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## Adsorption of Lead in Aqueous Solution using Montmorillonite-silica Nanocomposite

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**Abstract** In this study, the locally available materials which include; montmorillonite clay and rice husks were used to synthesize montmorillonite-silica nanocomposite as adsorbent in removal of lead from aqueous solution. Fourier transform infra-red (FTIR), was used to characterize the adsorbent. Batch method of adsorption was employed in the study and parameters that influence the adsorption such as adsorbent dose, initial concentration and contact time have been studied. The optimum conditions of the study were found at the initial concentration 500 mg/L, adsorbent dosage (0.3g), contact time 40 (minutes) and constant stirring at 200 rpm. The experiments were carried out at the natural pH  $5 \pm 0.3$  of the solution and room temperature (309 K). The results showed the maximum percentage of lead removal to be 99.99%. The equilibrium data for the adsorption was analyzed using both Langmuir and Freundlich isotherms models with  $R^2=0.9375$  and  $R^2=0.9275$  respectively and both fitted the experimental data. The maximum adsorption capacity ( $q_{max}$ ) using Langmuir isotherm was found to be 132.802mg/g. The kinetics study was carried out by employing pseudo-first order and pseudo-second order kinetics, the result of the kinetic studies showed that pseudo-second order kinetic model was found to correlate well to experimental data with  $R^2=1$ . The results indicate that montmorillonite-silica nanocomposite is a cost effective adsorbent that can employ for the adsorption of Lead from aqueous solution.

**Keywords** Clay, Silica, Nanocomposite, Adsorption, Heavy metal

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### Introduction

Different contaminants are released to wastewater with the rapid industrialization of human society, including heavy metal ions, organics, bacteria, viruses, and so on, which are serious harmful to human health. Wastewater are generated from many industries, including pharmaceutical, chemical manufacturing, battery manufacturing industries, metallurgical, leather tanning, and mining and contains pharmaceutical emerging contaminants and heavy metal ions. These wastewater with heavy metal ions are discharged into natural water directly, not only threat the aquatic organisms, but may be enriched by precipitation, adsorption, and harmed human health through the food chain. Thus, the removal of such toxic metal ions from wastewater is becoming crucial issue.

The conventional methods for treatment of lead waste includes; precipitation, adsorption with activated carbon, ion-exchange, membrane processes, oxidation and reduction, but the adsorption via nanocomposite become more effective than all due its less financial expenses contribute to its cost effectiveness, [1].

The adsorption of various pollutants such heavy metal ions and organic pollutants (including dyes and pharmaceutical emerging contaminants) from the contaminated water with the help of nanocomposites has attracted significant attention [2]. [1], nanoscale materials have the potential to improve the environment, both through direct application of those materials to detect, prevent and remove pollutions as well as indirectly by using nanotechnology to design clearer industrial processes and create environmentally responsible products.



Recently, various methods lead removal from water has been extensively studied. Hafne *et al.*, [2008], [3], investigated the potential adsorption of lead using commercial natural Bentonites (NB) in the removal of lead from aqueous solution. The effect of different variable such as concentration of the lead, mass of natural bentonites, pH, time, NB washing and heat treatment and temperature was investigated. The experiment was carried out using batch process, and was found that NB had a higher adsorption capacity ( $q_m$ ) of 107,110 and 120mg<sup>-1</sup> at 293,313 and 333K respectively compared to others adsorbents. Season leafy was investigated as adsorbent material using batch process model, for the removal of lead from aqueous solution. The bio-sorbent was characterized by thermogravimetric analysis and Fourier transforms infrared spectroscopy. The influence of phase contact time, pH, adsorbent dosage and initial concentrations were investigated to optimize condition for maximum adsorption. The Koble-carrigan and Langmuir isotherm best represented the measure biosorption data. The biosorption capacity of the biosorbent was found to be 279.86mg<sup>-1</sup> which was higher or comparable to the adsorption capacity of various adsorbents reported the by Liu *et al.*, [2012], [4].

The aim of this research was to investigate the use of montmorillonite-silica nanocomposite in the removal of lead from aqueous solutions. Rice husk is a low cost adsorbent which is a waste material from agriculture and montmorillonite clay is a low cost natural adsorbent. Rice husk ash is known to have high silica content ranging from 60% and above. Silica content of the rice husk ash was extracted using sodium hydroxide and obtained as sodium silicate [5]. The montmorillonite-silica nanocomposite was synthesized in-situ by precipitating sodium silicate with acid in the presence of montmorillonite clay. The study involved examination of experimental conditions such as effect of adsorbent, Initial concentration of lead and contact time on the removal of lead from aqueous solution. The Langmuir and Freundlich adsorption isotherms were used to investigate the adsorption process. Kinetic study was carried out based on pseudo first and second order.

### Theories of Adsorption Isotherms

The isotherm of adsorption indicates how much molecules are distributed between the liquid and the solid phase when the adsorption process reach equilibrium. Its employed to establish the maximum capacity of adsorption of metal on adsorbents and which is express in terms of quantity of metal adsorbed per unit mass of adsorbent used (mg g<sup>-1</sup>).

#### Langmuir Theory

The Langmuir was the first to point out that in the chemical adsorption of gas on solid surface, a layer single molecule in thickness is formed. He proposed that the adsorption process consist of two opposing action – condensation of molecule from gas phase on the solid surface and the evaporation of the molecules from solid surface back to the gas surface which at equilibrium the rate of two opposite actions are equal. He also derived an equation base on certain assumptions of surface homogeneity:

- the adsorbent side adsorbs a layer single molecules in thickness
- the adsorption of the molecule on this side is restricted.
- there is no interaction between the adsorbed molecules.
- that all adsorption sites have the same affinity for the sorbent.

Equation

$$C_e/q_e = 1/\varphi_0 b + C_e/\varphi_0$$

Where  $C_e$  is final concentration is the Langmuir equilibrium constant,  $C_o$  is initial concentration,  $q_e$  is the amount adsorbed.

However, the essential behavior of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor, RL, which is expressed as

$$RL = 1/(1+bC_o)$$

Where 'b' is the Langmuir constant and  $C_o$  is the initial concentration of metal. it is known that RL values between zero and one ( $0 < RL < 1$ ) is indicating favourable adsorption, where as RL value above one ( $> 1$ ) is indicating unfavourable adsorption, and the plot of  $1/q_e$  against  $1/C_o$  gives the Langmuir isotherm graph.



### Freundlich Theory

The Freundlich equation is the empirical relationship whereby it is assumed that the adsorption energy of a metal ion binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied.

$$\log q_e = \log k + 1/n \log C_e$$

Where  $q_e$  and  $C_e$  are the equilibrium adsorption capacity of the adsorbent and the equilibrium concentration in the aqueous solution, respectively.

$K$  and  $n$  are the Freundlich constants related to adsorption capacity. And the plot of  $\log q_e$  against  $\log C_e$  gives the Freundlich isotherm graph.

The limitation of the Freundlich model is that the amount of adsorbed solute increases indefinitely with the concentration of the solute in the solution.

### Adsorption Kinetics

The relationship between the adsorption capacity and adsorption time, that is used to describe the rate of chemical reaction in the adsorption process is referred to as adsorption kinetics, which is one of the most important characteristics defining the efficiency of adsorption of an adsorbent. In analyzing the mechanism of a metal ion on the surface of the solid, liquid or gaseous adsorbent, available adsorption kinetics are applicable but pseudo-first order, second order are the most widely used in the adsorption process. The pseudo-first order equation is represented as follows.

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

Where  $k_1$  is the Lagergren rate constant of adsorption (1/min). The plot of  $\log(q_e - q_t)$  against  $t$ , gives a linear relationship from which  $q_e$  and  $k_1$  are determined from the intercept of the plot respectively.

The pseudo-second order model can be represented by the following linear form;

$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

Where  $k_2$  is the second order rate constant of adsorption (g/mgmin). The values of  $k_2$  and  $q_e$  are determined from the intercept of the plot of  $t/q_t$  against  $t$ .

### Materials and Method

#### Sample Collection and Preparation

About 1000g of rice husk sample was collected from a milling machine at Talasse Balanga local government in Gombe State. The rice husk was washed thoroughly with tap water; five times to remove the adhesive dirt, rewashed with distilled water and dried in the air overnight. And then oven dried overnight at 95°C until its constant weight has been obtained being the starting material for the preparation of rice husk ash.

#### Preparation of Rice Husk Ash

About 250g of a clean dried rice husk was refluxed with 1000ml of 1M hydrochloric acid for 1 hour at 95°C in a 2000ml beaker to remove some metallic impurities. After the reaction was completed, the acid was removed from the rice husk by washing it with distilled water. It was then dried overnight at 110°C in an oven. The treated rice husk was calcined in a muffle furnace at 650°C for seven (7) hours, then the white rice husk ash (WRHA) was obtained and kept for further preparation of nanocomposite [6].

#### Collection and Preparation of Clay

The montmorillonite clay, 500g was collected from Talasse, and was washed with tap water five times and rewashed with distilled water. It was dried, ground and sieved using 250µm sieve, 250g of the powdered clay was refluxed with 1M HCl, in a 500ml solution at 120°C for one hour, it was rewashed to remove the acid, then dried and ground for the preparation of montmorillonite/silica nano-composite, by adopting the procedure [7].

#### Synthesis of Montmorillonite-Silica Nanocomposite

30g of white rice husk ash was refluxed with 250ml of 2.5M NaOH solution for one hour with continuous stirring and filtered; a clear sodium silicate solution was obtained.

Into the 200ml of sodium silicate solution, 75g of acidified clay was added with constant stirring and precipitated with concentrated sulphuric acid in a drop wise and measuring the pH until its equal to 8.9. It was then aged for 24



hours and then rewashed with distilled water five times until the pH=7. The montmorillonite-silica nanocomposite was dried in an oven overnight, grounded and sieved using 250um (micrometer seive), the adopted procedure, [8] and kept for further analysis.

### Batch Adsorption Method

All the experiments in these studies were carried out in 500ml conical flask containing 200ml of Lead solution. After adding the amount of adsorbent, the flasks were agitated using magnetic stirrer while studying the parameters such as the effect of adsorbent dosage, initial concentration and contact time effect. The filtrate obtained was analyzed using atomic absorption spectrophotometer (AAS). The adopted procedure [9] was used in order to study the quantity adsorbed at equilibrium ( $q_e$ ) by the adsorbent. The percentage of lead adsorbed at equilibrium,  $q_e$ (mg/g) and  $q_t$ (mg/g) at time t, were calculated according to the equation as follows:

$$\% \text{ Lead removal} = \frac{(C_o - C_e)}{C_o} \times 100$$

$$q_e = \frac{(C_o - C_e)}{C_o} \times V$$

$$q_t = \frac{(C_o - C_t)}{m} \times V$$

## Result and Discussion

### Characterization of Montmorillonite-Silica Nanocomposite

The Fourier Transform Infrared Spectroscopy (FT-IR) spectra are used in this study as a qualitative measurement to analyze the chemical composition of the montmorillonite-silica nanocomposite. From the spectra observed, montmorillonite-silica nanocomposite spectrum is presented Fig: 1, the bands at about  $3700 \text{ cm}^{-1}$  corresponds to the stretching vibration of surface hydroxyl groups, and the bands at  $1198$  and  $798 \text{ cm}^{-1}$  attribute to the -OH bending vibration. These have also been reported by [10-12].

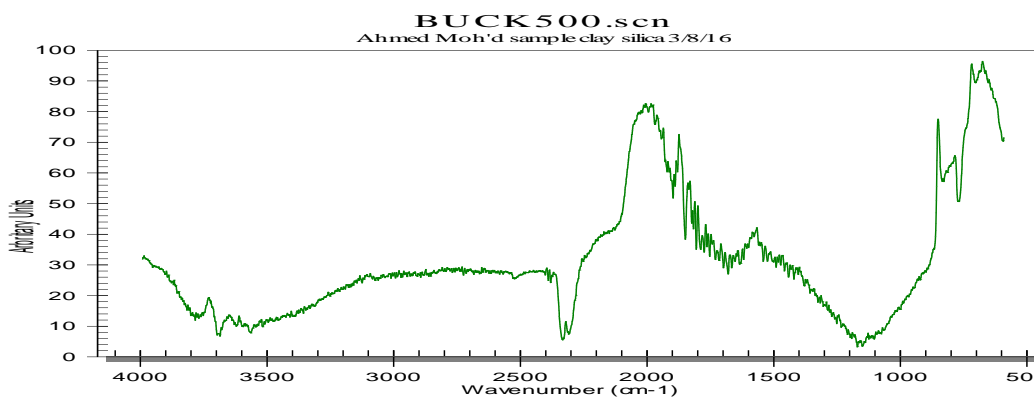


Figure 1: FTIR Montmorillonite-silica nanocomposite spectrum

### Effect of Adsorbent Dose

The effect of adsorbent dosage on the amount of metal ion was determined by batch method, at 500mg, 309 K, pH  $5 \pm 0.3$ , 200 rpm and contact time 60 minutes. It is evident from the observation in the Table 1; below that the amount of lead absorbed increases with the increase in the adsorbent dose from 0.1 to 0.3g at removal % from 99.979 to 99.992, beyond that the removal percentage fall with the increase in adsorbent dosage may be due to the adsorption sites remaining saturated during adsorption at equilibrium or adsorption reaction. And hence optimum dosage can be taken as 0.3g in all calculations in this study since even at high adsorbent dosage conditions does not improved the adsorption due to the interference between binding sites and reduced mixing at high adsorbent densities as realized in Fig 4. Therefore, it may be suggested that a more economical designed for the removal of lead ion can be carried out using small amount of adsorbent than in a large quantity.



**Table 1:** The result of effect of adsorbent dose

Adsorbent dose(g)	C <sub>o</sub> (mg/L)	C <sub>e</sub> (mg/L)	C <sub>o</sub> C <sub>e</sub> (mg/g)	%Removal	q <sub>e</sub> (mg/g)	Logq <sub>e</sub>	LogC <sub>e</sub>	C <sub>e</sub> /q <sub>e</sub>
0.1	500	0.102	499.898	99.979	999.76	3.999	-0.991	0.00012
0.2	500	0.089	499.911	99.982	499.911	2.698	-1.051	0.00019
0.30.	500	0.035	499.965	99.982	333.31	2.523	1.456	0.00011
0.4	500	0.108	499.892	99.978	249.949	2.39	-0.967	0.00043
0.5	500	0.158	499.842	99.973	199.946	2.30	-0.876	0.00066

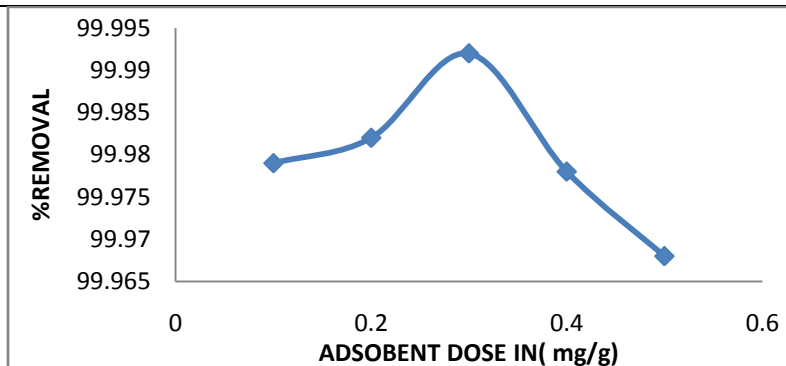


Figure 2: Effect of Adsorbent Dose; 0.3g, initial concentration 500mg, contact time 60 minute, pH 5±0.3, temperature 309 K

### Effect of Initial Concentration

The effect of initial concentration was carried out at various concentrations from 500 to 700 mg/L, 0.3 g adsorbent, contact time;60, pH 5±0.2, 200 rpm and temperature 309 K. Table 2; below represent the specific lead adsorption in which the percentage removal of metal ion decreased with the increased in initial concentration of the solution. This is assumed to be due to driving force of i.e. concentration gradient. At lower concentration most of the lead ions present in the solution could interact with the binding site of the adsorbent, and thus the percentage removal was higher. Whereas at higher concentration, the decreased in the removal percentage may be due to lack of sufficient number of adsorption site in the adsorbent to accommodate the incoming metal ions available in the solution as we can see in Fig 3.

**Table 2:** The result of the effect of initial concentration

Adsorbent dose(g)	C <sub>o</sub> (mg/L)	C <sub>e</sub> (mg/L)	C <sub>o</sub> C <sub>e</sub> (mg/g)	% Removal	q <sub>e</sub> (mg/g)	Logq <sub>e</sub> (lg)	LogC <sub>e</sub> (lg)	C <sub>e</sub> /q <sub>t</sub> (mg.L)
0.3	500	0.051	499.949	99.989	333.299	2,523	-1.292	0.00015
0.3	550	0.071	549.929	99.987	366.619	2.698	-1.149	0.00019
0.3	600	0.078	599.921	99.987	399.947	2.523	-1.108	0.00019
0.3	650	0.089	649.911	99.986	433.274	2.637	--1.105	0.00020
0.3	700	0.103	699.897	99.985	466.598	2.699	-0.987	0.00022

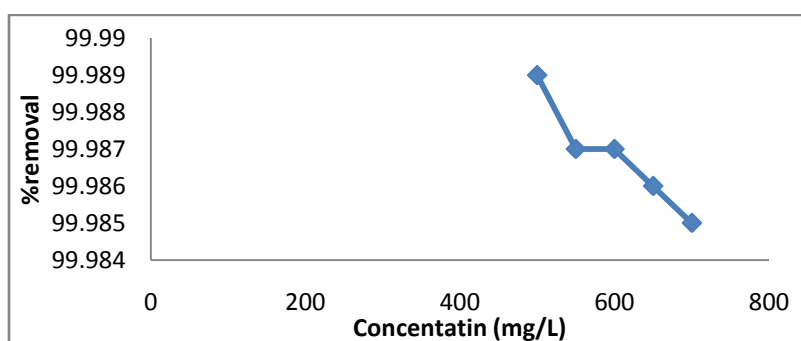


Figure 3: Effect of Initial Concentration; Adsorbent dose 0.3g, contact time 40 minutes, pH 5±0.3, and temperature 309 K.



### Effect of Contact Time

It was evident from the batch experimental result obtained in Table 3; below that the lead adsorption (uptake) was found to be increasing rapidly with the increase in contact time and the optimum percentage adsorption of the metal ion was found to occur at 40 minutes, achieving the % removal of 99.985 after which it remained constant for the rest of the adsorption duration, and the slow rate of adsorption by the adsorbent may be attributed to the lack of available vacant active site on the adsorbent to accommodate the metal ion species present in the solution.

In general the initial rate of adsorption was fast, and then the slow adsorption followed as the available adsorption sites were slowly decreased. Therefore, the obtained result signifies that the optimum contact time for lead adsorption on to the montmorillonite-silica nanocomposite in this study was fixed at 40 minutes time as represented in the Fig 4. Similar phenomena have been reported by, [8].

**Table 3:** The result of the effect of contact time

Time (mins)	Adsorbent dose(g)	C <sub>0</sub> (mg/L)	C <sub>e</sub> (mg/L)	C <sub>0</sub> C <sub>e</sub> (mg/g)	% Removal	q <sub>e</sub> (mg/g)	Logq <sub>e</sub> (1.g)	LogC <sub>e</sub> (1.g)	C <sub>0</sub> /q <sub>e</sub> (g/L)
10	0.3	500	0.091	499.909	99.981	333.273	2.523	-1.041	0.00027
20	0.3	500	0.084	499.916	99.983	333.277	2.523	-1.076	0.00025
30	0.3	500	0.078	499.922	99.984	333.281	2.523	-1.108	0.00023
40	0.3	500	0.073	499.927	99.985	333.285	2.523	-1.137	0.00022
50	0.3	500	0.072	499.928	99.986	333.285	2.523	-1.143	0.00022

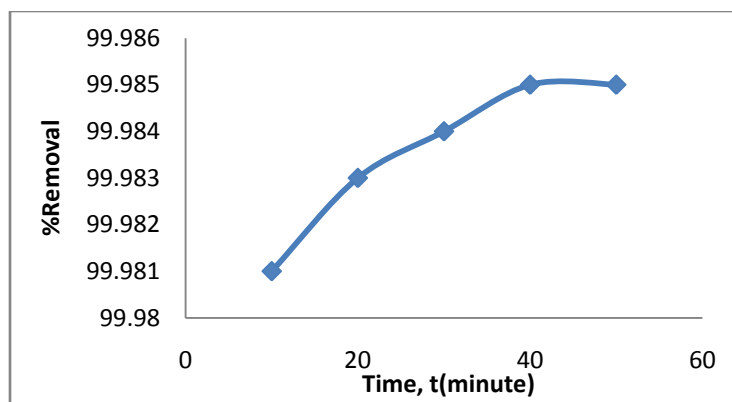


Figure 4: Effect of Contact Time; Contact time 40 min, adsorbent dose 0.3g, initial concentration 500 mg, pH 5 ±0.3, and temperature 309 K.

### Adsorption Isotherm Study

The equilibrium studies (isotherm) were carried out, the experimental data were analyzed using two most commonly used isotherms models, Langmuir and Freundlich. The equilibrium data was well presented by all the two models. The calculated isotherm constants, Table 4 were carried out from the plot of C<sub>0</sub>/q<sub>e</sub> against C<sub>e</sub> which represents the Langmuir model, whereas logq<sub>e</sub> against logC<sub>e</sub> represent the Freundlich model. The Langmuir model best fitted the experimental data with R<sup>2</sup>=0.9375 and followed by Freundlich isotherm model with R<sup>2</sup>=0.9275 as represented in the Table 4; may be due to uniform distribution of adsorption site on the montmorillonite-silica nanocomposite.

**Table 4:** The isotherm parameters of adsorption for Langmuir and Freundlich models.

Isotherm	Constant	Values
Langmuir	R <sup>2</sup>	0.9375
	q <sub>max</sub> (mg/g)	132.802
	b	0.0753
Freundlich	R <sup>2</sup>	0.9275
	q <sub>max</sub> (mg/g)	101.419
	n	0.00986



### Kinetic Adsorption Study

To determine the kinetic adsorption of the lead ions using montmorillonite-silica nanocomposite, pseudo-first order and pseudo-second order were tested on the experimental data by plot of  $\log(q_e/q_t)$  against  $t$ , for first-order kinetics and  $t/q_t(1/g)$  against  $q_e(\text{mg/g})$  for the second-order kinetics respectively. The regression correlation coefficient  $R^2$  obtained from the pseudo-first order kinetics graphs was observed to be ( $R^2=0.8201$ ) which is quite low than that of the second order ( $R^2=1$ ). This implied the lesser or non-applicability of the pseudo-first order kinetics model to the experimental data of the adsorption of Lead ions on to the montmorillonite-silica nanocomposite as represented in the Table 5; below.

**Table 5:** maximum adsorption values of Lead and pseudo-first order parameters at different time.

Parameters	Times (min)				
	10	20	30	40	50
Removal (%)	99.981	99.983	99.984	99.985	99.986
$K_1$	0.2253	0.12615	0.0841	0.06307	0.05046
$q_e$ exp. (mg/g)	333.275	333.277	333.281	333.285	333.285

The correlation coefficient of  $R^2 = 1$  was obtained by the pseudo-second order kinetic. This phenomenon signifies the conformity of the mechanism of adsorption of lead ions on the montmorillonite nanocomposite followed the pseudo-second order kinetic model, Table 6.

**Table 6:** maximum adsorption values of Lead and pseudo-second order parameters at different time.

Parameters	Time (min)				
	10	20	30	40	50
Removal (%)	99.981	99.983	99.984	99.985	99.986
$K_2$	0.63655	0.31827	0.212180	0.15914	0.12731
$q_e$ exp.(mg/g)	333.275	333.277	333.281	333.285	333.285

### Conclusion

The montmorillonite-silica nanocomposite obtained from montmorillonite clay and rice husk ash was characterized and utilized for the removal of lead from aqueous solution, as well as a cost effective adsorbent successfully. The experimental data were better fitted by both the Langmuir adsorption isotherm model as and the Freundlich isotherm models with  $R^2$  values 0.9357 and 0.9275 respectively. The maximum percentage removal of lead in from aqueous solution was found to be 99.989% at (0.3g) adsorbent dosage, initial concentration at (500mg/L) and contact time (40 min), pH  $5 \pm 0.3$ , 200 rpm, and temperature 309 K. Also, the adsorption capacity was found to be (132.208 mg/g-<sup>1</sup>) which is comparable with the commercial expensive adsorbent for lead removal from aqueous solution, [3]. The kinetics studies best correlation coefficient was obtained using pseudo-second order kinetic models (rate expression). The result presented here revealed that the montmorillonite-silica nanocomposite could be economically and cost effectively when employed as adsorbent for removal of lead ions from aqueous solution.

### Reccommendation

The prepared nanocomposite should be properly characterize using x-ray diffractometry (XRD), Scanning electron microscopy (SEM), and thermogravimetric analysis in order to understand and other applications of the material. It can be recommended that montmorillonite-silica nanocomposite produced from montmorillonite clay and rice husk can be used as adsorbents for industrial application due to its high percentage removal of lead ion from aqueous solution up to (99.989%).

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