PARAMETRIC STATISTICAL SIGNIFICANCE OF LEAD (II) IONS ADSORPTION BY RICE HUSK IN AQUEOUS SOLUTIONS

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Abstract: Batch experiments were performed to determine how Pb (II) ion adsorption was affected by contact time, adsorbent dosage, temperature, and pH. Adsorption increased with higher adsorbent doses and decreased with higher adsorbate doses. Time speeds up the adsorption process, with pH 6 and 650 °C showing the highest levels of adsorption. The Langmuir and Dubinin-Radushkevic isotherm models best fitted the sorption data, with R^2 values of 0.995 and 0.9956 and standard errors of regression of 1.8209 and 0.0298, respectively. The pseudo-first order kinetic model best captured the kinetics. Analysis of Variance (ANOVA) and the Bonferroni-Holm Posthoc significance test showed that the adsorption was statistically and parametrically justified.

Keywords: Rice husk, ANOVA, Adsorption capacity, Removal efficiency

1. INTRODUCTION

Many activities are consuming sizable amounts of harmful chemicals and producing sizable amounts of hazardous waste as a result of the rapid increase in agriculture, industry, commerce, hospitals, and healthcare institutions. There are currently over 110,000 different kinds of dangerous compounds that are sold commercially. Another 1000 new chemicals are released onto the market year for industrial and other purposes. Heavy metals are among the most dangerous environmental contaminants [1].

In general, the term "heavy metals" refers to substances like cadmium, chromium, copper, mercury, nickel, lead, ferox, and zinc that are frequently linked with toxicity and pollution issues. Each of these elements has a range of typical background concentrations associated with it in soils, sediments, waterways, and living creatures since heavy metals are naturally present in rock formation and ore minerals. These heavy metals are of particular concern because of their toxicity, propensity for bioaccumulation, and persistent nature.

Numerous researchers frequently employ the adsorption method to remove heavy metals from waste streams [2]. Although it is an extremely expensive substance, activated carbon has been utilized regularly as an adsorbent. As a result, research must be conducted to produce activated carbon substitutes that are more affordable and effective. The design and operation of the adsorption process are flexible, and it frequently results in treated effluent of good quality. A proper desorption process can also replenish adsorbents because it is occasionally reversible.

Numerous processes including metal finishing, electroplating, painting, dying, photography, surface treatment, and printed circuit board manufacturing allow pollutants to reach aquatic systems [3]. Aside from mining operations, agricultural runoff, and domestic waste all have the potential to deposit heavy metals into water bodies,

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increasing the number of metallic species in the ecosystem [4]. Recent years have seen a lot of emphasis focused on the removal of harmful and damaging heavy metals from mine waters, water supplies, and wastewater from industrial effluents. Industrial wastewaters frequently contain a significant amount of heavy metals that, if discharged without sufficient treatment, pose a risk to both public health and the environment. Rice husk had been used as a biosorbent for lead from various aqueous solutions, while physicochemical parameters such shaking time, various proportions of adsorbent and adsorbate were studied to optimize the conditions to be utilized on a commercial scale for the decontamination of effluents using a batch technique [5].

Mitra *et al.* [6] used rice husk as an adsorbent in continuous column mode for the removal of Pb(II) and Cr(VI) ions. The variations of column process parameters like influent metal concentration, bed height, rate of flow and so on were investigated to study the breakthrough behavior.

Adsorption has been demonstrated to be an excellent method for treating industrial waste effluents, offering important advantages over conventional methods, particularly from an economic and environmental standpoint, such as low cost, availability, profitability, ease of operation, and efficiency. The exploration of biologically derived materials as prospective metal biosorbents is the result of the search for an inexpensive and widely accessible adsorbent. The removal and/or recovery of hazardous metals from wastewater using current technologies is being challenged by biosorption [7].

This study examines the use of an inexpensive adsorbent made from rice husk for the removal of heavy metals (lead) from wastewater in batch systems since it is readily available locally, abundant, and reasonably priced. With precise physiochemical characterization of the rice husk specie, the variables that affect adsorption, such as biomass dosage, contact time, temperature, adsorbate dose, and pH, were also studied. Additionally, the features of the adsorption isotherm model, the adsorption kinetics model, and the thermodynamics for the removal of lead from the wastewater were also explored.

2. EXPERIMENTAL SETUP

2.1. Materials

The rice husk was locally sourced from the rice mining factory Saki, Oyo State, Nigeria.

2.2. Apparatus and reagents used

The following tools and materials were utilized: hydrochloric acid of the analytical grade (Epoxy Oilserv, 30 % w/w purity); analytical grade sodium hydroxide (Epoxy Oilserv, 98 % purity); analytical grade lead (II) nitrate (Indian Platinum, 98% purity); distilled water; rotary shaker (Bioevopeak SHK-O0310111, China); weighing balance (AL Mettler Toledo GmbH); furnace (Bioevopeak FNC-TB1700, China); oven (Gallenkamp, England); pH meter (HANNA Instrument pHep®); beaker (Pyrex, England); Conical flask (Pyrex, England); Measuring cylinder (Pyrex, England); atomic absorption spectrophotometer (Perkin Elmer Analyst 200); scanning electron microscope (Model Jeol-JXA 840 A, Japan); water bath shaker (Grant OLS 200); filter paper (Whatman); stop watch (Electronic Timer, TIME-Q118, China); sieve (B.S.S. 200- 100); FTIR spectrometer (Thermo Nicolet Avatar 330, England).

2.3. Adsorbent preparation

The procedure of Ositadinma *et al.* [8] was used to prepare the rice husk. It was properly cleaned with distilled water to eliminate dirt and dust before being dried in the sun for two days and then stored for 24 hours at 700 °C.

2.4. Carbonization

The carbonization process was done by the procedure adopted by Mondal *et al.* [9]. The rice husk was heated in the Muffle Furnace at 450 °C for 30 minutes then permitted to cool. The beans husk was then crushed with blender and sieved to a size smaller than 850 μm. The yield of carbon is defined as the ratio of final weight of the obtained product after carbonization to the weight of dried precursor initially used was calculated using:

$$Yield(\%) = \frac{product}{reac\tan t} \times 100 \tag{1}$$

2.5. Activation

The activation process was done by the procedure adopted by Hanum et al. [10]. The carbonized rice husk was impregnated with 1 M HCl at carbon to acid ratio of 1:3 (w/v) for 24 hours. Afterwards it was placed in a furnace and heated at 650 °C for 30 minutes. The resulting sample was allowed to cool and watched with distilled water until neutral pH was reached.

2.6. Fourier Transform-Infrared (FTIR) Spectroscopy

At room temperature, surface functional groups of the impregnated activated carbon were identified by FTIR spectra recorded on a Thermo Electron Corporation instrument. Over 500 to 4000 cm^{-1}, the percentage of sample transmission was observed.

2.7. Adsorbate

Lead (II) nitrate (Indian Platinum, 98 % purity) was used as the adsorbate and was obtained from Lagos University Teaching Hospital (LUTH). It was prepared by dissolving 1 g of $Pb(NO_3)_2$ in 1 liter of distilled water.

2.8. Batch experimental procedure

Batch adsorption experiments were conducted in 250 mL conical flask using 50 mL of prepared lead solution. The amount of lead (II) ion adsorbed by the rice husk was determined using.

$$q_e = \frac{C_o - C_t}{M} \times V \tag{2}$$

$$\mathrm{Re}\,moval(\%) = \frac{C_o - C_t}{C_o} \times 100 \tag{3}$$

where M represent mass of activated carbon in gram; V is volume of test solution in liter; Co is the initial concentration of lead; Ct represent final concentration of lead; q_e is the amount of solute removed or adsorbed.

2.8.1. Effect of contact time

In a conical flask, 50 mL of adsorbate containing 1000 mg/L was added. The conical flask containing the adsorbate received 2 g of the adsorbent, and it was shaken on a rotary shaker at 120 rpm for 10 minutes. This action was taken between 10 and 60 minutes of contact time. Filtered mixtures were produced, and their concentrations were determined using the AAS (atomic absorption spectrophotometer).

2.8.2. Effect of adsorbent dose

Separate conical flasks were filled with 50 mL of a produced adsorbate at a concentration of 1000 mg/L. Each beaker received different weighed additions of adsorbents (ranging from 0.5 to 3 g). The conical flasks were shaken for 20 minutes at 120 revolutions per minute on a rotary shaker. The filtered concentrations that were produced were then assessed using the AAS.

2.8.3. Effect of adsorbate dose

Distilled water was used to generate 50 mL of 100 mg/L adsorbate, and 2 g of adsorbents were added to the adsorbate solution. The conical flask was shaken for 20 minutes at 120 rpm on a rotary shaker. The adsorbate concentration used for this phase ranged from 200 to 1000 mg/L. The AAS was used to calculate the filtrates' final concentrations.

2.8.4. Effect of pH

The pH of the solution was adjusted using 0.1 M NaOH and 0.1 M HCl, then 50 mL of the 1000 mg/L adsorbate and 2 g of the adsorbents were added to a conical flask. For 20 minutes at 120 rpm, the conical flask was shaken on a rotary shaker. For pH ranges of 2 to 12, this was done. After filtering the results, the concentrations were calculated using the AAS.

2.8.5. Effect of temperature

Two grams (2 g) of the adsorbent and 50 mL of the produced adsorbate were put to a conical flask that held 250 mL. For 20 minutes at 120 rpm, the conical flask was shaken in a water bath. Then, this process was repeated with temperature ranges between 25 and 75 °C. Filter paper and funnels were used to remove the adsorbents, and the AAS was used to measure the concentrations of the filtrate.

3. RESULTS AND DISCUSSION

3.1. Characterization of activated carbon

The rice husk adsorbent had an ash content of 3.7 %, moisture content of 8.3 %, pH of 6.2 and a bulk density of 0.45 g/mL. Before and after the adsorption process, the surface functional groups of rice husk were characterized using an FTIR (Fourier transform infrared) spectrometer. FTIR spectra of sorbent obtained in the range of 4400–350 cm^{-1} wave number and major functional groups present in adsorbent before and after adsorption are listed below. The process of adsorption has been influenced by the presence of alcohol, carboxylic acid, aromatic compound, amine, alkene, carbon dioxide and halo compound on the surface of an adsorbent.

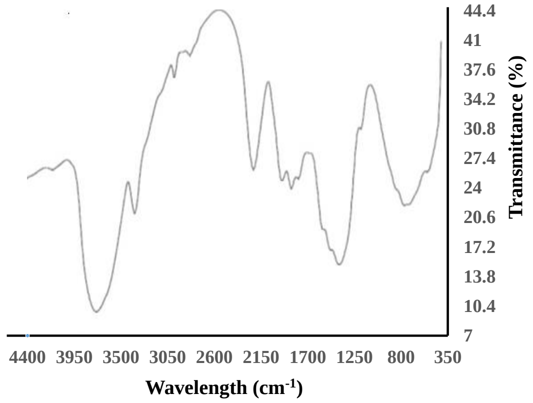

Fig. 1. FTIR of rice husk before adsorption.

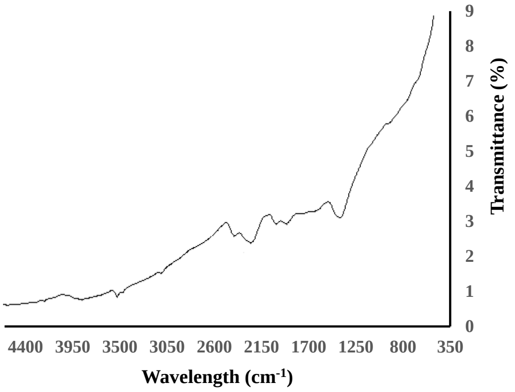

Fig. 2. FTIR of rice husk after adsorption.

Table 1. Identified functional groups present in rice husk by FTIR spectroscopy.

IR Peak	Possible Functional Group		Compound Name
	Before Sorption	After Sorption	
448	C-I stretching	-	Halo Compound
600.36	C-I stretching	-	Halo Compound
722.3	-	C-I stretching	Halo Compound
901	C- Br stretching	-	Halo Compound
901	-	C=C bending	Alkene
1048	C=H bending	-	Mono Substituted Alkene
1102.4	C-N stretching	-	Amine
1157.3	-	CO-O-CO	Anhydride
1328.6	C-O stretching	-	Secondary Alcohol
1375.5	-	C=H bending	Aldehyde
1375.8	-	C=H bending	Alkene
1439	-	C-C stretching	ConjugatedAlkene
1443	C-C stretching	C-C stretching	ConjugatedAlkene
1605	-	C-O stretching	ConjugatedAldehyde
1635.5	C=H bending	-	Aromatic Compound
1709.4	-	C=C=C stretching	Alkene
2144.2	O=C=O stretching	-	Carbon dioxide
2351.8	O=C=O stretching	-	Carbon dioxide
2358.8	-	O=H stretching	Carboxylic Acid
2901.6	O=H stretching	-	Carboxylic Acid
2919	-	O=H stretching	Alcohol
3368	-	O=H stretching	Alcohol
3428	O=H stretching	-	Alcohol
3850.6	-	O=H stretching	Alcohol
4027	-	O=H stretching	Alcohol

3.2. Effect of adsorbent dose

The variations of dose from 0.5-3.0 g for adsorbent are graphically represented in Figures 3 and 4. The mass appeared to have a significant impact on the adsorption procedure. At a dosage of 3 g of adsorbent, 49 % of the Pb^{2+} was observed to be removed. It is evident that increased surface area and active sites resulted in an increase in the percentage of heavy metal removal by rice husk when adsorbent dosage was increased [11]. The adsorption capacity decreased with increasing adsorbent dosage, this can be due to fact that at constant Pb concentration, increase in the adsorption dosage increased the sorption site, which could not cover the Pb molecules in the solution, hence the decrease in the adsorption capacity.

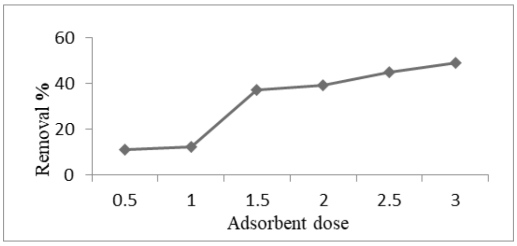

Fig. 3. Effect of pH on removal efficiency.

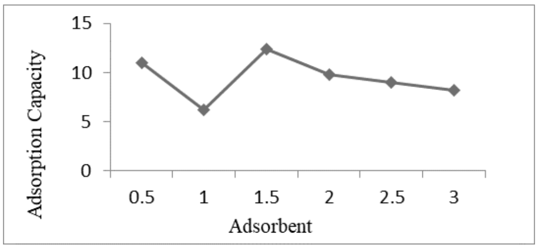

Fig. 4. Effect of pH on adsorption.

3.3. Effect of adsorbate concentration

The relationship between concentration and adsorption rate was examined under 27 °C room temperature, Pb^{2+}, and 120 rpm shaking conditions shown in Figures 5 and 6. The range (200-1000 ppm) of the initial concentration of heavy metals was investigated. It was shown that the percentage elimination fell off as the original lead concentration rose. It was observed that adsorption capacity of the Pb^{2+} increases with an increase in initial Pb^{2+} concentration which implies that adsorption process depends on initial concentration. A higher concentration of lead provides a higher driving force for the metal ion to approach adsorption sites more rapidly. This outcome was brought about by the saturation of active sites on rice husk over a particular level of heavy metal concentration.

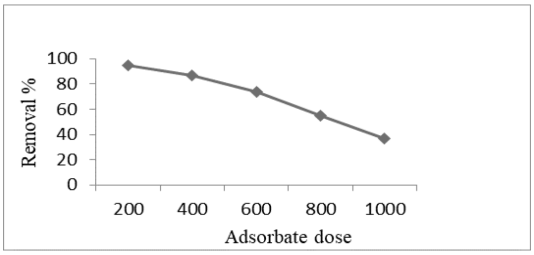

Fig. 5. Effect of adsorbent dose on removal efficiency.

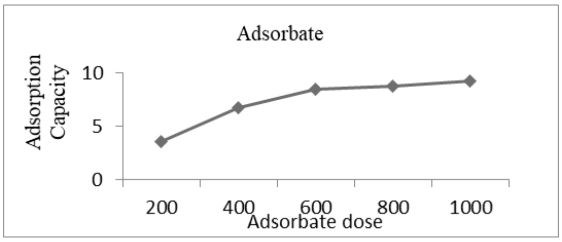

Fig. 6. Effect of adsorbent dose on adsorption capacity.

3.4. Effect of contact time

The elimination of Pb^{2+} by adsorption was shown to rise with increasing time and reached a maximum value at around 60 minutes (Figures 7 and 8). This was accomplished by observing the effect of contact time on the rate of adsorption using rice husk. The outcome showed that, at all concentrations, the absorption of adsorbate increased at the beginning of the contact time [12]. This is because all of the active sites on the adsorbent are empty at the start of the adsorption process. As a result, desorption occurs more slowly and adsorption occurs more quickly [13].

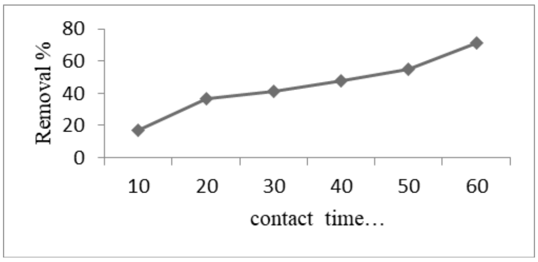

Fig. 7. Effect of contact time on removal efficiency.

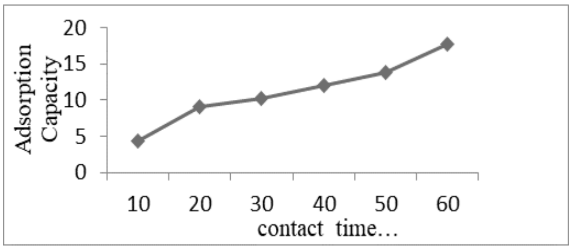

Fig. 8. Effect of contact time on adsorption capacity.

3.5. Effect of pH

One of the crucial variables controlling the metal ion adsorption is the pH of the effluent. The initial pH range of 6 to 8 was used to study the impact of pH on Pb^{2+} adsorption. Figures 9 and 10 illustrate the relationship between the initial pH of the solution and the proportion of these heavy metals removed. The difference in adsorption capacity in this pH range was mostly caused by pH effects on Pb^{2+} adsorption properties, indicating that the adsorption capacity of the adsorbent was unmistakably pH-dependent. The elimination of Pb^{2+} by rice husk at pH 6 roughly resulted in the best pH being recorded. Further increases in pH value decreased adsorption of the metal ions may be due to precipitation and lower polarity of Pb (II) at higher pH value, as reported by [14].

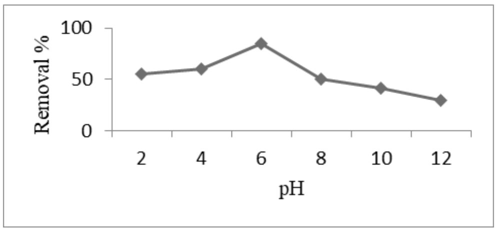

Fig. 9. Effect of pH on removal efficiency.

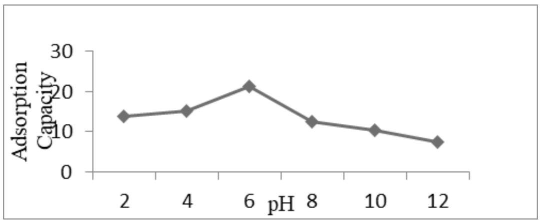

Fig. 10. Effect of pH on adsorption capacity.

3.6. Effect of temperature

Rice husk was studied at temperatures between 25 and 75 °C to determine how temperature affected Pb^{2+} retention onto the adsorbent. If the adsorption is exothermic or endothermic, depending on the thermodynamic parameters that depends on temperature. The rate at which Pb^{2+} was adsorbing increased as the system's temperature rose, indicating that the adsorption is endothermic (Figure 11 and 12).

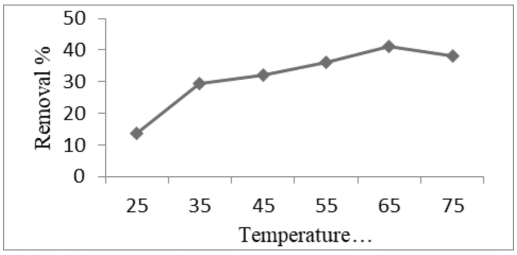

Fig.11. Effect of temperature on removal efficiency.

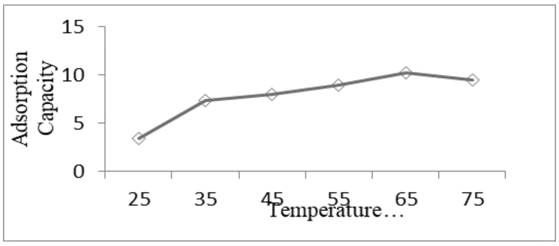

Fig. 12. Effect of temperature on adsorption capacity.

3.7. Analysis of variance and parametric statistical significance

Table 2 provides the results of the ANOVA and Bonferroni-Holm Posthoc significance test for the Pb^{2+} ion adsorption by rice husk under various conditions. Daniel's XL Toolbox Version 6.70 (© 2008–2013) software was used to execute the statistical computations presented.

Table 2. Bonferroni-Holm Posthoc significance test and analysis of variance (ANOVA) of Pb^{2+} adsorption with rice husk using varying parameters.

Group1	Group2	Analysis of Variance (ANOVA) Test						Bonferroni-Holm Posthoc Significance Test		
		S_{SB}	S_{SW}	D_{FB}	D_{FW}	F	P	P_C	P	Significant
W_A	P_R	1369914	135291.9	1	10	101.2562	1.5E-6	0.05	1.5E-6	Yes
C_A	P_R	217562.5	621800	1	8	2.799132	0.132853	0.05	0.132853	No
t	P_R	803418.8	167437.5	1	10	47.9832	4.06E-5	0.05	4.06E-5	Yes
T	P_R	1203333	49833.33	1	10	241.47I6	2.49E-8	0.05	2.49E-8	Yes
pH	P_R	632502.1	177338.8	1	10	35.6663	1.37E-4	0.05	1.37E-4	Yes

In Table 2, C_A is the adsorbate concentration (mg/L), W_A is the weight of the adsorbent (g), S_{SB} and S_{SW} are the sums of squares within and between the groups, t is the mixing time (min), F is Fisher's ratio, P and P_C are the probability and critical probability factors respectively, P_R is the percentage of ions removed (% removal), D_{FB} and D_{FW} are the degrees of freedom between and within the groups respectively, and T is the temperature (°C). The analyzed parameters display the actual sums of squares both within and between groups. Since the F and P values are generally within the predicted limits, there is a statistically significant difference between the individually studied parameters and the percentage removal of Pb (II) ion groups at the 95 % confidence interval. Fisher's F is a measure of the variation within and across the groups, and P is a probability factor, which in an

ANOVA analysis, must be less than 0.05. Between the groups, there was one degree of freedom throughout, while within the groups, there were 8 to 10 degrees of freedom. Except for the correlations between P_R and C_A, which had P values bigger than the P_C in the 95 % confidence interval, the Bonferroni-Holm Post-hoc parametric significance test for the other parameters revealed a strong dependency or importance on each other. The parametric factors that provided the maximum % removal of ions with identical adsorption systems complied with earlier works [15].

3.8. Adsorption isotherm for rice-husk

The distribution of the liquid and solid phases at equilibrium is shown by the adsorption isotherm. Five isotherm models (the Langmuir, Freundlich, Temkin, Dubinin-Radushkevic, and Henry's models) were used in the adsorption isotherm investigation. By looking at coefficients (R^2) value, it was determined whether isotherm equation could be used to describe adsorption process.

3.8.1. Langmuir isotherm

To depict chemisorption, the Langmuir isotherm of the ideal localized monolayer was created. For Pb^{2+} by rice husk, isotherm data had been linearized using the Langmuir equation and plotted between Ce/qe vs Ce (Figure 13). The rice husk's monolayer adsorption capacity, as measured by the Langmuir constant, was found to be 10.54 mg g^{-1} for Pb^{2+}. For Pb^{2+} adsorption by rice husk, the Langmuir constant, Km, which represents adsorption energy, was 0.0119 mg^{-1}. The rice husk yielded a high regression correlation coefficient R^2 of 0.995 Pb^{2+}, indicating that the experimental data and isotherm parameters agreed well. The results showed that the equilibrium data suited the Langmuir isotherm model nicely. The model's linear form is as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_L k} + \frac{1}{Q_L} C_e \tag{4}$$

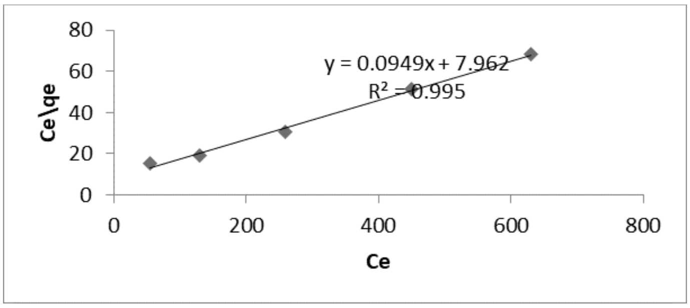

Fig. 13. Langmuir isotherm of Pb^{2+} by rice husk.

Table 3. Isotherm constant.

Parameter	Value
Q_l	10.5374
K_l	0.0119
R^2	0.995
S	1.82089
ε_H	1.9909
ε_L	0.3592

3.8.2. Freundlich isotherm

Utilizing the same equilibrium data of heavy metals from rice husk adsorption, the applicability of the Freundlich isotherm was examined based on adsorption on heterogeneous surfaces. The graph between lnqe and lnCe was used to calculate the Freundlich constants, $K_F$and n, which are displayed in Figure 14. By rice husk, the values of K_F and n were 0.9587 Pb^{2+} and 2.7144, respectively. The Freundlich isotherm model’s regression correlation coefficient for rice husk was reported to be 0.8706 Pb^{2+} by rice husk. Although frequently employed, the Freundlich isotherm model does not provide data on monolayer adsorption capacity.

The linear form of the model is:

$$\log q_e = K_F + \frac{1}{n} \log C_e \tag{5}$$

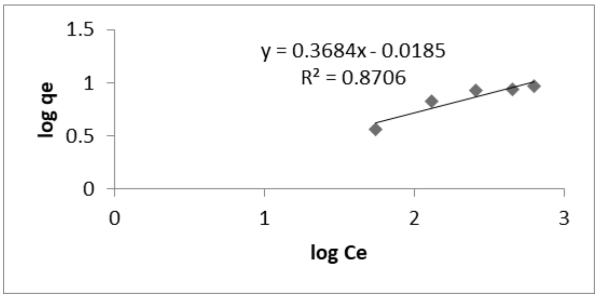

Fig. 14. Freundlich isotherm of Pb^{2+} ions by rice husk.

Table 4. Isotherm constant.

Parameters	Value
R^2	0.8706
K_f	0.9587
N	2.7144
S	0.06983
ε_H	1.1177
ε_L	1.7866

3.8.3. Temkin isotherm

The Temkin isotherm constants, A and B, were calculated using a plot of qe vs lnCe at constant temperature, as illustrated in Figure 15. The values of B and A for the Temkin isotherm mode were 2.2552 Pb^{2+} by rice husk and 0.1191 Pb^{2+} by rice husk, respectively. The Temkin isotherm model's obtained regression correlation coefficient was 0.9258 Pb^{2+} by rice husk.

The linear form of the model is:

$$q_e = A \ln B + A \ln C_e \tag{6}$$

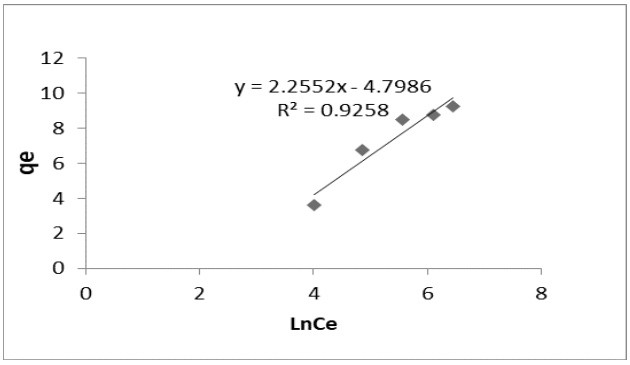

Fig. 15. Temkin isotherm of Pb^{2+} by rice husk.

Table 5. Isotherm constant.

Parameters	Value
R^2	0.9258
A	0.1191
B	2.2552
S	0.72302
ε_H	-0.6137
ε_L	-0.4878

3.8.4. Henry's isotherm

Plotting qe against Ce setting an intercept of zero to calculate the Henry's constant K_{HE} as shown in Figure 16. The constant gave a value of 0.0066, the regression correlation was 0.8311, which shows the Henry's isotherm doesn't fit the model.

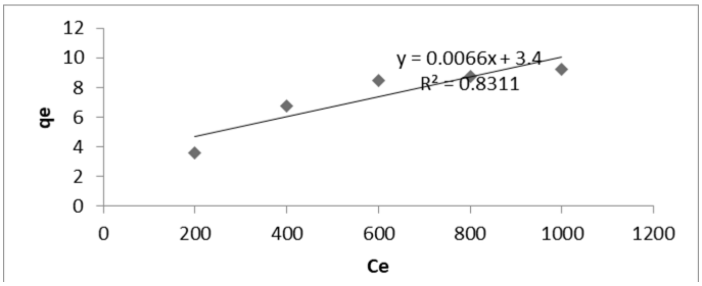

Fig. 16. Henry's isotherm of Pb^{2+} by rice husk

Table 6. Isotherm constant.

Parameters	Value
R^2	0.8311
Khe	0.0066
S	1.09068
ε_H	3.8
ε_L	19

3.8.5. Dubinin- Radushkevich isotherm

To depict adsorption mechanisms with Gaussian energy distribution onto heterogeneous surfaces, the Dubinin-Radushkevich isotherm empirical adsorption model is widely utilized [16].

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{7}$$

where q_m (mg/g) is the theoretical saturation capacity, β (mol^2/kJ^2) is a coefficient related to the mean free energy of adsorption, and is the ε Polanyi expressed as:

$$\varepsilon = RT \ln\left(1 + {}^{1}\!/_{C_e}\right) \tag{8}$$

$$E = {}^{1}\!/_{\sqrt{2\beta}} \tag{9}$$

where E is the means adsorption energy.

A plot of $\ln q_e$ against ε^2gives a straight line with β and q_m obtained from the slope and intercept respectively. The results showed a very good fit for this model (Figure 17 and Table 7).

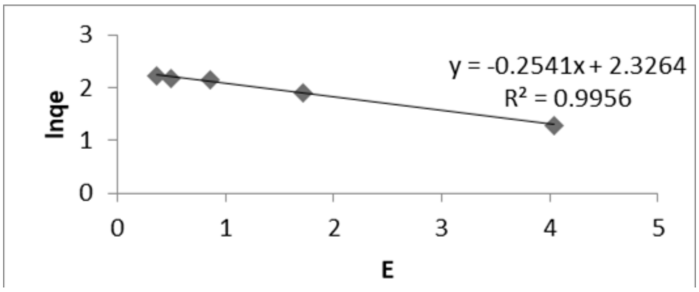

Fig. 17. Dubinin-Radushkevic isotherms of Pb^{2+} by rice husk.

Table 7. Isotherm constant.

Parameters	Value
R^2	0.9956
q_m	2.3264
B	-0.2541
S	0.0298
ε_H	-2.0663
ε_L	-0.1922

3.9. Adsorption Kinetics

Analyzing the heavy metals' uptake across various time intervals allowed researchers to identify the kinetics of adsorption. Adsorption kinetics offered information on the mechanism by which an adsorbate is adsorbed to an adsorbent. Pseudo-first-order, second-order, and intra-particle kinetic models are evaluated using experimental data to comprehend the kinetics of Pb^{2+} removal from rice husk.

3.9.1. Pseudo first-order kinetics

Plot of log (qe-qt) versus t gave a straight line which represented pseudo first-order kinetics for the removal of Pb2+ using rice husk (Figure 18). The values of first-order rate constants, k1 and qe for initial heavy metals concentration by rice husk were calculated to 0.0283 and 16.9981 respectively. The regression correlation coefficient was obtained to be 0.9762.

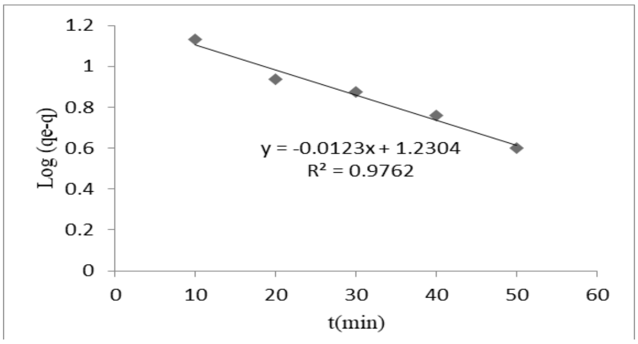

Fig. 18. Pseudo 1st order kinetic of Pb^{2+} by rice husk.

Table 8. Kinetics constants.

Parameters	Value
R^2	0.9762
K_l	0.0283
Q_e	16.9881
S	0.0369
ε_H	0.0229
ε_L	-0.0133

3.9.2. Pseudo second-order kinetics

The second-order kinetic model depicted in Figure 19 was also used to examine the kinetics of Pb^{2+} adsorption by rice husk. The second-order rate constant, k_2, the predicted equilibrium capacity, qe, and the regression correlation coefficient of Pb^{2+} by rice husk were obtained via the application of second-order kinetics by plotting t/qt vs. t. It was discovered that the regression correlation coefficient was 0.8043.

3.9.3. Intra-particle kinetics

Going further to test for the kinetics study using Intra-particle model as shown in Figure 20, a plot of q against $t^{1/2}$ yielded the intra-particle rate constant k_d of 2.615 and C of -3.7414 and a regression correlation of 0.544 of Pb^{2+} by rice husk.

Finally, for all starting lead concentrations, the pseudo first order kinetic model provided a substantially better correlation fit for the adsorption of lead than the pseudo second order and intra-particle models.

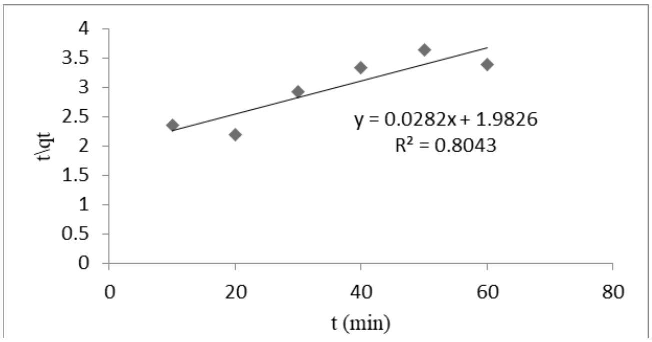

Fig. 19. Pseudo 2nd order kinetics for Pb^{2+} by rice husk.

Table 9. Kinetics constant.

Parameters	Value
R^2	0.8042
K_l	4.01*E-4
Q_e	35.461
S	0.2710
ε_H	0.0883
ε_L	-0.2943

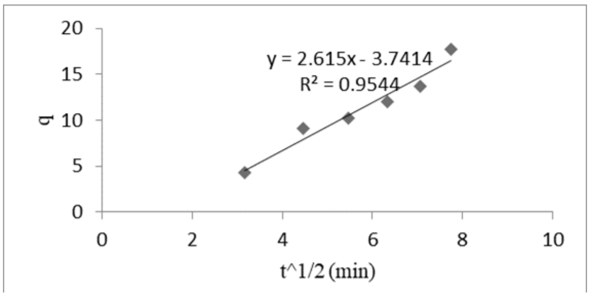

Fig. 20. Intra-particle kinetics for Pb^{2+} by rice husk.

Table 10. Kinetics constant.

Parameters	Value
R^2	0.9544
K_d	2,615
ε_H	-0.2780
ε_L	1.2357

3.10. Thermodynamic study

Thermodynamic parameters evaluated Pb^{2+} adsorption onto rice husk are the free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0). These parameters were calculated using the following equation:

$$K_d = \frac{q_e}{C_e} \tag{10}$$

$$\Delta G^0 = -RT \ln K_d = \Delta H^0 - T\Delta S^0 \tag{11}$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{12}$$

ΔS^0 and ΔG^0 of Pb^{2+} by rice husk sorption from the aqueous solution were calculated employing the above equations. The plot of $\ln K_d$ versus 1/T was linear over temperature range of 298-348 K. The value of ΔH, ΔS and ΔG^0 was calculated from the slope and intercept of Figure 21. The value of ΔH^0 confirmed the endothermic for Pb^{2+}. The spontaneous character of the adsorption process, which was more advantageous at low temperatures, was thought to be the cause of the increase in G with temperature.

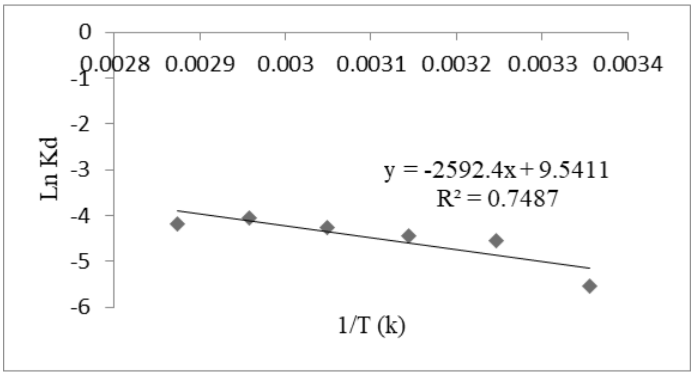

Fig. 21. Van't Hoff plot of adsorption of Pb^{2+} ions onto rice husk

Table. 11. Thermodynamic parameters for the adsorption of Pb^{2+} onto rice husk.

T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol)
298	-2085.55	21553.21	79.3247
308	-2878.79		
318	-3672.04		
328	-4465.29		
328	-5258.54		
348	-6051.78		

4. CONCLUSIONS

The rice husks are an agricultural waste substance. This product exhibits very good adsorption for heavy metal Pb^{2+} from wastewater. In this study, the adsorption of lead from wastewater was investigated using activated carbon from rice husk as adsorbent.

The findings demonstrated that as the dosage of adsorbent increased, so did the percentage of removal. It has been demonstrated that the pH, adsorbent dosage, temperature, and contact time all have a significant role in the adsorption of lead by rice husks. With R^2 values of 0.995 and 0.9956, respectively, the Langmuir and Dubinin-Radushkevic isotherms models were determined to be the most suitable ones for the heavy metals.

The pseudo-first-order reaction model, according to kinetic studies, best explained the adsorption process. The results of the current study demonstrated that rice husk may be employed as an efficient adsorbent for the treatment of wastewater because it can remove up to 99.02 % of Pb^{2+}. Utilizing ANOVA and the Bonferroni-Holm Posthoc significance test, statistical analysis was used to support the adsorption, confirming the critical role that process parameters play.

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Conflicts of Interest: *The authors declare no conflicts of interest.*

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