

ISOTHERM AND KINETICS STUDIES OF ADSORPTIVE REMOVAL OF LEAD FROM AQUEOUS SOLUTION BY ACTIVATED CARBON FROM PINEAPPLE PEEL

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Abstract: Lead is naturally occurring toxic metal found in the Earth's crust. Its widespread use has resulted in extensive environmental contamination, human exposure and significant public health problems. In this research, adsorption studies were carried out for the removal of Pb^{2+} from aqueous solution. The carbons were activated using 40% Phosphoric acid. It was characterized using BET, SEM and FTIR methods of characterization. The BET analysis was used to determine the surface area which was gotten to be $1383\text{ m}^2/\text{g}$. The surface area of the chemically activated carbon from the SEM image is found to consist of highly packed bundles of deep long cylindrical pores and some pits indicating the good adsorptive capacity. The peaks obtained from the FT-IR analysis are O-H band, C-H stretch and nitrile triple ($HC\equiv N$) bond. Equilibrium adsorption data were modeled using Langmuir, Freundlich, Redlich-Peterson and Elovich models, Langmuir model fitted more compared to other models. Adsorption kinetic data were tested using pseudo-first order and pseudo-second order, the adsorption followed the pseudo-second order mechanism with a correlation coefficient (R^2) of 0.9999.

Keywords: Adsorption; Lead; Pineapple peel; Isotherm; Kinetics

1. INTRODUCTION

The assessment of pollution has always been done frequently, and many people have looked into it. But cleanup is essential and required because it would be useless to try to estimate the level of pollution without also presenting feasible remedies for lowering or eliminating it. The tranquility of our environment depends on our society's discipline because our actions damage the air, land, and water.

Heavy metal contamination in the environment, such as that caused by Cu, Pb, Fe, Cd, and Mn, is primarily caused by industrial waste water. Such metal may be released into waste streams from a variety of companies, including those that plate metal, manufacture storage batteries, alloys, dye textiles, produce fertilizer, and engage in other chemical processes. Because pollution rises steadily as industrial technology advances, much effort has been made to reduce these toxic chemicals and, as a result, avoid their harmful impacts on people, plants, and animals (Sachin and Gaikwad, 2011).

Since then, these industries have been spewing pollutants into the air, water, and soil at a never-before-seen rate and have contaminated the surface water and groundwater with numerous harmful heavy metals. Pb is one of the very poisonous heavy metals that is produced by a variety of industrial processes, including those used in the production of explosives, lead batteries, glass, dye, and printing pigments (Azam et al., 2022). Because Pb is not biodegradable, it stays in water, builds

up in living things, sediments, and sludge, and enters the food chain (Azam et al., 2022). According to the World Health Organization and Environmental Protection Agency, the maximum allowable limit of lead in drinking water are 0.01 mg/L and 0.015 mg/L, respectively, and the permissible effluent discharge limit of lead in surface water bodies is 0.1 mg/L (Azam et al., 2022).

Although studies on the adsorption characteristics of carbon from organic waste have not yet been described in detail, particularly in the usage of fruit waste, there are several reports on the synthesis and characterization of carbon material. In reality, knowing what phenomena happen during the adsorption process and how to exploit them for other purposes is essential, especially when utilizing carbon as a catalyst and an adsorbent (Nandiyanto et al., 2020).

In the studies of the adsorption of Pb (II) on plantain peel biochar carried out by Nworie et. al., (2020), results showed that the adsorption of Lead from aqueous solution increased with an increase in pH and initial concentration. Equilibrium modelling studies suggested that the data fitted mainly to the Langmuir isotherm. Adsorption kinetic data tested using various kinetic models fitted the Weber and Moris intraparticle diffusion model. Boparai et al., (2017) investigated the adsorption of lead (II) ions from aqueous solutions using coir dust and its modified extract resins. Although several isotherm models were applied, the equilibrium data was best represented by Freundlich and Flory-Huggins isotherms due to high correlation coefficients.

Modified iron-kaolin clay was used by Awwad et. al., (2021) for the removal of Pb (II) and Cd (II) ions from aqueous solution. The batch adsorption parameters: pH of solution, adsorbent dose, contact time, initial metal concentration and temperature were found to be effective on the adsorption process. Langmuir isotherm model showed the best fit for the experimental data. Azmi et. al., (2020) investigated the adsorptive removal of Pb (II) ions from groundwater samples in Oman using carbonized Phoenix dactylifera seed. The RSM with Box-Behken design was used to optimize the variables to achieve the best response. The adsorption equilibrium data fitted well into both Langmuir and Freundlich isotherm models. The experimental data from the kinetic studies obeyed the Pseudo-second order model.

This present study aims to investigate the adsorption of Pb²⁺ ions from aqueous solution onto activated carbon prepared from pineapple peel. The methods employed in characterizing the Pineapple peel activated carbon are Scanning Electron Microscopy (SEM), Fourier Transformation Infrared Spectroscopy (FT-IR) and Brunauer-Emmett-Teller (BET). To avoid limitations accompanied by optimization of analytical methods like contact time, adsorbent loading and initial concentration, Response Surface Methodology (RSM) with Box-Behnken design was used for optimization of process variables to achieve the best response. Kinetic models were tested to identify potential adsorption mechanism.

2. MATERIALS AND METHODS

2.1 Instruments

FTIR Spectrophotometer (Agilent Technologies), Oven, Furnace, Scanning Electron Microscope (SEM) instrument, Atomic Absorption Spectrometer (PerkinElmer PinAAcle 900H), BET (Brunauer, Emmet and Teller) Instrument: Quantachrome NovaWin-Data Acquisition and Reduction for NOVA Instruments.

2.2 Reagents

All chemicals used in this research were obtained and used without further purification. They include: Phosphoric Acid (H₃PO₄) [Sigma] and Lead (II) Nitrate, Pb(NO₃)₂[Nice Chemical Laboratory].

2.3 Preparation of Pineapple Peel (Adsorbent)

The pineapple peel was cut into small pieces and washed thoroughly with deionized water and dried in oven for 2 to 3 hours at 105 °C. The dried pineapple peel was then sieved and stored for further studies.

2.4 Preparation of Adsorbent (Pineapple Peel) using Phosphoric Acid (H₃PO₄)

In preparing the adsorbent, procedures used by Selvanathan and Subki (2015) was employed with small modification. Oven dried pineapple peel was soaked in a boiling solution of 40% phosphoric acid for 1 hour. It was then transferred to the oven at 100°C to dry the raw materials which was then allowed to cool in a desiccator. The oven dried pineapple peel was carbonized in a furnace at 500°C for 1 hour. Finally, it was washed with hot deionized water and dried at 120°C for 2 hours and stored in a tight lid container.

2.5 Preparation of Stock Solution

In preparing the stock solution for this adsorption, 1.5984 g of Lead (II) Nitrate, $Pb(NO_3)_2$ was weighed and dissolved into 1 L of distilled deionized water to get 1000 ppm of Lead solution.

From the prepared stock solution, other concentrations used for the adsorption process was prepared using the dilution formula in Equation 1

$$C_1V_1 = C_2V_2 \dots \dots 1$$

Where: C_1 = Concentration of original stock solution, V_1 = The unknown or the amount to be taken from the stock solution, C_2 = Working concentration you want to prepare, and V_2 = Volume of the new solution you want to prepare.

2.6 Adsorption Studies

Instead of utilizing one variable at a time (OVAT) for varied conditions like adsorbent load, concentration, and time, which enables for the examination of a variable's effect with respect to only one variable while keeping the other variables constant. Response Surface Methodology (RSM), a statistical technique, was used in this work to offer a better route for the adsorption process' optimization. This is due to RSM's ability to show how each variable affects the others.

The concentration was set within the range of 10 mg/L to 100 mg/L, Adsorbent load was within the range of 0.5 g and 5 g, and the time was within the range of 30 minutes to 180 minutes. Table 1.0 shows the sequential strategies to carry out the experiment. The percentage adsorption is calculated using the relationship in Equation 2

$$\%R = \frac{C_0 - C_t}{C_0} \times 100 \dots \dots \dots (2)$$

Where C_0 (mg/l) and C_t (mg/l) are the initial concentration of the adsorbate and the concentration at time t.

2.7 Kinetic Studies

On concluding the adsorption studies, the experimental procedure with the highest equilibrium adsorption capacity (q_e) was employed. So this procedure was adopted with variation in time, that is, 30, 60, 90, 120, 150 and 180 minutes. The concentration was 100 mg/L and adsorbent load was 0.50 g.

3. RESULTS AND DISCUSSION

3.1 Adsorbent Characterization

3.1.1 Brunauer-Emmett-Teller (BET) Theory

By measuring nitrogen multilayer adsorption as a function of relative pressure with a completely automated instrument, BET analysis gives an accurate specific surface area evaluation of materials. The method includes evaluations of both the exterior area and the pore area to calculate the total specific surface area. This provides crucial information for researching the impacts of surface porosity and particle size in a variety of applications.

The BJH method was used to calculate the samples' surface area and pore size distributions. The well-developed mesoporosity was corroborated by the pore size distributions for both samples (2-50nm size). As seen, the surface area, pore volume, and pore size of the activated pineapple peel, APP sample were 1383 m^2/g , 0.667cc/g, and 2.072 nm, respectively. This finding suggests that the variation in experimental characteristics of a pineapple peel sample that had been chemically activated and had high BET surface area, low pore size, and high pore volume may have been caused by the impregnation of an activating agent, Demiral et al., (2021). A similar study was reported by Demiral et al. (2021), which revealed that the BET surface area of the activated carbon showed the highest surface area of 1399 m^2/g . Thus, the high value of the surface area of activated carbon in this study would allow for more adsorptive sites.

As a result, more adsorptive sites would be possible due to the high value of the activated carbon surface area in this study.

3.1.2 Fourier Transform- Infrared (FT-IR)

When assessing chemicals or materials, FTIR spectroscopy is a well-known tool for quality control. A change in the material's composition or the presence of contamination is clearly shown by a change in the pattern of absorption bands that characterizes the substance. FT-IR spectroscopy was used to investigate the interactions between different species and changes in chemical compositions of the mixtures of the activated pineapple peel.

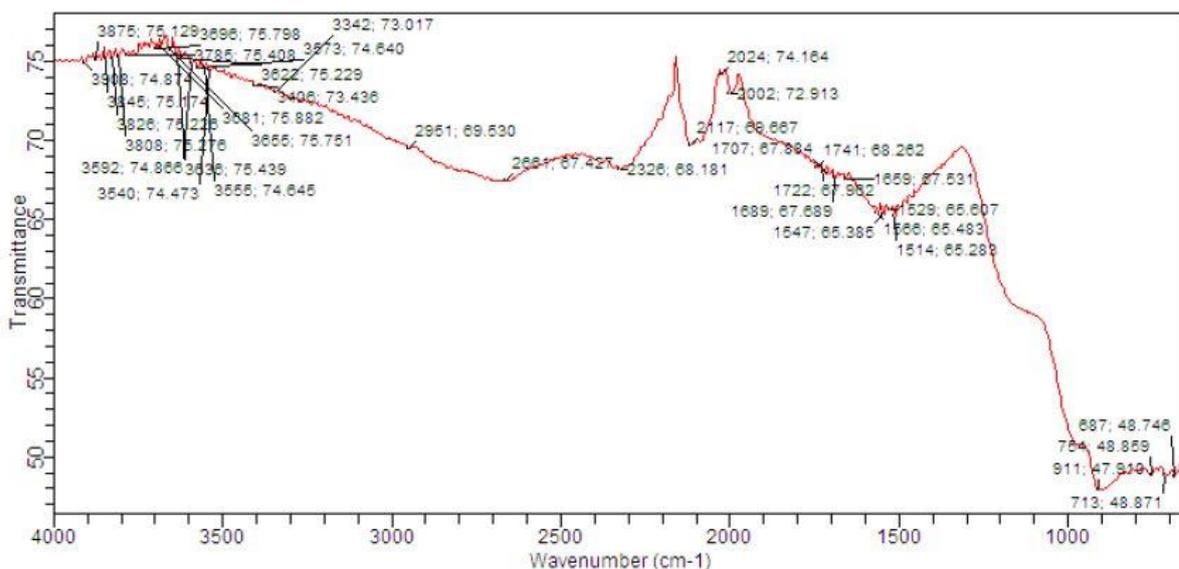


Figure 1: FTIR spectrum of activated adsorbent of PP

The peak at 2981.69 cm^{-1} may be caused by the existence of C-H stretch, that at 3540.74 cm^{-1} is the characteristic absorbance peak of the O-H band. A band at 2326.68 cm^{-1} can indicate the presence of a triple ($\text{HC}\equiv\text{N}$) nitrile bond (Fegousse et al., 2019).

3.1.3 Scanning Electron Microscopy (SEM)

One of the principal tools for in-depth micro area investigation in testing is scanning electron microscopy, or SEM. It benefits from having excellent stereoscopic vision, high magnification, a wide depth of field, and high resolution. In order to examine the surface morphology of the pineapple peel activated carbon, scanning electron microscopy, or SEM, was used. The porosity of activated carbon's surface, which serves as the active sites for adsorption and increases surface area, is depicted in Fig. 3. According to the SEM image, which shows the chemically activated carbon's surface area to be highly packed bundles of deep, long cylindrical pores and some pits, the material has a good adsorptive ability.

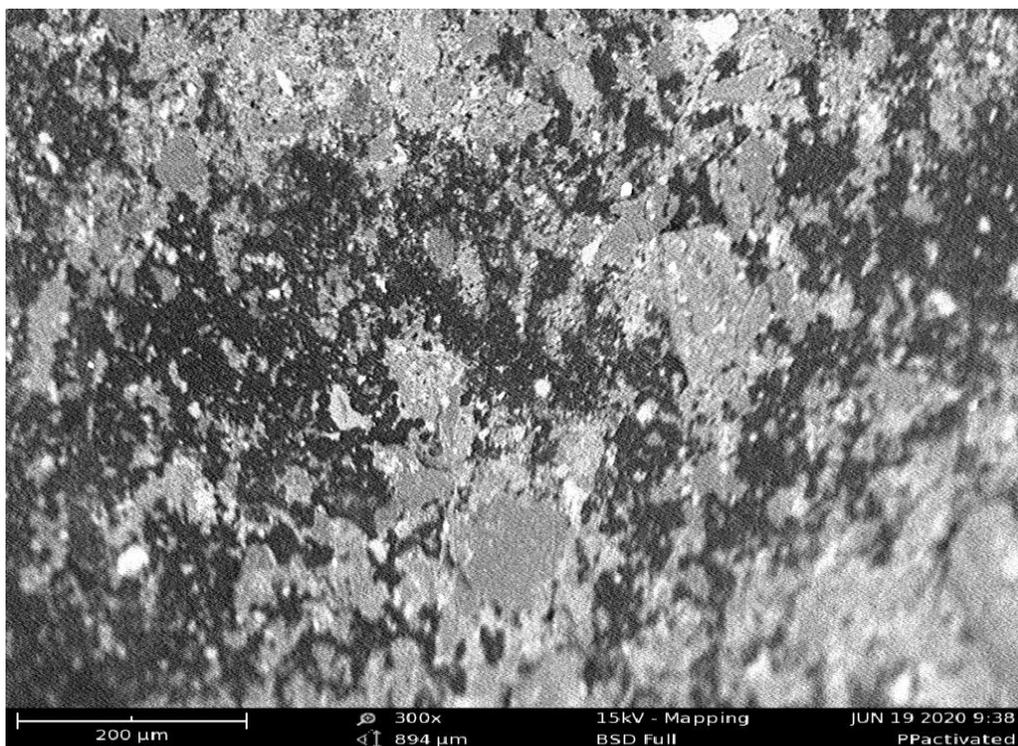


Fig. 3: SEM Image of chemically activated Pineapple Peel

3.2.0 Adsorption Studies

3.2.1 Response Surface Methodology

Response Surface Methodology, RSM and Box- Behnken Design, BBD are statistical techniques for experimental design that are used to assess complicated multi-variable systems, examine the interaction between two variables, and enhance the response of multiple variable processes. The adsorption parameters were optimized using RSM and BBD experimental design. In this study, three factors, initial concentration, adsorbent loading and contact time were investigated. Based on the BBD method, 17 sets of experimental trials were required for the adsorption process. All conditions were maintained constant, and experimental runs were randomized to reduce error and eliminate bias.

A second-order model polynomial equations were used to predict the relationship between the factors and stability as a function of concentration, adsorbent loading and contact time. The expression is shown in Equation 3.0

$$Y = n_0 + n_1X_A + n_2X_B + n_3X_C + n_4X_A^2 + n_5X_B^2 + n_6X_C^2 + n_7X_AX_B + n_8X_AX_C + n_9X_BX_C \dots \text{Equation (3.0)}$$

where Y is the response variable; A, B, and C are independent variables; n_0 is a model constant variable; $n_1, n_2,$ and n_3 are linear coefficients; $n_4, n_5,$ and n_6 represent the quadratic effects; and $n_7, n_8,$ and n_9 represent interaction effects of the model.

Table 1: RSM model of sequence for adsorption studies

Std	Run	Block	Factor 1 Concentration (mg/L)	Factor 2 Adsorbent Load (g)	Factor 3 Time (min)	Response % Removal
17	1	Block 1	55.00	2.75	105.00	36.56
10	2	Block 1	55.00	5.00	30.00	41.42
8	3	Block 1	100.00	2.75	180.00	51.2
1	4	Block 1	10.00	0.50	105.00	26.45
6	5	Block 1	100.00	2.75	30.00	50.98
4	6	Block 1	100.00	5.00	105.00	53.53
7	7	Block 1	10.00	2.75	180.00	23.88
5	8	Block 1	10.00	2.75	30.00	21.60
12	9	Block 1	55.00	5.00	180.00	42.82
14	10	Block 1	55.00	2.75	105.00	42.84
16	11	Block 1	55.00	2.75	105.00	43.62
9	12	Block 1	55.00	0.50	30.00	40.31
11	13	Block 1	55.00	0.50	180.00	40.24
3	14	Block 1	10.00	5.00	105.00	22.20
15	15	Block 1	55.00	2.75	105.00	42.69
2	16	Block 1	100.00	0.50	105.00	50.12
13	17	Block 1	55.00	2.75	105.00	42.42

Response ranges from 21.6 to 53.53. ratio of max to min is 2.47824, a ratio greater than 10 usually indicates a transformation is required. For ratio less than 3, the power transforms have little effect.

Table 2: Analysis of Variance (ANOVA) For the Quadratic Model

Source of Variation	Quadratic sum of Squares	Model degree of freedom (DF)	Mean Square	F-Value	P-Values Prob > F	Remarks
Model	1647.59	9	183.07	35.62	< 0.0001	Significant
A	1559.61	1	1559.61	303.48	< 0.0001	
B	1.83	1	1.83	0.36	0.5691	
C	1.02	1	1.02	0.20	0.6701	
A ²	64.59	1	64.59	12.57	0.0094	
B ²	2.66	1	2.66	0.52	0.4955	
C ²	0.56	1	0.56	0.11	0.7503	
AB	1.06	1	1.06	0.21	0.6633	
AC	14.67	1	14.67	2.85	0.1350	
BC	0.54	1	0.54	0.11	0.7552	
Residual	35.97	7	5.14			
Lack of Fit	3.10	3	1.03	0.13	0.9401	Not significant
Pure Error	32.88	4	8.22			
Cor Total	1683.57	16				

The Model F-value of 35.62 implies the model is significant. There is only 0.01% chance that a Model F-value this large could occur due to noise. Values of Prob > F less than 0.0500 indicate model terms are significant. In this case, A, A² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The “Lack of Fit” of 0.13 implies that the Lack of Fit is not significant to the pure error. There is a 94.01% chance that a “Lack of Fit F-value” this large could occur due to noise. Non-significant Lack of Fit is good. The “Pred R-squared” of 0.9401 is in reasonable agreement with the “Adj R-Squared” of 0.9512.

3.2.2.0 Adsorption Isotherms

Adsorption isotherms, which explain how pollutants interact with adsorbent materials, are crucial for maximizing the usage of adsorbents. Adsorption properties define how pollutants interact with adsorbent materials. In this study, isotherms such as Langmuir, Freundlich, Halsey, Elovich, and Redlich-Peterson were used to represent the equilibrium data.

3.2.2.1 Langmuir Isotherm

Linear regression is frequently used to determine the best-fitting isotherm, However, the Langmuir isotherm can be linearized as four different types

Table 3: Langmuir Isotherm showing the type 1,2,3 and 4 linear forms (Itodo et al.,2009)

Isotherm	General Form	Linear Form	Plot
Langmuir Type 1	$q_e = (q_m K_a C_e) / (1 + K_a C_e)$	$C_e / q_e = (1/q_m) C_e + 1/K_a q_m$	C_e / q_e Vs C_e
Langmuir Type 2		$1/q_e = (1/K_a q_m) 1/C_e + 1/q_m$	$1/q_e$ Vs $1/C_e$
Langmuir Type 3		$q_e = q_m - (1/K_a) (q_e / C_e)$	q_e Vs (q_e / C_e)
Langmuir Type 4		$q_e / C_e = K_a q_m - K_a (q_e)$	q_e / C_e Vs q_e

Where: k_a is the Langmuir adsorption constant (Lmg^{-1}), q_m is the theoretical maximum (monolayer) adsorption capacity (mgL^{-1}), q_e = amount of solute adsorbed per unit weight of solid at equilibrium (mg/g) and C_e = equilibrium concentration of solute remaining in solution (mg/L).

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (separation factor) R_L defined by

$$R_L = \frac{1}{(1 + C_0 K_L)} \text{-----(3.1)}$$

Where C_0 is the higher value of initial concentration (mgL^{-1}). R_L values indicate the type of isotherm: to be irreversible ($R_L=0$), favorable ($0 < R_L < 1$), linear ($R_L=1$), or unfavorable ($R_L > 1$) (Mahdi *et al.*, 2010).

In this research, Langmuir type 4 isotherm model was adopted. The slopes and intercepts of the linear plot with q_e as the abscissa and q_e/C_e as the ordinate are shown in Fig 4. These values were used to calculate the Langmuir parameters.

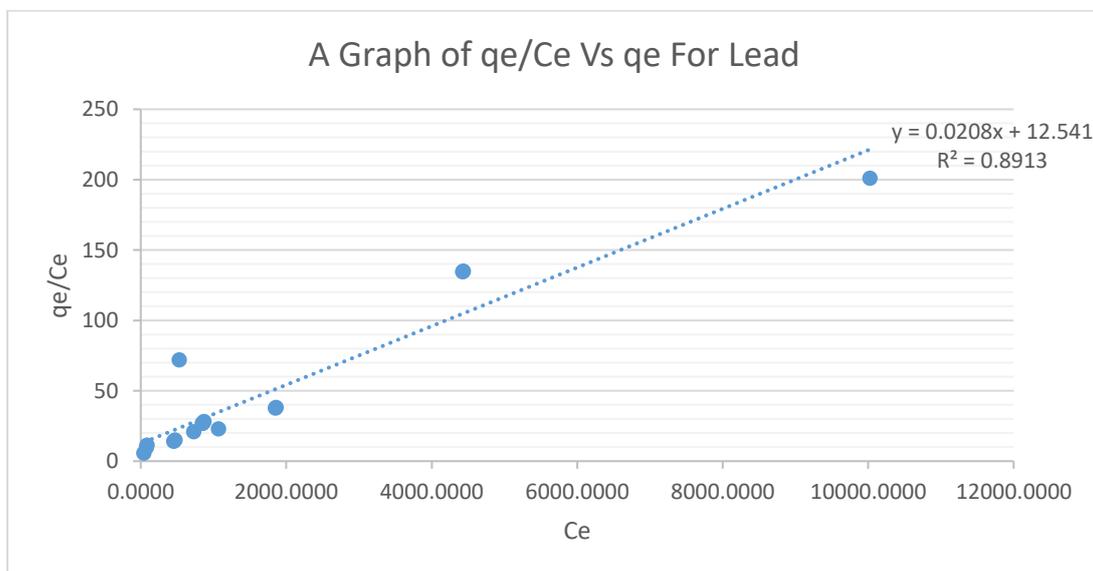


Fig. 4.: Langmuir isotherm for Pb²⁺ ion removal at various concentrations

From this research work, the maximum monolayer coverage capacity (Q_{max}) from Langmuir Isotherm model for Nickel ion was determined to be Pb^{2+} (602.93 mg/g). The correlation coefficient (R^2) was 0.8913. This proves that the sorption data fitted well to Langmuir Isotherm model. The estimated statistics show that the Langmuir isotherm is advantageous since the R_L is larger than 0 but less than 1 (0.325).

3.2.2.2 Freundlich Isotherm

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. The Linear equation of Freundlich isotherm is given in Equation 3.2:

$$\log q_e = \log K_f + \frac{1}{n_f} \log C_e \text{-----(3.2)}$$

Where K_f is the Freundlich constant ((mg/g)/(mg/l)^{1/n}) and (1/n_f) is the heterogeneity factor. $\frac{1}{n_f}$ and K_f constants are determined from the slope and intercept of the plot of log q_e against log C_e. The value of 1/n_f (heterogeneity factor) is between 0 and 1. If n = 1 then the partition between the two phases are independent of the concentration. If value of 1/n is below one, it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption (Mohan, and Karthikeyan, 1997). This constant can be one or any integer or decimal number. If n =1 (linear), n<1 (Chemisorption process), and n>1 is physisorption process (Hameed et al., 2009).

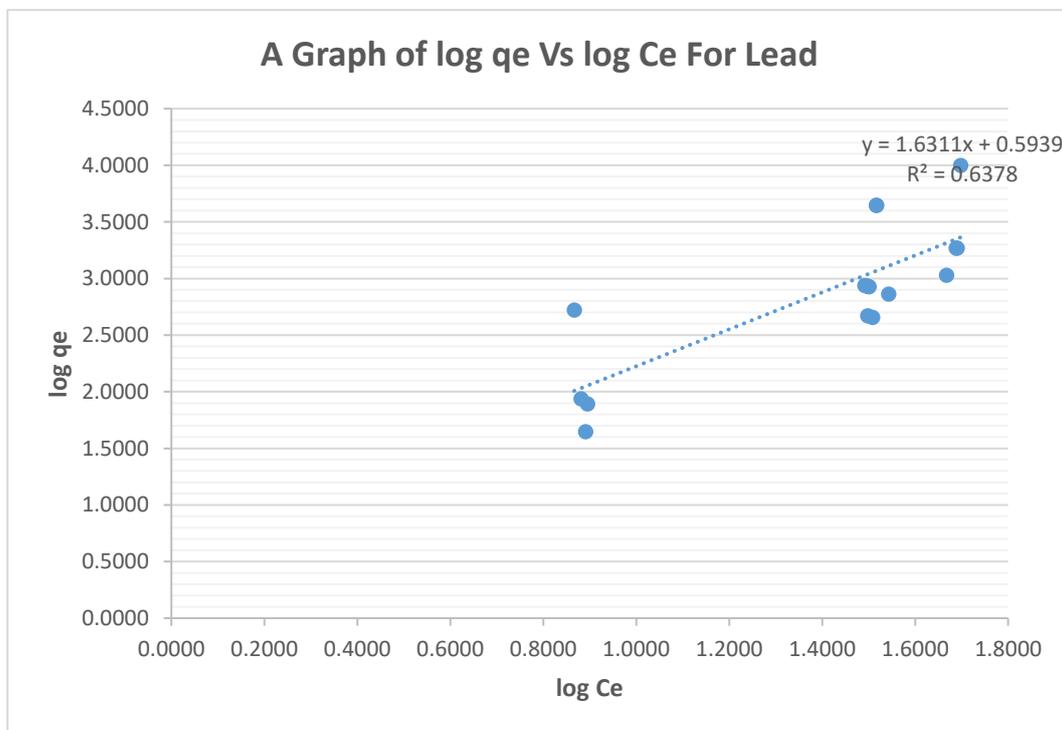


Fig. 5: Freundlich isotherm for Pb^{2+} ion removal at various concentrations

The adsorption intensity ($n = 0.6130832$) as calculated shows that the adsorption is chemisorption. The correlation coefficient (R^2) for Lead ion Pb^{2+} (0.6378) proves that the sorption data partially fitted into the Freundlich Isotherm model. Freundlich constant, K_f is 3.9255mg/g.

3.2.2.3 Halsey Isotherm Model

This model is used to evaluate multilayer adsorption in a system where metal ions are located relatively far from the surface. This model can be expressed using Equation 3.3.

$$q_e = \exp\left(\frac{\ln K_H - \ln C_e}{n_H}\right) \text{-----(3.3)}$$

Its linear form is represented in Equation 3.4:

$$\ln(q_e) = -\frac{1}{n_H} \ln \frac{1}{C_e} + \left[\left(\frac{1}{n_H}\right) \ln(K_H)\right] \text{-----(3.4)}$$

Where; n_H = constant of equation, and K_H =Halsey's equilibrium constant.

These constants can be obtained from the slope and intercept of the plot $\ln(q_e)$ versus $\ln C_e$. From the straight line obtained, the slope is n_H , and the intercept represents K_H .

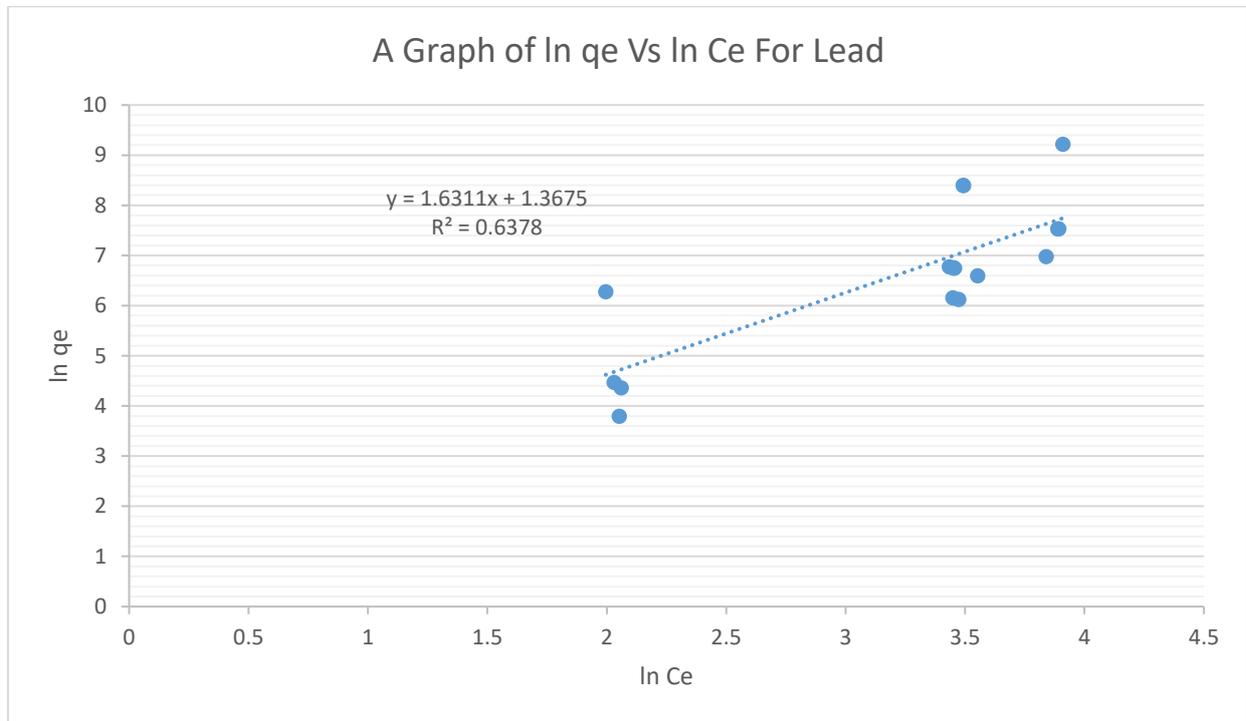


Fig. 6: Halsey isotherm for Pb^{2+} ion removal at various concentrations

The correlation coefficient (R^2) for the metal ion Pb^{2+} (0.6378) proves that the sorption data partially fitted into the Halsey Isotherm model, which may be attributed to heterogeneous distribution of active sites and multilayer adsorption on Pineapple peel. The Halsey's equilibrium constant, K_H is 0.1451 and constant of equation, n_H is -0.61308.

3.2.2.4 Redlich-Peterson Isotherms

The Redlich-Peterson isotherm is a mix of the Langmuir and Freundlich Isotherms. The numerator is from the Langmuir isotherm and has the benefit of approaching the Henry region at infinite dilution. This isotherm model includes three parameters and is empirical. The process of adsorption is consequently a mix and does not adhere to ideal monolayer adsorption because it integrated features from the Langmuir and Freundlich equations.

The model is defined by the expression in Equation 3.5:

$$q_e = \frac{AC_e}{1+BC_e^\beta} \dots\dots\dots (3.5)$$

Where: A= Redlich-Peterson isotherm Constant (Lg^{-1}), B= Constant (Lmg^{-1}), B= exponent that lies between 0 and 1, C_e = equilibrium liquid-phase concentration of the adsorbent (mgL^{-1}), and q_e = equilibrium adsorbate loading on the adsorbent.

The linear form of the Redlich-Peterson isotherm is expressed in Equation 3.6.

$$\ln \frac{C_e}{q_e} = \beta \ln C_e - \ln A \dots\dots\dots (3.6)$$

A plot of $\ln (C_e/q_e)$ versus $\ln C_e$ enables the determination of Redlich-Peterson constants, where β is slope and A is intercept. Because of its adaptability, this isotherm model represents adsorption equilibrium over a wide range of adsorbate concentration by having a linear dependence on concentration in the numerator and an exponential function in the denominator. It can be used in both homogeneous and heterogeneous systems (Ayawei et al., 2017).

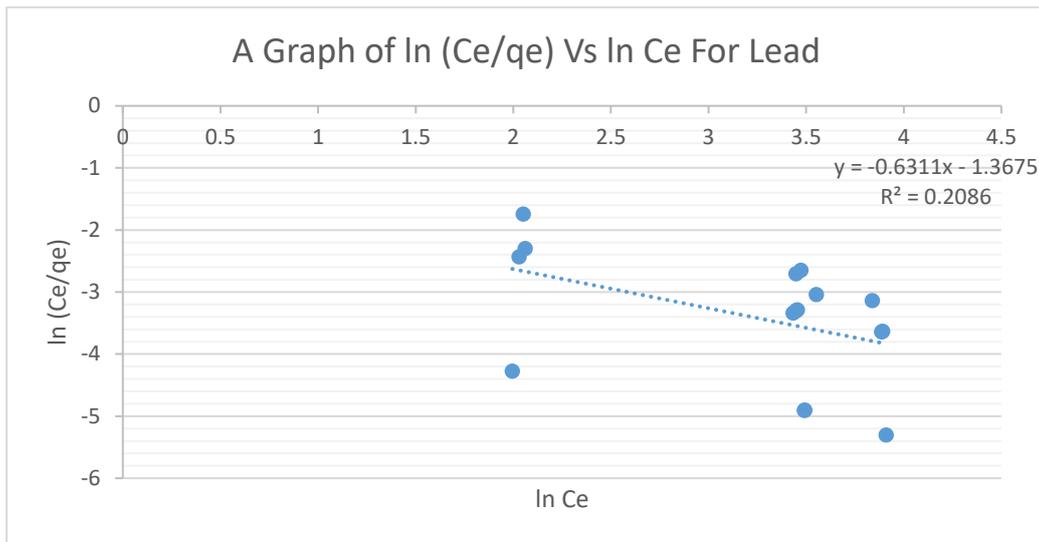


Fig. 7: Redlich-Peterson isotherm for Pb^{2+} ion removal at various concentrations

From the correlation coefficient (R^2) value, 0.2086, Pb^{2+} does not fit into the Redlich-Peterson isotherm model. Other Redlich-Peterson constants are A (-1.3675 Lg^{-1}) and β (-0.6311 $L mg^{-1}$).

3.2.2.5 Elovich Isotherm Model

According to Elovich model, mechanism of adsorption is based on chemical reactions which are responsible for adsorption. The equation that defines this model is based on a kinetic principle which assumes that adsorption sites increase exponentially with adsorption, meaning a multilayer adsorption. The linear form of the Elovich model is expressed in Equation 3.7:

$$\ln \frac{q_e}{C_e} = \ln K_E q_m - \frac{q_e}{q_m} \dots\dots\dots(3.7)$$

Where: q_m = Elovich maximum adsorption capacity (mgg^{-1}), and K_E = Elovich equilibrium constant (Lmg^{-1}). Both the Elovich maximum adsorption capacity and Elovich constant can be calculated from the slope and intercept of the plot of $\ln \frac{q_e}{C_e}$ versus q_e . The correlation coefficient (R^2) for Pb^{2+} (0.6601) proves that the sorption data relatively fits into the Elovich isotherm model. The Elovich maximum adsorption capacity, q_m is 3.97865 mgg^{-1} and the Elovich equilibrium constant, K_E is 3333.333 Lmg^{-1} .

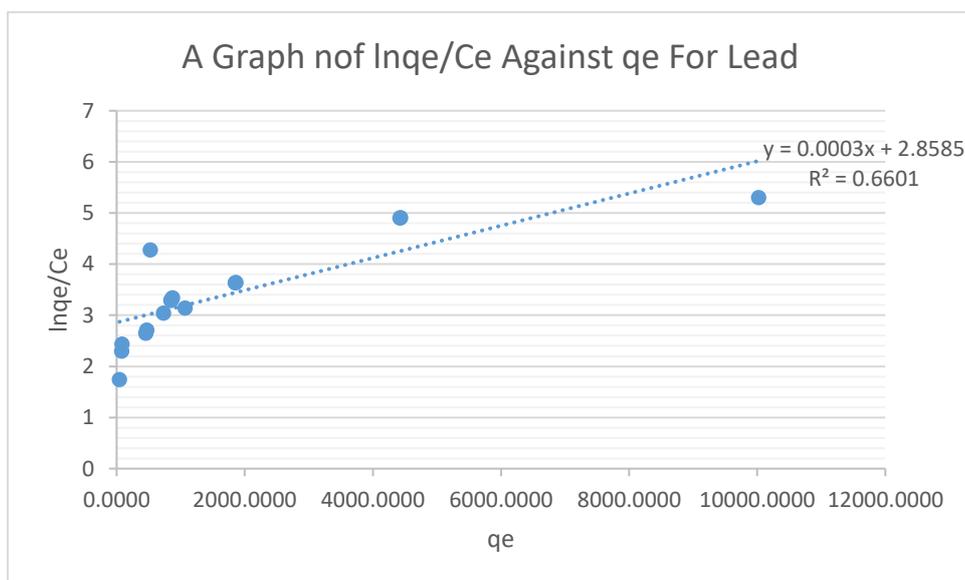


Fig. 8: Elovich isotherm for Pb^{2+} ion removal at various concentrations

Table 4: Adsorption Isotherm Models' Parameters

Langmuir Isotherm		Freundlich Isotherm		Halsey Isotherm		Redlich-Peterson Isotherm		Elovich Isotherm	
q_{max} (mg/g)	1.9721	n	0.16983	n	-0.16983	A (Lg ⁻¹)	-2.13216	A (L mg ⁻¹)	2000
R_L	0.128	K_F (mg/g)	2.175×10^{-4}	K	27.0516	B (L mg ⁻¹)	-4.8883	B (mg/g)	3.8056
K_L	0.0681	R^2	0.7037	R^2	0.7037	R^2	0.6208	R^2	0.6078
R^2	0.9984								

3.3.0 Adsorption Kinetics

The optimal adsorbent for the treatment of wastewater must have a rapid adsorption rate in addition to a high adsorption capacity. Effective adsorbent selection criteria include efficiency and adsorption rates. In this study, the experimental findings were fitted by conventional kinetic models, including pseudo-first-order and pseudo-second-order kinetic models, in order to assess the specific characteristics of each model and understand the adsorption mechanism. Following adequate linearization procedures, the parameters of the kinetic models can be obtained using either linear or nonlinear regression analysis (McKay *et al.*, 1985).

3.3.1 Pseudo-first-order equation

Pseudo first order integrated rate equation can be represented by the linear Equation 3.8:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \text{-----(3.8)}$$

Generally, by plotting $\log(q_e - q_t)$ vs. t (linear relationship), k_1 and q_e can be evaluated from the slope and intercept of the respective line. The equilibrium adsorption capacity (q_e) value for the metal ion Pb^{2+} is 5.47559 while the k_1 value for the Pb^{2+} ion is 2.2222×10^{-7} . The small R^2 value, coupled with the difference between the intercept and q_e means that the adsorption is not likely to be pseudo first-order reaction.

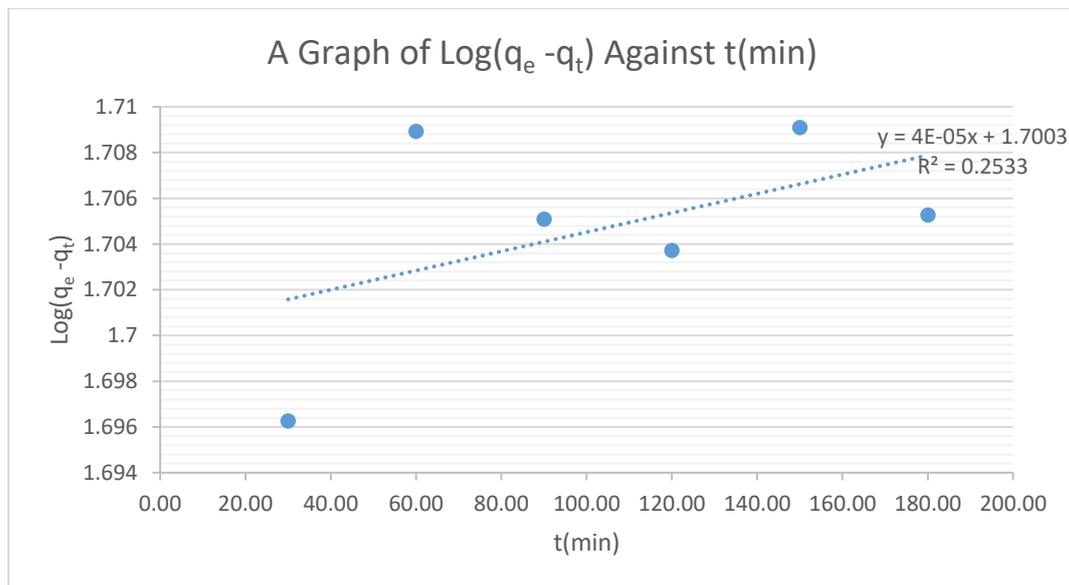


Fig.9: First order plot $\ln(q_e - q_t)$ against time (min) of adsorption of Pb^{2+}

3.3.2 Pseudo-second Order Equation

Pseudo second order integrated rate equation is defined by the relation in Equation 3.9:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \text{-----(3.9)}$$

Where: q_e = Maximum amount of adsorbed Pb^{2+} at equilibrium, q_t = Maximum amount of adsorbed Pb^{2+} at time t , and k_2 = Rate constant. Values of k_2 and equilibrium adsorption capacity (q_e) were calculated from the intercept and slope of the plots of $\frac{t}{q_t}$ vs. t , respectively. The values of R^2 and q_e also indicate that this equation leads to better results. The R^2 values

for the pseudo-second order kinetic model was found to be 0.9999 and the calculated q_e value is 49.0196 which is close to the experimental data which strongly support the idea of applicability of this model for real fitting experimental data concerning the Lead (II) ion.

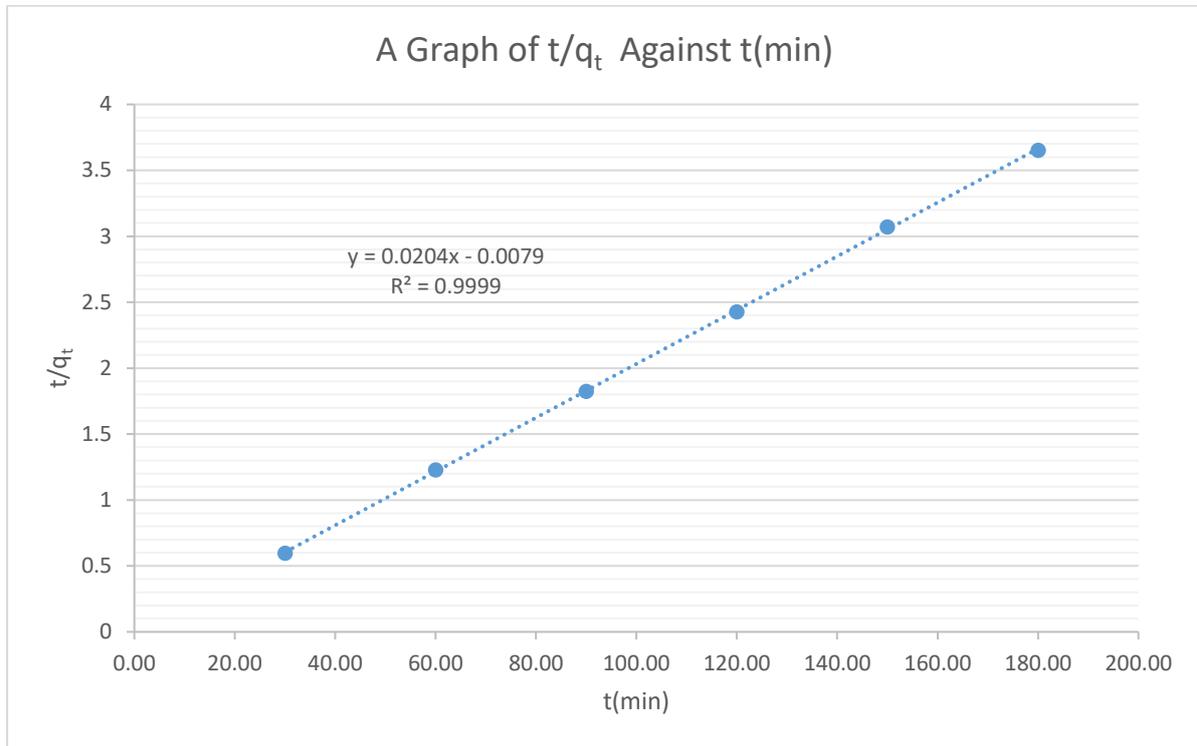


Fig. 10: Second order plot t/q_t against time (min) of adsorption of Pb^{2+} from aqueous solution

4. CONCLUSION

Pineapple peel acid activated carbon is a very good adsorbent for the removal of Lead (II) ions, Pb^{2+} from aqueous solution. The synthesized pineapple peel was characterized via Fourier Infrared Spectrophotometry (FT-IR), Brunauer-Emmett-Teller (BET) analysis and Scanning Electron Microscope (SEM). From the results of the BET analysis, the specific surface area was found as a predominant factor in determining the adsorption capacity of investigated carbon, $1382.664 \text{ m}^2\text{g}^{-1}$.

Also, adsorption studies were carried out to test for different isotherm models like Langmuir, Freundlich, Elovich, and Redlich-Peterson isotherm models. The metal ion was tested to see the isotherm model that will perfectly fit in, the Langmuir model fitted perfectly compared to other models. Furthermore, the data obtained for kinetic studies showed that it followed the pseudo-second-order mechanism ($R^2 = 0.999$) compared to the pseudo-first-order mechanism ($R^2 = 0.2533$).

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