



## **Thiourea Doped Silica Composite for Lead Removal: Isotherm, Kinetic, and Thermodynamic Studies**

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### **Authors' contributions**

This work was carried out in collaboration between both authors. Authors OIO and BWO designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors OIO and BWO managed the analyses of the study and the literature searches. Both authors read and approved the final manuscript.

### **Article Information**

DOI: 10.9734/CSJI/2018/40922

#### Editor(s):

(1) Pradip K. Bhowmik, Professor, Department of Chemistry, University of Nevada Las Vegas, USA.

#### Reviewers:

(1) Julian Cruz-Olivares, Autonomous University of State of Mexico, Mexico.

(2) Naoki Kano, Niigata University, Japan.

Complete Peer review History: <http://www.sciencedomain.org/review-history/24308>

**Received 3<sup>rd</sup> February 2018**

**Accepted 16<sup>th</sup> April 2018**

**Published 24<sup>th</sup> April 2018**

**Original Research Article**

### **ABSTRACT**

In this study, series of experiments were carried out in batch in order to examine the possibility of thiourea doped silica composite for the removal of lead under different experimental conditions. Adsorption of lead (II) ions was investigated with the difference in the parameters of pH, contact time, and lead (II) ions concentration. The adsorption of lead followed pseudo-second-order rate kinetics. Intra-particle diffusion was established not to be the sole rate-controlling step. Thermodynamic studies tell that the adsorption of lead was endothermic and spontaneous, with a good affinity of the adsorbent. Various isotherm models viz, Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Harkins-Jura isotherms were used to evaluate the equilibrium data. The Freundlich and Temkin models were established to be in actual agreement with the experimental data with high  $R^2$ , low RMSE, and low  $\chi^2$  values. The maximum adsorption capacity calculated from Langmuir isotherm was 42.31 mg/g at optimum condition of pH 4 and contact time of 60 min.

**Keywords:** Lead; silica; isotherm; composite; thiourea.

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## 1. INTRODUCTION

Heavy metals pollution has always been a significant challenge in developing countries. The quality of water supply is affected by the discharged of heavy metals into water bodies resulting into serious pollution concern in the environment. Accumulations of these metals in the water constitute a severe health hazard mainly due to their noxiousness and non-degradability [1]. Lead, copper, nickel, zinc, and aluminum are common metal ions in industrial wastewater because of their enormous uses in industries such as metal finishing, batteries manufacture, electroplating, brewery and pharmaceutical [2].

Lead is usually used in many important industrial applications, such as storage battery, printing pigments, manufacturing, fuels, photographic materials and explosive manufacturing. This has created a wide range of toxicity leading to hypertension, impaired blood synthesis, severe stomach ache, brain, and kidney damage in the human body [3,4]. According to US Environmental Protection Agency (EPA), the permissible level for lead in drinking water is  $0.05 \text{ mg L}^{-1}$ . Therefore, a very low concentration of lead in water is very toxic [5].

Adsorption has advantages over other wastewater removal techniques because it solves problems of sludge removal and it renders the system more economically viable especially if low-cost adsorbents are used. This system is also effective in the removal of trace components from a liquid phase and can be used to recover the component or simply to remove toxic substance from industrial wastes [6].

Silica gels have added advantages over other adsorbents because, they are characterized by a highly porous texture, their particle sizes affect the value of their specific surface area and their compactness of binding influences the absorption volume of the pores [7]. According to Castro et al., sulfur- and nitrogen-containing ligands are characterized by a high selectivity towards heavy metals [8]. For this reason, the modification of silica gel by S- and N- containing organic substances is of great interest. The purpose of this present work is to synthesize silica gel derived from maize husk ash doped with thiourea, containing sulfur and nitrogen as donor atoms, expecting selectivity toward Pb (II) adsorption.

## 2. MATERIALS AND METHODS

### 2.1 Preparation and Characterization of Adsorbent

The maize husks used were obtained after the harvest seasons, was first dried at ambient air. After this, the husk was washed with water, dried at  $105^{\circ}\text{C}$ . The combustion was carried out at  $650^{\circ}\text{C}$  for 3 hours in a muffle furnace. Silica gel was extracted from the ash [9]. Impregnation method was used to synthesize the composite. The silica aquagel was acid treated to activate the surface silanol (Si-OH) groups while stirring continuously at a temperature of  $60^{\circ}\text{C}$ . Thiourea was added to the activated gel in (3:7) and the mixture was stirred continuously at room temp for 6 hours. The pH of the resulting mixture was adjusted to 7. The gel was broken and the slurry was centrifuged for 5 mins at 4000 rpm. The composite was dried at  $80^{\circ}\text{C}$  for 24 hours to produce xerogels. Additional washing was done with deionized water to effectively remove minerals and impurity from the composite.

### 2.2 Characterization of the Adsorbents

Fourier transform infrared spectrometry (PerkinElmer FTIR-RX1) with KBr pellets was used to study the functional groups available on the surface of the composite. Scanning Electron Microscopic analysis of the adsorbent studied was obtained using Model (Philips XL30 FEG), was used to characterize the surface morphology of the composite.

### 2.3 Batch Adsorption Experiment

Series of batch experiments were conducted by adding 25 mg of the composite to 20 ml of 100 mg/L lead (II) solution. The experiments were performed at pH values of 2-7 and the effect of contact time was studied at various time intervals and the residual Pb (II) were analyzed by atomic absorption spectrometry model 200A. Various metal ions concentrations (25-100 mg/L) and different ranges of temperatures ( $299\text{-}313 \text{ }^{\circ}\text{K}$ ) were also conducted to determine the equilibrium adsorption of Pb (II) ions.

## 3. RESULTS AND DISCUSSION

### 3.1 Characterization of the Adsorbents

In order to verify the successful impregnation of the silica gel with thiourea, FTIR spectrum of the

thiourea doped silica composite was obtained (Fig. 1). At  $3375\text{ cm}^{-1}$ , the composite exhibited associated water (-OH) and at  $959.84\text{ cm}^{-1}$ , a silanol group (Si-OH) was present. This is as a result of the interaction between hydroxyl groups on the silica surface and water existing in the surrounding atmosphere [10]. The bands at 1156, 800.91 and  $453.73\text{ cm}^{-1}$  were due to various types of Si-O-Si stretching of the siloxane

groups [10,11]. The presence of the thiol group (-SH) and amine group (-NH) were observed at the band at  $2697.14$  and  $1596\text{ cm}^{-1}$  respectively.

The SEM image (Fig. 2) revealed the rough and porous nature of the composite. The seemingly rough surface and porosity of the adsorbent is assigned to a high surface area which can promote the bonding of lead ions.

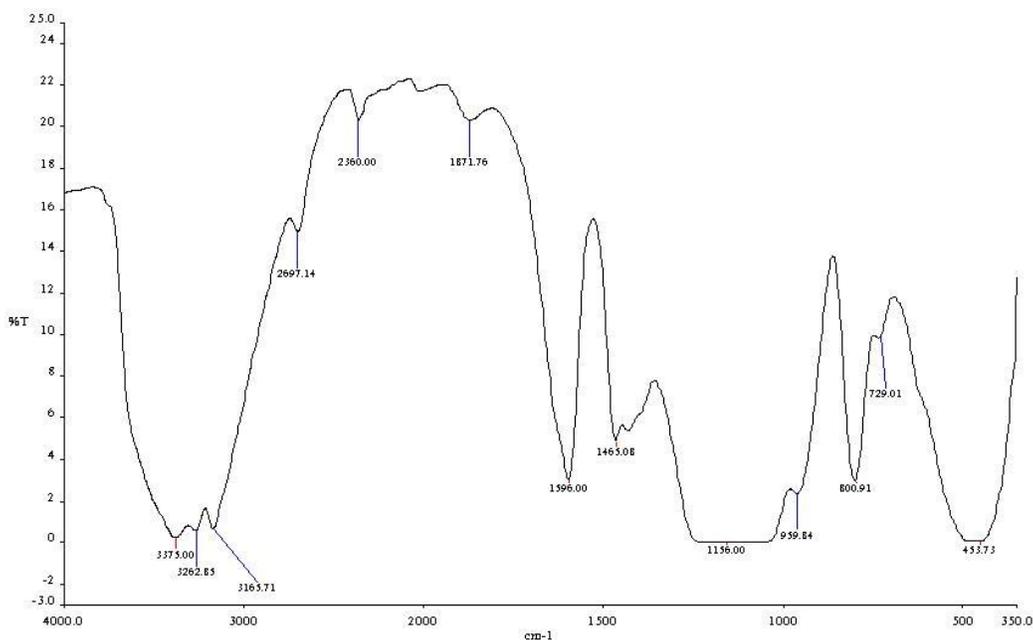


Fig. 1. FTIR Spectrum of thiourea doped silica composite

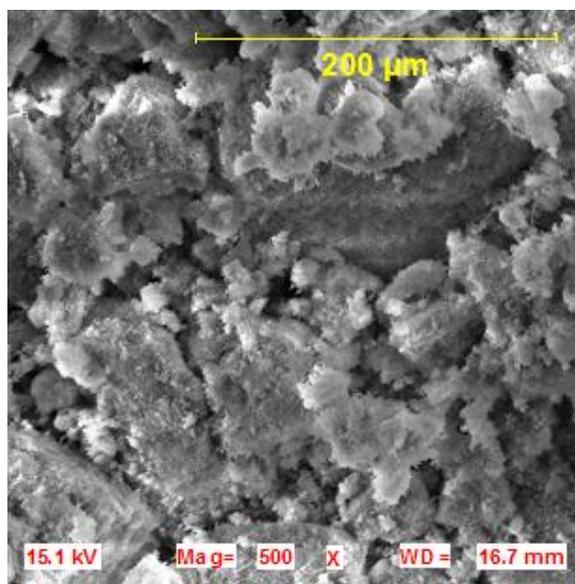


Fig. 2. SEM image of thiourea doped silica composite

### 3.2 Effect of pH on Adsorption

The acidity of solution pH is one of the key parameters controlling the uptake of heavy metals from wastewater and aqueous solutions. The uptake and percentage removal of lead from the aqueous solution is strongly affected by the pH of the solution as illustrated in Fig. 3. The lead adsorption percentage was found to increase with an increase in pH from 2 to 4 and attained a maximum uptake percentage at 91.45% for the adsorbent and then found to decrease with further increase in the solution pH, thus, optimum pH is found to be 4.

The effect of pH can be explained considering the surface charge of the adsorbent material. At low pH, the solution is highly acidic, due to high positive charge concentration the electrostatic repulsion will be high, resulting in lower uptake of positively charged metal ions, also the protonation of the active sites was enhanced and this refused the formation of links between cationic metals and protonated active sites [12]. As the pH of the solution increased, the active sites become deprotonated and free for lead ions to bind, this reduces the competition between metal ions and protons leading to an increase in adsorption with an increase in pH and hence uptake of metal ions increases. It was confirmed by some authors that most Pb (II) species exist as  $Pb^{2+}$  ions, and only a small portion of  $Pb(OH)^+$  is also present in case of pH approaching 6 [12,13].

### 3.3 Effect of Contact Time on Adsorption

The effect of contact time on the adsorption of the lead ion on thiourea doped silica composite was explored in order to achieve the optimum equilibrium time for adsorption. The rate of adsorption of the lead ion on the composite was

rapid during the first 5-15 min and attained equilibrium at 1 h (Fig. 4), the equilibrium uptake percentage of the adsorbent was 87%, thereafter and no significant increase in adsorption with an increase in contact time was noticed. This suggests that at the initial stage, adsorption take place rapidly due to the accumulation of Pb ions on the surface and the availability of abundant active sites on the surface of the composite. The adsorption process slows down with time as the active sites were used up and the remaining vacant surface sites are difficult to be occupied by Pb ions due to the formation of repulsive forces between the Pb on the solid surface and the liquid phase. Beside the mesopores becomes saturated at the initial stage of adsorption where the metal ions are adsorbed. As a result, the driving force of mass transfer between the liquid and a solid phase in an aqueous adsorption system decreases as time elapsed. Further, the metal ions have to pass through the deeper surface of the pores for binding and encounter much larger resistance which slows down the adsorption during the later phase of adsorption [14].

### 3.4 Adsorption Kinetics

In order to investigate the mechanism of adsorption, kinetic models such as; pseudo-first-order, pseudo-second-order kinetics model, and intra-particle diffusion model were applied to study the adsorption dynamics. The agreement between the experimental data and the model-predicted values was expressed by coefficients of determination ( $R^2$ ).

The rate constant of adsorption was determined from Pseudo-first-order rate expression given in Eq. 1,

$$\log (q_e - q_t) = \log q_e - (k_1 / 2.303)t \quad (1)$$

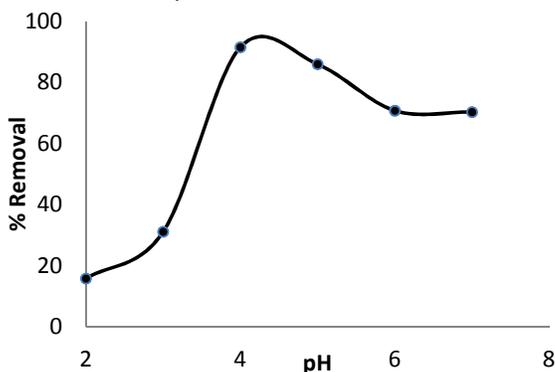


Fig. 3. Effect of pH

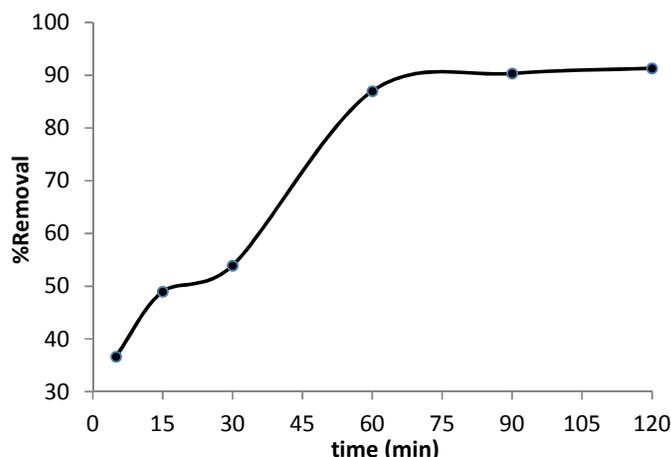


Fig. 4. Effect of contact time

where  $q_e$  and  $q_t$  are the amounts of Pb adsorbed at equilibrium and at the time ( $t$ ) (mg/g) respectively and  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of adsorption. The values of the  $k_1$  and  $q_{e,cal}$  were calculated from the slope and the intercept of the plot of  $\log (q_e - q_t)$  versus  $t$  (Fig. 5) and reported in Table 1, which shows that there is a large difference in the value of  $q_{e,cal}$  and  $q_{e,exp}$  and  $R^2$  is not close to unity for the adsorbent. This established that the pseudo-first-order model was not suitable to describe the kinetic profile of the adsorption.

The Pseudo-second-order kinetic model given in Eq. 2 considers the rate-limiting step as the formation of a chemisorptive bond involving sharing or exchange of electrons between the adsorbate and the adsorbent.

$$t / q_t = 1 / k_2 q_e^2 + 1 / q_e t \quad (2)$$

where  $k_2$  is the pseudo-second-order rate constant (g/mg min).

This model predicts the performance over the entire range of studies supporting a pseudo-second-order equation and is in agreement with chemisorption being the rate controlling step. The parameters,  $q_{e,cal}$ , and  $k_2$  were calculated from the linear plot of  $t/q_t$  versus  $t$  (Fig. 6). The calculated  $q_e$  value of this model agreed well with the experimental  $q_e$  values. Furthermore, the correlation coefficient  $R^2$  for pseudo-second-order model was much closer to unity than the correlation coefficient for pseudo-first order model as shown in Table 1. These suggest that the pseudo-second-order adsorption mechanism is more effective and that the overall rate reaction of the Pb ion adsorption process maybe predominantly controlled by the chemisorption process, which may involve valence forces through sharing or exchange of electron between adsorbent and adsorbate and also by the interaction between polar functional groups on the adsorbent surface and the metals.

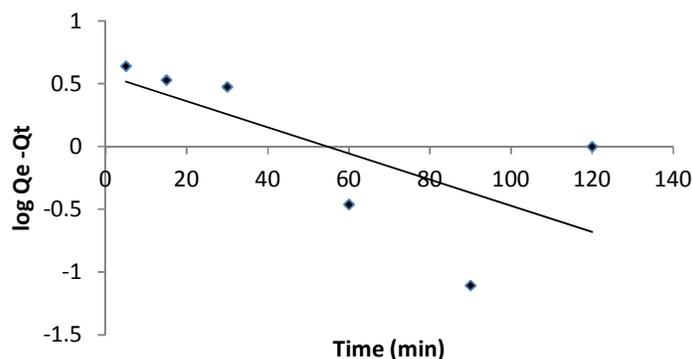
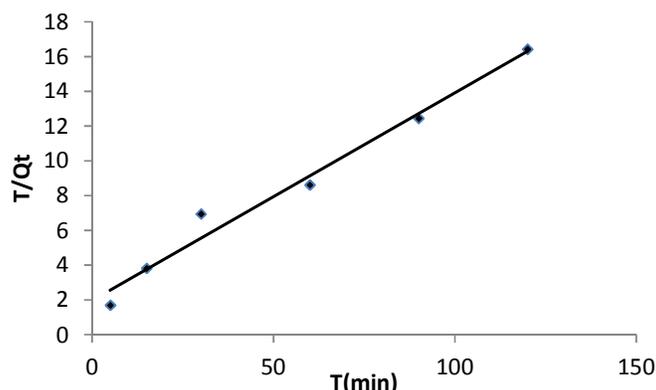


Fig. 5. Pseudo first order plot



**Fig. 6. Pseudo-second order plot**

Intra-particle diffusion model given in Eq. 3 states that if the plot of  $q_t$  versus  $t^{1/2}$  is linear and passes through the origin then intra-particle diffusion is the sole rate-limiting step.

$$q_t = k_{id}t^{1/2} + C \quad (3)$$

where the  $k_{id}$  is the intra-particle diffusion rate constant. It has also been suggested that in the instance when  $q_t$  versus  $t^{1/2}$  is multilinear, two or more stages govern the adsorption process [15]. As the plot did not pass through the origin, intra-particle diffusion was not only the rate controlling step, it may be concluded that the surface adsorption and intra-particle diffusion were concurrently operating during the Pb ion and adsorbent interaction. Values of C (Table 1) give an idea about the thickness of the boundary layer i.e., the larger the intercept, greater the contribution of the surface sorption in the rate controlling step.

**Table 1. Kinetic parameters for adsorption of lead ions**

Parameters	Thiourea doped silica composite
<b>Pseudo-first-order</b>	
$q_{e,exp}$ (mg g <sup>-1</sup> )	7.306
$q_{e,cal}$ (mg g <sup>-1</sup> )	3.704
$k_1$ (min <sup>-1</sup> )	0.024
$R^2$	0.469
<b>Pseudo-second-order</b>	
$q_{e,cal}$ (mg g <sup>-1</sup> )	8.36
$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	1.955
$R^2$	0.979
<b>Intra-particle diffusion</b>	
$k_{id}$ (mg g <sup>-1</sup> min <sup>-1/2</sup> )	0.857
$C$ (mg g <sup>-1</sup> )	1.75
$R^2$	0.927

### 3.5 Adsorption Isotherms

It is important to have a satisfactory description of the equilibrium state between the two phases in order to successfully represent the dynamic behavior of an adsorbate from solution to the solid (adsorbent) phase. The Langmuir [16], Freundlich [17], Temkin [18], Dubinin-Radushkevich [19] and Harkins-Jura [20] Isotherm models were respectively used to analyze the equilibrium experimental data for adsorption of Pb ions onto thiourea doped silica composite by varying initial metal ion concentrations from 25-100 mg/L at room temperature. To evaluate the fit of isotherm equations to the experimental data, different error functions of non-linear regression basin were used to measure the isotherm constants and compare them with the less accurate linearized analysis values. The residual root mean square error (RMSE) and the chi-square test were used. RMSE can be defined as [21]:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (q_{e,exp} - q_{e,calc})^2} \quad (4)$$

The subscripts “exp” and “calc” show the experimental and calculated values and n is the number of observations in the experimental isotherm. The smaller the RMSE value, the better the curve fitting. The chi-square test [22] is given as:

$$\chi^2 = \sum_{i=1}^n \frac{(q_{e,exp} - q_{e,calc})^2}{q_{e,exp}} \quad (5)$$

The lower the value of  $\chi^2$ , the higher the accuracy, validity, and fitness of the model.

The better fit of the model was checked by the correlation coefficient ( $R^2$ ), root mean square error ( $RMSE$ ) and chi-square ( $\chi^2$ ) values and summarized in Table 2.

The model equations are shown below (Equations 6-10)

$$C_e / q_e = 1 / K_L q_{max} + C_e / q_{max} \quad (6)$$

(Langmuir)

$$\log q_e = \log K_F + 1/n \log C_e \quad (7)$$

(Freundlich)

$$q_e = (RT / b_T) \ln A_T + (RT / b_T) \ln C_e \quad (8)$$

(Temkin)

$$\ln(q_e) = \ln(q_s) - k_{ad} \epsilon^2 \quad (9)$$

(Dubinin and Radushkevich)

$$1 / q_e^2 = (B/A) - (1/A) \log C_e \quad (10)$$

(Harkins-Jura)

Where  $q_e$  is the adsorption capacity in equilibrium ( $\text{mg g}^{-1}$ ),  $C_e$  is the adsorbate equilibrium concentration ( $\text{mg L}^{-1}$ ),  $K_L$  ( $\text{L mg}^{-1}$ ) is the Langmuir constant associated to energy of adsorption and  $q_{max}$  denotes the theoretical monolayer adsorption capacity ( $\text{mg g}^{-1}$ ).  $K_F$  is the Freundlich constant ( $\text{mg g}^{-1}$ ) ( $\text{L mg}^{-1}$ )<sup>1/n</sup> while  $1/n$  represents dimensionless heterogeneity factor.  $b_T$  is the Temkin constant related to heat of adsorption ( $\text{J mol}^{-1}$ ).  $A_T$  is the equilibrium binding constant ( $\text{L g}^{-1}$ ) corresponding to the maximum binding energy.  $q_s$  is the D-R isotherm constant ( $\text{mg g}^{-1}$ ),  $\epsilon$  represents the Polanyi potential constant ( $\text{Kj}^2 \text{Kmol}^{-2}$ ) is given as  $RT \ln(1 + 1/C_e)$ ,  $R$  is the universal gas constant,  $T$  is the temperature (k) and  $k_{ad}$  ( $\text{mol}^2 \text{Kj}^{-2}$ ) indicates the

activation energy,  $E$  ( $\text{Kj mol}^{-1}$ ) of adsorption per molecule of sorbate when it is transferred to the surface of the solid from infinity in the solution, where  $E = 1/ \sqrt{-2k_{ad}}$ .  $A$  and  $B$  are Harkins-Jura isotherm parameter and constant.

The Langmuir isotherm model describes quantitatively the buildup of a layer of molecules in an adsorbent surface as a function of the concentration of the adsorbed material in the liquid phase in which it is contact. It also assumes that a surface consists of a given number of equivalent sites, and the adsorbate is adsorbed homogeneously without interaction. The value of  $q_{max}$  and the value of  $k_L$  ( $\text{L/mg}$ ) parameter of the Langmuir model are shown in Table 2. To determine whether the adsorption is favorable, a dimensionless constant, commonly known as separation factor ( $R_L$ ) is calculated. The obtained  $R_L$  value for the adsorption of Pb onto thiourea doped silica composite is less than 1 and greater than zero, as shown in Table 2, indicating favorable adsorption. A plot of  $C_e/q_e$  against  $C_e$  for the adsorption of Pb ion was shown in Fig. 7. The Langmuir isotherm was found to be linear over the entire concentration range with good linear correlation coefficients and also the chi-square,  $\chi^2$ , and  $RMSE$  values gave a good fit to the experimental data of Langmuir model for the adsorbent. The maximum adsorption capacity for Langmuir isotherm was 42.32 mg/g.

The Freundlich isotherm model is used for determining the applicability of heterogeneous surface energy in the adsorption process. The Freundlich exponent,  $n$ , should have a value lying in the range of 1 to 10 for classification as favorable adsorption; the adsorbent indicated

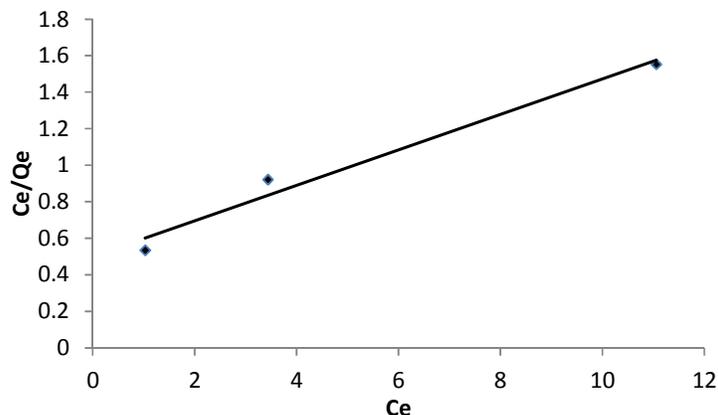


Fig. 7. Langmuir isotherm plot

that the adsorption of Pb was favorable as shown in Table 2. Fig. 8 showed that the Freundlich isotherm presented a better fit to the experimental data as indicated by  $R^2$ ,  $\chi^2$ , and RMSE (Table 2), resulting in a better fit to adsorption data than the other isotherm models used. The presence of chemisorption is confirmed if  $1/n < 1$ .

**Table 2. Isotherms constants of different isotherm models**

	Parameters	Thiourea doped silica composite
<b>Langmuir</b>	$q_{max}$ (mg/g)	42.31
	$k_L$ (L/mg)	0.193
	$R_L$	0.05 - 0.172
	$R^2$	0.9766
	$\chi^2$	0.592
	RMSE	0.351
<b>Freundlich</b>	$k_F$ (mg/g)L/mg <sup>1/n</sup>	1.89
	$n$	1.81
	$1/n$	0.552
	$R^2$	1
	$\chi^2$	0.267
	RMSE	0.106
<b>Temkin</b>	$B$ (mg/L)	2.184
	$b_T$ (Kj/mol)	1.138
	$A_T$ (L/mg)	2.067
	$R^2$	0.9667
	$\chi^2$	0.559
	RMSE	0.294
<b>Dubinin-Radushkevich</b>	$q_s$ (mg/g)	5.724
	$k_{ad}$ (mg/kj <sup>2</sup> )	3.95
	$E$ (Kj/mol)	11.32
	$R^2$	0.8489
	$\chi^2$	69.8
	RMSE	1.99
<b>Harkins-Jura</b>	$A$	4.08
	$B$	1.02
	$R^2$	0.9032
	$\chi^2$	1.328
	RMSE	0.165

The derivation of the Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. Temkin isotherm also takes into account the molecular interaction among the adsorbed particles and adsorbent surface and the degree of heterogeneity of the adsorbent surface. The value of maximum binding energy ( $A_T$ ) and the Temkin isotherm,  $B$ , of the adsorbent is shown in Table 2. The obtained

correlation coefficient for the adsorbent was high and with low values for chi-square  $\chi^2$ , and RMSE confirms the better fit of Temkin model to the experimental data.

The Dubinin-Radushkevich model describes the adsorption nature of the sorbate on the adsorbent and is used to calculate the mean free energy of adsorption. The slope and intercept of plots of  $\ln q_e$  versus  $\epsilon^2$  were used to calculate the D-R isotherm parameters as shown in Table 2. The value of  $q_s$  for the adsorbent was 5.724 mg/g. The mean adsorption energy,  $E$ , is very useful in predicting the type of adsorptions, if the values are less than 8 kj/mol, then the adsorption is physical in nature due to weak Vander Waals forces and if it is in between 8-16 kj/mol, then the adsorption is due to exchange of ions [23]. The calculated  $E$  from D-R isotherm for the adsorbent was shown in Table 2, they are found to be in the range of 8-16 kj/mol. This may be due to different chemical process accompanying the ion exchange process. The high values of chi-square  $\chi^2$ , RMSE and the magnitude of the correlation coefficient ( $R^2$ ) of D-R isotherm is the lowest when compared to the other isotherm models used. This suggests that the Pb adsorption onto thiourea doped silica composite does not show a satisfactory fit to the experimental data for the Dubinin-Radushkevich isotherm model.

The Harkins-Jura adsorption isotherm accounts to multilayer adsorption and can be explained by the existence of a heterogeneous pore distribution. This method can be employed when different types of pores are involved in an adsorbent. Harkins-Jura isotherm constants  $A$  and  $B$  were calculated from a linear plot of  $1/q_e^2$  versus  $\log C_e$  and data are presented in Table 2 along with  $R^2$ , RMSE, and  $\chi^2$  values. The correlation coefficient obtained for the adsorbent indicated the existence of multilayered adsorption.

On the basis of low RMSE and low chi-square value and high correlation coefficients (Table 2), it was found that Freundlich Isotherm and Temkin Isotherm models fitted the result substantially better than the Langmuir Isotherm, Harkins-Jura, and Dubinin-Radushkevich Isotherm models. The applicability of Freundlich and Temkin Isotherms showed that there were effectively multilayer adsorption and heterogeneous distribution of active sites on the surface of the adsorbent. In all the cases, the Dubinin-Radushkevich Isotherm represented the poorest fit of experimental data in comparison to the other Isotherm equations.

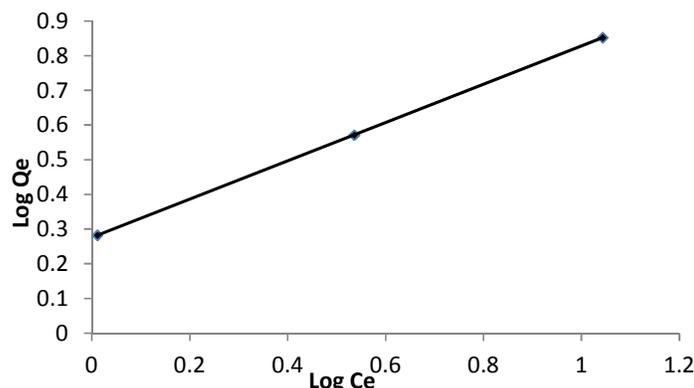


Fig. 8. Freundlich isotherm plot

### 3.6 Effect of Competitive Ions

Drinking water and wastewater contain cations, therefore, it was thought beneficial to study the effect of competitive ions on the removal of lead (II) by thiourea doped silica composite. Effect of competitive ions like sodium, potassium, and calcium on the removal of Pb (II) was carried out at ambient temperature, varying from 0.01 to 0.1 M. Thiourea doped silica composite showed a slight enhancement in adsorptive performance in the presence of competing ions, but as the concentration of the competing ions increased further, lead adsorption decreased, these results may suggest lead attraction is electrostatic and hence influenced strongly by high concentration of the competing ions. The cations reduced the lead (II) adsorption in the order of calcium > potassium > sodium.

### 3.7 Thermodynamic Studies

In order to fully understand the nature of adsorption, the thermodynamic parameters were calculated. The Gibbs free energy change,  $\Delta G^\circ$ , is an indication of the spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Also, enthalpy,  $\Delta H^\circ$ , and entropy,  $\Delta S^\circ$  factors must be considered in order to determine the Gibbs free energy of the process. The thermodynamic parameters of Gibbs free energy change,  $\Delta G^\circ$ , enthalpy change,  $\Delta H^\circ$ , and entropy change,  $\Delta S^\circ$ , for the

adsorption processes are calculated using this equation.

$$\Delta G^\circ = -RT \ln K \quad (11)$$

Where  $R$  is the universal gas constant and  $T$  is the absolute temperature (K).  $\Delta H^\circ$  (kJ/mol) and  $\Delta S^\circ$  (kJ/mol/K) of adsorption can be calculated from the slope and intercept of the plot of  $\ln K$  and  $1/T$  (Van't Hoff plot). The Van't Hoff plot gave a straight line.

As shown in Table 3, the negative value of  $\Delta G^\circ$  showed that, the adsorption process was feasible and spontaneous thermodynamically. However, the decrease of the values of  $\Delta G^\circ$  with increase temperatures suggested that, the adsorption was favourable at higher temperature. The positive values of  $\Delta H^\circ$  suggest the endothermic nature of adsorption which was also supported by the increase in values of  $Pb^{2+}$  uptake of the adsorbent with the rise in temperature. The positive value of  $\Delta S^\circ$  shows increased randomness at the adsorbent-solution interface during the adsorption of metal ions on thiourea doped silica composite and also reflected the affinity of the adsorbent towards  $Pb^{2+}$  ions under consideration. During the adsorption of Pb (II), the  $H^+$  ions, which are displaced by the Pb (II) ions gain more entropy than is lost by adsorbate species, thus allowing the prevalence of randomness in the system.

Table 3. Thermodynamic parameters for adsorption of lead ions

	$C_o$ (mg/L)	$-\Delta G^\circ$ (kJ/mol)				$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol/K)
		299°K	303°K	308°K	313°K		
Thiourea doped silica composite	25	7.831	9.057	14.207	19.885	257.460	0.884
	50	6.480	7.520	9.728	11.068	95.436	0.341
	100	5.183	5.881	7.899	8.487	70.999	0.254

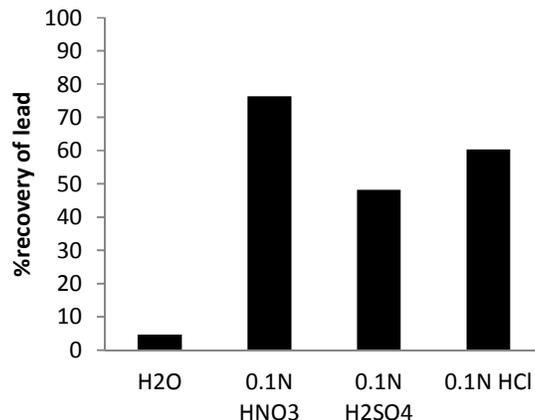


Fig. 9. Desorption of Pb ions

### 3.8 Desorption Study

Desorption studies help explain the nature of adsorption and regeneration of the spent adsorbent and metal ions. The effects of various reagents used for desorption studies are shown in Fig. 9. Among the solvents, distilled water had a limited amount of Pb ion recovery (<5%), it is evident that desorption of adsorbed lead (II) was very less, which indicates that the process of adsorption is predominately chemical or ion-exchange in nature. The highest (76%) recovery was found with the use of 0.1 N HNO<sub>3</sub>. The adsorption-desorption cycle of the metal ion was repeated five times using the various reagents. The adsorption capacities for the composite did not noticeably change during the repeated adsorption-desorption operations, but 2-6% change was observed after the fifth cycle. This can be attributed to the decomposition effects of the acid solution. These results show that the composite has good regeneration ability.

### 4. CONCLUSION

In this study, the ability of thiourea doped silica composite to adsorb lead from aqueous solution has been investigated. The doping of the adsorbent has been shown to enhance the adsorption capacity. The chemical stability of the adsorbent material in acidic medium allows the reuse of the composite for several cycles. The kinetic studies revealed that the adsorption process best fit the pseudo-second-order kinetic model for the adsorbent. In addition, the intra-particle diffusion constant was not the sole rate-controlling step. Equilibrium adsorption data fitted best both in Freundlich isotherm and Temkin isotherm with high  $R^2$ , low RMSE and low  $\chi^2$

values confirming good agreement between the theoretical models and the experimental results. The correlation coefficient for Freundlich isotherm was the highest in comparison to the values gotten from other isotherms and was an indicator of the heterogeneity of the surface of the adsorbent and the multilayer adsorption nature of the lead ions onto the adsorbent. The adsorption of Pb (II) on the adsorbent shows the chemical nature of the adsorption process in this study. Thermodynamics studies revealed that the adsorption process was endothermic and spontaneous in nature, with good affinity toward the adsorbent. This study shows that the composite is a promising adsorbent for the removal of Pb ions from aqueous solution.

### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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 The peer review history for this paper can be accessed here:  
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