

Original Research Article**Thiourea Doped Silica Composite for Lead Removal: Isotherm, Kinetic,
And Thermodynamic Studies**

In this study, a series batch experiments were carried out 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, 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 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 χ^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.

1. Introduction

Heavy metals pollution has always been a significant challenge in developing countries. The quality of water supply are 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 are usually used in many important industrial applications, such as storage battery, printing pigments, manufacturing, fuels, photographic materials and explosive manufacturing. This has created wide range of toxicity leading to hypertension, impaired blood synthesis, severe stomach ache, brain, and kidney damage in human body ^[3, 4]. According to US Environmental Protection Agency (EPA), the permissible level for lead in drinking water is 0.05 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

40 components from a liquid phase and can be used to recover the component or simply to
41 remove toxic substance from industrial wastes ^[6].

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

50 **2. Materials and Methods**

51 **2.1 Preparation and Characterization of Adsorbent**

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

62 **2.2 Characterization of the Adsorbents**

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

67 **2.3 Batch Adsorption Experiment**

68 Series of batch experiments were conducted by adding 25mg of the composite to 20ml of
69 100mg/L lead(II) solution. The experiments were performed at pH values of 2-7 and the
70 effect of contact time was studied at various time intervals and the residual Pb(II) were
71 analyzed by atomic absorption spectrometry model 200A. Various metal ions concentrations
72 (25-100mg/L) and different ranges of temperatures (299-313°K) were also conducted to
73 determine the equilibrium adsorption of Pb(II) ions.

74 **3. Results and Discussion**

75 **3.1 Characterization of the Adsorbents**

In order to verify the successful impregnation of the silica gel with thiourea, FTIR spectra of the thiourea doped silica composite was obtained (Fig. 1). At 3375 cm^{-1} , the composite exhibited associated water (-OH) and at 959.84 cm^{-1} , 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 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 cm^{-1} respectively.

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

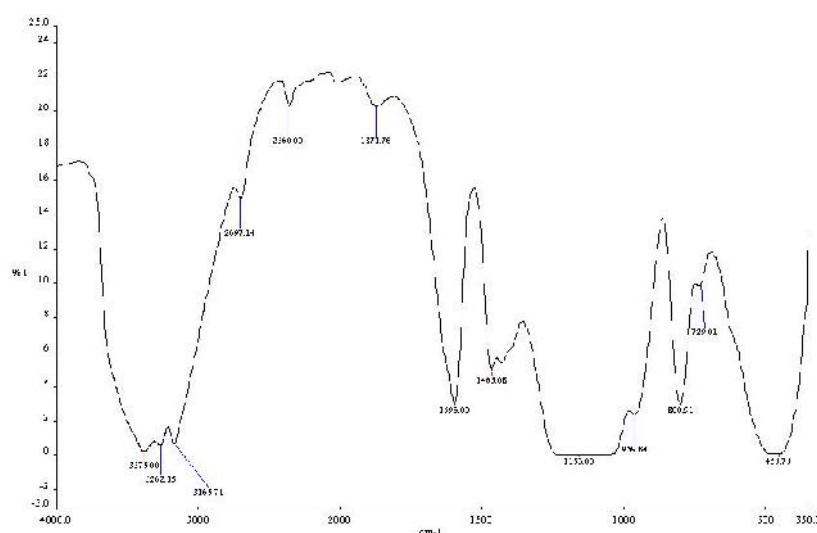


Figure 1: FTIR Spectra of thiourea doped silica composite

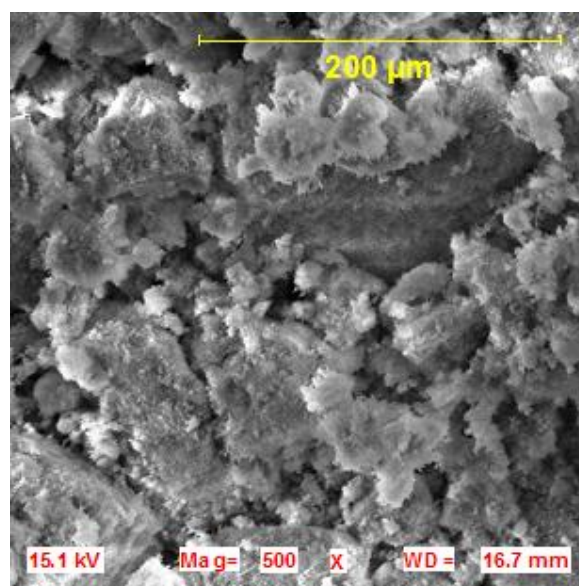


Figure 2: SEM image of thiourea doped silica composite

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 are 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 on 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. As the pH of the solution increased, the active sites becomes deprotonated and free for lead ions to bind, this reduces the competition between metal ions and protons leading to an increase in adsorption with increase in pH and hence uptake of metal ions increases.

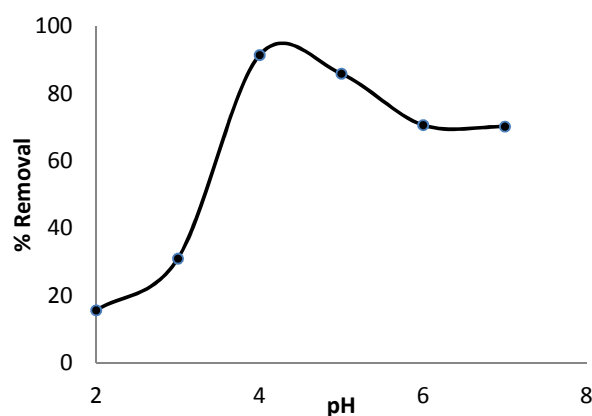


Figure 3: Effect of pH

3.3 Effect of Contact Time on Adsorption

The effect of contact time on the adsorption of lead ion on thiourea doped silica composite was explored in order to achieve the optimum equilibrium time for adsorption. The rate of adsorption of lead ion on the composite was rapid during the first 5-15 min and attained equilibrium at 60 min Fig. 4, the equilibrium uptake percentage of the adsorbent was 87%, thereafter and no significant increase in adsorption with increase in contact time was noticed. This suggests that at the initial stage, adsorption took 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.

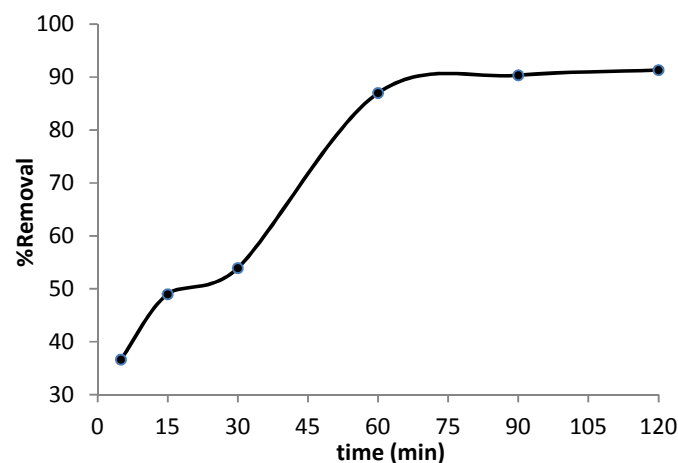


Figure 4: Effect of contact time

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,

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

where q_e and q_t are the amount of Pb absorbed at equilibrium and at time (t) (mg/g) respectively and k_1 (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.

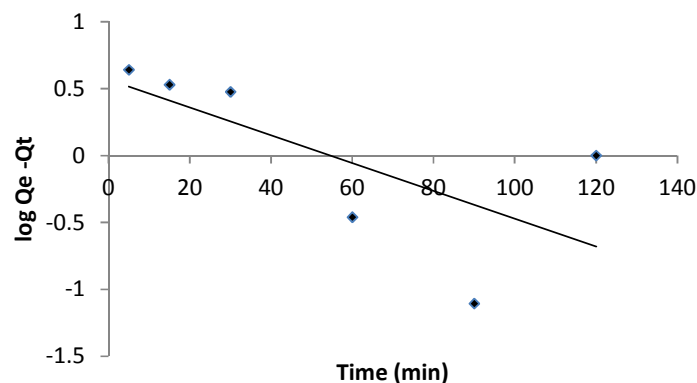


Figure 5: Pseudo first order plot

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 of the Pb ion adsorption process maybe predominantly controlled by the chemisorption process.

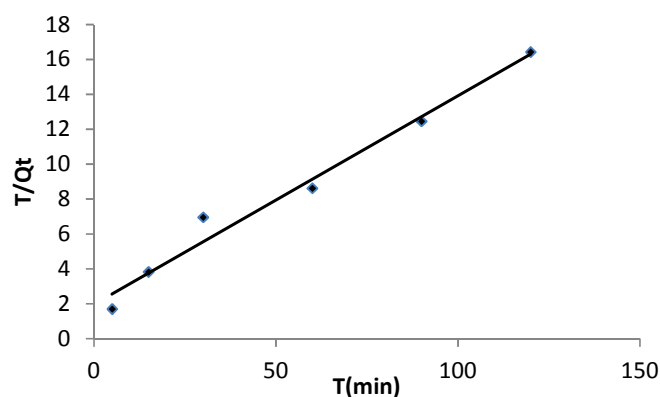


Figure 6: Pseudo second order plot

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 k_{id} is the intra-particle diffusion rate constant. It has also been suggested that in instance when q_t versus $t^{1/2}$ is multilinear, two or more stages govern the adsorption process [12]. 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.

163

Table 1: Kinetic parameters for adsorption on lead ions

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

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165 3.5 Adsorption Isotherms

166 It is important to have a satisfactory description of the equilibrium state between the two
 167 phases in order to successfully represent the dynamic behavior of any adsorbate from solution
 168 to the solid (adsorbent) phase. The Langmuir ^[13], Freundlich ^[14], Temkin ^[15], Dubinin-
 169 Radushkevich ^[16] and Harkins-Jura ^[17] Isotherm models were respectively used to analyze the
 170 equilibrium experimental data for adsorption of Pb ions onto thiourea doped silica composite
 171 by varying initial metal ion concentrations from 25-100 mg/L at room temperature. To
 172 evaluate the fit of isotherm equations to the experimental data, different error functions of
 173 non- linear regression basin were used to measure the isotherm constants and compare them
 174 with the less accurate linearized analysis values. The residual root mean square error (RMSE)
 175 and the chi- square test were used. RMSE can be defined as ^[18]:

$$176 \quad RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (q_{e,exp} - q_{e,calc})^2} \quad (4)$$

177 The subscripts “exp” and ‘calc” show the experimental and calculated values and n is
 178 the number of observations in the experimental isotherm. The smaller the *RMSE* value, the
 179 better the curve fitting. The chi square test ^[19] is given as:

$$180 \quad \chi^2 = \sum_{i=1}^n \frac{(q_{e,exp} - q_{e,calc})^2}{q_{e,exp}} \quad (5)$$

181 The lower the value of χ^2 , the higher the accuracy, validity and fitness of the model.

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

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

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

$$\log q_e = \log K_F + 1/n \log C_e \quad (\text{Freundlich}) \quad (7)$$

$$q_e = (RT / b_T) \ln A_T + (RT / b_T) \ln C_e \quad (\text{Temkin}) \quad (8)$$

$$\ln(q_e) = \ln(q_s) - k_{ad} \varepsilon^2 \quad (\text{Dubinin and Radushkevich}) \quad (9)$$

$$1 / q_e^2 = (B/A) - (1/A) \log C_e \quad (\text{Harkins-Jura}) \quad (10)$$

where q_e is the adsorption capacity in equilibrium (mg g^{-1}), C_e is the sorbate equilibrium concentration (mg L^{-1}), K_L (L mg^{-1}) is the Langmuir constant associated to energy of adsorption and q_{max} denotes the theoretical monolayer adsorption capacity (mg g^{-1}). K_F is the Freundlich constant ($\text{mg g}^{-1})(\text{L mg}^{-1})^{1/n}$ while $1/n$ represents dimensionless heterogeneity factor. b_T is the Temkin constant related to heat of adsorption (J mol^{-1}). A_T is the equilibrium binding constant (L g^{-1}) corresponding to the maximum binding energy. q_s is the D-R isotherm constant (mg g^{-1}), ε 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 (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 numbers of equivalent sites, and the adsorbate is adsorbed homogeneously without interaction. The value of q_{max} and the value of k_L (L/mg) parameter of the Langmuir model are shown in Table 2. To determine whether the adsorption is favourable, 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 favourable 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, χ^2 and $RMSE$ values gave a good fits to the experimental data of Langmuir model for the adsorbent. The maximum adsorption capacity for Langmuir isotherm was 42.32 mg/g.

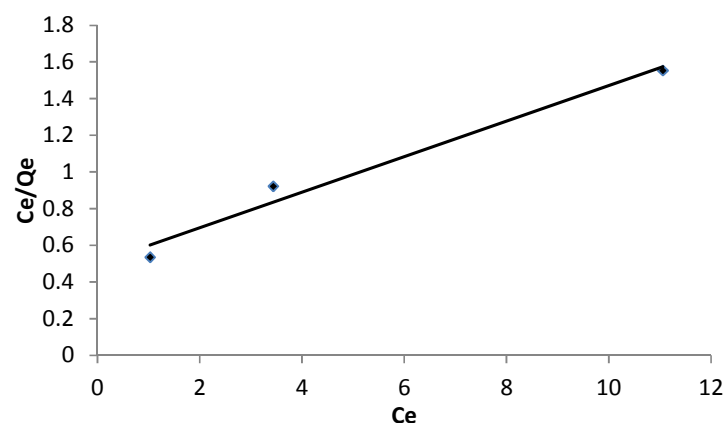


Figure 7: Langmuir isotherm plot

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 favourable adsorption; the adsorbent indicated that the adsorption of Pb was favourable 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 , χ^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 $1/n < 1$

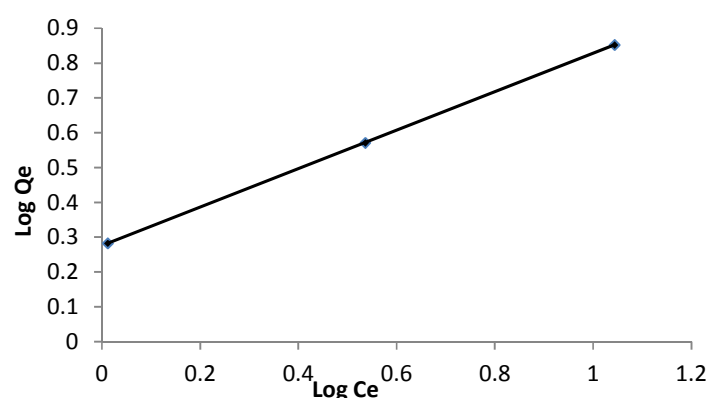


Figure 8: Freundlich isotherm plot

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 χ^2 , and RMSE confirms the better fit of Temkin model to the experimental data.

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Table 2: Isotherms constants of different isotherm models

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

236

237 The Dubinin-Radushkevich model describes the adsorption nature of the sorbate on the
 238 adsorbent and is used to calculate the mean free energy of adsorption. The slope and intercept
 239 of plots of $\ln q_e$ versus ε^2 at different temperature were used to calculate the D-R isotherm
 240 parameters as shown in Table 2. The value of q_s for the adsorbent was 5.724 mg/g. The mean
 241 adsorption energy, E , is very useful in predicting the type of adsorptions, if the values is less
 242 than 8 kj/mol, then the adsorption is physical in nature due to weak Vander Waals forces and
 243 if it is in between 8-16 kj/mol, then the adsorption is due to exchange of ions^[20]. The
 244 calculated E from D-R isotherm for the adsorbent was shown in Table 2, they are found to be
 245 in the range of 8-16 kj/mol. This may be due to different chemical process accompanying the
 246 ion exchange process. The high values of chi-square χ^2 , RMSE and the magnitude of the
 247 correlation coefficients of D-R isotherm is the lowest when compared to the other isotherm
 248 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 with 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 χ^2 values. The correlation coefficient obtained for the adsorbent indicated 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 sorption 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.

3.6 Thermodynamic Studies

In order to fully understand the nature of adsorption, the thermodynamic parameters were calculated. The Gibbs free energy change, ΔG° , is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Also, enthalpy, ΔH° and entropy, ΔS° factors must be considered in order to determine the Gibbs free energy of the process. The thermodynamic parameters of Gibbs free energy change, ΔG° , enthalpy change, ΔH° , and entropy change, ΔS° , for the adsorption processes are calculated using this equation.

$$\Delta G^\circ = -RT \ln K$$

(11)

where R is the universal gas constant and T is the absolute temperature (K). ΔH (kJ/mol) and ΔS (kJ/mol/K) of sorption 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.

Table 3: Thermodynamic parameters for adsorption of lead ions

	C_e (mg/L)	$-\Delta G^\circ$ (kJ/mol)				ΔH° (kJ/mol)	ΔS° (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

As shown in Table 3, the negative value of ΔG° showed that, the adsorption process was feasible and spontaneous thermodynamically. However, the decrease of the values of ΔG° with increase temperatures suggested that, the adsorption was favourable at higher temperature. The positive values of ΔH° suggest the endothermic nature of adsorption and the

positive value of ΔS° shows increased randomness at the adsorbent-solution interface during the adsorption of metal ions on thiourea doped silica composite.

4. Conclusion

In this study, the ability of thiourea doped silica composite to adsorbed lead from aqueous solution has been investigated. The doping of the adsorbent has been shown to enhance the adsorption capacity. 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 χ^2 values. 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.

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