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Kinetic and equilibrium modelling of lead sorption from aqueous solution by activated carbon from goat dung

Mambo Moyo*, George Nyamhere, Edith Sebata, Upenyu Guyo

Department of Chemical Technology, Midlands State University, Private Bag 9055, Senga, Gweru, Zimbabwe, Tel. +263712500488, +27839847553; email: moyom@msu.ac.zw (M. Moyo), Tel. +263712548061; email: nyamhereg@gmail.com (G. Nyamhere), Tel. +263775153177; email: sebatae@msu.ac.zw (E. Sebata), Tel. +263778015360; email: guyou@msu.ac.zw (U. Guyo)

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ABSTRACT

The potential of goat dung-derived activated carbon as an adsorbent for the removal of lead from aqueous solution in a batch system was studied. Physicochemical properties of the biosorbent were characterized by means of X-ray diffraction, scanning electron microscopy and Fourier transform infrared spectroscopy. Batch adsorption experiments were carried out as a function of pH, contact time, adsorbent dosage, initial concentration and temperature. The adsorption showed a pH dependent profile and an optimum value at pH 4.5. The adsorption isotherm modelling showed that the equilibrium data fitted better to the Freundlich than the Langmuir model. Kinetic data were properly fitted with the pseudo-second-order kinetic model. Furthermore, the thermodynamic parameters indicated that the adsorption reaction was endothermic and a spontaneous process.

Keywords: Lead; Goat dung; Adsorption; Isotherms; Kinetics; Thermodynamics

1. Introduction

The presence of toxic metals in environmental wastewater can be harmful to humans and living species even in low concentration. The aqueous toxic heavy metals are non-degradable, can accumulate in living bodies, and get concentrated through the food chain and cannot be detoxified biologically [1]. Among the toxic metals, Lead may be found in wastewaters from many industries involving metal plating; painting, mining operations and battery manufacture [2]. Lead poisoning causes the nervous system, gastrointestinal system, cardiovascular system, blood production, kidneys and reproductive system problems [3]. The World Health Organization recommends that the

amount of lead should be 0.01 mg L^{-1} for safe drinking water and the permissible level of lead in wastewater given by the Environmental Protection Agency is 0.05 mg L^{-1} [4,5].

In recent years, various physicochemical methods for heavy metal removal from aqueous solution, including ion exchange, precipitation, oxidation, reduction and membrane filtration, have been reported [6–8]. Compared with the aforementioned methods, adsorption technology, using some cheap, easily available agricultural plants, algal biomass, and cyanobacteria, has undoubtedly been one of the preferable techniques to remove some trace metal ions [9]. However, the use of raw sorbents in adsorption may cause problems since most plants and animal waste contain a pigment (sparingly soluble in water) and some organic matter, may be leached out,

^{*}Corresponding author.

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consequently affecting the taste and colour of the treated waters [10,11]. In spite of the efficacy of commercial activated carbon as an adsorbent in wastewater treatment with its high surface area, microporous characteristics, and high adsorption capacity; its high cost and loss during the regeneration restrict its applications in developing countries [12,13]. In order to address the aforesaid problems, a search for alternative activated carbon from abundant and low cost precursors has increased in recent years. The activated carbon has mainly been derived from plant-based carbonaceous locally available materials such as *Ceiba pentandra* hulls [12]; coconut coir [13], rice hush ash [14], maize tassel [15]; peanut shells [16]; *Sterculia alata* nutshell [17]; and hazelnut husks [18] just to mention a few.

In addition to plant-derived activated carbons, little information is reported in literature concerning the exploitation of animal waste for the adsorption of aqueous metal ions [18-24]. Zinc was adsorbed from activated carbon derived from heat treated grinded sheep manure waste [20]. Elsewhere, Zaini et al., (2009) reported on the use of activated carbon prepared from cattle manure compost using ZnCl₂ as an activating agent to remove Cu(II) and Pb(II) from aqueous solution [24]. It is important to extend the investigation on the potential of other animal manurebased carbons to fill a much-needed niche in the overall carbon market which is extremely high. Therefore, the focus of the present study was to assess the potentiality of activated carbon derived from goat dung for the adsorption of lead from aqueous solution. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to elucidate the adsorption process. The effects of pH, adsorbent dosage, contact time, initial metal concentration and temperature were investigated. The adsorption isotherm, sorption kinetics and thermodynamics of lead onto activated carbon are presented. FTIR, XRD and SEM were also used to elucidate the adsorption process.

2. Materials and methods

2.1. Preparation of the adsorbent

The goat dung was collected from Manhede farm, Gweru, Zimbabwe. The sample was sealed in clean plastic bags. The sample was then sun dried for 2 d to obtain significant loss of moisture. The activated carbon was prepared using a simple and convenient reported procedure [15]. Briefly, the goat dung powder (200 g) was weighed in a clean dry beaker of capacity 1 L containing (200 mL, 97% H₂SO₄ for 24 h) followed by refluxing in a fume hood for 4 h. After cooling, the reaction mixture was filtered, and the filtrate was washed repeatedly with distilled water and soaked in 1% NaHCO₃ solution to neutralize any remaining acid. The sample was then washed with distilled water until the pH was neutral and became free from SO_4^{2-} ion (negative BaCl₂ test), dried overnight in an oven at 120°C, and kept in a glass bottle until use.

2.2. Preparation of metal ion solution

A stock solution of 1 g L^{-1} of lead (II) ions was prepared by dissolving appropriate amount of Pb (NO₃)₂ in distilled water. The used concentrations were obtained by dilution of the stock solution. All the necessary chemicals used in the study were of analytical grade.

2.3. Adsorption experiments

Batch adsorption experiments were carried out in 250 mL conical Erlenmeyer flasks containing 50 mL of lead solutions. The flasks with adsorbent dosage of 0.50 g were shaken at 30 °C at 150 rpm on a shaker for 60 min. Through batch adsorption experiments the following parameters were used pH (3–8), contact time (2–300 min), temperature (30–45 °C), adsorbent dosage (0.1–2.0 g) and initial lead (II) concentration (10–50 mg L⁻¹). The samples were centrifuged at 3,000 rpm for 10 min to separate the solid phase from the liquid phase after each batch experiment.

2.4. Analysis

XRD studies were carried out using an X-ray diffractometer (D8 Bruker, Germany) with Cu K α radiation at 40 kV and 40 mA. The morphology of activated carbon was studied by SEM-Hitachi S-4500 SEM machine (Japan). The functional groups responsible for lead binding were obtained in the range 4 000–480 cm⁻¹ with an IR-Prestige-21 Shimadzu FTIR spectrophotometer, by KBr pellet method. The pH measurements were carried out with a Crison 2001 micro pH-meter (Spain). The supernatant liquid was analyzed by Shimadzu AA-680 AAS. The percentage removal of lead was calculated according to Eq. (1):

$$R = \frac{(C_0 - C_e)}{C_0} \times 100\%$$
(1)

The adsorption amount (q_e) was calculated according to Eq. (2):

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{2}$$

where q_e is the amount (mg g⁻¹) of lead adsorbed by activated carbon, C_0 and C_e are the metal concentrations (mg L⁻¹) in the solution initially and after adsorption, respectively, *V* is the volume (L) of the solution and *M* is the mass (g) of adsorbent used in the experiment.

3. Results and discussion

3.1. Surface characterization

3.1.1. XRD and SEM analysis

The composition and physical properties of the goat dung-derived activated carbon were determined using XRD (Fig. 1). From the XRD pattern, it can be suggested that the activated carbon consist of a mixture of amorphous and crystalline structure. The SEM image of activated carbon (Fig. 2(a)) confirms the morphology and microstructure. Some pores were found on the surface of the activated carbon. Fig. 2(b) shows that no residual metal ions were present on the goat dung-derived activated carbon.

3.1.2. FTIR spectral analysis

The shift in the spectra, reduction and disappearance of the peaks can be used to see whether there was an effect of lead adsorption by different functional groups. The FTIR spectrum was obtained for activated carbon before (a) and after (b) lead adsorption (Fig. 3).

The bands at 3,409 and 3,422 cm⁻¹ could be due to the –OH stretching of polymeric compounds or presence of N-H groups. The peaks at 2,924 and



Fig. 1. XRD of activated carbon derived from goat dung.

2,854 cm⁻¹ indicate presence of both methylene (-CH₂-) bridges and aromatic C-H stretching vibrations. The peaks at 1,451 and 1,456 cm⁻¹ indicate C=C groups present in carbon. The additional small peaks at 1,244 and 1,058 cm⁻¹ indicate the S=O. The band at 1,648 cm⁻¹ corresponds to carbonyl stretching vibration of amide considered to be due to the combined effect of double-bond stretching vibration and -NH deformation band for lead loaded activated carbon. The C=O and S=O functional groups have been reported to show very high coordination with trace metals [12], hence some shifts in the lead loaded were observed at 1,622 and 1,107 cm⁻¹. Similar observations were observed in Pb(II) and Cu(II) removal using activated maize tassel and mimosa Tannin gel, respectively [12,15].

3.1.3. Mechanism of sorption

The sorption mechanism might be partly a result of the ion exchange or complexation between the Pb^{2+} ions and functional groups of oxygen and aromatic compounds on the activated carbon. Thus, the Pb^{2+} ions/activated carbon reaction may be represented in two ways as shown in Fig. 4. From Fig. 4, lead ion (Pb^{2+}) can attach itself to two adjacent hydroxyl groups, and release two hydrogen ions (H^+) into solution. On the other hand, the two oxyl groups can donate two pairs of electrons to Pb^{2+} ion. In both reactions, a four coordination number compound is formed.

3.2. Effect of sorption parameters

3.2.1. Effect of pH

During adsorption process, pH of an aqueous solution is an important factor that influences the surface properties of adsorbent [15]. As shown in Fig. 5, the adsorption of lead varies with pH and consequently, lead adsorption on activated carbon is highly pH dependent. The percentage of lead adsorption on activated carbon increased with increasing pH and reached a maximum value at around pH 4.5. Around pH 4.5, the surface of activated carbon is negative, and there is a strong electrostatic attraction between surface groups and lead species. Below and above pH 4.5, the adsorption process was decreased. At highly acidic pH, the surface of activated carbon becomes positive due to protons in solution. As a result, the Pb²⁺ ions are repelled from the positively charged surface due to the repulsive force [24]. As pH increases, protons are lost from the ionizable active site of the activated carbon which results in the negatively



Fig. 2. (a) SEM image of activated carbon (b) EDX of activated carbon derived from goat dung.



Fig. 3. FTIR spectra of activated carbon before (a) and after (b) lead adsorption.

charged surface. The maximum adsorption for activated carbon was found to be 92.5% at pH 4.5. Beyond

the optimum pH, the biosorbent shows a decrease in sorption attributed to lead hydrolyzing and precipitating instead of the adsorption process taking place [13]. Hence, further adsorption experiments were carried at an optimum pH 4.5.

3.2.2. Effect of contact time

The influence of contact time on the adsorption capacity of activated carbon is shown in Fig. 6. The results obtained from the adsorption of lead onto activated carbon showed that adsorption increases with an increase in contact time. It is obvious that there is a rapid uptake of lead within the first the 20 min. The fast uptake of lead ions might be due to the creation of more active sites on the surface of activated carbon by the treatment process during the preparation of activated carbon from goat dung [25]. The maximum removal was 95.08% and thereafter there was no significant adsorption of lead ions onto the activated



Fig. 4. Possible mechanisms for adsorption of Pb²⁺ ion onto activated carbon surface.



Fig. 5. Effect of pH on lead adsorption ([Lead] = $10 \text{ mg} \text{ L}^{-1}$, activated carbon dosage = 0.5 g, temperature = $30 \degree$ C, contact time = 60 min).



Fig. 6. Effect of contact time on lead adsorption ([Lead] = 10 mg L^{-1} , pH 4.5 activated carbon dosage = 0.5 g, temperature = $30 \degree$ C).

carbon with increasing contact time as the active sites were saturated. The equilibrium contact time for lead adsorption was found to be 60 min.

3.2.3. Effect of adsorbent dosage

The dosage of a biosorbent strongly influences the extent of sorption [26]. The results obtained from varying biosorbent dosages are presented in Fig. 7.

As shown in Fig. 7, adsorption percentage increased from 78.2 to 97.1% and thereafter become constant. The optimum adsorbent dosage was 0.5 g. The observed trend can be attributed to the increase in the available exchangeable sites when activated carbon was increased during adsorption, thereby enhancing lead sorption capacity.



Fig. 7. Effect of dosage on lead adsorption ([Lead] = 10 mg L^{-1} , pH 4.5, temperature = 30° C, contact time = 60 min).

3.2.4. Effect of initial lead concentration

The effect of initial metal concentration on the adsorption rate was analyzed within the range $10-50 \text{ mg L}^{-1}$ for lead (Fig. 8).

As shown in Fig. 8, a decrease in the removal of the lead with increasing initial concentrations was observed. The lead removal went down from 85.33 to 69.43%. At lower metal concentration, the ratio of the number of moles of lead in an aqueous solution to the available surface area on activated carbon is low showing adsorption is independent of the initial concentration. However, at higher concentration, the number of available sites for adsorption decreases and, hence, lead removal is dependent on the initial concentration [15].

3.2.5. Effect of temperature

The adsorption of lead on activated carbon was investigated as a function of temperature and the maximum removal was obtained at 45°C (Fig. 9). An increase in temperature is known to increase the uptake of lead due to the increase in chemical interaction between the lead ions and activated carbon or creation of some new sorption sites on the activated carbon. It might also be suggested that the lead ions were able to overcome the activation energy barrier for adsorption on activated carbon. As a result, the process was endothermic. Similar results have been obtained for adsorption of Cr(VI) using activated cow dung carbon [19].

3.3. Thermodynamic parameters

Thermodynamics assumes that in a system that is kept isolated, where energy cannot be gained or lost



Fig. 8. Effect of initial concentration on lead adsorption (pH 4.5, activated carbon dosage = 0.5 g, temperature = 30°C, contact time = 60 min).



Fig. 9. Effect of temperature on lead adsorption (pH 4.5, activated carbon = 0.5 g, contact time = 90 min).

to the surroundings, the entropy change is the driving force [26]. The change in the reaction should be considered when developing an adsorption system and is achieved through the thermodynamic concept. Hence, in environmental chemical engineering practice both energy and entropy factors must be considered so that spontaneous processes will be determined. In the current study, the effect of temperature on adsorption of lead onto activated carbon was explained on the basis of thermodynamic parameters, such as change in Gibbs free energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS), using the following equations:

$$K_d = \frac{C_a}{C_e} \tag{3}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{4}$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{5}$$

where K_d is the distribution coefficient for the biosorption, C_a is the amount of lead adsorbed onto activated carbon at equilibrium (mg L⁻¹) and C_e is the equilibrium concentration of the lead ions in solution (mg L⁻¹). *T* is the solution temperature (K) and *R* is the gas constant. ΔH° and ΔS° were calculated from the slope and intercept of van't Hoff plots of ln K_d vs. 1/T (Fig. 10). The thermodynamic parameters are shown in Table 1.

The free energy change (ΔG) obtained were all negative, confirming that the adsorption of lead is spontaneous and thermodynamically favourable. Furthermore, the change in free energy increases in negativity with increase in temperature. The positive value of change in enthalpy (ΔH) infers the endothermic nature of the process showing it consumes energy. The positive value of change in entropy (ΔS) reflects



Fig. 10. van't Hoff plot for the adsorption of lead on activated carbon ([lead] = 10 mg L^{-1} , activated carbon dosage = 0.5 g, pH 4.5, contact time = 60 min, temperature = 30° C).

the increased randomness at the solid/solution interface.

3.3.1. Adsorption isotherms

Adsorption isotherms are very useful for analyzing the nature of adsorbate–adsorbent interaction and are important in optimizing the use of adsorbents. Adsorption isotherms are one of the most useful data to understand the mechanism of an adsorption, and the mathematical analysis of isotherms is needed before the interpretation of the kinetics of an adsorption process [26–28]. As a result, in order to optimize the design of a successful adsorption unit to remove trace metal ions from industrial wastewaters, it is significant to establish the best correlation for the equilibrium isotherms. The Langmuir and Freundlich models were used to determine the appropriate isotherm required for lead adsorption from aqueous onto activated carbon.

The Langmuir isotherm model describes the monolayer adsorption onto the surface of an adsorbent with finite number of identical sites and is the most widely used isotherm for adsorption studies in recent years [15]. The linear form of the Langmuir isotherm model[29] can be represented by

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \left(\frac{1}{bq_{\max}}\right) \frac{1}{C_e} \tag{6}$$

where $C_e \,(\text{mg L}^{-1})$ is the equilibrium concentration, q_e is the amount of metal ion adsorbed at equilibrium, q_{max} is the maximum adsorption capacity and *b* is the equilibrium Langmuir constant. A plot of $1/q_e$ vs. $1/C_e$ was found to be a straight line with $1/q_{\text{max}}$ as intercept and $1/bq_{\text{max}}$ as slope, and hence q_{max} and b can be calculated. Fig. 11 shows Langmuir adsorption with the coefficient of determination ($R^2 = 0.9784$).

In addition, a dimensionless constant called separation factor, R_L , can be used to express an essential feature of Langmuir isotherm:

$$R_L = \frac{1}{1 + bC_m} \tag{7}$$

where C_m is the initial concentration (10 mg L⁻¹, in this case) of lead. The value of R_L indicates the type of the isotherm to be either unfavourable when $R_L > 1$, linear if $R_L = 1$, or favourable if $0 < R_L < 1$ or $R_L = 0$. The calculated R_L value was 0.826, indicating that the adsorption of the lead was a favourable process.

A monolayer sorption with a heterogeneous energetic distribution of active sites, coupled by interaction between the adsorbed molecules, is one of the assumptions of the Freundlich isotherm. The linearized Freundlich isotherm equation [30] is given by

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{8}$$

where q_e (mg g⁻¹) is the amount of metal ion adsorbed at equilibrium by the adsorbent, C_e (mg L⁻¹) is the equilibrium concentration, K_F (mg g⁻¹) and n are constants representing the adsorption capacity and intensity of adsorption. A plot of ln q_e vs. ln C_e gives a

Table 1 Thermodynamic parameters for adsorption of lead onto activated carbon

Tomporatura (K)	Thermodynamic parameters					
Temperature (K)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹	R^2		
303	-8.89	+15.65	+0.081	0.998		
308	-9.23					
313	-9.70					
318	-10.11					



Fig. 11. Langmuir isotherm for lead adsorption (activated carbon dosage = 0.5 g, pH 4.5, contact time = 60 min, temperature = 30 °C).



Fig. 12. Freundlich isotherm for lead adsorption (activated carbon dosage = 0.5 g, pH 4.5, contact time = 60 min, temperature = $30 \degree$ C).

straight line, and K_F and n can be calculated from the intercept and slope, respectively. Fig. 12 shows that adsorption of lead on activated carbon obeys Freund-lich isotherm model and the constant K_F and n were determined as 0.0912 and 0.858, respectively. The value of n was between 1 and 10, which means favourable adsorption of lead on activated carbon. The

Table 2 Langmuir and Freundlich constants for lead adsorption onto activated carbon

Parameter	Activated carbon
$q_{\max} (\operatorname{mg} \operatorname{g}^{-1})$	14.99
b (L mg ⁻¹)	0.021
R^2	0.9784
$K_F (mg g^{-1})$	0.0912
n	0.858
R^2	0.9992
	Parameter $q_{max} (mg g^{-1})$ $b (L mg^{-1})$ R^2 $K_F (mg g^{-1})$ n R^2



Fig. 13. Pseudo-second-order plot for Pb(II) adsorption onto activated carbon.

coefficient of determination was found to be 0.9992. A summary of the parameters for both Langmuir and Freundlich isotherm plot is shown in Table 2.

The comparison of maximum monolayer adsorption capacity of lead ions onto activated carbon derived from different precursors is given in Table 3. It should be noted that adsorption capacity varies and depends on the characteristics of an individual adsorbent, the extent of surface modification, heat treatment temperatures and the initial concentration of the adsorbate used. As can be seen from Table 3, activated

Table 3

Performance of activated carbons from various precursors for adsorption of lead from aqueous solutions

Precursor	Activation agent	$q_{\rm max} \ ({\rm mg \ g}^{-1})$	Ref.
Maize tassel	Chemical activation by H_2SO_4	37.31	[15]
Hazelnut husks	Chemical activation by ZnCl ₂	13.05	[18]
Tea waste	Chemical activation by Na_2S	1.3510	[31]
Eichhornia	Physical activation-500°C	16.61	[32]
Militia ferruginea plant leaves	Chemical activation: H_2SO_4	3.3	[33]
Coconut shell	Chemical activation by H_2SO_4	26.50	[34]
Goat dung	Chemical activation by H_2SO_4	14.99	This study

Adsorbent	Pseudo-first-or	Pseudo-first-order kinetic model		Pseudo-second-order kinetic model		
	$q_e \ (\mathrm{mg \ g}^{-1})$	$k_1 \; (\min^{-1})$	R^2	$q_e \ (\mathrm{mg \ g}^{-1})$	$k_1 (g mg^{-1} min^{-1})$	R^2
Activated carbon	2.562	0.0125	0.8752	4.735	1.95×10^{-2}	0.9992

 Table 4

 Rate constants for lead adsorption on activated carbon

carbon from goat dung has reasonable adsorption capacity but is not the best one for lead removal, while if taking account, the availability and cheapness of goat dung, it is also a good candidate for adsorbent preparation.

3.3.2. Adsorption kinetics

The solute uptake rate in kinetic analysis, which determines the residence time required for the completion of the adsorption reaction, may possibly be established. In the present study, the pseudofirst-order and pseudo-second-order model were used for determining the mechanism of the adsorption process.

The pseudo-first-order model described by the Lagergren equation is shown in Eq. (9):

$$\log(q_e - q_t) = \log q_e - \frac{t \cdot k_1}{2.3}$$
(9)

where q_e and q_t are the amount of lead adsorbed (mg g⁻¹) activated carbon at equilibrium and at any time t, k_1 (min⁻¹) is the rate constant of pseudo-first-order model and t is the time (min).

The pseudo-second-order model assumes that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites. The second-order kinetic model can be expressed as follows [34]:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2(q_e)^2}$$
(11)

where k_2 is the equilibrium rate constant of pseudosecond-order model (g mg⁻¹ min⁻¹). The values of q_e and k_2 are determined from the slope and intercept of the plot of (t/q_t) vs. t, respectively (Fig. 13). The adsorption kinetic parameters are presented in Table 4. The coefficient of determination for the pseudo-firstorder was $R^2 = 0.8752$, indicating that it could not be used to describe the entire adsorption process well. On the other hand, the correlation coefficient (R^2) value of the pseudo-second-order kinetic model was Table 5

Characteristics of effluent from a round cell manufacturing industry

Parameter	Effluent
pH TDS (mg L^{-1}) Lead (mg L^{-1})	3.68 100.44 3.18

0.9992. Therefore, it can be concluded that the adsorption system of lead followed a pseudo-second-order reaction rather than pseudo-first-order reaction.

3.3.3. Application on commercial effluent

The performance of goat dung-derived activated carbon was evaluated for the removal of lead by using effluent from a round cell manufacturing industry. Characteristics of the round cell manufacturing industry effluent are provided in Table 5. The quantity of lead present in the effluent was determined to be 3.18 mg L^{-1} . An adsorbent dosage of 0.5 g L^{-1} of the effluent and an agitation time of 1 h resulted in 85% removal of the lead from the wastewater. The results indicate the efficacy of animal waste for cleaning environmental wastewaters.

4. Conclusions

The adsorption of lead onto goat dung-derived activated carbon was found to be depending on factors such as pH, adsorbent dosage, contact time, concentration of lead and temperature. The results obtained are:

- (1) pH 4.5 was deduced as optimum for the removal of lead for activated carbon.
- (2) Adsorption rate increased with increasing biosorbent dosage and decreased with increasing lead concentration.
- (3) The equilibrium for activated carbon was 60 min.
- (4) Adsorption followed the pseudo-secondorder model.

- (5) Freundlich isotherm model best described the adsorption mechanism.
- (6) Thermodynamic parameters such as ΔG , ΔS and ΔH showed that the adsorption process was feasible, spontaneous and endothermic.

The results from the present study show that goat dung may be used as a low-cost, eco-friendly and effective biosorbent to remove lead from aqueous solution. Further study could be conducted to examine the feasibility of using goat dung-derived activated carbon as adsorbents for other toxic heavy metals.

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