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Comparative Adsorption Isotherm Study of the Removal of Pb2+ and Zn2+ Onto Agricultural Waste

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Abstract— The removal of lead (II) ions (Pb2+) and Zinc (II) ions from aqueous solution by phosphoric acid modified rice husk has been investigated. Isotherms studies were carried out by considering the equilibrium sorption of Pb2+ and Zn2+. The adsorption isotherms of Pb2+ and Zn2+ ions fitted the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models well. The highest coefficient of determination values (R2) for Pb2+ was obtained from the Temkin model as 0.997 while that of Zn2+ was obtained from the Langmuir model as 0.990 respectively. The maximum adsorption capacity predicted by the Langmuir Isotherm for Pb2+ and Zn2+ are 142.857 mg/g and 100 mg/g respectively. Isotherm parameters estimated from Langmuir, Freundlich Temkin and Dubinin-Radushkevich showed better adsorption of Pb2+ than Zn2+ under the same experimental conditions. The study showed that rice husk modified with phosphoric acid is an effective low-cost adsorbent for the removal of Pb2+ and Zn2+ from wastewater.

Index Terms— Adsorption, Heavy metals, Rice husk, Langmuir isotherms, Freundlich isotherm, Temkin isotherm, Freundlich isotherm, Dubinin-Radushkevich isotherm .

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1 INTRODUCTION

Increase in industrial and mining activities has led to various deterioration of the ecosystem and therefore posed dangers to human health and environment [1]. Heavy metals are some of the toxic pollutants released into water bodies due to various anthropogenic activities. There are many physical and chemical processes for removing metal ions from solution. Examples of such processes include chemical precipitation, ultra-filtration, solvent extraction, and membrane separation [2]. The major disadvantage of these processes is their high operational cost. However, Adsorption, a surface phenomenon, has shown great promise in removing metal ions from solution of wastewater. Commercial activated carbon has been proven as an efficient adsorbents but its cost is prohibitive [3]. Several biosorbents such as rice husk, spent grain, peat, sawdust, and green algae have been researched for the adsorption of metal ions in aqueous solutions [2] ,[3], [4], [5], [6]. They combine the advantages of being readily available in large quantities, cheap and are environmentally friendly [7].

In this study, rice-husk modified with phosphoric acid was tested for its ability to remove Pb^{2+} and Zn^{2+} from synthetic wastewater. Rice husk is the hard covering of rice grains obtained from the threshing of rice. An estimated world production of rice husk in 2010 was given as 154 million tons [8].

The objective of this study is to investigate the adsorption of Zn^{2+} and Pb^{2+} by modified rice husk from aqueous solution. Isotherms of their sorption were studied and compared.

2.0 Materials and Methods

2.1. Sorbents and sorbates

Rice husk collected at a mill in Ilorin, Kwara, Nigeria, was screened and washed with deionized water to remove impurities and thereafter dried in the oven at 105^0C for 2 hours. It was then ground and sieved in a sieve between the range of 150 μm and 250μm. The sieved rice husk was then treated with 1.0M phosphoric acid (H_3PO_4) and then heated on the magnetic stirrer at 100^0C till it formed a paste. The rice husk paste was the washed in deionized water until the pH is about 6. It was then dried in the oven at 80^0C. The modified rice husk was tagged phosphoric acid modified rice husk (PRH).

2.2. Preparation of aqueous solution

Stock solutions containing 1000mg/l each of Pb^{2+} and Zn^{2+} were prepare with distilled water using $Pb(NO_3)_2$ and $Zn(NO_3)_2$ respectively. Working concentrations in the range of 10 – 200 mg/l were prepared through serial dilution.

2.3. Adsorption Experiments

The experiments were carried out in the batch mode. 0.1 g of the adsorbent, PHR was added to a $100cm^3$of the different concentra-

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tions of the synthetic wastewater samples in a 250 cm^3 Pyrex conical flask. The conical flasks were shaken in a orbital shaker at room temperature for 90minutes at 200rpm.The mixtures were filtered with whatman filter paper No 42, and the residual concentration of the filtrate was analyzed using Atomic Absorption Spectrophotometer (2380 UNICAM AAS). The amount of metal ion adsorbed (mg/g) was calculated using the formulae reported by Vanderborght and Van Grieken [9]:

$$q_e = \frac{v(C_i - C_e)}{w} \quad (1)$$

where q_e is the amount of metal ion sorbed (mg/g); C_e is equilibrium concentration (mg/dm^3); C_i is initial concentration(mg/dm^3); w is the weight in gram of the adsorbent.

3. Results and Discussion

The sorption isotherms of Zn^{2+} and Pb^{2+} were studied by fitting the obtained data to Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Isotherm models.

3.1. Langmuir isotherms

The Langmuir isotherm [10] has been widely applied in adsorption studies. It assumes a monolayer adsorption in which adsorbates are adsorbed to a finite number of definite localized sites that are identical and equivalent with no lateral interaction [1].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

Where C_e is the equilibrium concentration (mg/dm^3); q_e is the amount of metal ions adsorbed (mg/g); q_m is the maximum monolayer coverage (mg/g); K is the Langmuir constant (dm^3/mg).

Foo and Hameed [1] gave the linear forms of the equation as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (3)$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \quad (4)$$

$$q_e = q_m - \frac{q_e}{K_L C_e} \quad (5)$$

$$\frac{q_e}{C_e} = K_L q_m - K_L q_e \quad (6)$$

Parameters such as q_m, and K_L are obtained by making the appropriate plots using any of the equations (3) – (6).

For Pb^{2+}, applying the linear form of Langmuir equation, Equation (3), with the plot of C_e/q_e against C_e gave a value of R^2. For Zn^{2+}, Equation (4) gave the best R^2 with the plot of $1/q_e$ against $1/C_e$. With these, isotherms parameters which are useful for adsorption system design were obtained and reported in Table 1.

Webber and Chakkravorti [11] defined a dimensionless constant R_L known as Separation factor as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

Where K_L (L/mg) is the Langmuir constant and C_0 is the adsorbate initial concentration. The value of R_L indicates the nature of adsorption as either unfavourable (R_L>1), linear (R_L=1), favourable (0<R_L<1) or irreversible (R_L = 0). From the estimated values of R_L in Table 1, it can be concluded that Zn^{2+} and Pb^{2+} adsorption on modified rice husk is favourable. However, the i smaller value for Pb^{2+} compared to that of Zn^{2+} indicates that the sorption of Pb^{2+} is more favourable.

3.2. Freundlich isotherm

Freundlich isotherm was developed to study the adsorption of a material onto animal charcoal [12]. It is, however, presently applied in heterogeneous systems especially for organic compounds or highly interactive species on activated carbon and molecular sieves. It is n empirical model which applies to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface [1].

The equation is expressed as:

$$q_e = K_F C_e^{1/n} \quad (8)$$

The equation can be expressed in its linear form as:

$$\ln q_e = \ln K_F + {}^{1}/_{n} \ln C_e \quad (9)$$

K_F is the Freundlich constant related to the adsorption capacity, where $1/n$ is related to the adsorption intensity. A plot of $\ln q_e$ against $\ln C_e$ gives $1/n$ and $\ln K_F$ as the slope and the intercept respectively. $1/n$ value below one implies chemisorptions while a value above one indicates cooperative adsorption [1]. Also, $1/n$ is a heterogeneity parameter. The smaller the value, the greater the heterogeneity of the adsorption process. If the value n lies between one and ten, then adsorption is said to be favourable [13]. The values of $1/n$ for Zn^{2+} adsorption is 0.631 while that of Pb^{2+} is 0.178. This shows that the adsorption of Pb^{2+} is more unto heterogeneous surface than that of Zn^{2+}. Sorption of $Zn^{2+}$and Pb^{2+} onto modified rice husk is favourable as the values of n in both cases lie between 1 and 10.

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modified rice husk is favourable as the values of *n* in both cases lie between one and ten.

3.3. Temkin isotherm

Temkin isotherm contains a factor that takes into account the adsorbent-adsorbate interactions [14]. The model is given as:

$$q_e = \frac{RT}{b_T} lnA_T C_e \qquad (10)$$

The linear form is expressed as:

$$q_e = \left(\frac{RT}{b_T}\right) lnA_T + \left(\frac{RT}{b_T}\right) \qquad (11)$$

where

A_T = Temkin isotherm equilibrium binding constant (L/g),

b_T = Temkin isotherm constant,

R = universal gas constant (8.314 J/mol.K),

T = Temperature at 298 K.

The equilibrium adsorption of Pb^{2+} is better represented by Temkin isotherm than for Zn^{2+}. However, Temkin isotherm gives a good fit for both Pb^{2+} and Zn^{2+} with high R^2 values. In fact, the isotherm gave the best fit for Pb^{2+} out of the all the isotherms fitted to the adsorption data with an R^2 value of 0.997.

3.4. Dubinin-Radushkevich isotherm

Dubinin-Radushkevich isotherm [15] is an empirical model generally applied to express the adsorption of subcritical vapours onto micropore solids following a pore filling mechanism [16]. It is expressed as:

$$q_e = (q_s)exp(-k_{ad})\varepsilon^2 \qquad (12)$$

where

q_e = amount of adsorbate in the adsorbent at equilibrium(mg/g);

q_s = theoretical isotherm saturation capacity (mg/g);

K_{ad} = Dubinin–Radushkevich isotherm constant (mol^2/kJ^2)

ε can be correlated as:

$$\varepsilon = RT ln\left[1 + \frac{1}{C_e}\right] \qquad (13)$$

where R, T and C_e are the gas constant (8.314 J/mol.K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L) respectively.

The linear form of the Dubinin–Radushkevich isotherm is obtained by taking the logarithm of the equation.

$$ln(q_e) = ln(q_s) - k_{ad}\varepsilon^2 \qquad (14)$$

The model has often successfully fitted high solute activities and the intermediate range of concentrations data well.

K_{ad} is related to the free energy of sorption / mole of the sorbate as it migrates to the surface of the adsorbent from infinite from infinite distance in the solution [18]. The apparent energy of adsorption from Dubinin–Radushkevich model can be computed using the relationship [20]:

$$E = \frac{1}{\sqrt{2k_{ad}}} \qquad (15)$$

The apparent energy of adsorption of Pb^{2+} is much lower than that of Zn^{2+}. This explains why higher adsorption of was observed.

The model gave a better fitting for Pb^{2+} with a high R^2 of 0.944 while a R^2 of 0.793 was obtained for Zn^{2+}. Dubinin–Radushkevich isotherm constant was obtained and reported in Table 1.

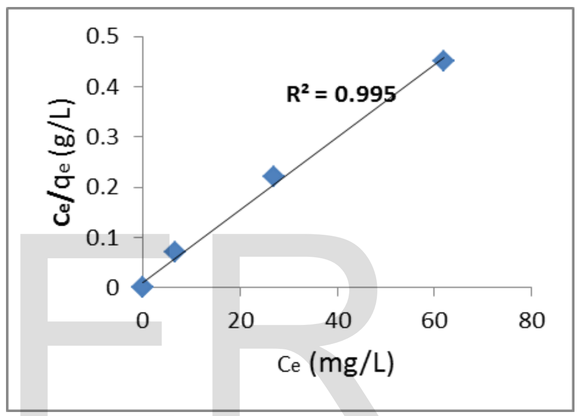

Fig. 1. Langmuir isotherm plot for Pb^{2+}

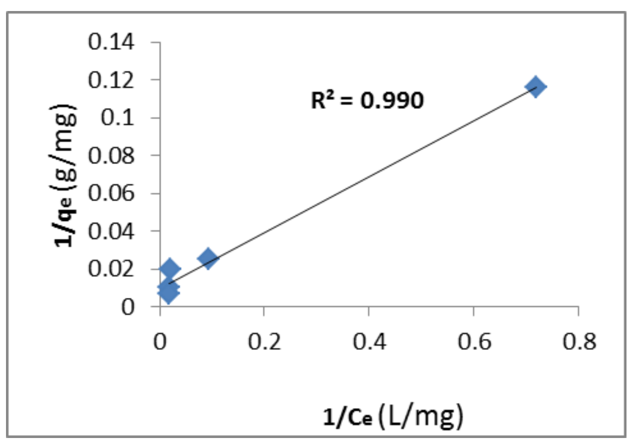

Fig 2. Langmuir isotherm plot for Zn^{2+}

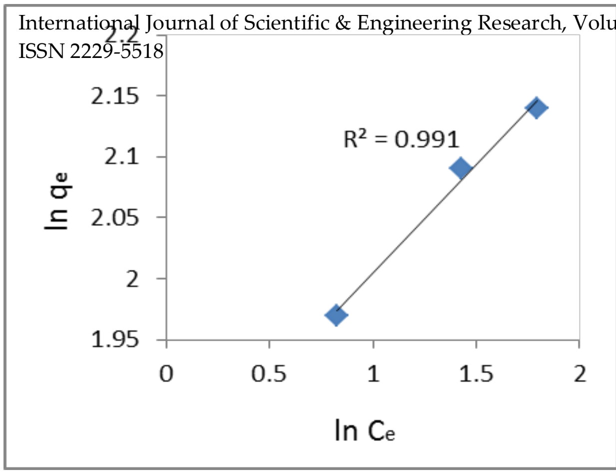

Fig. 3. Freundlich isotherm plot for Pb^{2+}

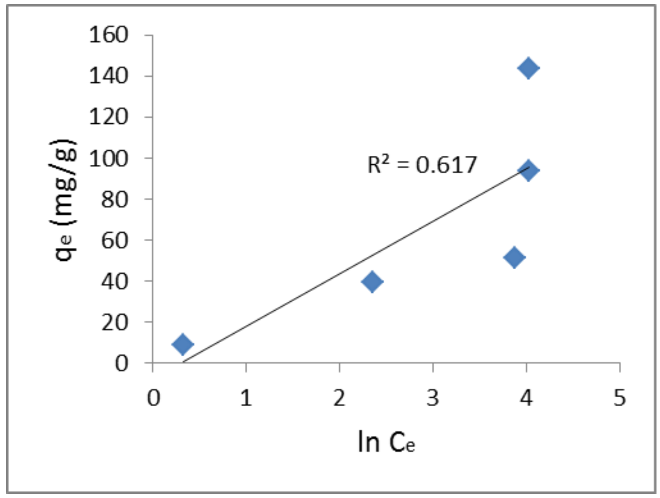

Fig. 6. Temkin isotherm plot for Zn^{2+}

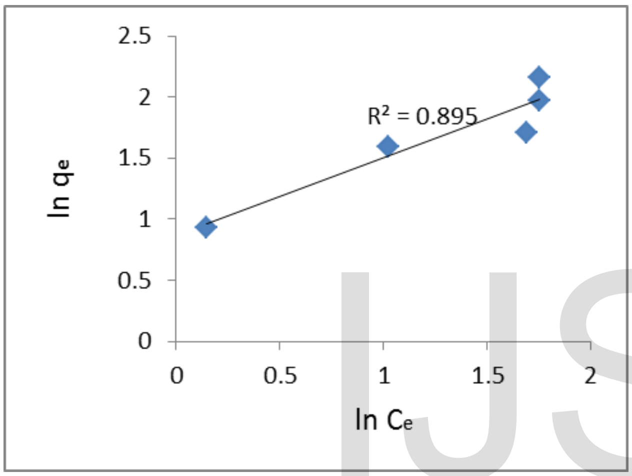

Fig. 4. Freundlich isotherm plot for Zn^{2+}

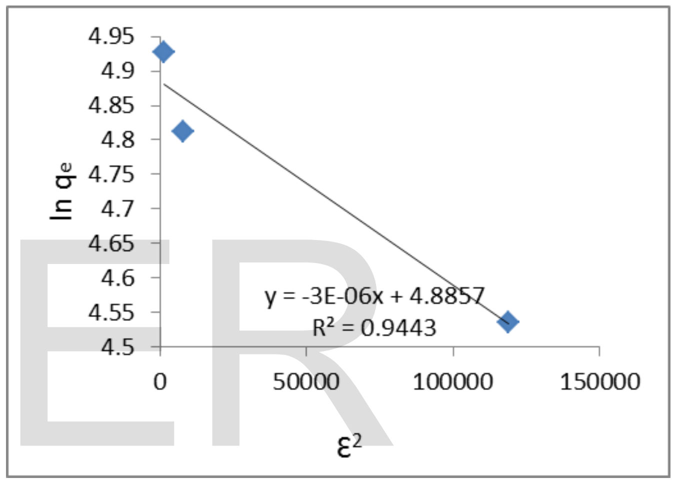

Fig.7. Dubinin-Radushkevich isotherm plot for Pb^{2+}

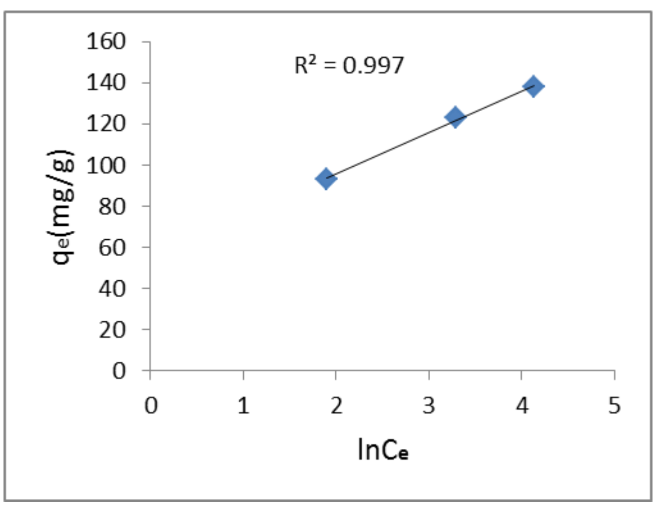

Fig. 5. Temkin isotherm plot for Pb^{2+}

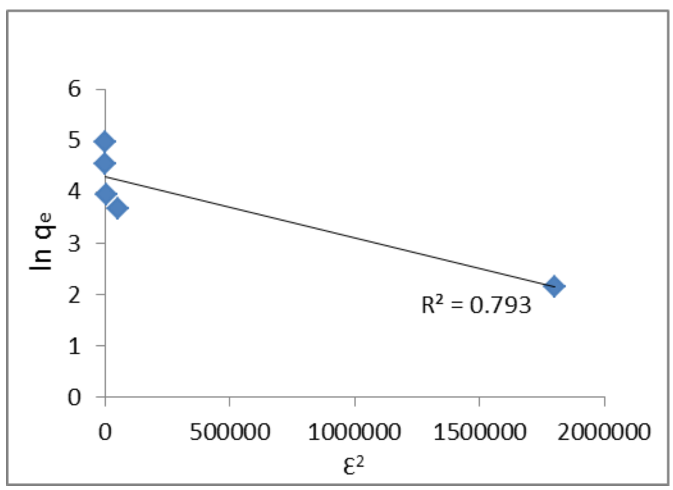

Fig. 8. Dubinin-Radushkevich isotherm plot for Zn^{2+}

Table 1

Equilibrium sorption isotherm parameters for Pb^{2+} and Zn^{2+}

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Isotherm	Parameters	Pb^{2+}	Zn^{2+}
Langmuir	q_m	142.857	100
	K_L	0.777	0.068
	R_L	0.068	0.006
	R^2	0.995	0.99
Freundlich	K_F	6.209	2.633
	1/n	0.178	0.631
	n	5.618	1.585
	R^2	0.991	0.895
Temkin	b_T	122.652	97.16
	A_T	15.45	0.748
	R^2	0.997	0.617
Dubinin-Radushkevich	K_{ad}	3.00E-06	1.00E-06
	q_s	132.29	73.626
	E	707.109	408.248
	R^2	0.944	0.793

4.0 Conclusion

All applied isotherms fitted the adsorption data well for both Pb^{2+} and Zn^{2+}. From the results obtained, it can be concluded that rice husk modified with phosphoric acid has a good potential as adsorbent for the removal of Pb^{2+} and Zn^{2+} from wastewater water. It was observed that the order of adsorption affinity on rice husk is $Pb^{2+} > Zn^{2+}$. This is related to the difference in their electronegativity. Adsorption of rice husk surface is due to ion exchange at the surface level, as such, it is expected that the more electronegative metal will show a higher adsorption tendency. The electronegativity of Pb^{2+} and Zn^{2+} is 2.33 and 1.65 respectively [2]. The adsorption of heavy metal with a larger ionic radius is greater than those with smaller radius [2]. The ionic radius of Pb^{2+} and Zn^{2+} is 1.33 and 0.88 respectively. The suitability of both Langmuir and Freundlich isotherms in representing the adsorption data for the sorption of Pb^{2+} and Zn^{2+} is an indication that a monolayer of metal ions was formed on the rice husk surface.

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