

## Adsorption of Pb(II) Ions from Aqueous Solutions Using Chemically Treated and Untreated Cow Dung Ash

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Batch experiments were conducted to evaluate the removal of Pb(II) ions from aqueous solutions using chemically and thermally activated cow dung (CTAC) ash and non-chemically but thermally activated cow dung (NTAC) ash under various experimental conditions. The optimum pH for the adsorption process using CTAC and NTAC was 5, while the optimum times using CTAC and NTAC were 240 and 180 min, respectively. Freundlich, Temkin, and Langmuir isotherm models were used to analyze the generated adsorption data. The Freundlich model had the highest coefficient of determination ( $R^2$ ) values that ranged from 0.989 to 0.999. The values of separation factor ( $R_L$ ) deduced from Langmuir isotherm were between 0 and 1 for both CTAC and NTAC ashes for the whole temperature range, which indicated favourable adsorption. Adsorption of the Pb(II) ions followed the pseudo-second-order kinetic model based on the  $R^2$  values that approached unity. Thermodynamic analyses revealed that the  $\Delta H^\circ$  values for CTAC and NTAC ashes were -8.69 and -11.39 kJ/mol, respectively, which indicated that ion adsorption was exothermic. Negative  $\Delta S^\circ$  values for the two adsorbents showed that the level of entropy was low at the solid/solvent interface during the adsorption process.

*Keywords:* Adsorption; Heavy metal; Cow dung ash; Adsorbent; Isotherm

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### INTRODUCTION

Heavy metals are toxic cations that can have devastating effects on human health at low concentration levels because they tend to build up in living tissues (Rao *et al.* 2010). The advancement in the use of heavy metals in recent decades has inevitably resulted in their release into the aquatic environment. The industrial revolution with respect to manufacturing and transportation sectors has harnessed some metals, such as Fe, Pb, Cu, *etc.*, which have invariably polluted the environment (Fraile *et al.* 2005). Leaching, electroplating, dyeing, effluent discharge, and run-off from farmland have all contributed to the dispersion of metal cations into the aquatic environment (Aksu and Kustal 1990).

The use of heavy metals and other metal-containing chemicals in industries often results in the generation of aqueous effluents with various concentration levels of heavy metal cations, which pose certain environmental challenges (Antunes *et al.* 2003). For instance, lead cations can be found in the effluents from electroplating processes. Plastic, paint, mining, metallurgical, petrochemical, pulp and paper, and battery production also generate wastewater that contains lead cations. The presence of heavy metal cations, such

as lead, in aquatic systems is often influenced by factors such as pH, salinity, and biological transformation (US EPA 2005).

Pavithra *et al.* (2017) and Kumar *et al.* (2018) reported that a good number of processes, both physical and chemical, have been employed to mitigate industrial effluent laden with heavy metal such as hexavalent chromium, and thereby reduce the metal load to within industrial effluent permissible limits. Among the established separation methods are ion exchange (Pakzadeh and Batista 2011; Li *et al.* 2017) and chemical precipitation (Golbaz *et al.* 2014; Yang *et al.* 2016). Others include electrochemical technologies (Liu 2011) and adsorption (Anbalagan *et al.* 2016), *etc.* The financial implications of some of these methods are on the high side. However, it is important to embrace low-cost and effective alternatives. Kumar *et al.* (2018) asserted that adsorption method has an edge over other separation methods, in the sense that it is eco-friendly and cost effective. Regeneration of adsorbent is possible with adsorption technique, which will however solve the problem of sludge (Borna *et al.* 2016). The removal of toxic metals using adsorption system is a viable alternative, mostly used in soil and wastewater treatment. In choosing a particular adsorbent for adsorption process, factors such as potency, cost, and availability of materials must be taken into cognizance. In their submission, Jeppu *et al.* (2012) examined some viable adsorbents for the removal of heavy metals, and kinetic and adsorption isotherms of the process were as well investigated. Jeppu and Clement (2012) reported optimizing the favourable conditions for optimum adsorption capacity; the variation of process factors such as temperature, initial metal concentration, dosage, and residence time on the adsorption of Cu, Ni, Cr, and Zn from aqueous solution was carried out by Xue *et al.* (2009).

For a long time now, activated carbon has been highly effective for the removal of toxic cations from industrial effluent, but it has been found to release soluble compounds under extreme pH (Wasewar 2010). Suganya and Kumar (2018) reported that activated carbon, having so many active sites and pores is useful in the purification of wastewater by removing contaminants of varying concentrations. Synthesis of activated carbon centres mainly on the processing of agricultural bio-wastes (Vishnuganth *et al.* 2016). Domestic and industrial wastes from kitchen, breweries, plastic industries, paper and pulp industries, wood industries, *etc.* into activated carbon will lessen the pressure on living carbonaceous materials (Rangabhashiyam *et al.* 2016). Anbalagan *et al.* (2016) reported that adsorbing materials synthesised from natural agricultural materials such as fishtail palm *Caryota urens* seeds, can be used to remove both organic and inorganic pollutants due to high active sites, light weight, and porosity. *C. urens* seeds, consisting of glucose, sucrose, and fructose which are all simple sugars enhance the adsorption of heavy metals from wastewater and simulated aqueous solution.

Researchers have intensified efforts in discovering more potent adsorbents, with little cost, and which will compete with other established adsorbents. Some of the naturally and abundantly available materials which have been experimented in heavy metal removal include *Glebionis coronaria*, *Diploaxis harra*, vegetable and fruit peels, rice and wheat straw, *Salvinia* plant, *etc.* (Dhir and Kumar 2010; Hossain *et al.* 2012; Seniunait *et al.* 2014; Derbe *et al.* 2015; Jain 2015; Tounsadi *et al.* 2015).

Adsorption of Pb(II) ions onto different adsorbents typically increases with higher pH values. At a high pH, Pb(II) ions precipitate as Pb(OH)<sub>2</sub> (Weber 1993; US EPA 2005). Conversely, at a low pH, Pb(II) ions are not highly sorbed onto solid substrates due to protonated acidic groups on the solid's surfaces (Gao *et al.* 2003; US EPA 2005).

Living organisms require trace amounts of some essential metal ions. However, when such ions are supplied at higher concentrations, they become toxic, causing different damages to tissues and organs, as the ions cannot be easily secreted (Crini 2005).

The research presented in this report focuses on other ways of harnessing the use of cow dung, apart from being used as compost manure. Since cow dung is readily available in large mass at cow ranches, its use as adsorbent (ash) will also add to the research database.

Cow dung ash is friendly to the environment, readily available, and cheap to obtain. Its components include 12.5% CaO, 0.9% MgO, 0.3% CaSO<sub>4</sub>, 20% Al<sub>2</sub>O<sub>3</sub>, 20% FeO, and 61% SiO<sub>2</sub> (Vasanthakumar and Bhagavanalu 2003). SiO<sub>2</sub> has the highest percentage of all the components, and this gives cow dung ash the ability to attract metal ions (Qian *et al.* 2008). Treatment of cow dung with sodium carbonate before incineration not only prevents environmental effects of repulsive odour, but it also activates the adsorbent thereafter (Qian *et al.* 2008).

The objectives of this research were to: prepare chemically and thermally activated cow dung (CTAC) ash and non-chemically but thermally activated cow dung (NTAC) ash; determine the effects of pH, residence time, temperature, initial metal ion concentration, adsorbent dosage, and sorption capacity on Pb(II) ions removal using cow dung ashes; establish the kinetic and isotherm parameters, as well as the thermodynamic properties of the sorption process.

## EXPERIMENTAL

### Materials

#### *Preparation of adsorbent*

Cow dung was collected from the Sango Cattle Ranch in Akure, Nigeria. Fresh cow dung was sundried to reduce its moisture content, and the air-dried dung was oven-dried to a constant weight. The oven-dried sample was ground into powder, which was sieved through a 425- $\mu$ m screen.

Two different ashes were prepared. One was prepared by treating 1 g of the sieved powder with a 30% Na<sub>2</sub>CO<sub>3</sub> solution (10 mL) and it was heated to 90 °C  $\pm$  2 °C for 2 h; after treatment, the solids were filtered and washed several times with distilled water until the filtrate had a neutral pH. The treated solid was oven-dried at 105 °C, and then ashed in a muffle furnace (S30 2RR; Carbolite, Sheffield, England) at 800 °C for 1 h. The resulting ash was further treated by soaking it overnight in 1 M HCl. The supernatant was decanted from the solid residue, which was washed continuously with distilled water until the filtrate had a neutral pH.

The resulting solid was oven-dried at 105 °C and later calcined for 2 h at 750 °C. The final ash was labelled as chemically and thermally activated cow dung (CTAC) ash. The other dung ash was prepared by heating the oven-dried dung powder in a muffle furnace at 800 °C for 1 h without subjecting it to any chemical treatment. The resulting ash was labelled non-chemically but thermally activated cow dung (NTAC) ash. After the ash adsorbents were produced, they were characterised for their functional groups, morphologies and mineral compositions using a Fourier transform infrared (FTIR) spectrometer, scanning electron microscope coupled with energy dispersive X-ray spectrometer (SEM-EDX; EVO MA-10, Carl Zeiss, Jena, Germany), respectively.

### *Preparation of metal solution*

The stock solution of Pb(II) was prepared by dissolving an appropriate amount of lead nitrate,  $\text{Pb}(\text{NO}_3)_2$  into deionized water in a 1-L standard flask. The experimental solutions used were prepared from the above stock solution by diluting it with distilled deionized water to obtain the desired Pb(II) concentration levels.

## **Methods**

### *pH studies*

An aqueous solution of 100 mg/L Pb(II) ions was prepared from the stock solution. An amount of 50 mL was transferred to a beaker, and the pH was adjusted to 1 using dilute NaOH and  $\text{HNO}_3$ . This was repeated to obtain solutions of pH 2, 3, 4...7. The CTAC ash (0.5 g) was added into each of the beakers containing the Pb(II) solutions. These slurries were agitated at regular intervals for 6 h.

At the adsorption time, the solutions were filtered, and the filtrates were taken for analysis using an atomic absorption spectrometer (AAS Buck Scientific 210, Buck Scientific Inc., Norwalk, CT, USA). The above procedure was repeated for the NTAC ash in place of the CTAC ash.

### *Time dependence study*

The effects of contact time on Pb(II) ion removal from the aqueous solutions using modified cow dung ashes were investigated using different time intervals. A Pb(II) ion solution (50 mL of 100 mg/L) was added to a beaker and its pH was adjusted to 5; this solution was for the experiments at room temperature.

The CTAC ash (0.5 g) was added, and the suspension was shaken and allowed to stand for 5 min. Similar experiments were also conducted at different time intervals of 15, 30, 90, 120, 180, 240, 300, and 360 min. At the end of each time interval, the slurries were filtered, and the resulting filtrates were taken for analysis using AAS. The same procedure was repeated for the NTAC ash.

### *Studies on varied initial concentration of Pb(II) ions*

The effects of varying initial Pb(II) ion concentration were examined using concentrations of Pb(II) of 10, 25, 50, 100, and 200 mg/L in different beakers. The pH of the solutions were adjusted to 5 (optimum pH) and replicate experiments were performed. A dung ash adsorbent (0.5 g) was added to 50 mL of each Pb(II) solution. The suspensions were shaken and allowed to sit at room temperature for 180 min (optimum time for NTAC) and 240 min (optimum time for CTAC). The suspensions were filtered at each time interval and the filtrates were analysed using AAS.

### *Temperature dependence study*

The effects of temperature were studied at 28, 35, 45, and 55 °C. A Pb(II) ion solution (50 mL of 100 mg/L) was adjusted to the optimum pH of 5 and transferred into a beaker. The dung ash adsorbent (0.5 g) was added, shaken, and allowed to stand for the optimum time. The ash suspensions were filtered, and the filtrates were analysed using AAS.

## RESULTS AND DISCUSSION

### Characterisation of CTAC and NTAC Ashes

The FTIR scans for the CTAC and NTAC ashes are presented in Figs. 1 and 2, respectively. For the CTAC ash, the following absorption peaks were noted at wavenumbers of 3445.0, 1454.4, 1639.2, and 1066.2  $\text{cm}^{-1}$ , which indicated a hydroxyl (HO-) stretch, C-H bend, N-H bend, and C-O stretch, respectively. The notable wavenumber peaks in the NTAC ash were 3442.0, 1628.0, and 1060.0  $\text{cm}^{-1}$ , which corresponded to a hydroxyl (HO-) stretch, N-H bend, and C-O stretch, respectively. Adsorption process can only be achievable if these notable functional groups are embedded in the adsorbent. Nacke *et al.* (2016) reported that functional groups indicated by the OH-stretch, N-H bend, among others play important roles in the process of adsorption, and effectively remove heavy metals as a result of ion exchange. Kumar and Jena (2015) reported that wavenumbers in the range 3725 to 2950  $\text{cm}^{-1}$  indicate the availability of OH-group, which can be linked to phenolic, alcohols, as well as carboxylic acids.

The morphologies and mineral compositions of the samples were evaluated using scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX). The SEM images of the CTAC and NTAC ashes are shown in Figs. 3 and 4, respectively. The SEM images were captured at 100  $\mu\text{m}$ . It was observed that the surface particles of CTAC appeared as irregular blocks that formed aggregates (Fig. 3); the surfaces also appeared coarse, which could have been due to the chemical and heat treatments. However, the particle surfaces of NTAC appeared smoother (Fig. 4) than those of CTAC (Fig. 3). It was also observed that the NTAC surface particles appeared as fluffy fibres. Figures 5 and 6 show the EDX spectra of CTAC and NTAC, respectively. The results indicated the CTAC ash contained the elements of K, C, Ca, O, Fe, Si, Na, Mg, and Al. Similar elements were found in the NTAC ash, along with S, P, and Cl.

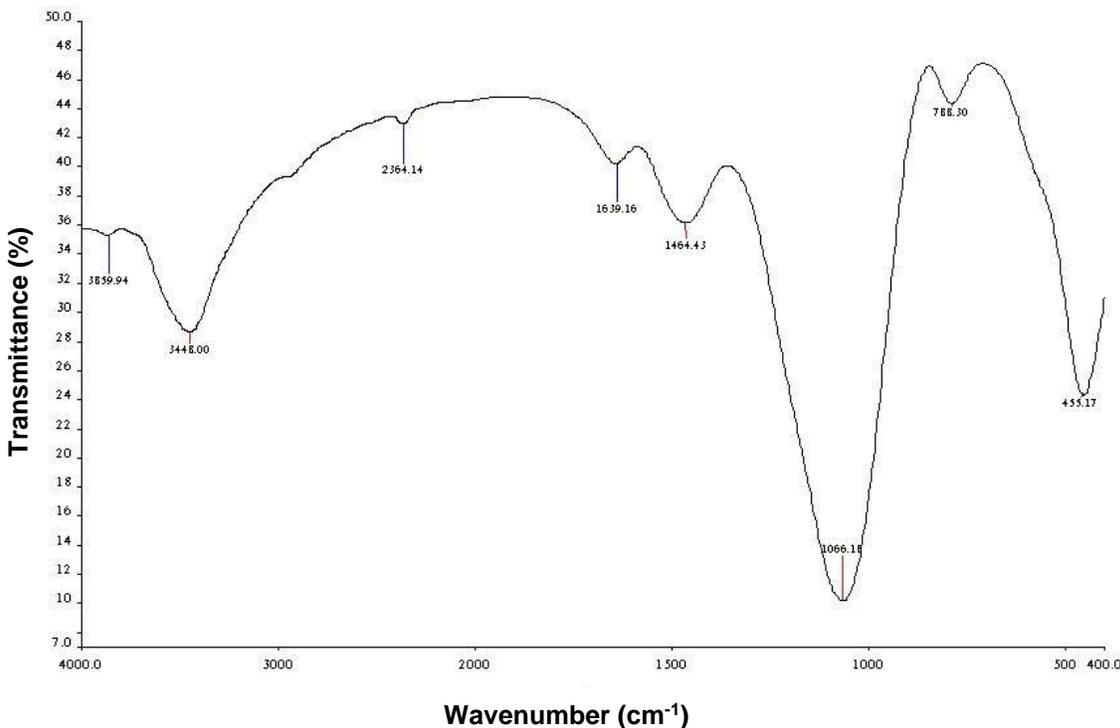


Fig. 1. FTIR spectra of CTAC ash

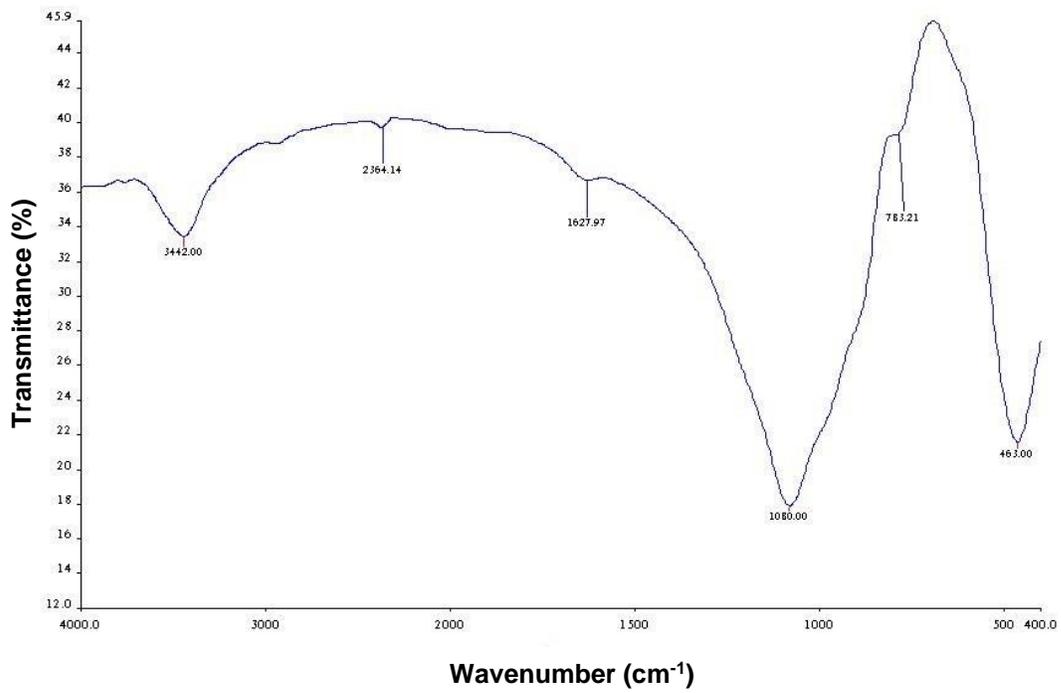


Fig. 2. FTIR spectra of NTAC ash

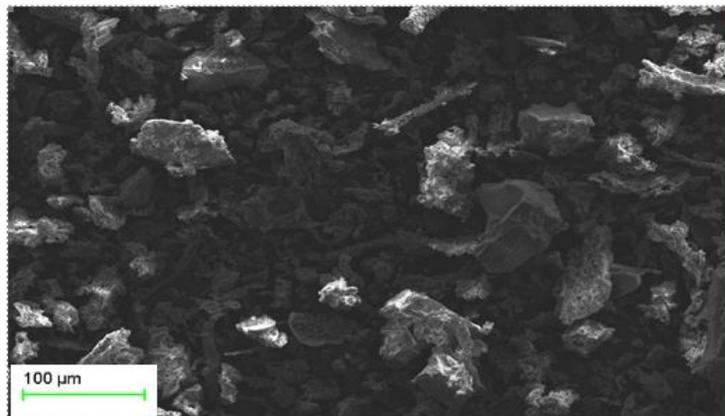


Fig. 3. Scanning electron micrograph of CTAC ash

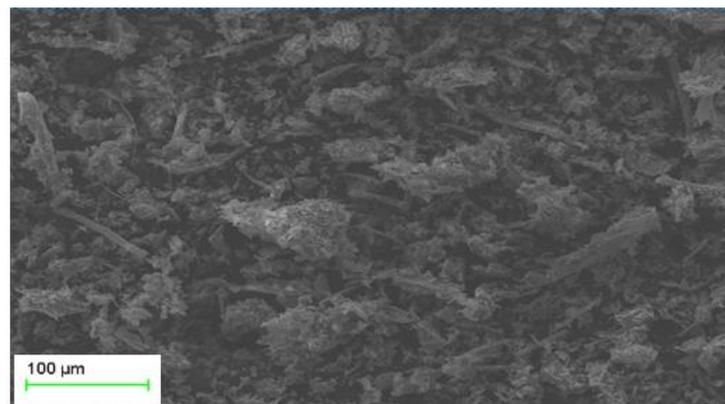


Fig. 4. Scanning electron micrograph of NTAC ash

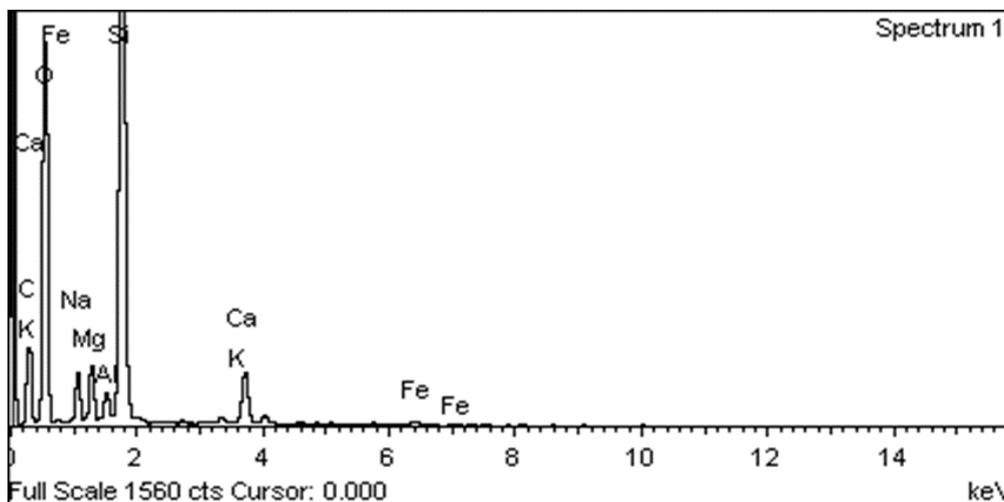


Fig. 5. EDX spectra of CTAC ash

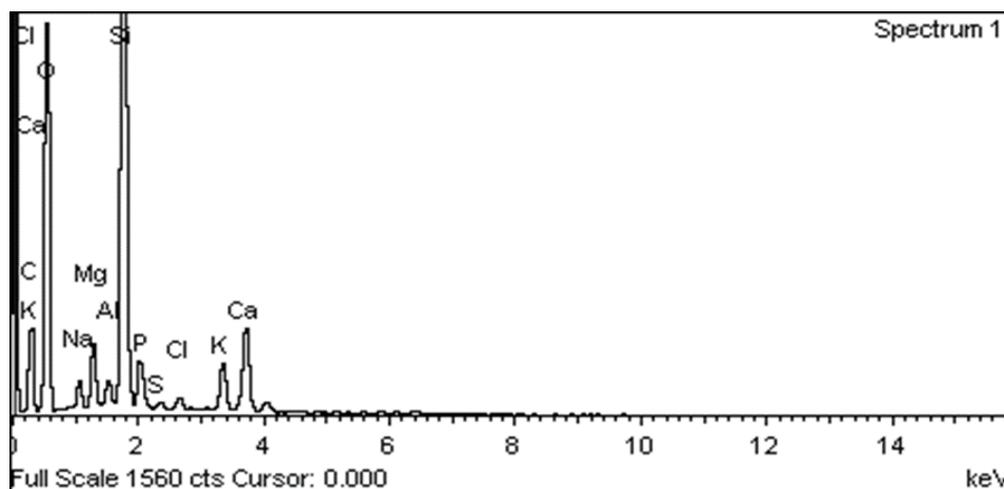


Fig. 6. EDX spectra of NTAC ash

### Effects of pH Variation

The percentage removal of Pb(II) ions increased from 27.3% to 69.9% using CTAC ash, and from 33.0% to 81.0% using NTAC ash when the solution pH was increased. Figure 7 clearly shows that the sorption efficiency increased as the pH was increased from 1 to 7 for both adsorbent ashes. At pH > 5, a Pb(OH)<sub>2</sub> precipitate was formed. The uptake capacities for the Pb(II) ions by CTAC and NTAC ashes at a pH of 5 were 6.60 mg/g and 7.93 mg/g, which corresponded to a 66.0% and 79.3% reduction of aqueous Pb(II) levels, respectively. As the pH of the solution was increased, the acidic groups on the adsorbent surfaces were ionized, allowing them to bind with the Pb(II) ions. Okoronkwo *et al.* (2009) reported a decrease in metal ion removal at pH values lower than 5, which is similar to the observed results of this work. Gupta *et al.* (2001) indicated that at pH values as low as 2.0, virtually all of the binding sites on the adsorbent surface were protonated, which released all the originally sorbed metal cations. Aksu (2001) reported that when pH is increased, more functional groups (such as amino and carboxyl groups) would be deprotonated, which would enhance the binding of metal cations onto the active sites of the adsorbent.

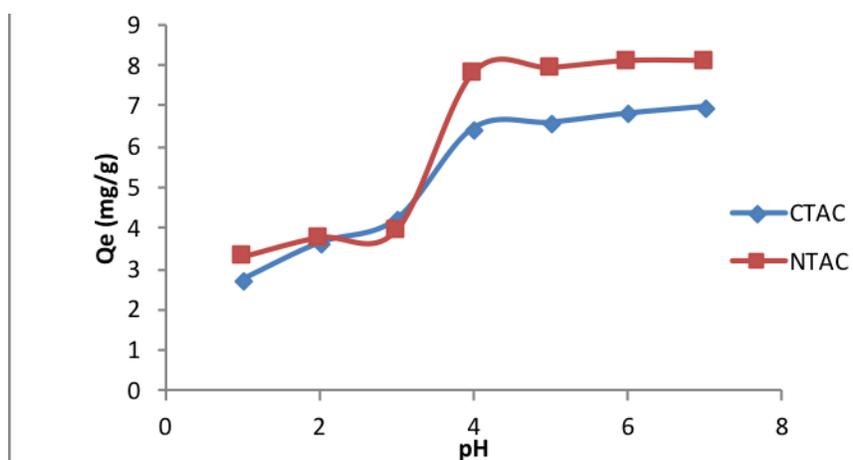


Fig. 7. Effect of pH on the adsorption of Pb(II) using CTAC and NTAC ash

### Time Dependence Studies of Adsorption

The effects of contact time on the adsorption of Pb(II) ions using CTAC and NTAC ash were investigated to determine the minimum time required to achieve sorption equilibria. Contact times with the adsorbent ashes of 5, 15, 30, 90, 120, 180, 240, 300, and 360 min were examined. Figure 8 shows that the rate of sorption of Pb(II) ions onto the CTAC ash was rapid for the first 180 min, and it attained equilibrium at 240 min. Adelaja *et al.* (2011) reported similar findings for *Moringa oleifera* seed pods for the sorption of Pb(II) ions. The sorption equilibrium time for Pb(II) ions onto NTAC ash was 180 min. The equilibrium uptake capacities for both CTAC and NTAC ash were 6.78 mg/g and 7.82 mg/g, which corresponded to a 67.8% and 78.2% reduction of aqueous Pb(II) levels, respectively.

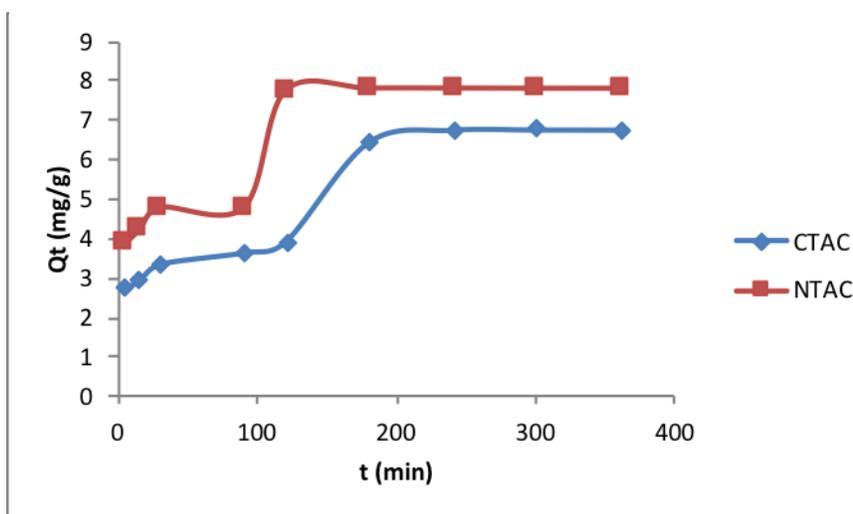


Fig. 8. Effect of contact time on the adsorption of Pb (II) ions using CTAC and NTAC ash

After the equilibrium time, there was minimal additional uptake of Pb(II) ions. This behavior suggested that the initial phase of cation sorption takes place rapidly due to the availability of abundant porous sites on the adsorbent surface. Similar observations have been reported in scientific literature (Saravanne and Sundarajan 2002; Narsi *et al.* 2004).

Furthermore, metal ions could also encounter some resistance in adhering to the surface as the remaining active sites could no longer accommodate additional ions; this invariably slowed the cation removal process in the later phases of the adsorption process (Srivastava *et al.* 2013).

### Kinetics of Pb(II) Ion Removal

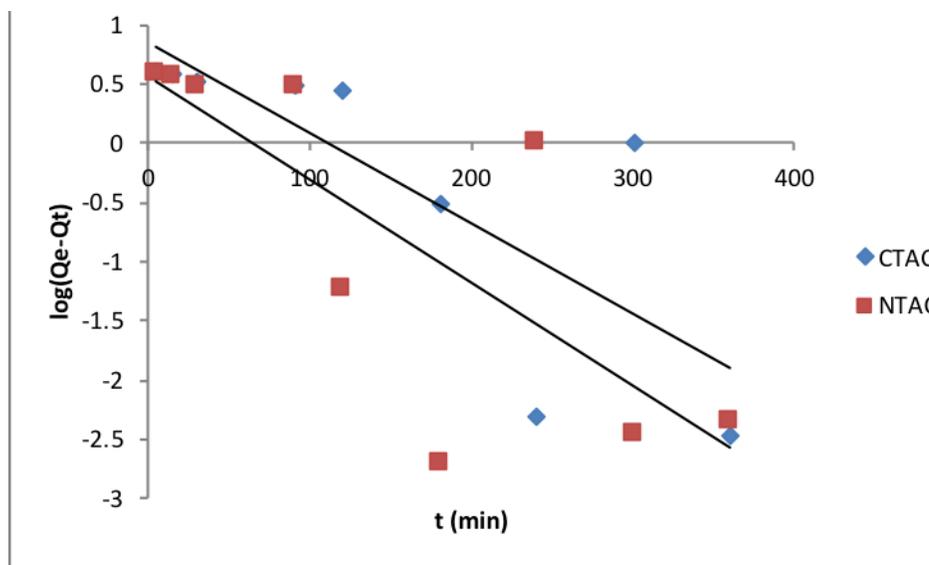
#### *Pseudo-first-order kinetic model for Pb(II) removal*

The rate of adsorption was first modeled as a pseudo-first-order rate, which is presented as,

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

where  $q_e$  (mg/g) and  $q_t$  (mg/g) are the quantities of the cation removed at equilibrium and at a given specific time  $t$  (min), respectively. The term  $k_1$  ( $\text{min}^{-1}$ ) is a pseudo-first-order constant. The values of  $k_1$  and  $q_{e,cal}$  were determined from the slope and the intercept of the plot of  $\log (q_e - q_t)$  versus  $t$  (Fig. 9); the results from the linear regression analysis are given in Table 1.

The results showed that the values of  $q_{e,cal}$  and  $q_{e,exp}$  were very close to one another for the CTAC ash, but the  $R^2$  value for this regression was far from unity. There was a large difference in the value of  $q_{e,cal}$  versus  $q_{e,exp}$  for the NTAC ash, which resulted in a  $R^2$  value that was also far from unity. This observation suggested that the pseudo-first-order model was not an appropriate model for the sorption behavior of Pb(II) ions by the adsorbent ashes.



**Fig. 9.** Pseudo-first-order plot of the adsorption of Pb (II) using CTAC and NTAC ash

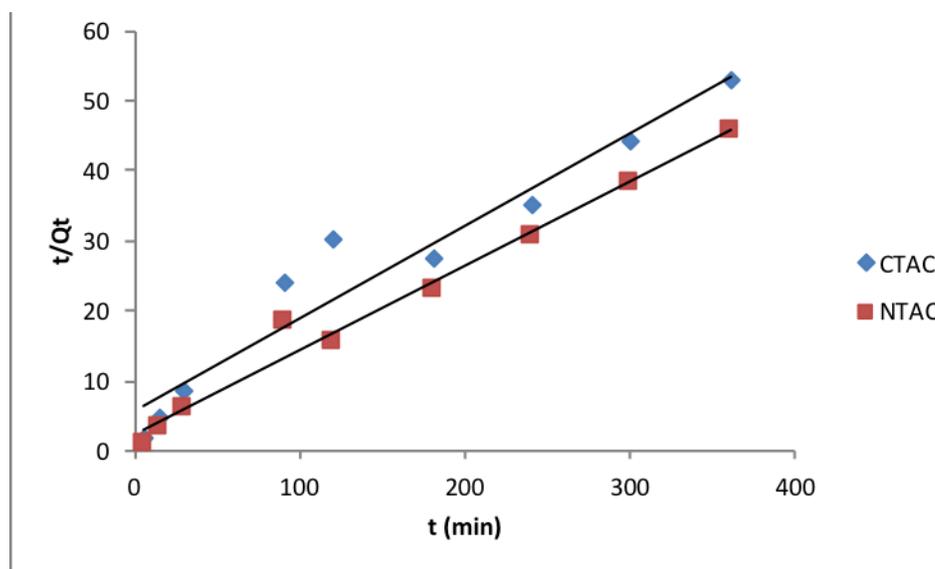
#### *Pseudo-second-order for Pb(II) ion adsorption*

A pseudo-second-order model, in its linearized form, was tested with the data; the expression is given as:

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

Plots of  $t/q_t$  versus  $t$  for both the CTAC and NTAC ashes are shown in Fig. 10. The values of  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ),  $q_e$ , and  $R^2$  were calculated from the regression plots; the results are

presented in Table 1. The data appeared to follow a pseudo-second-order kinetic model more so than the pseudo-first-order model based on the higher  $R^2$  values. Additionally, the experimental  $q_e$  value ( $q_{e,exp}$ ) was very close to the regression calculated  $q_e$  value ( $q_{e,cal}$ ) for both ash adsorbents. Okoronkwo *et al.* (2014) noted similar observations for chitosan as an adsorbent for the adsorption of  $Cu^{2+}$  and  $Ni^{2+}$  ions in a binary system. Furthermore, the pseudo-second-order rate constant,  $k_2$ , for the CTAC ash was lower than that for the NTAC ash, which indicated that the uptake of Pb(II) by NTAC ash was more rapid and favorable.



**Fig. 10.** Plot of pseudo-second-order kinetic model for Pb(II) ion adsorption by CTAC and NTAC ash

#### *Intra-particle diffusion model*

The kinetic data were also evaluated by an intra-particle diffusion model to determine if the phenomenon was diffusion-controlled. The model was expressed as,

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

where  $C$  ( $mg\ g^{-1}$ ) is a constant (intercept) and  $K_i$  ( $mg\ g^{-1}min^{-1/2}$ ) is the intra-particle diffusion constant. A large value of  $C$  increased the contribution of the surface in the rate-determining step. The  $K_i$  and  $C$  values for the two adsorbents are given in Table 1.

Intra-particle diffusion will be the rate-limiting step if the regression of the plots is linear, and if the curve goes through the origin. It has been suggested that if the plot of  $q_t$  versus  $t^{1/2}$  is multi-linear, then, two or more steps are involved in the adsorption system (Boparai *et al.* 2010). The  $R^2$  values obtained from the data regression to Eq. 3 for CTAC and NTAC ashes were 0.866 and 0.821, respectively (Table 1). As a result of continuous agitation and equilibration of the adsorbing species onto the surface active sites of the adsorbent, it was assumed that the surface adsorption and the intra-particle diffusion took place concurrently during the interactions of Pb(II) ions and the ash adsorbents, and that chemical and physical adsorptions were involved in the overall process.

**Table 1.** Kinetic Parameters for Adsorption of Pb(II) ions onto CTAC and NTAC Ash Adsorbents

Parameters	CTAC	NTAC
<i>Pseudo-first-order</i>		
$q_{e,exp}$ (mg·g <sup>-1</sup> )	6.788	7.826
$q_{e,cal}$ (mg·g <sup>-1</sup> )	6.902	3.614
$k_1$ (min <sup>-1</sup> )	0.016	0.018
R <sup>2</sup>	0.626	0.607
<i>Pseudo-second-order</i>		
$q_{e,cal}$ (mg·g <sup>-1</sup> )	7.576	8.333
$k_2$ (g·mg <sup>-1</sup> ·min <sup>-1</sup> )	0.003	0.006
R <sup>2</sup>	0.935	0.981
<i>Intra-particle Diffusion</i>		
$K_{id}$ (mg·g <sup>-1</sup> ·min <sup>-1/2</sup> )	0.282	0.271
C (mg·g <sup>-1</sup> )	1.790	3.376
R <sup>2</sup>	0.866	0.821

### Adsorption Mechanism – Isotherm Studies

Adsorption isotherms are often expressed as linear equations of Langmuir, Freundlich, Temkin, as well as Dubinin-Radushkevich models. These models are good tools to establish the adsorption mechanism. The mostly suited model can be established by comparing the correlation coefficient R<sup>2</sup> of all the models used in an adsorption process (Kamaraj and Vasudevan 2016).

#### *Langmuir isotherm for Pb(II) ion removal*

The Langmuir isotherm model is based on the principle of surface homogeneity, with respect to the following characteristics of equally available adsorbent active sites, monolayer coverage of the surface, and sorbent-sorbate interaction (Arica *et al.* 2004). The mathematical expression for this isotherm model is:

$$C_e/q_e = C_e/q_{max} + 1/(q_{max}K_L) \quad (4)$$

On the basis of the Langmuir isotherm adsorption model, an important parameter was the separation factor ( $R_L$ ) (Ozer and Ozer 2004; Malkoc and Nuhoglu 2007), which was defined as:

$$R_L = 1/1 + K_L C_o \quad (5)$$

where  $C_o$  (mg L<sup>-1</sup>) denotes the initial metal ion concentration and  $K_L$  (L mg<sup>-1</sup>) is the Langmuir constant (from Eq. 4).

The separation factor is considered a more reliable parameter for the adsorption system based on four different scenarios: (1) favorable adsorption when  $0 < R_L < 1$ ; (2) unfavorable adsorption when  $R_L > 1$ ; (3) linear adsorption when  $R_L = 1$ ; and (4) irreversible adsorption when  $R_L = 0$ . The plots of  $C_e/q_e$  versus  $C_e$  (Figs. 11 and 12 for CTAC and NTAC ash adsorbent, respectively) showed that the data were modeled reasonably well by this isotherm model. The coefficient of determination (R<sup>2</sup>),  $q_{max}$ , and  $K_L$  were determined from the data regression during the curve fitting, and their values are given in Table 2. The results showed that the NTAC ash had higher R<sup>2</sup>,  $q_{max}$ , and  $K_L$  values, which suggested that the NTAC ash was a better adsorbent for Pb(II) ion removal from aqueous solutions than the CTAC ash. The  $R_L$  values were greater than 0 but less than 1 for both the CTAC and NTAC ashes for every temperature value examined, which indicated a favorable adsorption phenomenon. Anbalagan *et al.* (2016) reported that the range of values of separation factor

( $R_L$ ) estimated from Langmuir isotherm was  $R_L = 0 < 1$ . This shows that the adsorption process was a favourable one. Ojedokun and Bello (2016), using cow dung ash for the removal of Cr(VI) ion, observed that the experimental data fitted well into both Langmuir and Freundlich isotherms. Baral *et al.* (2006) reported that optimum uptake and strong bonding were observed in the removal of hexavalent chromium from aqueous solution using treated sawdust under experimental conditions used. Iftikhar *et al.* (2009) and Barkat *et al.* (2009) submitted similar reports in their studies on the adsorption of  $\text{Cu}^{2+}$  and  $\text{Cr}^{3+}$  using rose waste biomass as adsorbent, and  $\text{Cr}^{6+}$  using activated carbon, respectively.

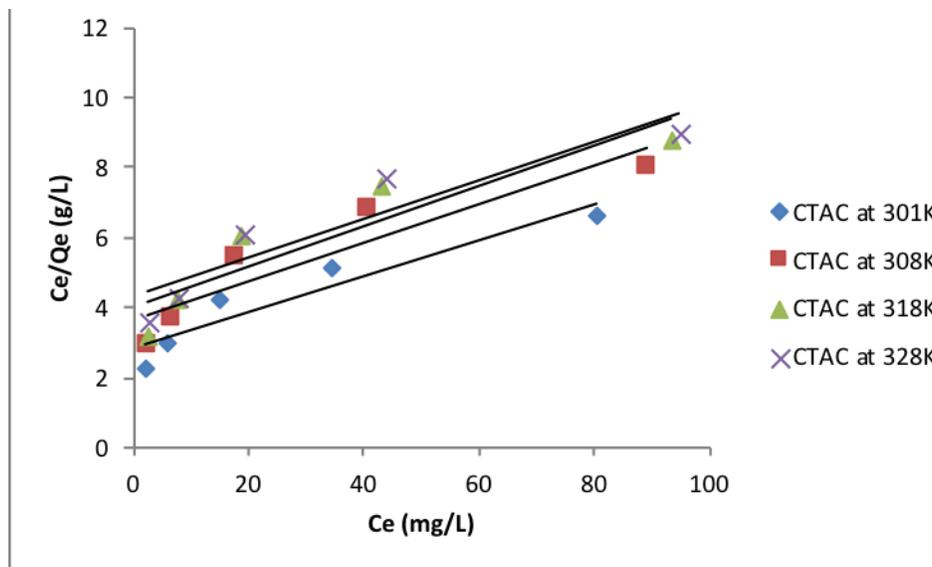


Fig. 11. Langmuir isotherm model for CTAC ash adsorbent at different temperatures

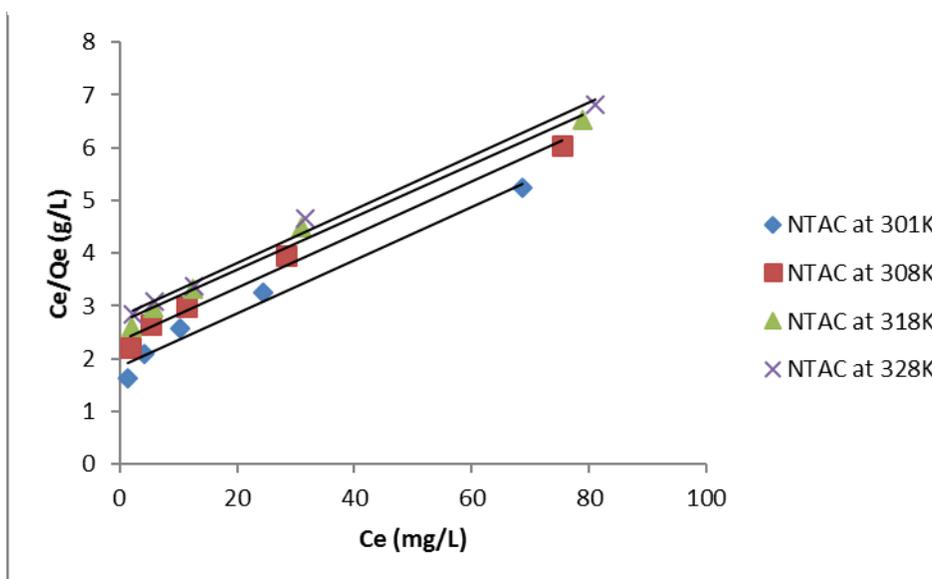


Fig. 12. Langmuir isotherm model for NTAC ash adsorbent at different temperatures

### Freundlich isotherm

The empirical Freundlich isotherm model for sorption is based on the heterogeneity of the sorbent surface; the model is expressed as:

$$\log q_e = \log K_F + (1/n) \cdot \log C_e \quad (6)$$

where  $n$  and  $K_F$  are the Freundlich exponent and constant, respectively.

The plots of Freundlich isotherm for CTAC and NTAC are presented in Fig. 13 and 14, respectively. When the value of  $n$  is between 1 and 10, then the adsorption process is favorable. The values of  $R^2$ ,  $K_F$ , and  $n$  were determined from the data regression to Eq. 6, and the results are given in Table 2. The magnitudes of  $K_F$  and  $n$  indicated adsorption of Pb(II) ions, and high adsorption capacity. High  $R^2$  values for Pb(II) ion removal using both CTAC and NTAC ashes showed that the data were modeled well by the Freundlich isotherm model. Christopher *et al.* (2016) in their study, reported that Freundlich isotherm was obeyed, based on the higher correlation coefficient over other models, when using chitosan functionalised magnetic nanoparticles as adsorbent. Christopher *et al.* (2016) also reported that the adsorption of Pb(II) ion using chitosan functionalised magnetic nanoparticles was favourable due to high adsorption capacity.

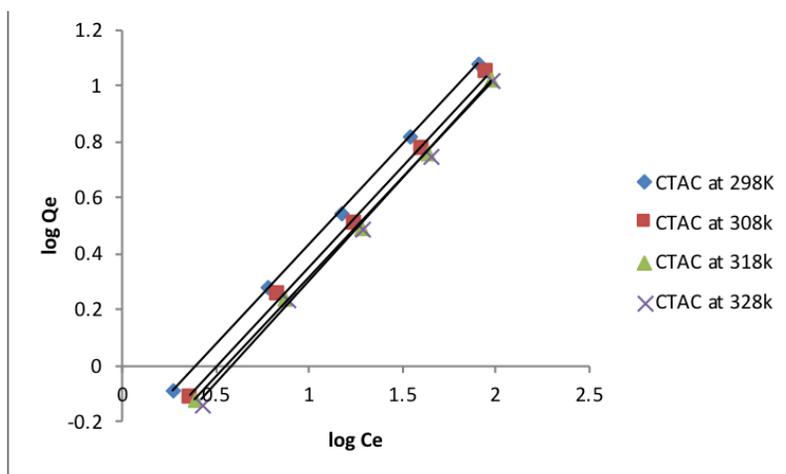


Fig. 13. Freundlich isotherm model for CTAC ash adsorbent at different temperatures

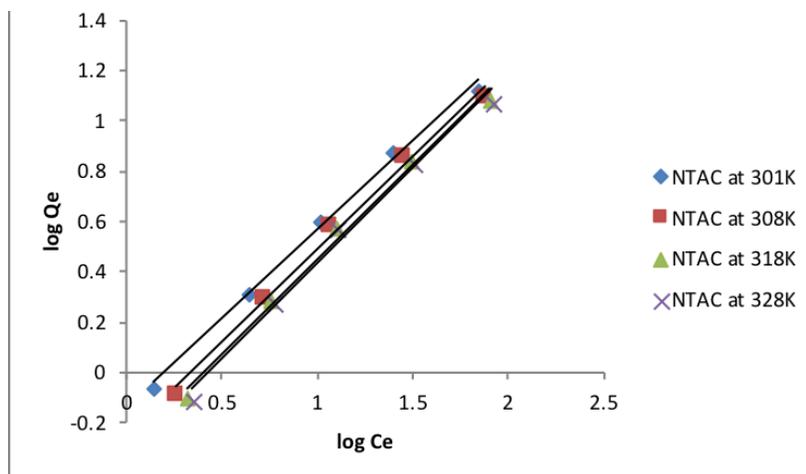


Fig. 14. Freundlich isotherm model for NTAC ash adsorbent at different temperatures

### Temkin isotherm

A Temkin isotherm models the interactions between the porous bed adsorbent and the ionic species to be adsorbed. The model also assumes that the free energy involved in the sorption process depends on the coverage of the surface (Deng and Ting 2005). The model is given as:

$$q_e = B_T \cdot \log K_T + B_T \cdot \log C_e \quad (7)$$

where  $K_T$  is the equilibrium binding constant (L/mg),  $q_e$  is the amount adsorbed (mg/g),  $C_e$  is the equilibrium concentration of the metal ion (mg/L), and  $B_T$  is Temkin constant related to the heat of adsorption (kJ/mol). The model suggests that the heat of adsorption among the molecules decreases linearly with increased coverage of the adsorbent due to the interactions between the adsorbent and the ionic species of the metal solution. The model also predicts that adsorption is often characterized by an even distribution of energies involved in binding, up to the optimum binding energy. Figures 15 and 16 are the Temkin plots for CTAC and NTAC ash, respectively, for a range of adsorption temperatures. Temkin constants,  $B_T$  and  $K_T$ , were determined from the data regression to the model (Table 2). The higher coefficient of determination,  $R^2$ , for the Freundlich isotherm model indicated that it represented the adsorption data better than both the Langmuir and Temkin isotherm models.

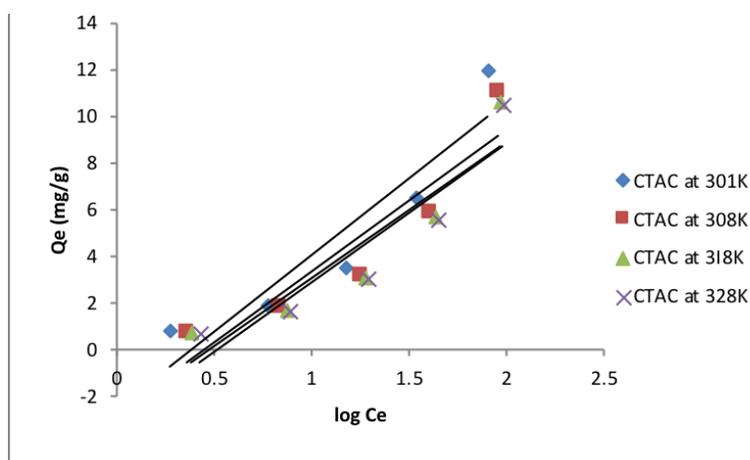


Fig. 15. Temkin isotherm model for CTAC ash adsorbent at different temperatures

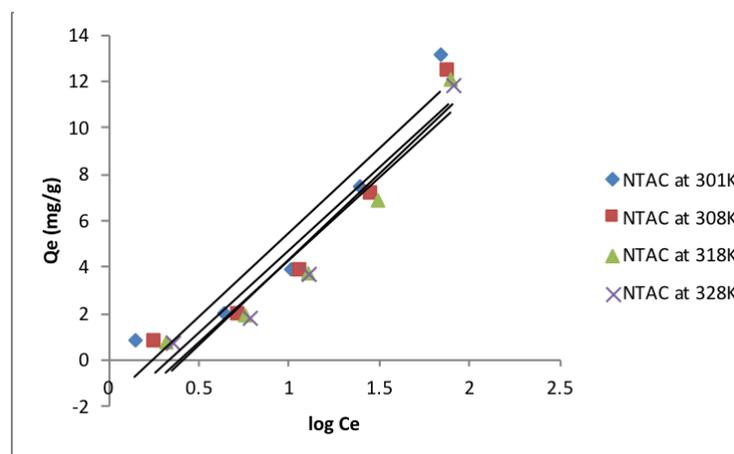


Fig. 16. Temkin isotherm model for NTAC ash adsorbent at different temperatures

**Table 2.** Adsorption Isotherm Parameters for Adsorption of Pb(II) Ions onto CTAC and NTAC Ash Adsorbents

	Parameter	CTAC				NTAC			
		28 °C	35 °C	45 °C	55 °C	28 °C	35 °C	45 °C	55 °C
Langmuir	$q_{max}$ (mg·g <sup>-1</sup> )	19.608	18.519	18.182	18.182	20.000	20.000	20.408	20.000
	$K_L$ (L·mg <sup>-1</sup> )	0.018	0.015	0.013	0.013	0.027	0.021	0.018	0.018
	$R_L$	0.357	0.400	0.417	0.435	0.270	0.476	0.357	0.357
	$R^2$	0.894	0.849	0.862	0.862	0.979	0.989	0.989	0.993
Freundlich	$K_F$	0.532	0.438	0.407	0.366	0.724	0.577	0.505	0.479
	$n$	1.410	1.404	1.357	1.357	1.414	1.360	1.335	1.323
	$1/n$	0.709	0.712	0.710	0.737	0.707	0.735	0.749	0.756
	$R^2$	0.999	0.998	0.998	0.998	0.995	0.992	0.992	0.989
Temkin	$B_T$ (mg/L)	6.521	6.078	5.951	5.951	7.217	7.154	7.081	7.049
	$K_T$	0.429	0.357	0.309	0.309	0.578	0.459	0.406	0.387
	$R^2$	0.868	0.856	0.863	0.863	0.912	0.920	0.920	0.928

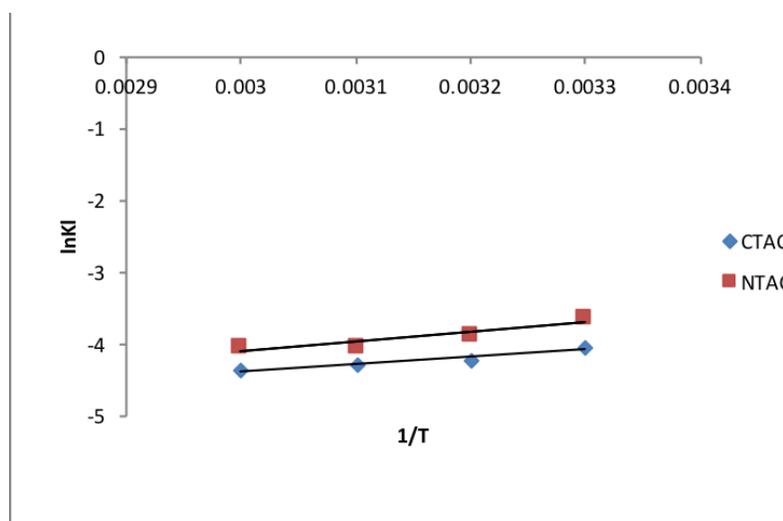
### Adsorption Thermodynamics for Pb(II) Ion Removal

The effects of temperature on ion adsorption are linked with many thermodynamic quantities. To clearly describe the influence of thermodynamic parameters on the removal of Pb(II) ions from solution, the enthalpy of adsorption ( $\Delta H$ ), entropy of adsorption ( $\Delta S$ ), and Gibb's free energy of adsorption ( $\Delta G$ ) were calculated from the Langmuir isotherm model,

$$\ln K_L = \Delta S^\circ/R - \Delta H^\circ/RT \quad (8)$$

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \quad (9)$$

where  $R$  represents the universal gas constant (8.314 J·mol<sup>-1</sup>·K<sup>-1</sup>) and  $T$  is the absolute temperature (K). The enthalpy of adsorption,  $\Delta H$  (J·mol<sup>-1</sup>), and entropy of adsorption,  $\Delta S$  (J·mol<sup>-1</sup>·K<sup>-1</sup>), were calculated from the slope and the intercept of plots of  $\ln K_L$  versus  $1/T$  (based on a Van't Hoff relationship (*i.e.*,  $\ln K_L = -\Delta G^\circ/RT$ )) as shown in Fig. 17.

**Fig. 17.** Van't Hoff plots for CTAC and NTAC ash adsorbents

The estimated thermodynamic quantities of adsorption from the plots are given in Table 3. The  $\Delta H^\circ$  values obtained for the CTAC and NTAC adsorbents were -8.69 kJ mol<sup>-1</sup>

<sup>1</sup> and  $-11.39 \text{ kJ mol}^{-1}$ , respectively, which confirmed that ion adsorption was an exothermic process. The  $\Delta G^\circ$  values were positive. The negative  $\Delta S^\circ$  values for the two adsorbents showed that the level of randomness was low at the solid/solution interface. Because  $\Delta S^\circ$  was very small under the experimental conditions examined, it can be concluded that its contribution to the ion adsorption phenomenon was negligible. Fabian *et al.* (2014) reported similar findings for the adsorption of Cr(III) ion onto sweet orange peels.

**Table 3.** Thermodynamic Parameters for Pb(II) Ion Adsorption by CTAC and NTAC Ash Adsorbents

Adsorbent	$\Delta H$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )	$\Delta S$ ( $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ )	$\Delta G$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )			
			301 K	308 K	318 K	328 K
CTAC	-8.688	-0.0623	10.078	10.515	11.138	11.762
NTAC	-11.390	-0.0681	9.115	9.592	10.274	10.955

## CONCLUSIONS

1. This study investigated the viability of the conversion of cow dung into a useful biosorbent ash for the removal of Pb(II) ions from aqueous solutions. The characterization of the adsorbent revealed the presence of hydroxyl, amine, and carbonyl groups, the functional groups enabled the adsorption process as they offer active sites for metal ions.
2. The data were analyzed by three isotherm models: Langmuir, Freundlich, and Temkin. The analyses indicated that the experimental data was modeled well by the Freundlich model with a high coefficient of determination ( $R^2$ ).
3. Determination of the thermodynamic parameters of adsorption indicated that the adsorption process was exothermic, not only that, the entropy of the system which was low (negative), which allowed the adherence of the ionic species onto the adsorbent active sites.
4. Additional analyses of the experimental data revealed that the adsorption phenomenon by the adsorbent ashes could be modeled by pseudo-second-order kinetics.
5. Lastly, as proven by the efficacy of the cow dung ash for Pb(II) ion removal, it can be observed that that the usefulness of cow dung is not only limited to being used as compost manure, but also as potent adsorbent for heavy metal. Further study is however needed on the use of cow dung ash for the removal of other heavy metals.

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