metal uptake was observed.

### 3.3.2. Desorption studies

For desorption purposes, the wet-loaded polymer in the column was subjected to further treatment. It was treated with the following eluting agents separately: 0.1 M nitric acid and 0.1 M EDTA. The eluting solution was collected in five portions, 10 mL at a time. Later on, these portions were analyzed using AAS to determine the desorbed metal ion concentration. Nitric acid and EDTA behave in different manners in their actions as eluting agents; the first is considered a proton-exchange agent, and the other is considered a chelating agent. During the recovery, EDTA can form a precipitate with divalent ions while nitric acid cannot, this implies that the EDTA-metal complex is more stable than the nitrate-metal complex, and the higher the complex stability, the lower the desorption efficiency. Thus, the regeneration process seems to be governed by the solubility effect [40]. Based on the % accumulative recovery shown in Table 9, it was concluded that HNO<sub>3</sub> is more able to recapture metal ions from the polymer surface.

### 3.4. Selectivity of the polymer in multi-component systems

The selectivity of the polymer was studied in multi-component systems to examine the polymer selectivity toward the three metals using the procedure mentioned in Section

2.7 – Metal uptake by poly(pen-py) using batch method. The results are shown in Table 10.

It is noticeable from Table 10 that the selectivity of the polymer towards the three metals is evident from the fact that the selectivity of Pb(II) is higher than that of Cd(II), which, in turn, is higher than Zn(II). This can be deduced from the % uptake for all the mixtures mentioned. In addition, these results correspond to the  $q_m$  behavior achieved by the Langmuir isotherm, in which (Pb(II)) > (Cd(II)) > (Zn(II)) at pH = 5 in all temperatures (Table 6).

### 3.5. Reusability

The use of an adsorbent in the adsorption process depends not only on its adsorptive capacity but also on how well the adsorbent can be regenerated and used again. For multiple uses of an adsorbent, adsorbed metal ions should be easily desorbed under suitable conditions. Desorption of the adsorbed Pb(II) and Cd(II) ions from the poly(pen-py) was also studied in a batch experimental system. Five cycles

Table 10  
% Uptake of the three metal ions by the polymer in different mixtures at 25°C, and pH 5

	% Uptake of Pb(II)	% Uptake of Cd(II)	% Uptake of Zn(II)
Mixture 1 [Pb(II), Cd(II), Zn(II)]	16.33%	9.47%	4.43%
Mixture 2 [Pb(II), Cd(II)]	27.22%	15.78%	N/A
Mixture 3 [Pb(II), Zn(II)]	22.27%	N/A	7.39%
Mixture 4 [Cd(II), Zn(II)]	N/A	12.91%	6.05%

Table 8  
Metal ion uptake using column experiment

Metal ion (II)	Initial concentration (ppm)	Final concentration (ppm)	Loaded concentration (ppm)	% uptake
Pb	100.0	58.40	41.60	41.60
Zn	100.0	90.90	9.10	9.10
Cd	100.0	79.30	20.70	20.70

Table 9  
Desorption of the three metal ions from the polymer using two different eluting agents

Metal ion	Eluting agents	% Recovery (1st portion)	% Recovery (2nd portion)	% Recovery (3rd portion)	% Recovery (4th portion)	% Recovery (5th portion)	% Cumulative recovery
Pb(II)	0.1 M HNO <sub>3</sub>	68.2	24.7	5.0	0.3	–	98.2
	0.1 M EDTA	58.1	17.8	4.3	3.5	0.1	83.8
Cd(II)	0.1 M HNO <sub>3</sub>	65.9	28.0	3.2	0.8	–	97.4
	0.1 M EDTA	56.0	19.3	3.7	2.1	0.7	81.8
Zn(II)	0.1 M HNO <sub>3</sub>	64.3	27.8	5.7	–	–	97.1
	0.1 M EDTA	54.0	20.5	6.2	1.9	0.1	82.7

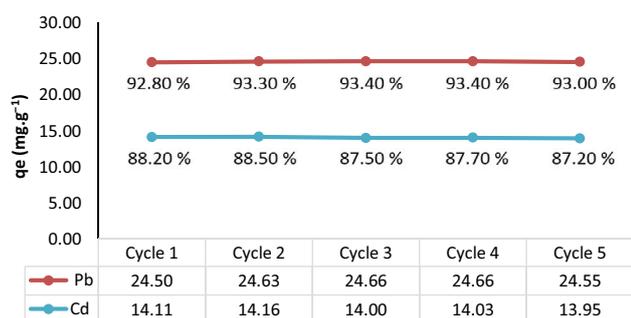


Fig. 13. Reusability of the polymer represented by the number of cycles vs. adsorption capacity at equilibrium (% Uptake is placed next to each metal line).

of adsorption–desorption experiments were conducted to examine the potential toxic metal uptake of the poly(pen-py) for practical applications. Each time the polymer was completely saturated with the metal ions (initial concentration 100 ppm) at optimum pH, it was then treated with a 0.1 M  $\text{HNO}_3$  solution for regeneration purposes. The uptake percentages were: 92.8%, 93.3%, 93.4%, 93.4%, and 93% for Pb(II) ions, and for Cd(II) ions, these percentages were: 88.2%, 88.5%, 87.5%, 87.7%, and 87.2%. These results indicate that the desorption efficiency was generally high and that poly(pen-py) could be reused many times for adsorption (Fig. 13).

#### 4. Conclusions

In the current study, poly(pentamethylene pyridine-2,6-dicarboxylate) (poly(pen-py)) polyester has been prepared and characterized. Metal-polymer adsorption relationships, including kinetics and isotherm studies, were also investigated. The ability of the prepared polyester to adsorb the three heavy metals: Pb(II), Zn(II), and Cd(II) from aqueous solutions was tested under different experimental parameters. Batch and column methods were used for this purpose. The efficiency of the desorption process was also studied using two different eluting agents: 0.1 M  $\text{HNO}_3$  and 0.1 M EDTA. It was found that poly(pen-py) has high uptake percentages toward Pb(II) ions but a low uptake percentage toward Zn(II) ions. Where the effect of pH values on metal loading by the polymer is viewed, the amount of sorbed ions increases very slowly as pH values increase (no significant effect). The degree of metal ion uptake at all temperatures and pH values and the selectivity of the polymer in multi-component systems can be summarized in the following order: Pb(II) > Cd(II) > Zn(II). Moreover, it was found that the data best fit the pseudo-second-order kinetics model, and the best adsorption isotherm model to represent the resulted data was the Langmuir model with a correlation coefficient > 0.990. The adsorption capacity of poly(pen-py) increases as temperature increases, and the trend in adsorption capacity obtained by column experiments was in agreement with that obtained by batch method at the optimum pH for each metal and a flow rate of 1 mL 4 min<sup>-1</sup>. Desorption of adsorbed metal ions would be efficient, and the percentages of recovery were higher by using 0.1 M  $\text{HNO}_3$  as the

eluting agent, and the prepared polymer can be reused at least five cycles and give high desorption percentages.

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