Adsorption of lead (II) from aqueous solution by using polysiloxane surfaces modified with ortho-, meta-, or para-nitrophenyl moieties

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ABSTRACT

The efficiency of polysiloxane surfaces modified with ortho, meta and para-nitrophenyl moieties as a low cost adsorbent for removing lead ions from aqueous solution has been investigated in this paper. Batch experiments were conducted to study the effects of the main parameters such as contact time, initial concentration of Pb(II), adsorbent dose, solution pH, and temperature on the adsorption of Pb(II) by polysiloxane surfaces. The maximum removal of lead(II) is found to be 97 % at pH 8 for (Si-p-NO$_2$), 95.9 % for(Si-o-NO$_2$) and 93.7% for (Si-m-NO$_2$) initial Pb(II) concentration of 10 mg·L^{-1}, adsorbent dose of 1 g·L^{-1}, agitation speed of 200 rpm, and temperature of 25 °C. The same study was done for the effect of dose (5 mg) and showed 99 % removal using the (Si-p-NO$_2$).Dynamics of the adsorption process were studied, and the values of rate constants of pseudofirst-order and pseudosecond-order were calculated. Equilibrium isotherms for the adsorption of Pb(II) were analyzed by the Langmuir and Freundlich isotherm models. The Langmuir isotherm model was found to represent better the data of Pb(II) sorption onto polysiloxane surfaces. Different thermodynamic parameters, namely, changes in standard Gibbs energy, enthalpy, and entropy, were also evaluated from the temperature dependence, and the results suggest that the adsorption reaction is non-spontaneous and endothermic in nature. The prepared compound was characterized using solid ^{13}C-NMR, TGA, FT-IR, UV-vis and SEM.

Keywords: groundwater, adsorption, isotherm, desorption, heavy metals, kinetics.

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INTRODUCTION

Environmental contamination with heavy metal ions is a considerable problem owing to their tendency to accumulate in living organisms and toxicities in relatively low concentration [1]. Many methods, such as reduction and precipitation, ion exchange, reverse osmosis and adsorption, have been proposed to remove heavy metal ions from wastewater [2]. Among these technologies, many researches concentrated on metal ion recovery using appropriate chelate polymer surfaces, because they are reusable, easy handing and have higher adsorption capacities, efficiencies as well as high selectivity to some metal ions [3]. Hence, numerous chelating resins have been prepared through the polymerization of conventional chelating monomers, such as acrylic acid [4], allylthiourea [5], vinyl pyrrolidone [6], and vinyl imidazole [7]. Additionally modification of a synthetic polymer [8] or a natural polymer matrix [9] by functionlization reactions has also been used to form a chelating polymer. Around the vinyl monomers, glycidyl methacrylate (GMA) is a commercial industrial material, which is cheaper than any other vinyl monomers possessing an epoxy ring in the side chain. Thus, numerous chelating resins have been successfully prepared via an epoxy group reaction of poly(glycidyl methacrylate) with amines. In addition, glycine is a low-

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priced amino acid that possesses an amino and a carboxyl groups to share electron pairs with a metal ion [10]. In general, Heavy metals toxicity depends on a number of factors. These are, the total dose absorbed, speciation, the route of exposure and the age of person. For example, young children are more susceptible to the effects of lead exposure because their organs absorb several times the percent ingested compared with adults [11].

Lead contamination in drinking water is a major source of concern due to its detrimental effect on human health when ingested, its pollution results from textile dyeing, ceramic and glass industries, petroleum refining, battery manufacture and mining operations.

Polysiloxanes are one of the most important organosilicon polymers that are used in polymer chemistry. The silanolSiO(CH$_3$)$_2$ is the key functional group for the synthesis of these polymers. Silicon (Si) is a semi-metallic element. It makes up 27% of the earth's crust by mass, and it is the second in abundance in the world (after oxygen). Silicon plays an important role in industry. Such as, solar energy and computers.

Adsorption process is usually studied through graph known as adsorption isotherm. That is the amount of the adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. Analysis of the isotherm data is important to develop an equation, which accurately represents the observed results. The most common isotherms that are applied in solid/liquid systems are the theoretical equilibrium isotherm models, which are Langmuir and Freundlich isotherms [12].

In this work, a chelating polysiloxane surfaces derived from carbaldehyde derivatives and 3-aminopropyl trimethoxysilane were synthesized and then functionalized with ortho-,meta- or para-nitrophenyl moieties for the removal of Pb(II) from an aqueous solution. The effects of solution conditions including pH value, temperature, contact time, adsorbent dose and metal ion concentration, on the adsorption behaviour were investigated. Also, the adsorption isotherm models, kinetics and thermodynamics parameters were studied.

MATERIALS AND METHODS

2. Experimental Part
2.1 Chemical Materials
All of the chemical substances that are employed in this work were of analytical grade and are used without any further purification. The required chemicals involve: silica gel (E. Merck) with particle size in the range of (70–230) mesh, and a median pore diameter of 60 Å, was activated for 24 hours before use by heating it at 150˚C, 3-aminopropyltrimethoxysilane that is purchased from Janssen Chimica, ethanol, toluene, SnCl$_2$, dichloromethane, acetonitrile, dry diethyl ether, HCl solution, NaOH solution, andPb(NO$_3$)$_2$ all with pure and analytical gardes.

2.2 Instrumentations
The required instrumentations for this research include the following: shaking water bath (DaihanLabtech, 20 to 250 rpm Digital Speed Control), pH meter (model: 3510, JENWAY), glassware, thermometer, AAS instrument, UV spectrometry, (model: UV-1601, SHIMADZU), IR Spectrometer (Nicolet iS5, iD3 ATR, Thermo Scientific), TGA (Q50 V20.10 Build 36 instrument at a heating rate of 10˚C.min^{-1} and in N$_2$ gaseous atmosphere).

2.3. Preperation of polysiloxane surfaces modified with ortho-, meta-, or para-nitrophenyl moieties
The preparation of porous materials as adsorbents has generated considerable interest, because of their regular pore structure, unique large specific surface area and well-modified surface properties. In addition, these substances can be regenerated for many times after adsorption saturation [13].

This research involves the modification of porous SiO$_2$ with functional *ortho-*, *meta-* or *para*-nitrophenyl receptors using heterogeneous route that involves reaction of carbaldehyde derivatives with 3-aminopropyl trimethoxysilane prior to immobilization on the support [14].

In general, porous silicas are usually modified by post-synthesis or one-pot synthesis. In both methods, the organic functional groups are used. The aptitude of the resulting attached chelate is mainly owed to the presence of sulfur, oxygen or nitrogen donor atoms [15].

The first step in the preparation of (SiNH$_2$) was the reaction between the silylating agent (3-aminopropyltrimethoxysilane) and the silanol groups on the silica surface. Such that, 25 g of activated silica gel (SiG) suspended in 150 mL of toluene was refluxed and mechanically stirred under nitrogen atmosphere for 3 hours. Then, 10 mL of aminopropyltrimethoxysilane was added dropwise. After that, 1 g of SnCl$_2$ was used as catalyst and the mixture was kept under reflux for 48 hours.

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The resulting solid matrix was filtered, washed with toluene and ethanol, then, it was soxhlet extracted with a (1:1) mixture of ethanol and dichloromethane for 24 h in order to remove the silylating reagent residue. The obtained immobilized silica gel was dried in vacuum at 20°C.

A mixture of 10 g of 3-aminopropylsilica (SiNH$_2$) with 3 g of each of *ortho*-nitroacetophenone, meta-nitroacetophenone or para- nitroacetophenone respectively in 100 mL of dry diethyl ether was stirred at room temperature for 24 hours. This process results in the formation of the three required adsorbents including (Si-o-NO$_2$), (Si-m-NO$_2$) and (Si-p-NO$_2$) respectively. After being filtered, the solid products were soxhlet and extracted with acetonitrile, methanol and dichloromethane for 15 hours. Then, these products were dried under vacuum at 70˚C over 40 hours.The synthesis procedures are shown in Fig. 1.
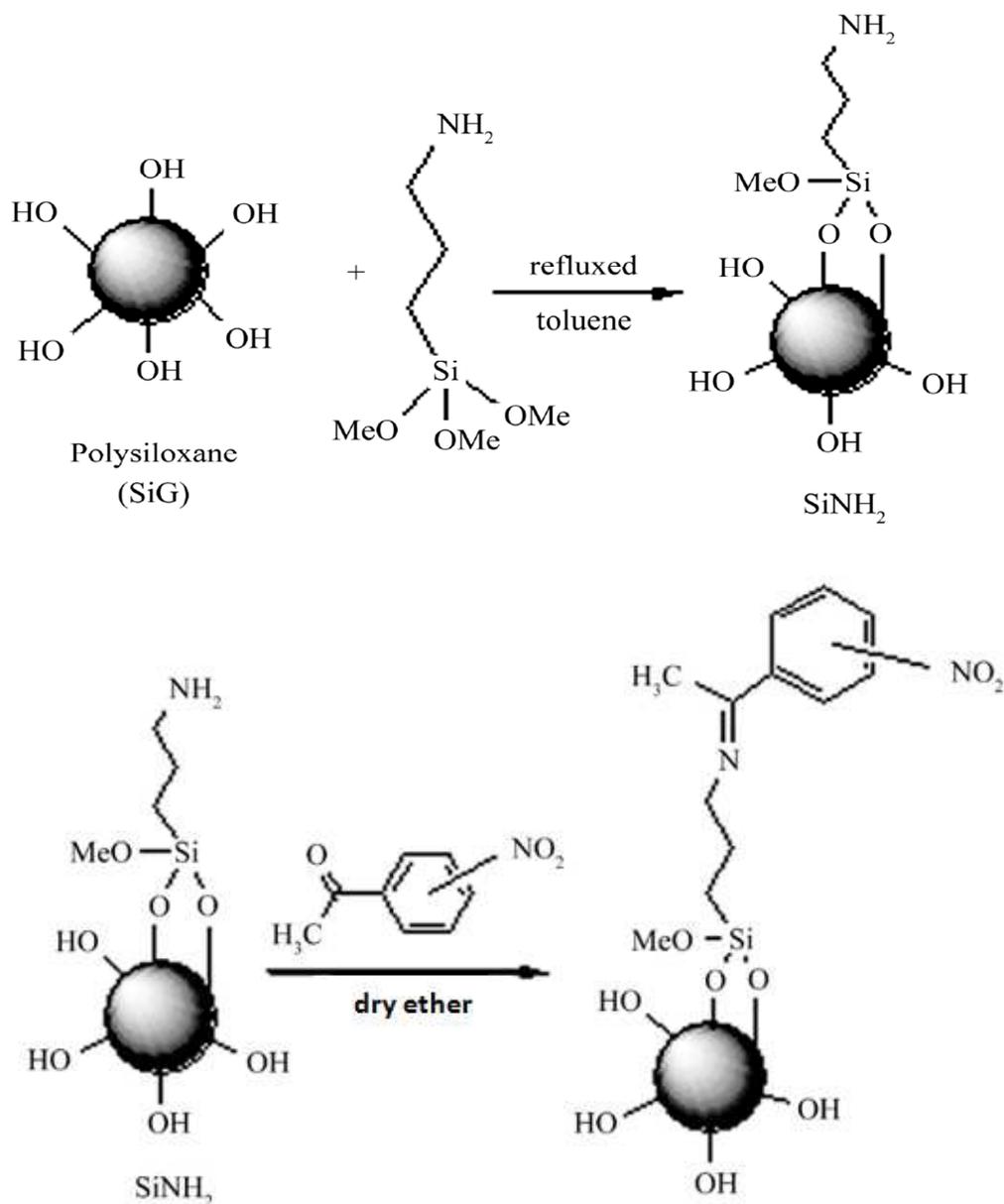
Figure.1: The synthesis route of modified nitrophenyl-substituted silicas

2.4 Preparation of Standard Solutions
Lead nitrate Pb(NO$_3$)$_2$ (331.2098 g/mol) was used to prepare several calibration standard solutions of Pb(II).

The prepared initial concentrations of lead ions are: 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 ppm. The standard solutions of calibration are used in batch experiments in order to study the effect of different factors such as; time,

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pH and temperature on each adsorption process. And hence to know what are theoptimum conditions for having effectient adsorption of Pb(II) on ortho-, meta-, or para-nitrophenylsilicas.

By using AAS measurements and depending upon the resulting calibration curves, the concentrations of lead ions in the used ground water (without any treatment) equal zero.

2.5.Batch Experiments
A mixture of 1 mg sample of (Si-o-NO$_2$), (Si-m-NO$_2$) or (Si-p-NO$_2$) adsorbent with 7 mL of distilled water containing known concentration of Pb(II) toxic metal was shaken.

The effect of solution conditions including; contact time, temperature, pH value, the amount of modified polymer and the concentration of toxic metal ion was discussed.

Atomic absorption measurements were used for the filtrate mixture of each sample in order to determine the remained amount of the toxic metal ion and hence investigating the extent of the adsorption efficiency.

2.5.1 Effect of Contact Time
The adsorption of toxic heavy metals on each adsorbent was studied as a function of shaking time at 20 $^{\circ}$C. A sample of 10 ppm of standard solutions at pH value equals 6 was taken in a volumetric flask and shaken with 1 mg of an adsorbent. At the end of time intervals (1 minute to 30 hours), each sample was filtered off and the amount of each adsorbate is determined using AAS apparatus.

2.5.2 Effect of pH
The effect of pH value on the adsorption behavior was investigated using different pH values ranging from 2 to 12. The pH value was adjusted using roughly concentrations of 0.1 M HCl and 0.1 M NaOH solutions.

A 1 mg of an adsorbent sample was added to 7 mL of the prepared standard solution with a concentration of 10 ppm. The prepared mixtures were placed in shaking water bath at constant temperature (20°C), with considering into account the resulting optimum time for each previous adsorption process.

2.5.3 Effect of Temperature
To study the effect of temperature on each adsorption process. A 1 mg of the adsorbent was added to 7 mL of the standard solution of Pb(II) with a concentration of 10 ppm at the optimum value of pH.

Each mixture was placed in shaking water bath at desired temperature (the range was 5 to 80°C) for optimum contact time. At the end of time intervals, each sample is filtered off , and the amount of each adsorbate is determined using AAS instrument.

2.5.4 Effect of Adsorbent Dose
In order to find out the optimum amount of adsorbent that is required for the adsorption of Pb(II) on modified silicas, A (1, 2, 3, 4 or 5 mg) of the modified silica was added to five vials containing 7 mL of 10 ppm of toxic metal standard solution. The mixtures were placed in shaking water bath at the optimum temperature, pH and time.

Then, the concentration of each toxic ion in the filtrate is measured using AAS instrument.

2.5.5 Effect of Adsorbate Concentration
To find the optimum concentration of cadmium, nickel and lead metal ions. The resulting optimum mass of each adsorbent was added to a number of vials, each contains 7 mL of different standard concentrations ofPb(II) . Such that, all optimum condition of pH, contact time, temperature and the amount of adsorbent must be taken in consideration. After that, the concentration of these toxic ions in each filtrate is measured using AAS apparatus.

<div style="text-align:center">

RESULTS AND DISCUSSION

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3.1 Materials Characterization
All material characterization like SEM, TGA, FT-IR, UV-Vis, BET have been done and published previously [14].

3.2 Adsorption Results
This study aimed to use the synthesized modified silicas for removing heavy metal ions from groundwater, and hence to compare the adsorption efficiency of these polymers. This process is done by studying the adsorption

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capacities for nitrophenyl substituted silica towards lead adsorbates. The extracted concentrations of heavy metal ions were determined using atomic absorption measurements.

After finding the remaining concentrations, the percentage removal for each adsorption process must be determined. This value is defined as the ratio of difference in the adsorbate concentration before and after adsorption ($C_I - C_F$), to the initial concentration of the metal ion in the aqueous solution (C_I), as shown in the following equation :

$$\% \ of \ Removal = \frac{C_I - C_F}{C_I} * 100\% \qquad (1)$$

Where;
C_I and C_F are the initial and finial concentrations of heavy metal ion in groundwater, respectively (ppm).

The adsorption processes are compared according to using the same adsorbent with lead ions or using the same heavy metal with different adsorbents including (Si-o-NO$_2$), (Si-m-NO$_2$) or (Si-p-NO$_2$).

The effect of solution conditions for the adsorption of lead ions on (Si-o-NO$_2$), (Si-m-NO$_2$) or (Si-p-NO$_2$) adsorbents is determined. As the adsorbent is changed, the adsorption dependence on the polymer nature is investigated.

3.2.1 Effect of Contact Time
To establish an optimum contact time between lead ions and each of the adsorbents , adsorption capacities of Pb(II) were measured as a function of time (Figure 2).

As shown in this plot, the highest percent of Pb(II) removal was for (Si-p-NO$_2$) after only 1 minute of shaking, this percentage is 97.01%. While when (Si-o-NO$_2$) is used for removing lead metal ions , the percentage removal is 94.73% and the optimum contact time is after 30 minutes. The removal of Pb(II) from groundwater using (Si-m-NO$_2$) has a 90.86% as percent of metal ion removal and a optimum contact time of 5 minutes. For the three synthesized adsorbents, the remaining concentration of the lead ions after each optimum contact time becomes approximately constant. The extremely high percents of Pb(II) removal are due to the very high availability of vacant sites on the adsorbent external surface.
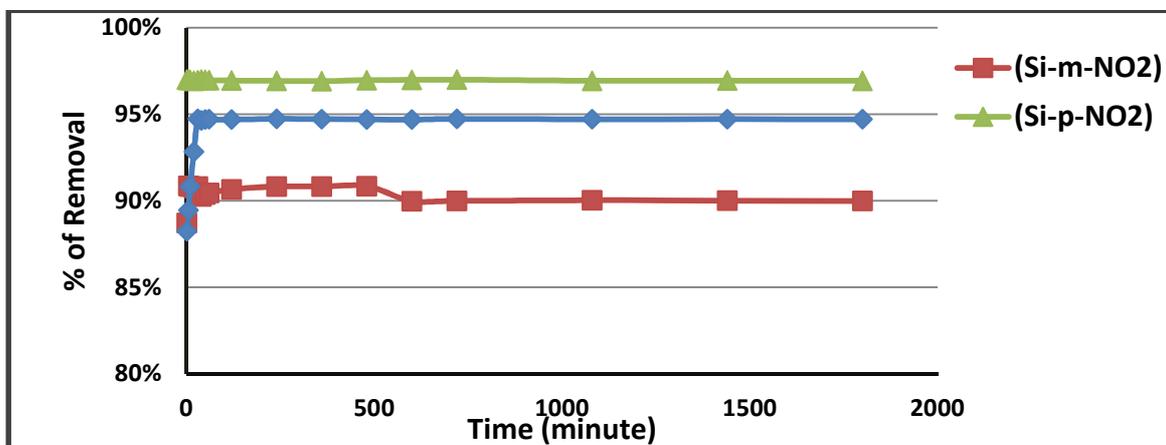
Fig. 2 Effect of contact time on the adsorption of Pb(II) on ortho-, meta- or para-nitrophenylsilicas (C$_I$ = 10 ppm, adsorbent dose = 1 mg, volume of groundwater = 7 mL, pH = 6, temperature = 20 °C)

3..2.2 Effect of pH Value
(Figure 3) showed the effect of pH value on Pb(II) removal efficiency on different adsorbents. These studies were conducted at the optimum contact times for (Si-o-NO$_2$), (Si-m-NO$_2$) and (Si-p-NO$_2$) with varying the pH value of the solution.

For (Si-p-NO$_2$) matrix, the percentage adsorption increases with pH to attain a maximum at pH 8, and thereafter it decreases with further increase in the value of pH. This adsorbent has the maximum percent of Pb(II) removal of 97.14% compared with that for (Si-o-NO$_2$) that equals 95.89% and (Si-m-NO$_2$) that equals 93.71%.

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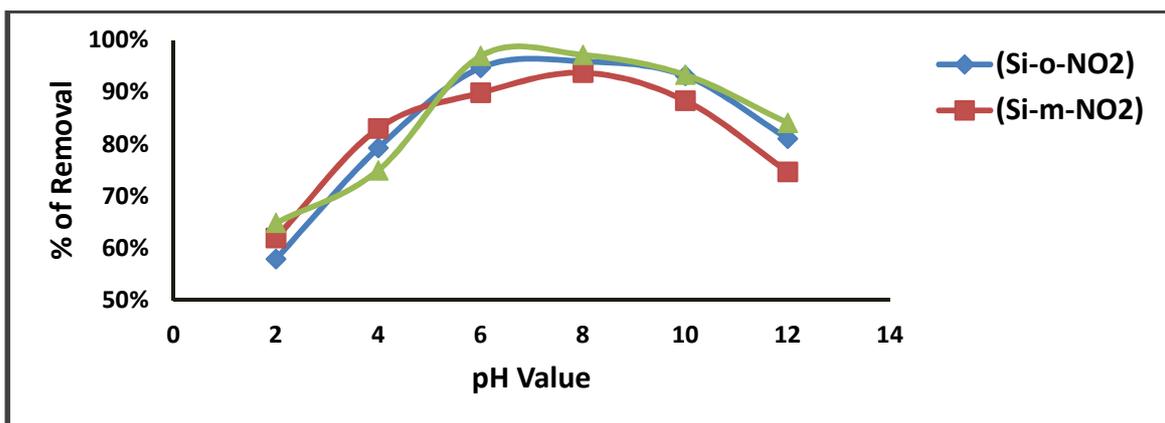
Figure 3: Effect of pH value on the adsorption of Pb(II) on ortho-, meta- or para-nitrophenylsilicas (C_I = 10 ppm, adsorbent dose = 1 mg, volume of groundwater = 7 mL, temperature = 20 °C)

Also, the effect of pH value on the adsorption efficiency of (Si-p-NO$_2$) and (Si-m-NO$_2$) polymers increases with pH until reaching a maximum at pH 8 and pH 7 respectively, and thereafter the percentage removal decreases with further increase in pH value.

The increase in metal ion removal as the pH increases can be due to decrease in competition between proton and lead ions for the same functional groups and also by the decrease in the positive surface charge, which results in a lower electrostatic repulsion between the surface and lead ions. While, the decreasing behavior of the percent of Pb(II) removal after each optimum pH for the three synthesized adsorbents is probably due to the formation of a soluble hydroxy complexes which lowers the adsorption efficiency to uptake lead ions from groundwater.

3.2.3 Effect of Temperature
To study the effect of temperature on the adsorption of Pb(II) using ortho-, meta- and para nitrophenylsilicas. The optimum conditions of contact time and pH value must be taken in consideration. In general, the adsorption efficiency becomes very low at high temperature values.
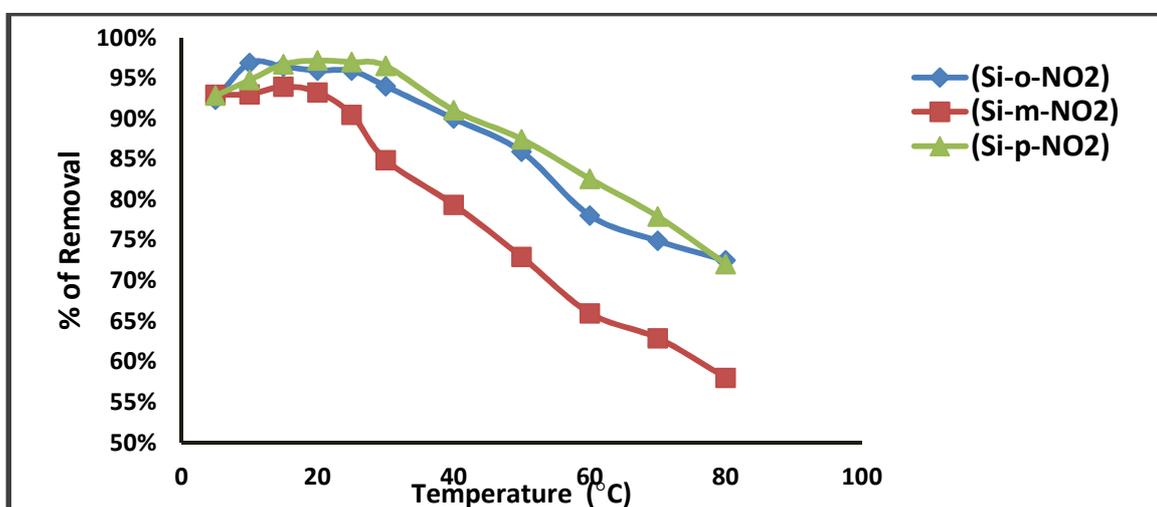
Figure 4: Effect of temperature on the adsorption of Pb(II) on ortho-, meta- or para-nitrophenylsilicas (C_I = 10 ppm, adsorbent dose = 1 mg, volume of groundwater = 7 mL)

As shown in (Figure 4), the adsorption oflead ions using the three different adsorbents including (Si-o-NO$_2$), (Si-m-NO$_2$) and (Si-p-NO$_2$) has been found to increase with an increase in temperature until reaching a maximum at 10 °C, 15°C and 20 °C respectively, and thereafter the percentage removal decreases with further heating. Such that, the percentages removal at the optimum temperature value are 96.89% for (Si-o-NO$_2$), 93.98% for (Si-m-NO$_2$) and 97.19% for (Si-p-NO$_2$).

In general, low temperatures of the solution enhance the complexation ability between lead ions and each of the matrix polymers and hence increase the adsorption efficiency.

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3.2.4 Effect of Adsorbent Dose
The experimental results for adsorptive removal oflead ions withrespect to each dose of (Si-o-NO$_2$), (Si-m-NO$_2$) and (Si-p-NO$_2$) adsorbents are shown in (Figure 5)over the range of 1 mg to 5 mg at the optimum values of time, pH and temperature.
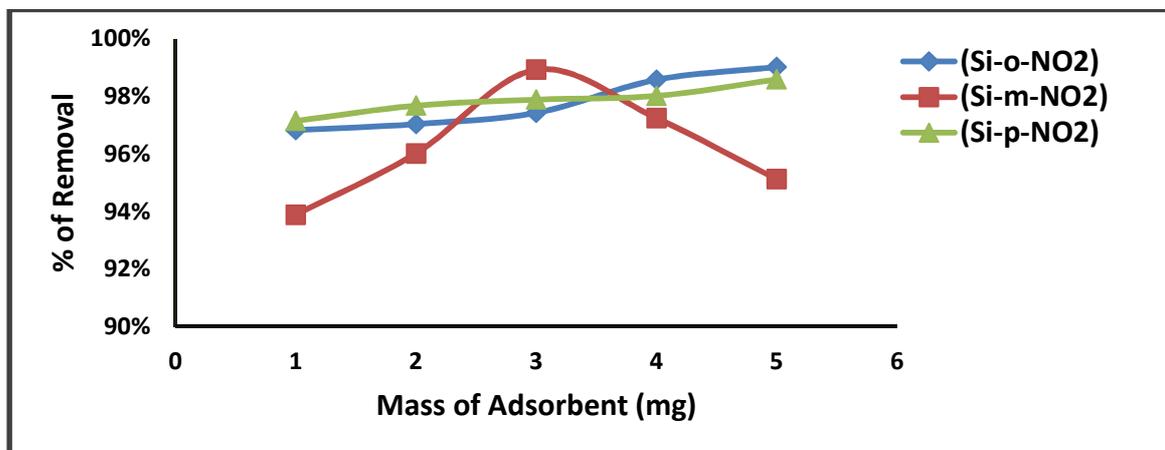
Figure 5: Effect of adsorbent dose on the adsorption of Pb(II) on ortho-, meta- or para-nitrophenylsilicas (C_I = 10 ppm, volume of groundwater = 7 mL)

The maximum percent of Pb(II) removal was 99.02% with using 5 mg of (Si-o-NO$_2$), such that, this polymer showed an increase in percentage removal with increasing the adsorbent dose. Also, the same relation between adsorption efficiency and dosage effect is observed for (Si-p-NO$_2$) with 5 mg amount of dose and 98.59% as percentage removal.

While (Si-m-NO$_2$) showed a different effect of adsorbent dose, such that, the maximum observed percent of Pb(II) removal was 98.59% with 3 mg dose.

The rapidly increased percentage removal of the metal ion with increase in the adsorbent dose is due to the greater availability of the exchangeable sites on the adsorbent surface area.

3.2.5 Effect of Adsorbate Concentration
The effect of the initial concentration of Pb(II) on the percentage removal of heavy metals using the three prepared adsorbents is shown in (Figure 6).
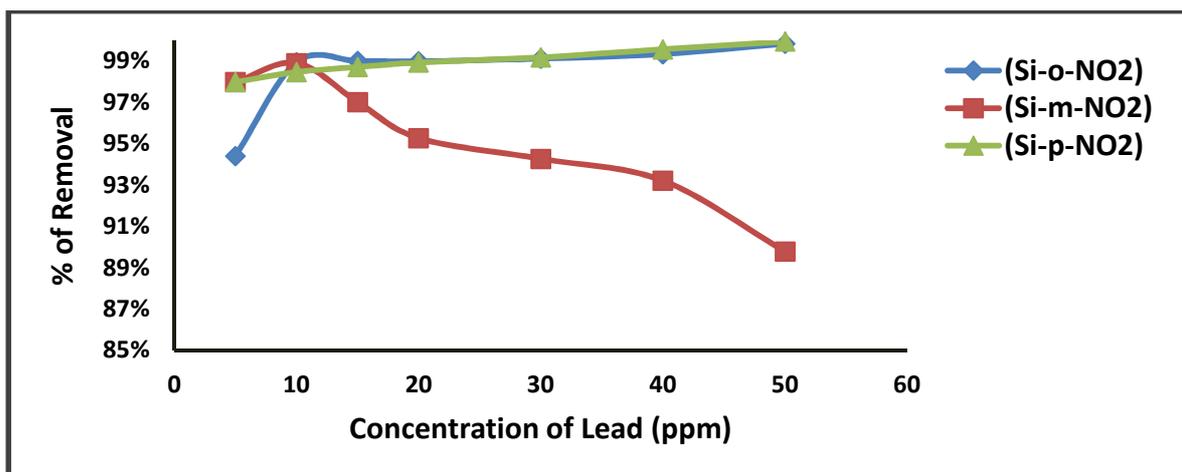
Figure 6: Effect of adsorbate concentration on the adsorption of Pb(II) on ortho-, meta- or para-nitrophenylsilicas (volume of groundwater = 7 mL)

As shown in this plot. For para-nitrophenyl silica, the adsorptive removal increases with the increase in the initial heavy metal concentration. The maximum percent of Pb(II) removal was 99.95% for (Si-p-NO$_2$) by using 50 ppm lead concentration. While the observed initial concentration for having maximum adsorption efficiency for (Si-o-

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NO_2) and (Si-m-NO_2) polymers is 50 ppm, and 10 ppm with percent of Pb(II) removal of 99.84% and 98.91% respectively.

3.3 Investigation of Adsorption Parameters
In order to investigate the adsorption efficiency for the adsorption of Pb(II) onto each of the synthesized polymers. The effect of solution conditions on the adsorption process were studied. These conditions involve the effect of shaking time, pH value, temperature, adsorbent dose and the concentration of adsorbate.

The best equilibrium isotherm model for each adsorption process was investigated according to the value of the correlation coefficient of Langmuir and Freundlich models. The kinetics of adsorption were also investigated using pseudo first-order, pseudo second-order and intra-particle diffusion kinetic models. In addition, Van't Hoff plot for each adsorption process was investigated in order to determine the values of enthalpy change and entropy change, and hence determining if the adsorption is spontaneous ($\Delta S > 0$) or not ($\Delta S < 0$), and if it is exothermic ($\Delta H < 0$) or endothermic one ($\Delta H > 0$).

Finally the effect of adsorbent recovery on the percent of heavy metal ion removal was investigated, and hence the adsorption process with the best regeneration is determined.

3.3.1Langmuir Adsorption Isotherm
This isotherm is called the ideal localized monolayer model, it was developed to represent chemisorption. Langmuir isotherm is based on the following assumptions. These are, adsorption is limited to monolayer coverage, such that; the adsorbed molecule cannot migrate across the surface or interact with neighboring molecules. Also, the surface of the adsorbent is uniform. This means that all the adsorption sites are equivalent in energy [16].

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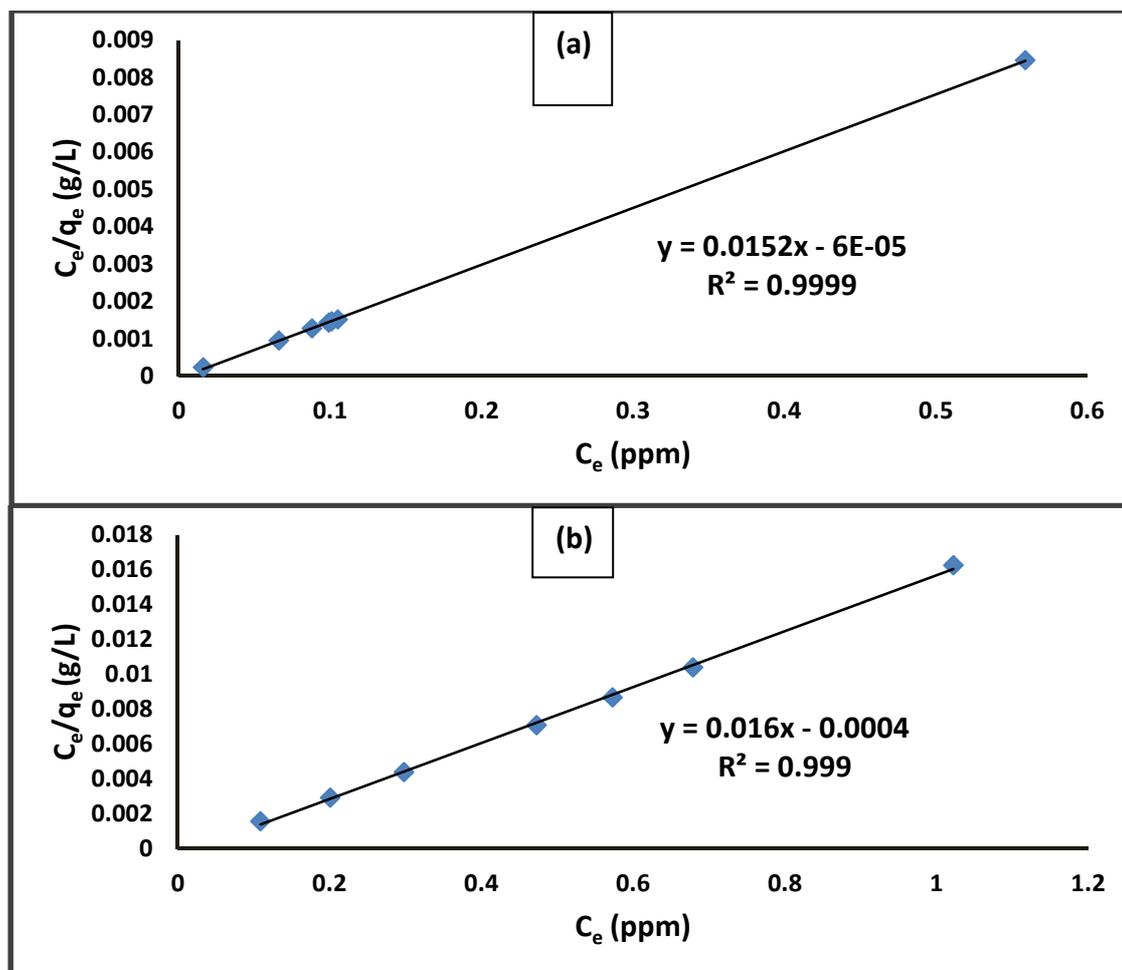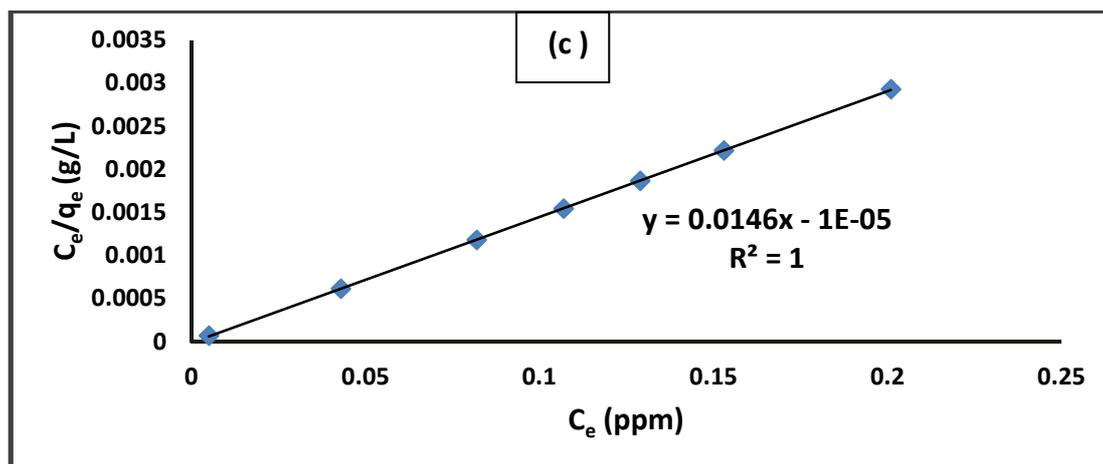
Figure 7: Langmuir plot for the adsorption of Pb(II) on a) (Si-o-NO₂), b) (Si-m-NO₂) and c) (Si-p-NO₂) ; (time = 50 minute, pH = 5, temperature = 25 °C, adsorbent dose = 4 mg, volume = 7 mL)

The Langmuir equation relates the coverage of molecules on a solid surface to the concentration of a medium above the solid surface at a fixed temperature. This equation can be written as:

$$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{1}{Q_o}C_e \qquad (2)$$

Where;
C_e is the equilibrium concentration of the adsorbate (mg/L).
b is the Langmuir affinity constant (L/mg).
Q_o is the adsorption capacity at equilibrium (mg/g).

q_e is the amount of adsorbate per unit mass of adsorbent (mg/g), and it can be calculated using the following relation:

$$q_e = (C_o - C_e)\frac{V}{m} \qquad (3)$$

Where;
C_o is the initial concentration of the adsorbate (mg/L).
V is the volume of the solution (L).
m is the mass of the adsorbent (g).

$(C_o - C_e)$ represents the adsorbed amount.
A graph of (C_e/q_e) values versus C_e is used in order to find the Langmuir parameters. Which are, $(1/bQ_o)$ as y-intercept and $(1/Q_o)$ as slope (Fig. 7) [17].

3.3.2 Freundlich Adsorption Isotherm
This isotherm was interpreted as adsorption to surfaces supporting sites of varied affinities or to heterogeneous surfaces. Freundlich isotherm assumed that stronger binding sites are occupied first, such that; the binding strength decreases with increasing degree of site occupation.

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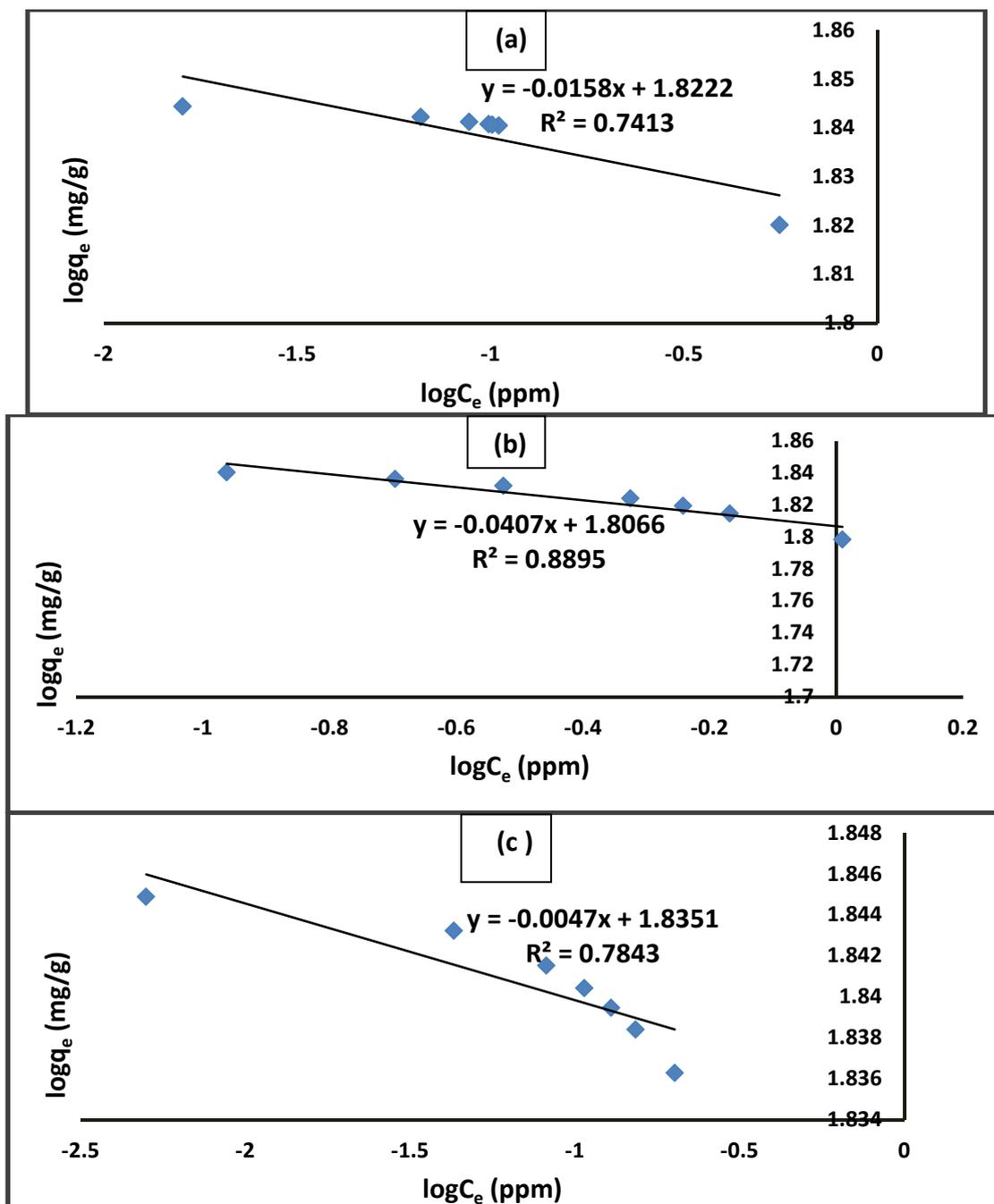
Figure 8: Freundlich plot for the adsorption of Pb(II) on a) (Si-o-NO₂), b) (Si-m-NO₂) and c) (Si-p-NO₂). (time = 50 minute, pH = 5, temperature = 25 °C, adsorbent dose = 4 mg, volume = 7 mL)

According to this statement, the adsorbed mass per mass of adsorbent can be expressed by the following equation [18].

Table 1: The parameters of Langmuir and Freundlich isotherms for the adsorption of Pb(II) on (Si-o-NO₂), (Si-m-NO₂) and (Si-p-NO₂).

Adsorbents	Adsorption of Pb(II)			
	Equilibrium Isotherm Models			
	Langmuir Isotherm		Freundlich Isotherm	
	Q_o(mg/g)	b (L/mg)	K_F (mg/g)	n (g/L)
Si-o-NO₂	65.789	-	66.405	-63.291
Si-m-NO₂	62.500	-40.000	64.062	-24.570
Si-p-NO₂	68.493	-	68.407	-212.766

$$logq_e = logK_F + \frac{1}{n}logC_e \qquad\qquad (4)$$

Where;

K_F is the Freundlich constant related to adsorption capacity(mg/g).

n is the heterogeneity coefficient that gives an indication of how favorable the adsorption process (g/L).

A plot of $\log q_e$ values versus $\log C_e$ is used to find Freundlich parameters. Which are, $\log K_F$ as y-intercept and (1/n) as a slope [19].

In order to determine the best adsorption isotherm for the adsorption of lead ions onto ortho-, meta-, or para-nitrophenylsilicas, the observed data were fitted to Langmuir and Freundlich isotherms which describe the relationship between the amounts of Pb(II) adsorbed and its equilibrium concentration insolution.

The adsorption parameters were investigated by plotting C_e/q_e versus C_e forLangmuir adsorption isotherm and $\log q_e$ versus $\log C_e$ forFreundlich adsorption isotherm, as shown in the following Figures (7-8) and Table. 1.

As shown from the previous figures, the values of R^2 using Langmuir adsorption isotherm are approximately one. This means that the adsorption of Pb(II) on ortho-, meta, or para-nitrophenylsilicas is chemical adsorption and follows Langmuir equation.

Table. 1 represents the values of Langmuir and Freundlich isotherm parameters for the adsorption of Pb(II) on (Si-o-NO_2), (Si-m-NO_2) and (Si-p-NO_2).

3.4 Adsorption Kinetic Models

The experimental kinetic data for Pb(II) adsorption on the prepared polymersare fitted with pseudo first-order, pseudo second-order and intra-particle diffusion kinetic models in order to investigate the mechanism of each adsorption process.

The kinetics parameters and correlation coefficients have been calculated from the linear plots of $\log(q_e - q_t)$ versus t for pseudo first order model, and t/q_t versust for pseudo second-order model and q_t versus t for intra-particle diffusion kinetic model, as shown in the following Figures (9-11).
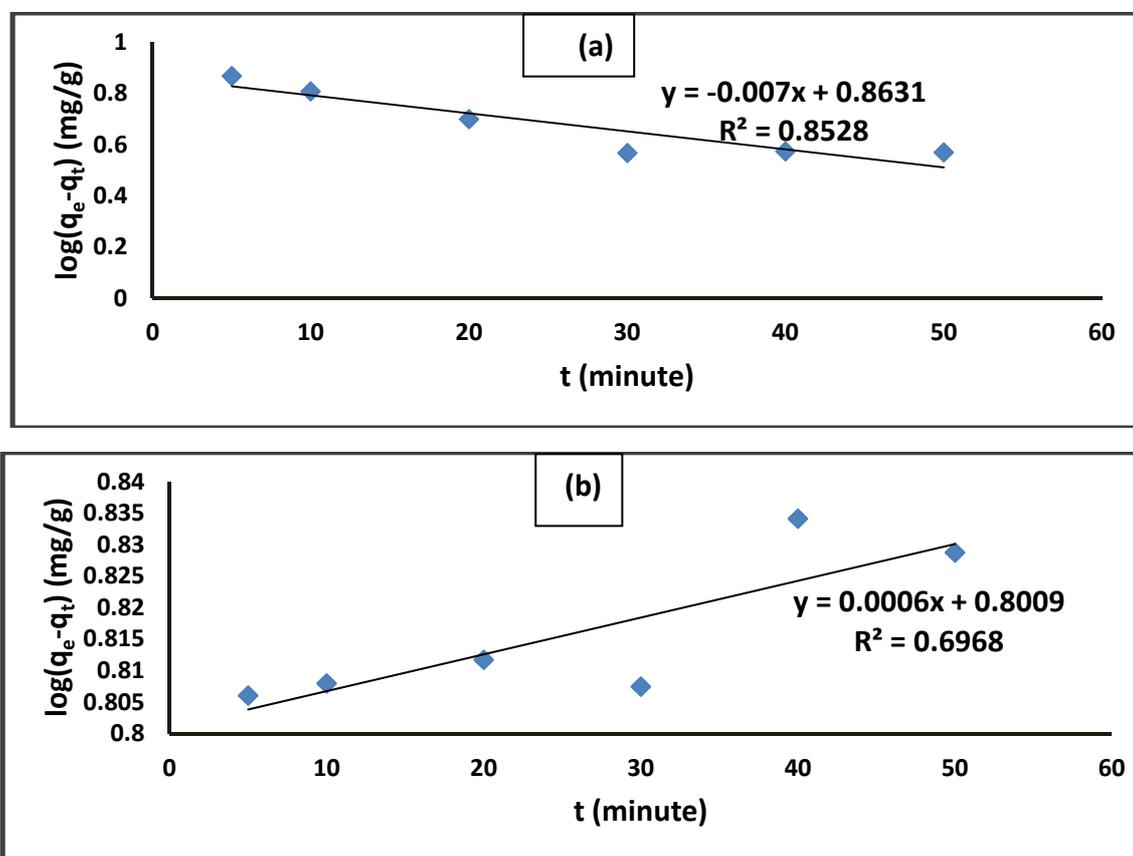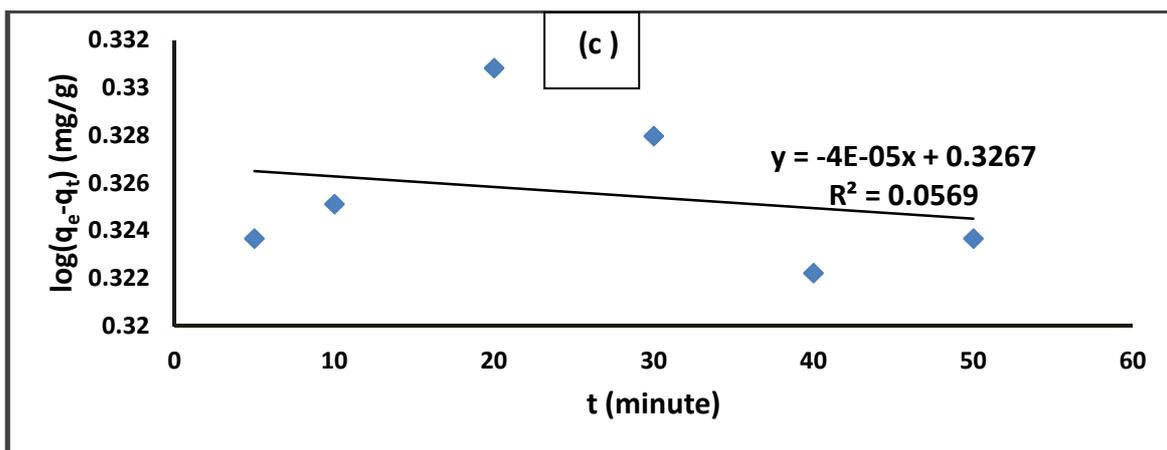
Figure 9: Pseudo first-order kinetic model for the adsorption of Cd(II) on (Si-o-NO₂). (C_I = 10 ppm, pH = 6, temperature = 20 °C, adsorbent dose = 1 mg, volume = 7 mL)

The kinetic of adsorption is defined as the process in which adsorbate molecules are transported from bulk solution to a boundary layer of the water surrounding the adsorbent particle by molecular diffusion through the stationary layer of water. Such that, the adsorbate particles are transported into an available site. Hence, an adsorption bond will be formed between the adsorbate and the adsorbent [20].

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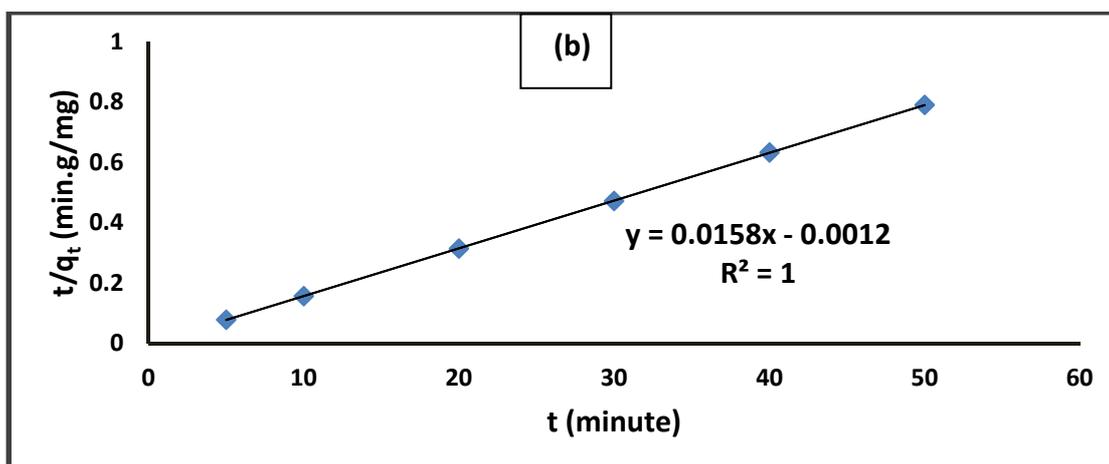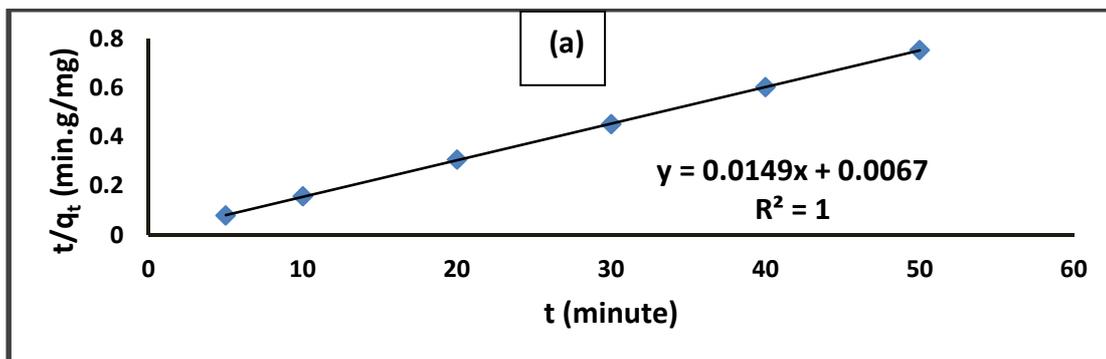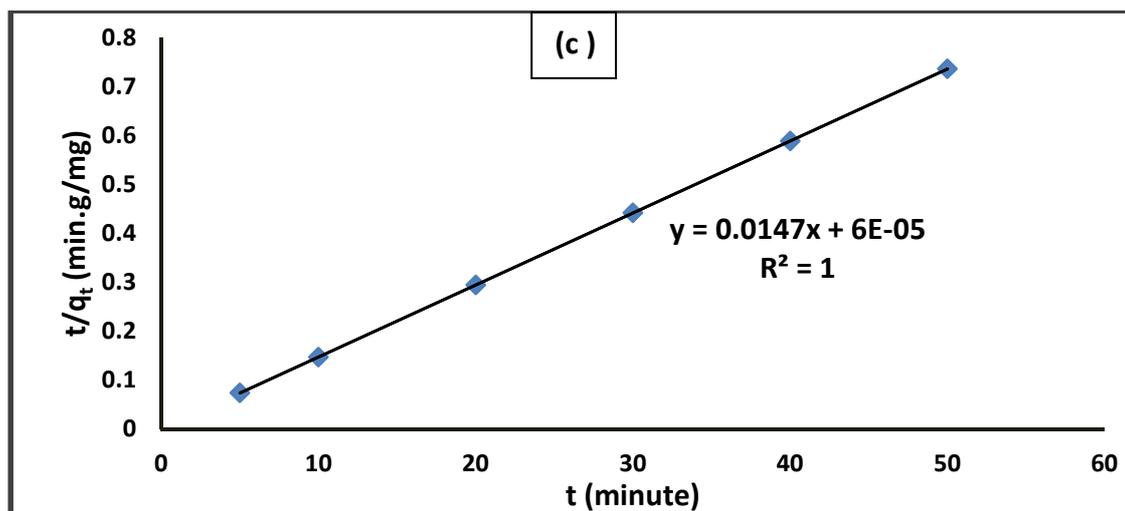
Figure 10: Pseudo second-order kinetic model for the adsorption of Pb(II) on (Si-o-NO₂). (C₁ = 10 ppm, pH = 6, temperature = 20 °C, adsorbent dose = 1 mg, volume = 7 mL)

Several adsorption kinetic models have been established in order to describe adsorption kinetics and rate-limiting step. These models give information about the adsorption system behavior and the rate at which specific constituent is removed using a certain adsorbent. In addition, they determine whether the adsorption process is a chemical or a physical one, and which specifically is the rate determining step.

Examples of the adsorption kinetic models include, external mass transfer model, pseudo first-order and pseudo second-order rate models, Adam–Bohart–Thomas relation, Weber and Morris sorption kinetics, first-order reversible reaction model, first-order equation of Bhattacharya and Venkobachar and Elovich's model [21].

3.4.1 Pseudo First–Order Kinetics
This kinetic model is considered as the earliest model developed for describing adsorption kinetics. The final integrated equation for this model can be written as:

$$log(q_e - q_t) = logq_e - \frac{K_1}{2.303}t \hspace{4cm} (5)$$

Where;
q_e and q_t are the masses of adsorbate per unit mass of adsorbent at equilibrium, and at time t respectively (mg/g).
k_1 is the rate constant of pseudo first-order adsorption model (mg.g^{-1}.min^{-1}).

A plot of $log(q_e–q_t)$ versus t will give a straight line for the pseudo first-order adsorption with $logq_e$ as y-intercept and (-k_1 /2.303) as the slope of the graph [22](Fig. 9).

3.4.2 Pseudo Second–Order Kinetics
This model of kinetics depends on the assumption that the rate-determining step may be chemical adsorption involving valence forces through sharing or exchange of electrons between the adsorbate and the adsorbent.

The rate equation for pseudo second-order kinetic model can be written as:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t \hspace{4cm} (6)$$

Where; k_2 is the equilibrium rate constant of pseudo second-order adsorption (g.mg^{-1}.min^{-1}) (Fig. 10).

The plot of t/q_t versus t should give a linear relationship that allows the computation of a second-order rate constants, k_2 and q_e[23].

Table 2: The parameters of pseudo first-order, pseudo second-order and intra-particle diffusion kinetic models for the adsorption of Pb(II) on (Si-o-NO₂), (Si-m-NO₂) and (Si-p-NO₂).

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Adsorbents	Adsorption of Pb(II)					
	Adsorption Kinetic Models					
	Pseudo First-Order Kinetics		Pseudo Second-Order Kinetics		Intra-Particle Diffusion Kinetics	
	q_e (mg/g)	K_1 (mg.g^{-1}.min^{-1})	q_e (mg/g)	K_2 (g.mg^{-1}.min^{-1})	C (mg/g)	K_p (mg.g^{-1}.min$^{-0.5}$)
Si-o-NO$_2$	7.296	0.0162	67.114	0.0331	61.078	0.8198
Si-m-NO$_2$	6.323	-1.382*10^{-3}	63.291	-0.208	63.833	-0.0799
Si-p-NO$_2$	2.122	-	68.027	-	67.878	0.0011

3.4.3 Intra-Particle Diffusion Kinetic Model

This model is based on the theory proposed by Weber and Morris. The final equation of this adsorption kinetic model is:

$$q_t = K_p t^{0.5} + C \tag{7}$$

Where;

K_p is the diffusion rate constant (mg/g.min$^{1/2}$).

C is a constant that gives an indication of the thickness of the boundary layer (mg/g) [24].

A plot of q_t versus $t^{0.5}$ should give a linear relationship for intra-particle diffusion kinetic model with constant C as a y-intercept and K_p as a slope as shown in Fig. 11.

According to the values for the correlation coefficient using the previous kinetic models. It is showed the adsorption of Pb(II) on (Si-o-NO$_2$), (Si-m-NO$_2$) or (Si-p-NO$_2$) followed the mechanism of pseudo second-order kinetic model. Such that, the values of R^2 in this kinetic model are approximately one.

Table 2 shows the kinetic parameters of pseudo first-order, pseudo second-order and intra-particle diffusion kinetic models for the adsorption of Pb(II) on (Si-o-NO$_2$), (Si-m-NO$_2$) and (Si-p-NO$_2$).

Comparing the value of q_e (experimentally) for all adsorption processes that equal 70, with the values of q_e (calculated) in pseudo first-order and pseudo second-order kinetic adsorption models, we conclude that the experimental values for all adsorptions are closer to the values of q_e (calculated) in pseudo second-order adsorption model. Hence, proving that this model represents the mechanism of the adsorption.

3.5 Adsorption Thermodynamics

Thermodynamic considerations of an adsorption process are necessary to determine whether this process is favorable or not.

This adsorption behavior can be expressed using the thermodynamic parameters including the change in Gibbs free energy (ΔG), enthalpy change (ΔH) and the change in entropy (ΔS).

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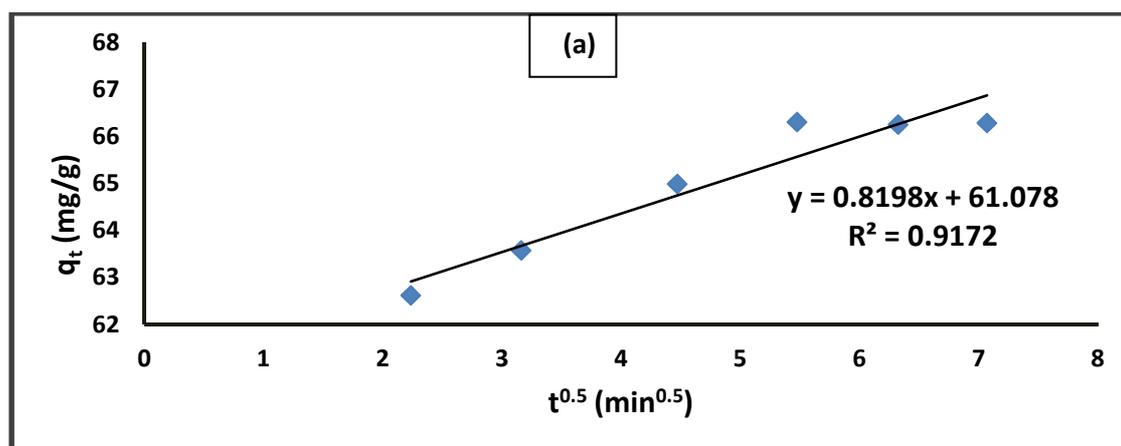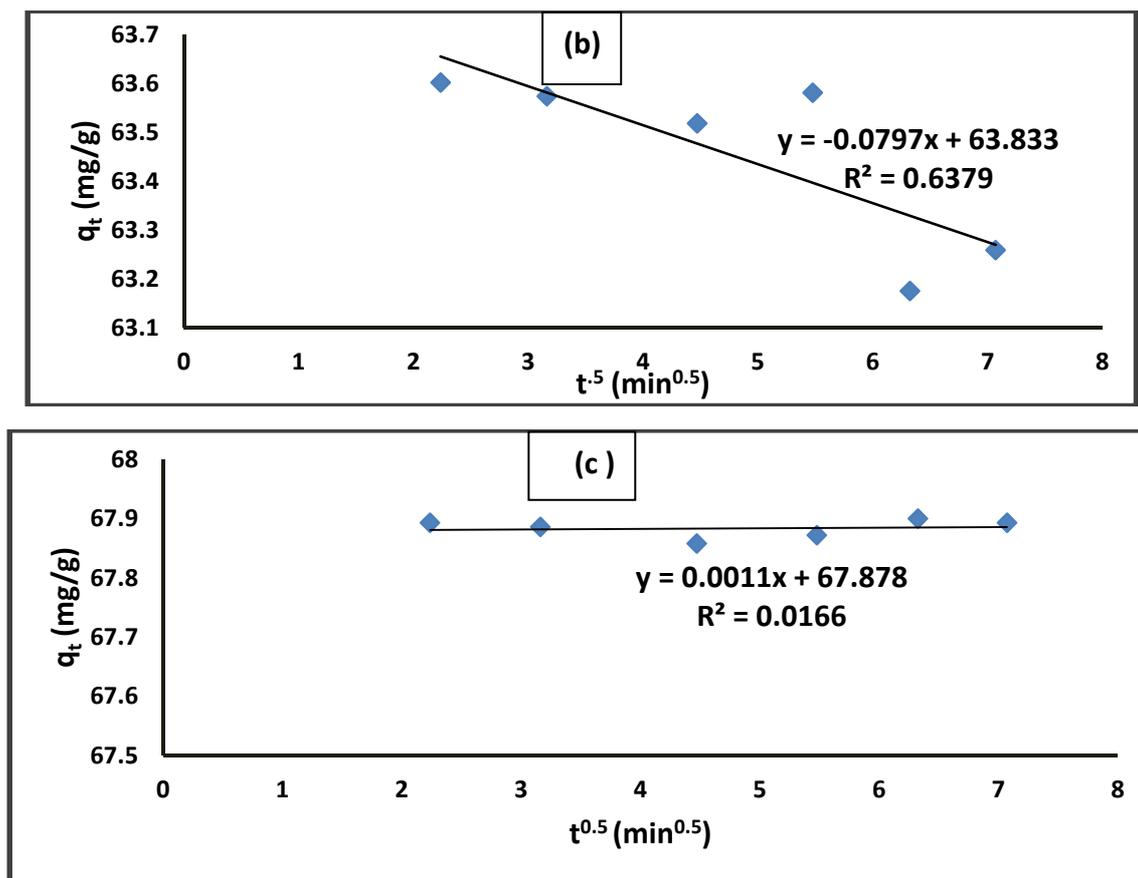
Figure 11: Intra-particle diffusion kinetic model for the adsorption of Pb(II) on (Si-o-NO₂). (C$_I$ = 10 ppm, pH = 6, temperature = 20 °C, adsorbent dose = 1 mg, volume = 7 mL)

Table 3: The thermodynamic parameters for the adsorption of Pb(II) on (Si-o-NO₂), (Si-m-NO₂) and (Si-p-NO₂)

Adsorbents	Adsorption of Pb(II)	
	Adsorption Thermodynamics	
	ΔH (kJ)	ΔS (J/K)
Si-o-NO₂	27.084	-52.316
Si-m-NO₂	29.499	-65.639
Si-p-NO₂	25.525	-46.077

Where; ΔG and ΔH are in (J) and the unit of ΔS is (J/K).

The following equation is the general equation that can be used to relate between the adsorption parameters [25].

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

Where; T is the absolute temperature (K).

The change in Gibbs free energy can be also calculated by the following equation:

$$\Delta G = - RT \ln K_d \tag{9}$$

Where;
R is the universal gas constant that equals 8.314 J.mol^{-1}.K^{-1}.

K_d is the thermodynamic equilibrium constant that equals (q_e/C_e) with a unit equals (mol) or (L/g).

The combination of the last two equations will result in the following equation:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{10}$$

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The plot of InK_d versus (1/T) will give a straight line with (-ΔH/R) as slope and (ΔS/R) as y-intercept. The resulting graph is known as Van't Hoff plot.

By using the thermodynamic equation of Van't Hoff plot .the thermodynamic parameters (ΔH and ΔS) for the adsorption of lead ions on (Si-o-NO₂), (Si-m-NO₂) or (Si-p-NO₂) can be calculated from the slope and intercepts of the graph of InK_d versus (1/T), as shown in the following Figure (12).
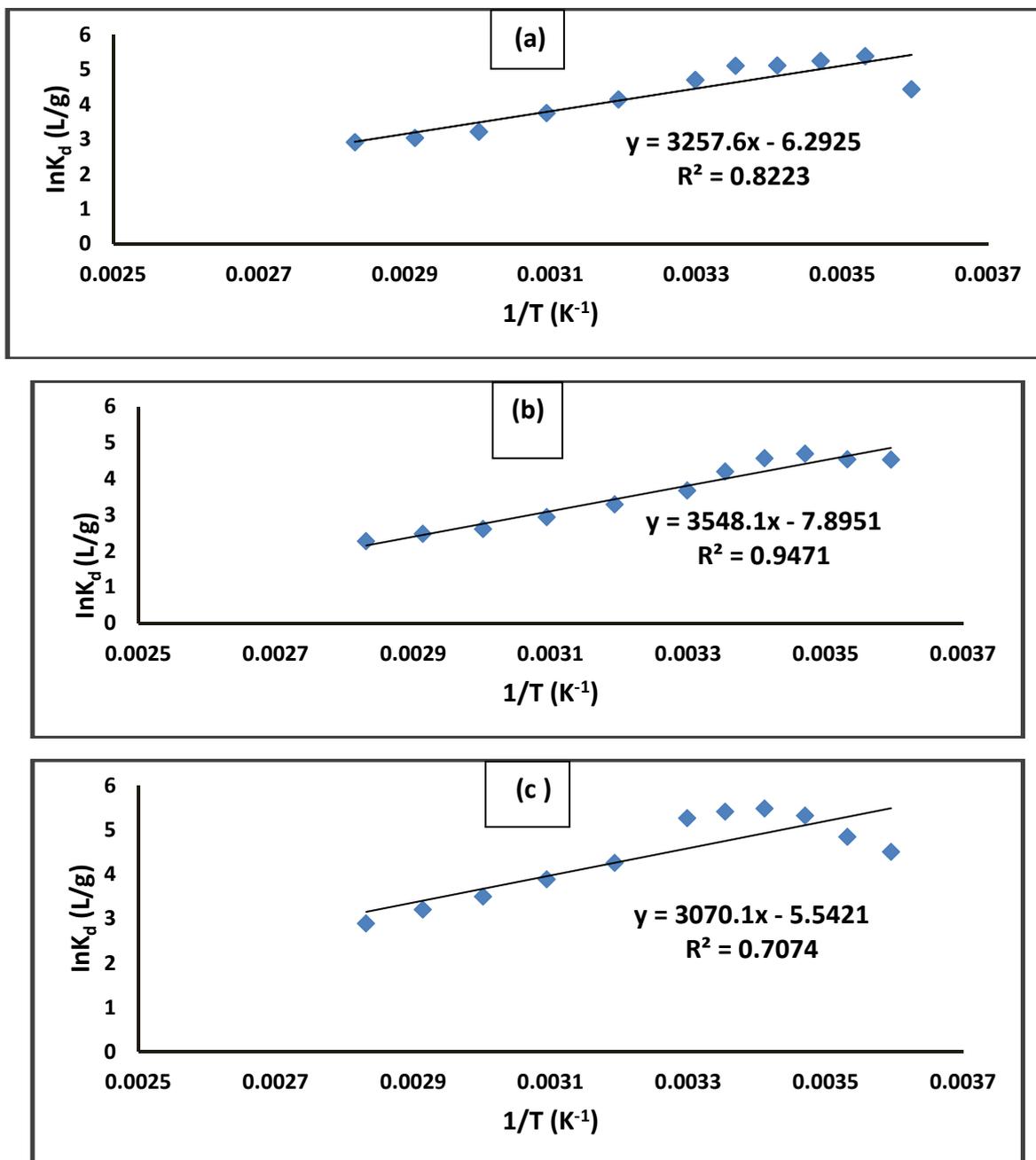
Figure 12: Van't Hoff plot for the adsorption of Pb(II) on (Si-o-NO₂). (time = 50 minute, C_I = 10 ppm, pH = 5, adsorbent dose = 1 mg, volume = 7 mL)

The following table represents the values of the thermodynamic parameters (ΔS and ΔH) for the adsorption of Pb(II) on ortho-, meta-, or para-nitrophenylsilicas.

As shown in table 3, the adsorption of Pb(II) on (Si-o-NO₂), (Si-m-NO₂) or (Si-p-NO₂) adsorbents is endothermic process (ΔH > 0) and non spontaneous (ΔS < 0).

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3.6 Adsorbent Regeneration

(Figure 13) shows the effect of adsorbent recovery on the adsorption of lead ions on ortho-, meta-, or para-nitrophenylsilicas. As shown in this plot, the difference between the percents of heavy metal ion removal after the first and second regeneration of each modified polymer is very low. This is a strong evidence that the three synthesized adsorbents can be recycled, and hence be used for several times.

	1 : (Si-o-NO$_2$)	2 : (Si-m-NO$_2$)	3 : (Si-p-NO$_2$)
	1	2	3
■ 1st use	96.12%	92.53%	97.84%
■ 1st regeneration	94.73%	90.97%	96.39%
■ 2nd regeneration	93.48%	90.22%	96.18%
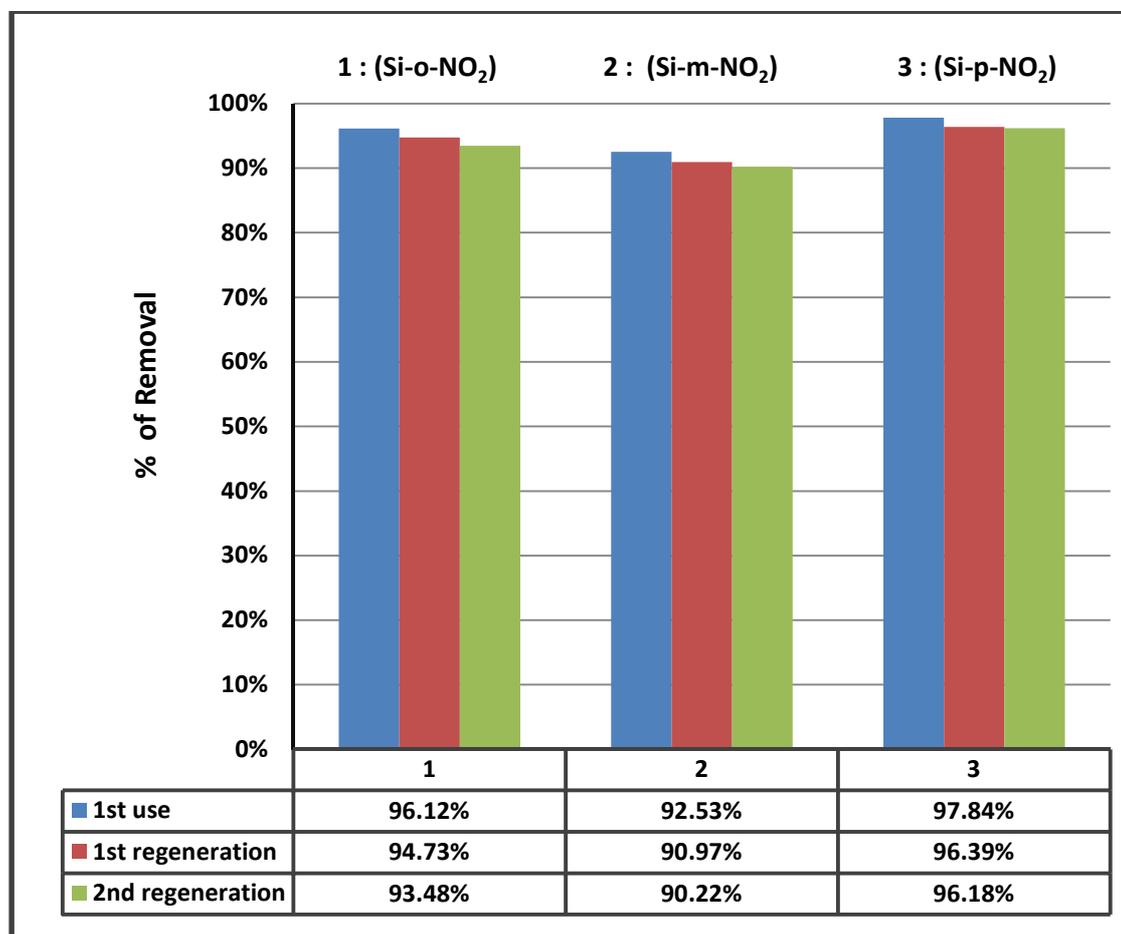
Figure 13: Effect of adsorbent recovery on the adsorption of Pb(II) on ortho-, meta-, or para-nitrophenylsilicas (contact time = 5 minute, C$_I$ = 10 ppm, adsorbent dose = 20 mg, volume of groundwater = 20 mL, pH = 6, temperature = 20 °C)

CONCLUSION

The synthesis and characterization of the new polysiloxane modified surfaces including (Si-o-NO$_2$), (Si-m-NO$_2$) and (Si-p-NO$_2$) showed that these polymers have very good thermal and chemical stabilities, and hence they can be used as perfect adsorbents to uptake Pb(II) from groundwater.

The observed results of this research include the following:
The maximum extent of adsorption was for (Si-p-NO$_2$) polymer in the presence of lead ions. This adsorption needed only 1 minute of shaking to have 99.95% as percent of Pb(II) removal at solution conditions of 20°C temperature, pH value equals 8, 5 mg adsorbent dose, 50 ppm of Pb(II) solution as initial concentration and 7 mL solution volume.Also, the results showed that all adsorptions followed Langmuir adsorption isotherm depending on the value of R^2.The mechanism of all adsorption reactions followed pseudo second-order kinetic adsorption model with correlation coefficient of approximately one.The thermodynamic parameters of all the adsorptions proved that these processes are endothermic ($\Delta H > 0$) and non spontaneous ($\Delta S < 0$).

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