Original Research

Removal of Pb(II) Metal Ions from Aqueous Solutions Using Chitosan-Vanillin Derivatives of Chelating Polymers

Fadi Alakhras[1]*, Hanin Al-Shahrani[1], Eman Al-Abbad[1], Fuad Al-Rimawi[2], Noureddine Ouerfelli[1]

[1]Department of Chemistry, College of Science, Imam Abdulrahman Bin Faisal University, Dammam, Saudi Arabia
[2]Depertment of Chemistry and Chemical Technology, Faculty of Science and Technology, Al-Quds University, Jerusalem, Palestine

Abstract

Our study investigates the removal of Pb(II) ions found in aqueous solutions using chitosan-vanillin polymeric material. The effects of pH, agitation time, adsorbent mass, and initial amount of studied ion on the chelation process have been carried out using batch experiments. The quantity of residual ions has been estimated via atomic absorption spectrometry. The polymers are characterized using infrared spectroscopy, TGA, SEM, and BET surface area.

The highest removal of Pb(II) ions achieved by polymers I and II was at pH 6. The Langmuir isotherm worked as the greatest explanation for the experimental outcome with highest chelation capability equal to 23.3 mg g^{-1} for polymer I and 66.23 mg g^{-1} for polymer II. Kinetic studies revealed that chemisorption was the rate-determining step, whereas the uptake was natural and endothermic.

Keywords: chitosan-vanillin Schiff base, chelating polymers, adsorption, wastewater treatment, lead removal

Introduction

Some factories and industries are responsible for producing the most dangerous, most highly soluble, and risky poisonous metal ions like Cd, Cr, Cu, Ni, As, Pb, and Zn as a result of getting rid of large amounts of metal-contaminated wastewater. All these toxic metals could be absorbed by living organisms. A large amount of these metals could be accumulated in the human body through the food chain. As these metals are being digested in the body, they might cause some health problems and disorders [1].

It has been found that as a challenging case, there is a low amount of poisonous metal ions in the liquid solutions. Furthermore, it has been stated that the method of metal ion separation from wastewater is a complicated process by pH, competing ions,

*e-mail: falakhras@iau.edu.sa

and the presence of organic substances. To get rid of the toxic species from liquid solutions, some methods were used like filtration, ion exchange, and precipitation and adsorption [2-5].

Plenty of approaches have been used to enhance the least expensive and most powerful technologies, with a specific goal of diminishing the produced wastewater and to build up the nature of the treated effluent. In recent years, a plethora of research has been conducted to find some of the most affordable and reasonable adsorbents. For example, the adsorption approach has been utilized as another treatment [6]. Biosorption is derived from biological substances and this technique has been professionally used and studied as a kind of treatment for wastewater that contained heavy metals [7-9]. Different types of biomass like seaweeds, molds, yeasts, bacteria, and crab shells have been tested for metal biosorption with very encouraging results.

Chitosan polymers are characterized as semi-artificially derived amino polysaccharides that have exceptional structures, very modern usefulness, and multi-dimensional properties, and an extensive variety of utilizations in biomedical and different fields in industry [10–12]. Chitosan is considered a natural sorbent for metal ions like Zn, Ni, Cu, Cr, and Pb. This can be due to the following reasons: 1) a large group of hydroxyls in chitosan, 2) the existence of primary amino groups that are considered sorption sites, and 3) the flexibility of a polymer chain structure that works as a suitable provider for complexity of metal ions [13]. A plethora of research has been conducted in the field of chitosan-based chelating polymers. It showed that the novel chitosan-based resins have enhanced sorption capacities for the target ions in single or mixed solutions with superior stability and reusability [14-24]. There are a number of reactions that have been carried out through using the reactive amine group. One of these examples is a reaction through which an aldehyde functional group reacts with the -NH2 group of chitosan by reductive amination [25].

Vanillin is also considered a biomass compound that plays a significant role as a renewable feed stock. Moreover, ortho-vanillin as a related compound is utilized in the organometallic polymers process, where a Schiff base is derived from ortho-vanillin, which has been chelated with other metal ions [26].

In spite of the environmentally friendly features of chitosan, its chelation capacity is still limited to the deacetylation degree, the metal ions nature, and the pH solution.

In this paper, we are going to exploit the sorption properties of the individual sorbents; chitosan- and vanillin-based polymers toward removal of Pb(II) ions by assembling two chitosan-derived Schiff bases. Metal ion uptake, sorption isotherm models, and kinetic and thermodynamic parameters will also be investigated.

Materials and Methods

Materials

Unless otherwise stated, all chemical materials are attained from trade sources and are utilized as obtained. vanillin (99%), *ortho*-vanillin (99%), sodium acetate anhydrous (99%), glacial acetic acid (99%), chitosan (not less than 85% glucosamine) with medium molecular weight, lead (II) acetate trihydrate (99%), ethanol (99%), acetone (99%), and methanol (99%)

Methods

Synthesis of Chitosan-Vanillin Resins; Polymers I-II

The sorbents were prepared by the process reported by Wang et al. [27]. About 5.70 g of starting material was refluxed with 13.69 g of vanillin (polymer I), 13.69 g of *ortho*-vanillin (polymer II) in a solution containing 90 mL methanol, and 9 mL glacial acetic acid for a period of 10 h. Afterward, the obtained polymers were refinement and rinsed with ethanol and acetone, correspondingly. The un-reacted materials were taken out using a soxhlet extraction apparatus filled with acetone and ethanol for 24 h. Finally, the resulting hard sorbents (beige for copolymer I, yellow for copolymer II) were desiccated at 70ºC overnight.

Characterization of the Resulting Polymers

The obtained sorbents have been analyzed and characterized using FTIR spectrometer (IRAFFINTT-2) by KBr discs. Thermal Gravimetric Analysis (Exstar, TG/ DTA 7300), BET Surface area (Quanta chrome), and SEM (INSPECT S50).

Preparing Buffer Solutions

A sequence of acetic acid/sodium acetate buffer solutions (pH values 3.0 to 7.0) was prepared. Metrohm pH meter model 525A (Herisau, Switzerland) was used for the pH measurements.

Preparing Metal Ion Solutions

Stock solution of Pb(II) ions with 1000 mg L^{-1} concentration was obtained by solving the appropriate quantity of metal salt in deionized water. Metal ion solutions with (10, 20, 30, 40, 50, 75, and 150 mg L^{-1}) have been fitted out from the stock solution in deionized water as well.

Sorption of Pb(II) Ions onto the Polymer Materials

The adsorption behavior of the two sorbents has been explored by the batch equilibrium process; 0.05 g

of adsorbent was suspended in a 100 mL conical vial, including 25.0 mL of buffer solution with pH ranging from 3.0 to 7.0, for a period of 2 h of constant trembling (Orbital Shaker, Steady Shake,757) to reach equilibrium. Then, 25.0 mL of Pb(II) solution with 20 mg L^{-1} was joined and the mixed solutions were shaken at 30ºC.

To find out the impact of time, comparable trials have been performed in diverse time periods (5, 10, 20, 30, 60, 120, 240, 480, and 1440 minutes). After that, the loaded polymers were removed by filtration and the quantity of residual metals ions was found out by atomic absorption spectrophotometry (Shimadzu, AA-7000). The same tests have been employed at various values of (30ºC, 50ºC, and 70ºC).

The effect of polymer dosage has also been investigated by using dissimilar doses (0.01, 0.05, 0.1, 0.2, 1.0 g) of the dehydrated polymers and applying the optimal conditions of exposure time and pH on metal adsorption.

Mathematical Treatment

In the isotherm trials, the quantity of metal ions adsorbed at balance, *Qe* (mg metal ion/g polymer), was evaluated by means of the subsequent equation:

$$Q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

...where *Co* represents the initial metal amount (mg L^{-1}), *Ce* is the final concentration after 24 h. The volume of solution (L) is represented by V, while W symbolizes the mass of waterless polymer utilized (g). For the sorption rate investigations, the value of metal ions chelated at several intervals was also studied using the succeeding formula:

$$Q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

…where *Ct* (mg L^{-1}) is the metal ions concentration in solution at different period *t*.
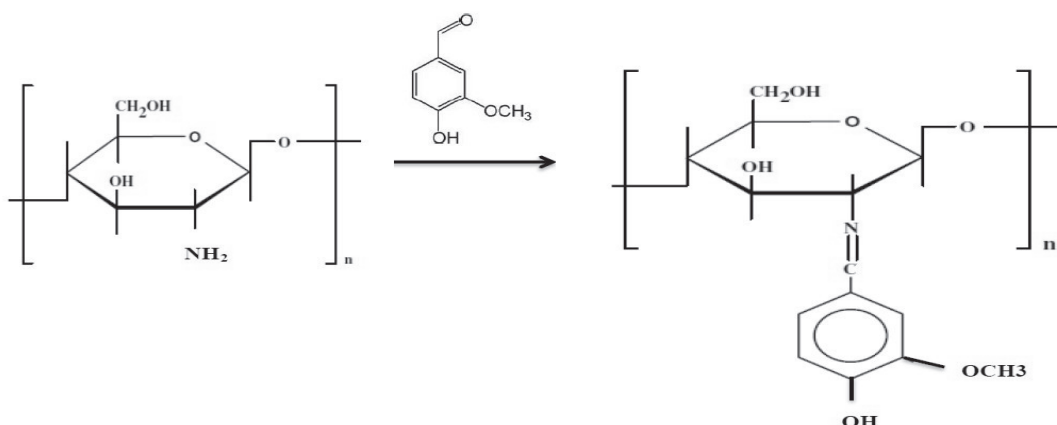
The following isotherm models have been used for fitting the experimental data [28].
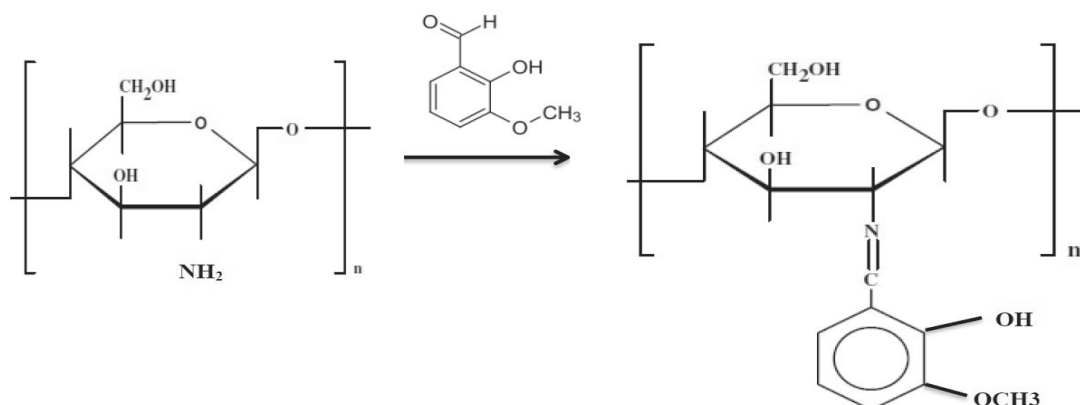
Langmuir isotherm: $C_e/q_e = 1/(q_0 K_L) + C_e/q_0$ (3)

Freundlich isotherm: $\log q_e = \log K_F + \frac{1}{n}\log C_e$ (4)

$$q_e = \frac{Rt}{b}\ln A + \frac{Rt}{b}\ln C_e$$

Temkin isotherm: $q_e = B\ln A + B\ln C_e$ (5)

Scheme 1. Preparation of Chitosan-Vanillin Schiff base (polymer I).

Scheme 2. Preparation of Chitosan-O-vanillin Schiff base (polymer II).

Table 1. Peaks of IR spectroscopy for chitosan, polymer I, and polymer II.

Probable assignment	Typical range (cm^{-1})	Chitosan	Polymer I	Polymer II
O-H stretching	3200-3500	3400	3440	3465
N-H stretching	3310-3400	3300	----	-----
Aromatic C-H stretching	3000-3100	----	3047	3060
Aliphatic C-H stretching	2850-2980	2870 - 2916	2880-2960	2886-2942
C=N stretching	1630-1660	----	1638	1631
Aromatic C=C stretching	1460-1650	----	1520	1470
C-O stretching	1000-1300	1085-1260	1024-1280	1075-1250

Separation factor:
$$R_L = \frac{1}{1 + K_L C_0} \qquad (6)$$

Furthermore, *pseudo* first-order and *pseudo* second-order equations have been used for sorption rate investigations. In addition, thermodynamic parameters, which give information about the heat of adsorption and the nature of surface and the adsorbed phase, have been evaluated using the Vant-Hoff equation:

$$\log\left(\frac{q_e}{C_e}\right) = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \qquad (7)$$

Results and Discussion

Synthesis and Characterization of Polymers

Synthesis

Imine assembly-based materials are normally created via condensation reaction between primary amine and dynamic carbonyl group. In this study, chitosan performs the principal amine with the purpose of interacting with vanillin (polymer I) and O-vanillin (polymer II) to produce the corresponding polymers as shown in schemes 1 and 2, respectively.

The incorporation of efficient moieties in the chitosan matrix may enhance the removal capacity with metallic ions or particles through complexation with analytical and environmental applications.

IR Spectroscopy

IR spectra provide productive data to investigate chelating polymers and to find the bonding sites in the metal complexes about these polymers. Those IR data of the obtained sorbents are in accord with the constructions allocated to them. The intense broad band between 3300-3500 cm^{-1} is assigned to the intramolecular hydroxyl stretching vibrations that clearly overlapped with N-H expansion groups. The peaks in the area of 3040-3060 cm^{-1} revealed in the spectrum of polymer I and II are assigned to the fragrant C-H stretching vibrations, where as the peaks allocated between 2870-2960 cm^{-1} are ascribed to the broadening of the aliphatic C-H. The confirmation of the imine (C=N) formation was represented between 1630-1640 cm^{-1} [21, 29]. The IR spectra of polymer I and II adsorbed with Pb(II) ions revealed that imine and hydroxyl groups became sharper with less intensity and relocated to less frequent demonstrations that the binding with Pb(II) ions has taken place throughout those sites. All IR data are reviewed in Table 1.

Thermogravimetric Analysis (TGA)

The thermo-grams for chitosan and the two copolymers are measured and shown in Figs 1-3, respectively; where these curves symbolized the major stage of weight loss for the investigated materials.

It is observed that chitosan and the obtained two copolymers afforded an endothermic band at almost 70ºC originated from the evaporation of solvent; vanishing of water was restricted in chitosan itself and may be a methanol solvent for polymer I and II. This peak is called the solvent peak [30]. The second period of the mass defeat is ascribed to the torrid ruin of the polymer materials with an exothermic peak.

Chitosan showed its degradation peak at around 308.5ºC [14] with 43% lack in polymer mass. The first polymer revealed degradation around 318ºC with 56% load lack, while the second polymer experienced a mass loss at 309°C with 71% absence [31].

Apparently, the degradation temperatures of polymers I and II are superior to those of untainted chitosan, which may lead one to conclude that the substance amendment of chitosan by the company of imine assembly in conjunction with phenolic aromatic rings improved its thermal stability, resulting in more rigid structures. Another noticeable feature is the highest degradation temperature of polymer I compared with polymer II, caused by P-hydroxyl group at the aromatic rings which can create extra H-bonding with outlying hydroxyl groups that finally crosslink the polymer template and improve thermal constancy. This kind of hydrogen linking should be conked out first
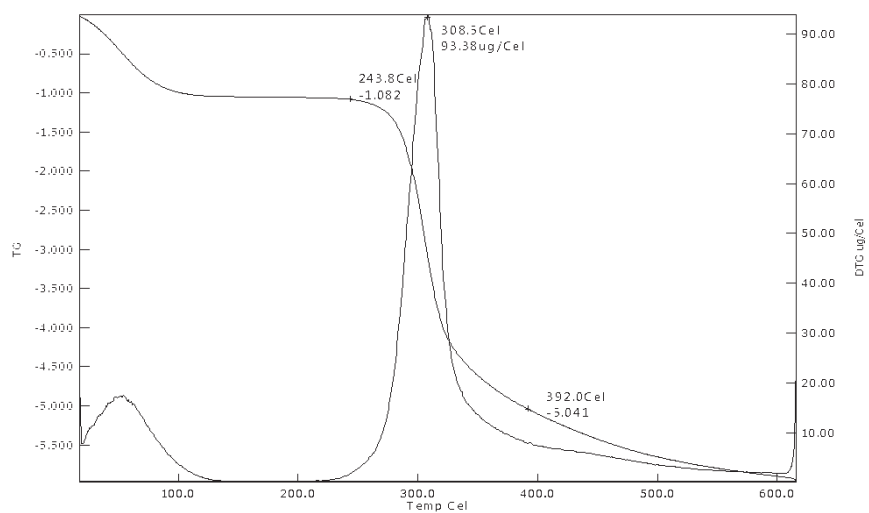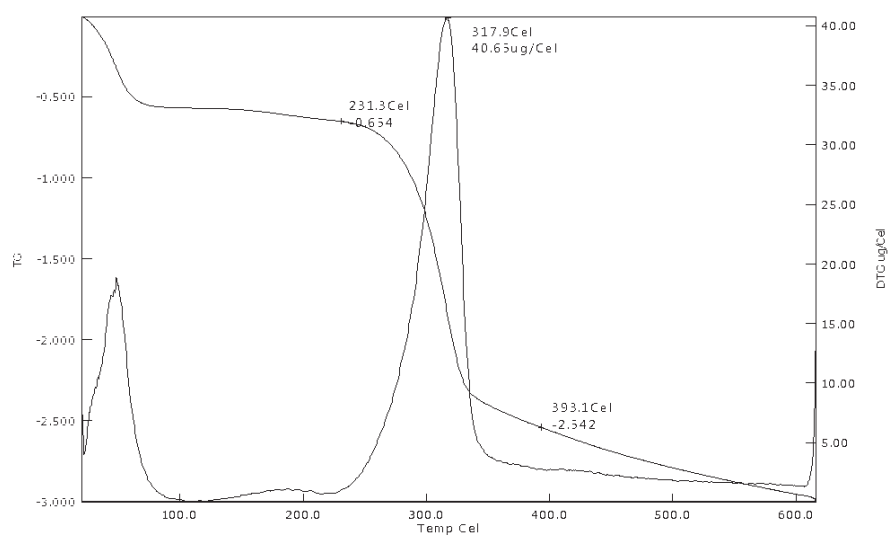
Fig. 1. TG-DTG curve of chitosan.
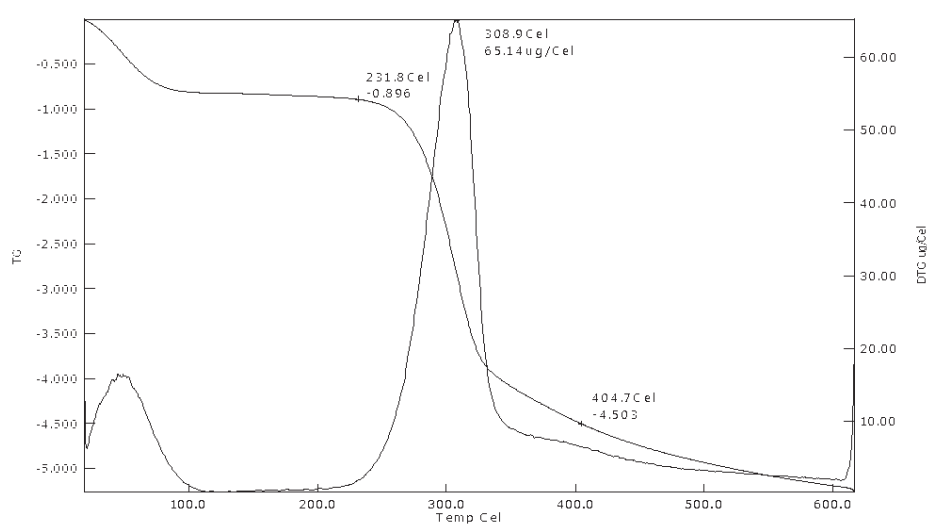

Fig. 2. TG-DTG curve of polymer I.

Fig. 3. TG-DTG curve of polymer II.

before consequent ruin.

This explanation can be better proven through the bigger solvent peak resembled to other materials which appears associated with the phenol hydroxyl group, which may assault polar solvent moieties via H-linking.

Scanning Electron Microscope (SEM)

Chitosan, and unloaded and loaded polymers were investigated through scanning electron microscopy. The SEM image of chitosan indicates numerous pores with average wide distribution of diameters in its surface. The BET surface area of chitosan obtained was discovered to be 0.064 m^2 g^{-1}, whereas the total pore volume was 0.1139 cm^3 g^{-1}.

After chemical alteration, polymers I and II appeared to surprisingly have more cracks and channels which go up the surface range and improve sorption capacity. The BET surface area of polymers I and II were observed to be 7.570 m^2 g^{-1} and 2.704 m^2 g^{-1}, separately, though the aggregate pore volume for polymer I is 0.6438 cm^3 g^{-1} and for polymer II is 0.2721 cm^3 g^{-1}.

SEM images (Fig. 4) demonstrated that the surface morphology of loaded polymers have been adjusted by adsorption of Pb(II) ions from cracked to almost smooth surfaces, which showed that the adsorption of substantial ions is a result of solid chemical connections between polymers' dynamic sites and metals ions [32].

Adsorption of Pb(II) by Polymer I and II

Influence of pH on Pb(II) Uptake

The impact of pH on Pb(II) sorption onto polymers I and II was examined between pH values 3-7 under continuous shaking for an altered contact time run about 24 h at 30ºC with initial concentration of 20 mg L^{-1}.
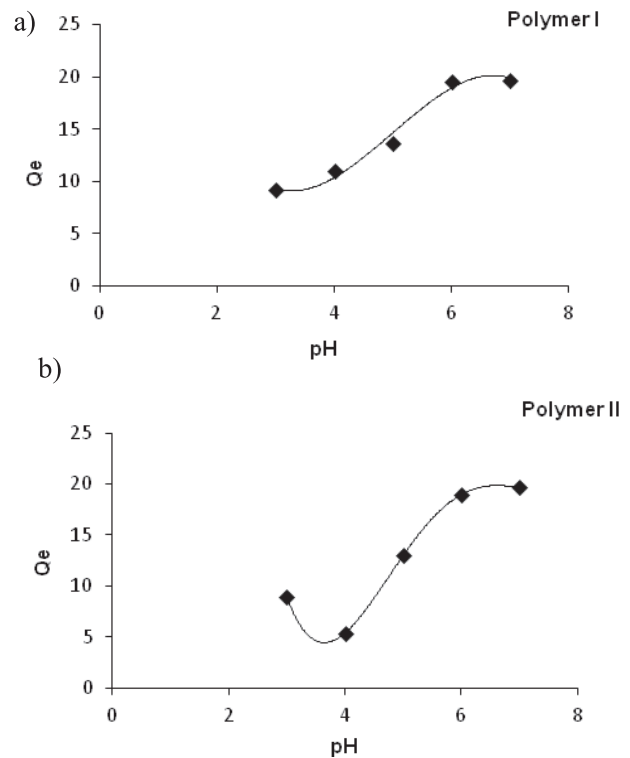
Fig. 5. Effect of pH on Pb(II) by: a) polymer I, b) polymer II (C_0 = 20 mg L^{-1}, T = 30ºC, W = 0.05 g, V = 0.05 L, Time = 24h).

When the pH values increased, hydrolysis of the Pb(II) ions became huge and contended with resin complex figuration. The pH-sorption outlines of polymers I and II would be clearly demonstrated in Fig. 5. The results showed that the uptake of Pb(II) ions is expanding with pH values.

The hydroxyl oxygen atoms, alternately those lone couple of electrons on the nitrogen atoms, are influenced eventually by the solution acidity. On the one hand, as
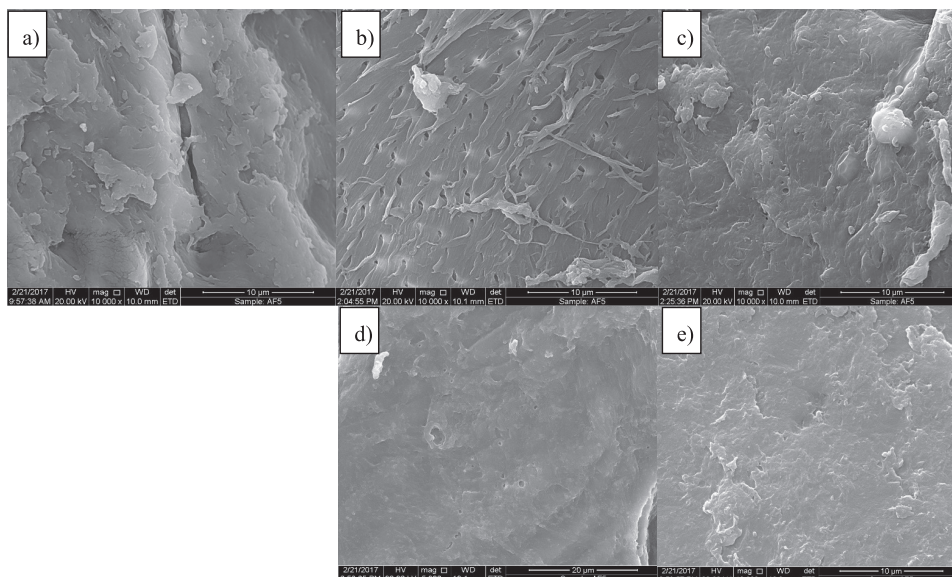
Fig. 4. SEM image of a) chitosan b) polymer I c) polymer II d) polymer I after Pb(II) adsorption, and e) polymer II after Pb(II) adsorption.
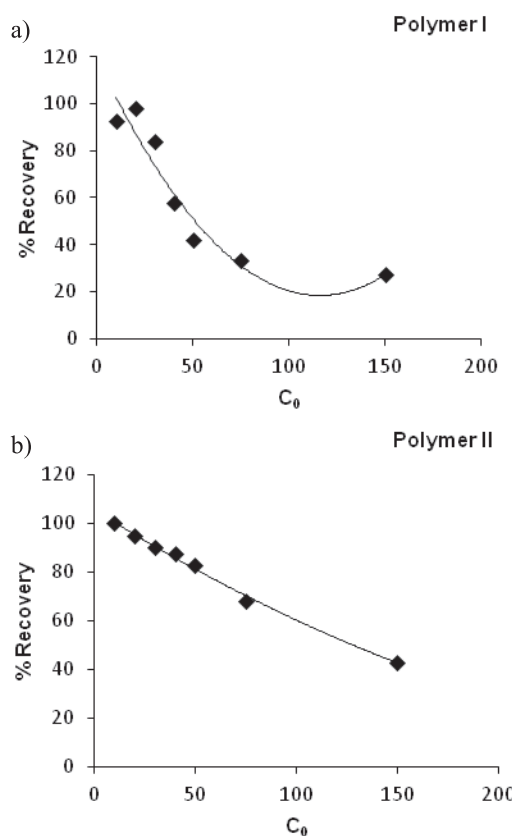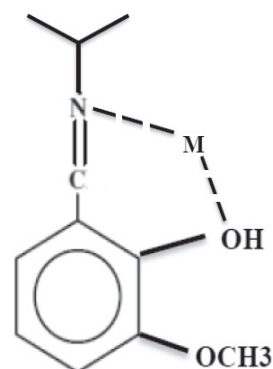
Fig. 6. Effect of initial Pb(II) concentration by: a) polymer I, b) polymer II (T = 30ºC, W = 0.05 g, V = 0.05 L, Time = 24h).

Scheme 3. Possible complexation of Pb(II) ions with polymer II .

concentration is high, the rate of adsorbed metal ions will be considered low. It is clearly shown that polymer II has considerably higher removal effectiveness over polymer I at high concentration. Moreover, the percentage rate for polymer I will be strikingly declined subsequent to C_0 = 30 mg L^{-1}, whereas for polymer II there may be a gradual diminishment upon initial concentration increase.

The above results can be explained depending on the chemical structure of polymer II (Scheme 3). The metal ion can strongly attach via two sites (N,O) at the same time, which certainly affects the obtained complex stability [19].

Influence of Polymer Amount
on Metal Removal

Table 2 illustrates the impact of polymer I and II dosages on the chelation of Pb(II) ions from aqueous solutions. It is clearly noticed that by expanding the adsorbent dosage, the sorption effectiveness of metal ions expands relentlessly. This might be demonstrated eventually by the increase of accessible polymer sites for adsorption of lead ions [33]. Additionally, as the polymer weight increment from 0.01 g to 0.05 g, the exclusion rate expanded drastically, while after expanding from 0.1 g up to 1.0 g, the ascent in uptake proficiency is nearly in a consistent state. Therefore, the ideal polymer dosage is around 0.05 g for polymer I and 0.1 g for polymer II.

Influence of Temperature
on Metal Removal

To examine the contact of heat on the uptake procedure, studies have been carried out at three distinct values (30-50-70ºC) with a Pb(II) concentration of 40 mg L^{-1}. The outcomes demonstrated that the sorption rate of lead ions rose as the temperature increased (Table 3).

Expanding the temperature of solutions will enhance movement of metal ions, and in addition produce the impact of swelling inside the inner structures

pH is raised, the hydroxyl might misplace its proton and also was contrarily charged and the imine gathering solitary combine will be more accessible for chelating with ion species. Therefore, the additional pull of metallic ions on top of the polymer exterior will take place [29].

Alternatively, while solution acidity increased, the adsorption of Pb(II) significantly decreased, which might be assigned to the complexation sites of protonation. The apparent prevalence of hydrogen ions will limit the approach of metal cations to be chelated onto the polymer surface [30]. The findings indicated that there is a concurrence for the pH behavior of chelating resins with N and O chelating sides. Accordingly, the ideal attempted pH domain for adsorption of Pb(II) onto polymer I and II was set at pH 6.

Influence of Metal Ion Concentration
on Removal Capacity

Metal ions removal is a mass relocation process characterized as those metal aggregations at the boundary through those solid/liquid segments. Consequently, the impact of the introductory metal amount has been analyzed eventually by changing its concentration from 10, 20, 40, 50, 75, until 150 mg L^{-1}, keeping other parameters constant (Fig. 6). It is plainly noticeable that though the introductory metal

Table 2. Adsorption of Pb(II) on polymer I and polymer II at different polymer weights.

W (g)	C_0 (mg L^{-1})	Polymer I		Polymer II	
		C_e (mg L^{-1})	R%	C_e (mg L^{-1})	R%
0.01		6.434	67.831	10.799	46.005
0.05		0.429	97.857	1.052	94.738
0.1	20	3.292	83.536	0.797	96.013
0.2		0.630	96.849	0.669	96.655
1.0		0.502	97.49	0.450	97.747

Table 3. Adsorption of Pb(II) on polymer I and polymer II at different temperatures.

T (ºC)	C_0 (mg L^{-1})	Polymer I			Polymer II		
		C_e (mg L^{-1})	Q_e (mg g^{-1})	R%	C_e (mg L^{-1})	Q_e (mg g^{-1})	R%
30		16.859	23.140	57.852	5.021	34.979	87.446
50	40	9.299	30.700	76.752	2.652	37.348	93.37
70		0.630	39.369	98.424	0.669	39.331	98.328
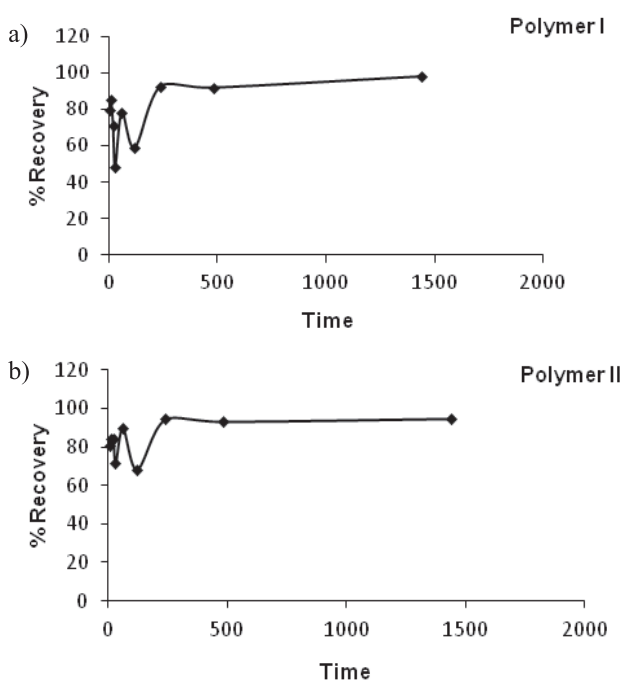
Fig. 7. Effect of contact time on Pb(II) adsorption by: a) polymer I, b) polymer II (C_0 = 20 mg L^{-1}, T = 30ºC, W = 0.05 g, V = 0.05 L)

of polymers I and II [30]. Along these lines, this empowers substantial metal particles to keep on being penetrated. The temperature additionally influenced the chelating rate by changing the molecular interactions and dissolvability. Moreover, the impact of temperature on metal expulsion for polymer I is more recognizable than for polymer II. For polymer I, the sorption rate goes up by 40% after changing the temperature from 30ºC to 70ºC, while for polymer II R% just upgrades by 10%.

Influence of Time on Metal Removal

The impact of adsorption time on Pb(II) ions being taken away has indicated that there is a fast uptake eventually by polymer I and II within the first 5 min to compass around 80%. The rate was higher at the start because of empty binding sites on the adsorbent surface and high electrostatic attraction [23]. Moreover, there was a gradual expansion in the uptake of Pb(II) ions and achieved equilibrium at 4 hours (92-94%), which disclosed the filling of the remaining active sites on the adsorbent surface (Fig. 7).

Table 4. Langmuir, Freundlich, and Temkin model parameters for the adsorption of Pb(II).

	Langmuir model				Freundlich model			Temkin model		
	Q_0 (mg g^{-1})	K_L (L mg^{-1})	R^2	R_L	n	K_f	R^2	B (J mol^{-1})	A (L g^{-1})	R^2
Polymer I	23.3	3.16	0.998	0.015	9.88	16.04	0.373	1.64	38294.01	0.399
Polymer II	66.23	0.27	0.995	0.156	2.78	16.04	0.844	11.416	3.71	0.979

Table 5. Kinetic constants for pseudo first-order and pseudo second-order for the adsorption of Pb(II).

	$(q_e)_{Exp}$	Pseudo first-order			Pseudo second-order		
		$(q_e)_{Cal}$	K_1	R_1^2	$(q_e)_{Cal}$	K_2	R_2^2
Polymer I	19.571	5.124	0.0032	0.458	18.762	0.0029	0.979
Polymer II	18.948	2.556	0.0064	0.423	18.832	0.0064	0.991

Isotherm Studies

Different isotherm models like Langmuir, Freundlich, and Temkin that have been utilized to depict the experimental results. These models were used to best describe the design of the sorption system for the exclusion of ion particles from aqueous media.

In order to check if the Langmuir isotherm model can be connected to the metals sorption onto polymer I and II, a straight line of C_e/q_e against C_e was plotted and the results of Q_0, K_L, and R_1^2 (correlation coefficient) were clearly shown in Table 4. The data demonstrated that Langmuir isotherm model is the best fit for polymer I with R^2 0.9977. The outcomes expressed that the chelation of Pb(II) ions by polymer I is portrayed by a layer with one molecule thick on the external surface of the polymer with equivalent activation energy for each adsorbed ion [24]. Similar conduct was found with polymer II with 0.9946 R^2.

The adsorption coefficient, K_L, which is identified with the noticeable energy of adsorption for Pb(II) ions by polymer I (3.16 L mg^{-1}), is more noteworthy than that of Pb(II) adsorbed by polymer II (0.27 L mg^{-1}). This could imply that the power of sorption is more positive for Pb(II) with polymer II than polymer I, which shows that not every single binding site might be accessible for Pb(II) ions with polymer I, even with larger surface area because of its generally larger hydration energy [34].

Depending upon the impact of the separation factor, R_L, that is represented by Equation 6 on the isotherm profile, it is indicated that the values of R_L are between $0<R_L<1$, which gives a reasonable sign and suggestion that the uptake of Pb(II) ions by the two polymers is constructive progression [32].

Plotting of log qe versus log Ce results in a straight line that represents the linearized Freundlich model. K_f values represent the adsorption limit and 1/n shows the positivity of adsorption [19]. From these qualities introduced in Table 4, one can state that the Pb(II) adsorption process is encouraging – particularly with polymer II.

The Temkin isotherm model can be utilized to clarify the adsorption procedure by polymer II ($R^2 = 0.9788$). This model expects that the adsorption energy diminished after expanding in surface scope with metal ions and the sorption procedure can be delineated by consistent sharing of linking energies up to maximum [35]. Heat of sorption (constant B) is equal
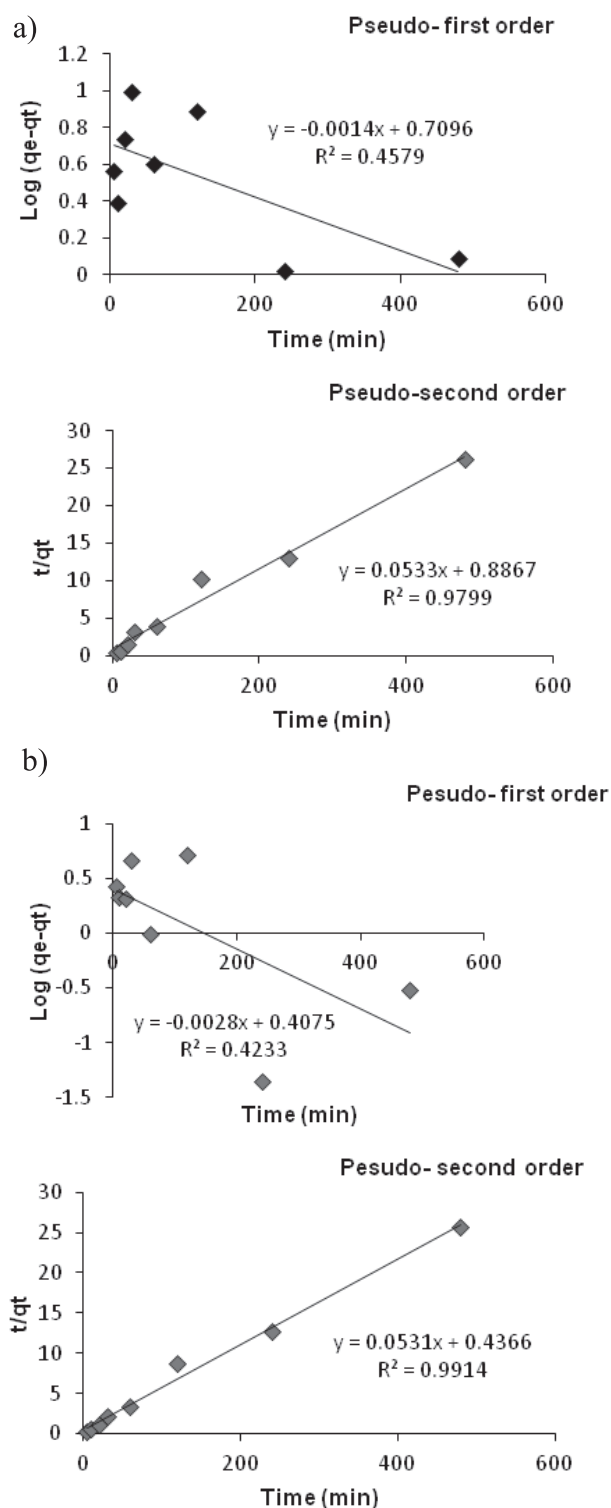
a)

Fig. 8. Pseudo first-order and pseudo second-order kinetics for adsorption of Pb(II) ions onto a) polymer I and b) polymer II.

Table 6. Thermodynamic parameters for the adsorption of Pb(II) for two polymers at different temperatures.

	ΔH (KJ mol⁻¹)	ΔS (J mol⁻¹K⁻¹)	ΔG (KJ mol⁻¹)		
			T = 30	T = 50	T = 70
Polymer I	81.529	268.590	-0.798	-3.209	-11.796
Polymer II	45.742	165.915	-4.892	-7.106	-11.624

to 11.42 Jmol⁻¹, whereas the greatest restricting energy (constant A) is 3.71 L g⁻¹.

It is clear from the given information of the Langmuir model for the studied polymers that the greatest chelation ability of polymer II (66.23 mg g⁻¹) of Pb(II) ions is around three times higher than that of polymer I (23.3 mg g⁻¹), which implies that polymer II has higher chelation capacity than polymer I. This outcome affirms our past clarification with respect to the chemical structure of this shaped complex (see scheme 3).

Kinetic Studies

The impact of time is a vital parameter for exploring the adsorption mechanism by deciding the rate-determining step of the adsorption process. To assess the kinetics and mechanism of the adsorption manner, *pseudo* first-order reaction (equation 8) and *pseudo* second-order reaction (Equation 9) have been utilized to clarify the investigational outcome [29, 32], which is presented in Table 5.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303\, t} \qquad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (9)$$

…where k_1 and k_2 are the rate constants of two models, respectively.

It can be seen from Fig. 8 that the correspondence coefficients from the two models are 0.4579 and

0.9799, individually for polymer I, and 0.4233 and 0.9914 separately for polymer II. Moreover, the calculated values of Q_e on account of the second-order model are near the exploratory quantities for Pb(II) ions. For instance, once the amount of Pb(II) ions was 20 ppm and the temperature was 30ºC, the investigational Q_e,exp values for the two sorbents after 24 h were 19.571 and 18.948 mg g⁻¹, separately. Then again, the calculated values for the two sorbents, $Q_{e,cal}$ by the pseudo second-order, were 18.762 and 18.832 mg g⁻¹, individually.

From the above data, we may propose that the sorption of Pb(II) ions onto chitosan-based polymers clearly follow the pseudo second-order kinetic model, which has been exploited for portraying chemisorption procedure.

Thermodynamic Studies

It can be expressed that the genuine indicator for convenient appliance of sorption progression is Gibbs energy (ΔG), enthalpy (ΔH), and entropy (ΔS). These thermodynamic parameters are resolved through utilizing equations (7, 10) and as given in Table 6. By plotting the diagram of log (Qe/Ce) versus1/T, the estimations of ΔH and ΔS can be accessed from the slopes and intercepts.

$$\Delta G = -RT \ln \left(\frac{Q_e}{C_e} \right) \qquad (10)$$

The positive change of enthalpy is accompanied by absorption of heat, whereas ΔS proposed the

Table 7. Adsorption capacities of Pb(II) ions by various adsorbents.

Adsorbent	Metal ions	Adsorption capacity	Ref.
Chitosan-GLA beads	Pb(II)	14.24 mg g⁻¹	[19]
Tree fern	Pb(II)	39.8 mg g⁻¹	[37]
Chitosan derivatives(notedasCS₈PA-GLA and CS₁₁PA-GLA)	Pb(II)	2.23 mg g⁻¹ for CS₈PA-GLA 2.29 mg g⁻¹for CS₁₁PA-GLA	[38]
Oryza sativa L. husk	Pb(II)	8.6 mg g⁻¹	[39]
Sawdust	Pb(II)	3.19 mg g⁻¹	[40]
activated carbon developed from Apricot stone	Pb(II)	21.38 mg g⁻¹	[41]
Chitosan- Vanillin Schiff base (polymer I)	Pb(II)	23.3 mg g⁻¹	This study
Chitosan-O-vanillin Schiff base (polymer II)	Pb(II)	66.23 mg g⁻¹	This study

expanded randomness at the boundary phase through the adsorption of lead ions on top of polymers I and II. The negative estimations of ∆G suggested the spontaneous behavior of the procedure of sorption. Besides, the decrease in ∆G values with expanding temperature demonstrated that sorption is more natural and unstructured at higher temperatures [36].

As seen in Table 7, the adsorption limit of Pb(II) ions of the obtained two polymers (I, II) is bigger than other chitosan subsidiaries and better over an extensive variety of adsorbents written in literature showing high potential as a proficient substance for the expulsion of harmful species from polluted liquid sources.

Conclusions

New Schiff-base materials were synthesized via condensation reaction of chitosan and two vanillin derivatives. The structure of the obtained polymers was confirmed by various spectroscopic techniques with enhanced thermal stability and surface area. The adsorption process followed Langmuir for polymer I and Langmuir and Temkin isotherm models for polymer II, suggesting a homogeneous sorption process. The kinetics followed the pseudo second-order prototype disclosing that the adsorption is chemisorption. The removal process was found to be spontaneous and endothermic in nature, with the highest chelation capacity equal to 23.3 mg g^{-1} for polymer I and 66.23 mg g^{-1} for polymer II. The above results may indicate that our investigated polymers have high potential as an efficient adsorbent for the removal of toxic metal ions from wastewater samples.

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Conflict of Interest

The authors declare no conflict of interest.

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