

Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn²⁺ Unto Phosphoric Acid Modified Rice Husk

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Abstract : Equilibrium sorption of the phosphoric acid modified rice husk was studied. The Physico-chemical properties of the modified rice husk were determined. The equilibrium sorption data were fitted into Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (DRK) isotherms. Of the four adsorption isotherm, the R² value of Langmuir isotherm model was the highest. The maximum monolayer coverage (Q_o) from Langmuir isotherm model was determined to be 101.01mg/g, the separation factor indicating a favourable sorption experiment is 0.133. Also from Freundlich Isotherm model, the sorption intensity (n) which indicates favourable sorption and the correlation value are 1.6 and 0,89 respectively. The heat of sorption process was estimated from Temkin Isotherm model to be 25.34J/mol and the mean free energy was estimated from DRK isotherm model to be 0.7KJ/mol which vividly proved that the adsorption experiment followed a physical process.

Keywords: Heavy metals, Isotherms, Rice husk and Sorption.

I. INTRODUCTION

Heavy metals are widely distributed in the environment and are ecologically important due to their high toxicity for living organisms including human beings [1]. Several industrial activities are important sources of environmental pollution due to their high content of several heavy metal ions. In particular, Zn²⁺ is a common metal ions found in effluents of a large number of industries. This metal is an essential element for life and is a micronutrient in trace amounts [2]. However, a chronic exposure to Zn²⁺ is detrimental for human health. The toxicological profile of this pollutant has been well documented in literature and its presence in water and wastewaters is a potential risk for the environment and public health [2,3]. Therefore, it is necessary to design feasible processes to minimize the pollution caused by Zn²⁺ discharges and to reduce the risks associated to its presence in the environment. A wide range of various treatment techniques such as ion exchange, biodegradation, oxidation, solvent extraction and adsorption have been reported to be used for removal of heavy metal ions from industrial effluents [4]. However, adsorption has been universally accepted as one of the most effective pollutant removal process, with low cost, ease in handling, low consumption of reagents, as well as scope for recovery of value added components through desorption and regeneration of adsorbent [5,6] A notable and growing trend is to evaluate the feasibility and suitability of natural, viable, renewable and low-cost materials which will be used as adsorbent to combat the menace of heavy metal pollution. The afore-mentioned growing trend is the main objective of this research via the modification of rice husk and evaluation of the equilibrium sorption data using the notable adsorption isotherms such as Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms.

Rice husk is an agricultural waste material, a hard protecting coverings of grains of rice obtained from the threshing of the rice and constitutes about 20% of 650 million tons of rice produced annually in the world [7]. Rice husk has found several applications in household, industries and even in the treatment of direct dyes [8].

II. EXPERIMENTAL METHODS

2.1 Collection and Preparation of Adsorbent and Adsorbate

All chemicals used were of analytical grade. Rice husk was obtained from a local mill in Ilorin, Kwara State and was pre-treated according to the method reported in the literature [9,10].

The rice husk was screened and washed with de-ionized water to remove dirt and metallic impurities after which it was dried in the oven at about 105°C for 2 hours. The dried rice husk was grounded and sieved in the mesh in the range between 250µm and 150µm in order to increase its surface area. The modification was

done by chemical treatment of 50g of the sieved rice husk with 1.0M orthophosphoric acid (H_3PO_4) heated on the magnetic stirrer at $100^{\circ}C$ until it totally formed a paste. The modified rice husk was washed with de-ionized water until the $pH \approx 6$. It was later dried in the oven at about $80^{\circ}C$ to remove moisture. The name given to the adsorbent is rice husk modified with phosphoric acid, RH – MP.

The Preparation of Adsorbate was carried out by preparing stock solution containing 1000 mg/L of Zn. 2.908g of $Zn(NO_3)_2$ in $1000cm^3$ of de-ionized water. Working concentrations in the range of 10mg/L – 200 mg/L were prepared by serial dilution.

The RH – MP was characterized by determining the following parameters: specific surface area, moisture content, loss of mass on ignition, pH and bulk density using standard procedures:

2.2 Specific surface area

Saers' method was used for the determination of the surface area [11, 12]. A sample containing 0.5g of the RH – MP was acidified with 0.1M HCl to $pH 3 - 3.5$, the volume was made up to $50cm^3$ with de-ionized water after addition of 10.0g of NaCl. The titration were carried out with standard 0.1M NaOH in a thermostatic bath at $298 \pm 0.5K$ to $pH 4.0$, and then to $pH 9.0$. The volume V required to raise the pH from 4.0 to 9.0 was noted and the surface area was computed from the following equation:

$$S(m^2 / g) = 32V - 25 \dots\dots\dots(1)$$

2.3 Determination the moisture content.

This was done by weighing 5g of RH – MP into a crucible. This was placed in the oven and heated for 5hours at constant temperature of $105^{\circ}C$. The sample was then removed and put rapidly into a desiccator in order to prevent more moisture uptake from atmosphere. The sample was re-weighed. This procedure was repeated several times until a constant weight was obtained. The difference in the mass constitutes the amount of moisture content of the adsorbent [13]

$$\% \text{ Moisture content} = \frac{w_2 - w_3}{w_2 - w_1} \times 100 \dots\dots\dots(2)$$

W_1 = Weight of crucible

W_2 = Initial weight of crucible with sample

W_3 = Final weight of crucible with sample

2.4 The determination of loss of mass

The determination of loss of mass on ignition was done by weighing 10g of the adsorbent (RH – MP) and put inside furnace at constant temperature of $600^{\circ}C$ for 2hours. After roasting, the sample was removed and put in a desiccator for cooling. The residual product is then weighed and the difference in mass represented the mass of organic material present in the sample. This operation was repeated four times.

2.5 pH Determination

The determination of pH of the samples was done by weighing 1g each of RH – MP, boiled in a beaker containing $100cm^3$ of distilled water for 5minutes, the solution was diluted to $200 cm^3$ with distilled water and cooled at room temperature, the pH of each was measured using a pH meter (model ATPH-6) and the readings were recorded [14]

2.6The Determination of bulk density

The bulk density of each of the samples of RH – MP was determined using Archimedes's principle by weighing a $10cm^3$ measuring cylinder before and after filling with the samples. The measuring cylinder was then dried and the sample was packed inside the measuring cylinder, leveled and weighed. The weight of the sample packed in the measuring cylinder was determined from the difference in weight of the filled and empty measuring cylinder. The volume of water in the container was determined by taking the difference in weight of the empty and water filled measuring cylinder. The bulk density was determined using the equation below [15]

$$\text{Bulk density} = \frac{w_2 - w_1}{v} \dots\dots\dots(3)$$

W_1 = Weight of empty measuring cylinder

W_2 = Weight of cylinder filled with sample

V = Volume of cylinder

2.7 Sorption Experiment

The equilibrium sorption of the Zn²⁺ ions unto RH – MP was carried out by contacting 0.1g of the substrate with 100cm³ of different concentrations from 10 mg/L – 200mg/L in 250cm³ Pyrex conical flask intermittently for 90 minutes on the orbital shaker. The mixture was filtered and the residual concentration of the filtrate was analyzed using Atomic Absorption Spectrophotometer (2380 UNICAM AAS). The amount of adsorbed (mg/g) was calculated using the formulae reported by Vanderborght and Van Griekenm [16]:

$$Q = \frac{v(c_i - c_e)}{w} \dots\dots\dots(4)$$

where Q = the amount of solute adsorbed from the solution.

V = Volume of the adsorbate, C_i = the concentration before adsorption, C_f = the concentration after adsorption and W = the weight in gram of the adsorbent. The data was fitted into the following isotherms: Langmuir, Freundlich and Temkin [17]. The removal efficiency was determined by computing the percentage sorption using the formulae in Eq. (5)

$$\% \text{ Sorption} = \frac{C_i - C_e}{C_i} \times 100 \dots\dots\dots(5)$$

III. Results And Discussion

3.1 The physico-chemical parameters of the rice husk modified with phosphoric acid, RH – PH are shown in table 1.

Table 1: Some physico-chemical parameters of the modified with phosphoric acid, RH – PH

Properties	RH – MP
pH	6.30 - 6.50
% Moisture Content	12
% Loss of mass on ignition	0.9
Bulk density (g/cm ³)	0.386
Particle size	300µm<Φ<250µm
Surface Area (m ² /g)	19.8

The physico-chemical parameters of RH – PH viz; pH, % Moisture Content, % Loss of mass on ignition, Bulk density (g/cm³), Particle sizes and Surface Area (m²/g). The values reported are in the range with those reported in the literature [7].

3.2 Sorption Isotherms Of Zn(Ii) Ion Unto Rh – Mp

The equilibrium sorption of the Zn²⁺ ions was carried out by contacting 0.1g of the RH – MP with 100cm³ of 1000 mg/L of different concentrations from 10 mg/L – 200 mg/L in 250cm³ Pyrex conical flasks intermittently for 90 minutes on the orbital shaker. The mixture was filtered and the filtrate analyzed for metal ions concentration using AAS. The data was fitted into the following isotherms: Langmuir, Freundlich, and Temkin and Dubinin-Raduskevich

3.2.1 Langmuir Adsorption Isotherm: This describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases [29]. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Based upon these assumptions, Langmuir represented the following equation:

$$q_e = \frac{Q_o K_L C_e}{1 + K_L C_e} \dots\dots\dots(6)$$

Langmuir adsorption parameters were determined by transforming the Langmuir equation (6) into linear form.

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{Q_o K_L C_e} \dots\dots\dots(7)$$

Where:

C_e = the equilibrium concentration of adsorbate (mg/L⁻¹)

q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).

Q_o = maximum monolayer coverage capacity (mg/g)

K_L = Langmuir isotherm constant (L/mg).

The values of q_{\max} and K_L were computed from the slope and intercept of the Langmuir plot of $1/q_e$ versus $1/C_e$ [13]. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L , which is a dimensionless constant referred to as separation factor or equilibrium parameter [31].

$$R_L = \frac{1}{1 + (1 + K_L C_o)} \dots\dots\dots(8)$$

Where:

C_o = initial concentration

K_L = the constant related to the energy of adsorption (Langmuir Constant). R_L value indicates the adsorption nature to be either unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$. From the data calculated in table 3, the R_L is greater than 0 but less than 1 indicating that Langmuir isotherm is favourable. From this research work, the maximum monolayer coverage capacity (Q_o) from Langmuir Isotherm model was determined to be 101.01mg/g, K_L (Langmuir isotherm constant) is 0.065 L/mg, R_L (the separation factor) is 0.133 indicating that the equilibrium sorption was favourable and the R^2 value is 0.99 proving that the sorption data fitted well to Langmuir Isotherm model.

3.2.2 Freundlich Adsorption Isotherm: This is commonly used to describe the adsorption characteristics for the heterogeneous surface [27]. These data often fit the empirical equation proposed by Freundlich:

$$Q_e = K_f C_e^{1/n} \dots\dots\dots(9)$$

Where K_f = Freundlich isotherm constant (mg/g)

n = adsorption intensity;

C_e = the equilibrium concentration of adsorbate (mg/L)

Q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g). Linearizing equation 9, we have:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \dots\dots\dots(10)$$

The constant K_f is an approximate indicator of adsorption capacity, while $1/n$ is a function of the strength of adsorption in the adsorption process [30]. 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 [28]. The function has an asymptotic maximum as pressure increases without bound. As the temperature increases, the constants k and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface. However, K_f and n are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting and whereas linear regression is generally used to determine the parameters of kinetic and isotherm models [26]. Specifically, the linear least-squares method and the linearly transformed equations have been widely applied to correlate sorption data where $1/n$ is a heterogeneity parameter, the smaller $1/n$, the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when $1/n = 1$. If n lies between one and ten, this indicates a favorable sorption process [25]. From the data in table 3, that value of $1/n = 0.625$ while $n=1.6$ indicating that the sorption of Zn^{2+} unto RH – MP is favourable and the R^2 value is 0.89.

3.2.3 The Temkin Isotherm

This isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage [18, 19]. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity sorbed q_e against $\ln C_e$ and the constants were determined from the slope and intercept. The model is given by the following equation [18]:

$$q_e = \frac{RT}{b} \ln(A_T C_e)$$

$$q_e = \frac{RT}{b_T} \ln A_T + \left(\frac{RT}{b} \right) \ln C_e$$

$$B = \frac{RT}{b_T}$$

$$q_e = B \ln A_T + B \ln C_e \dots\dots\dots(11)$$

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

b_T = Temkin isotherm constant

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

T = Temperature at 298K.

B = Constant related to heat of sorption(J/mol)

From the Temkin plot shown in fig 3, the following values were estimated:

$A_T = 1.075$ L/g, $B = 25.34$ J/mol which is an indication of the heat of sorption indicating a physical adsorption process and the $R^2 = 0.62$.

3.2.4 Dubinin–Radushkevich isotherm model

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [20, 21]. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well.

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

$$\ln q_e = \ln(q_s) - (K_{ad} \varepsilon^2) \dots\dots\dots(13)$$

Where q_e , q_s , K_{ad} , ε are 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) and ε = Dubinin–Radushkevich isotherm constant. The approach was usually applied to distinguish the physical and chemical adsorption of metal ions with its mean free energy, E per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity) can be computed by the relationship [22, 23]:

$$E = \left[\frac{1}{\sqrt{2B_{DR}}} \right] \dots\dots\dots(14)$$

Where B_{DR} is denoted as the isotherm constant. Meanwhile, the parameter ε can be calculated as:

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \dots\dots\dots(15)$$

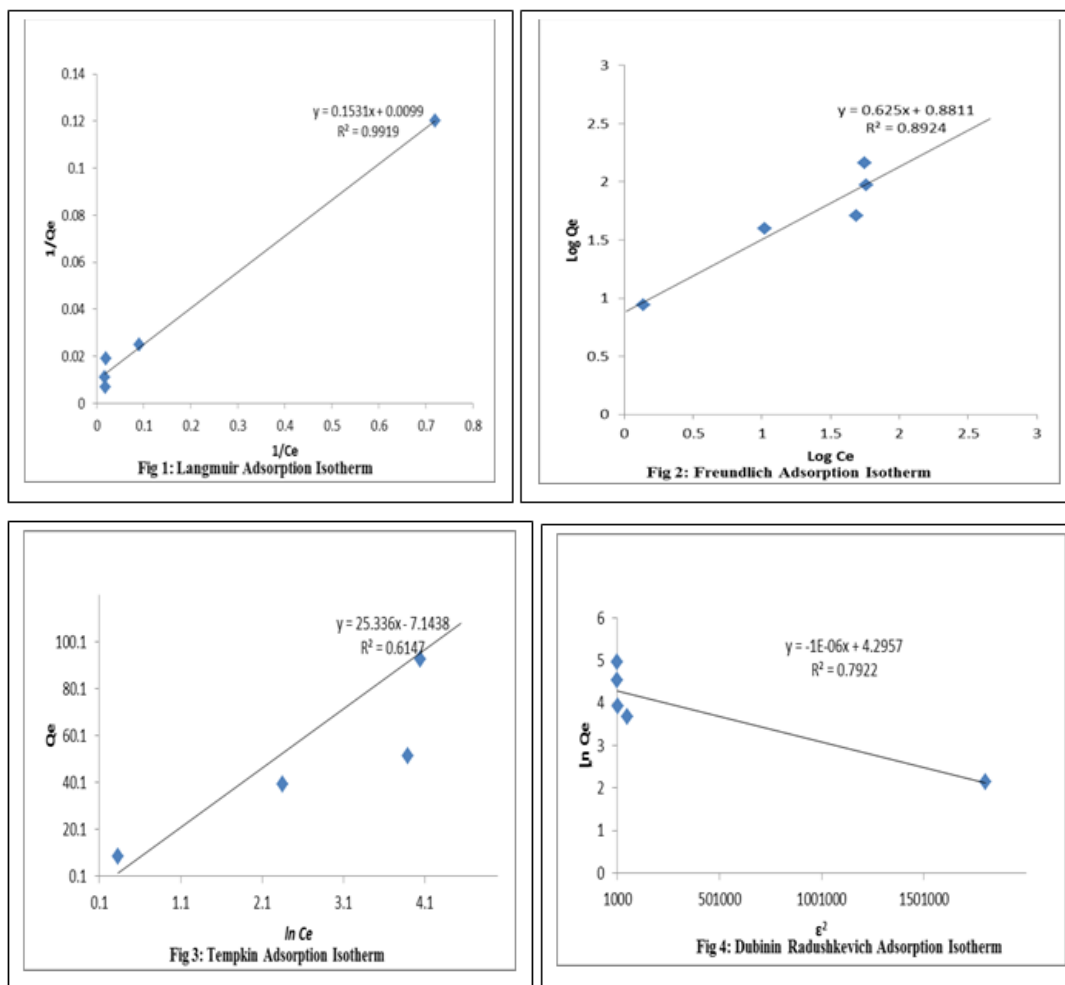
where R , T and C_e represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L), respectively. One of the unique features of the Dubinin–Radushkevich (DRK) isotherm model lies on the fact that it is temperature-dependent, which when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed ($\ln q_e$) vs ε^2 the square of potential energy, all suitable data will lie on the same curve, named as the characteristic curve [24]. The equation 12 is linearized to equation 13 which is used in the plot of DRK graph in figure 4 below. The constant such as q_s , and K_{ad} were determined from the appropriate plot using equation 13 above. From the linear plot of DRK model, q_s was determined to 70.579mg/g, the mean free energy, $E = 0.7$ KJ/mol indicating a physisorption process and the $R^2 = 0.79$ higher than that of Tempkin

Table 2: Parameters for plotting Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Adsorption Isotherms of Zn(II) ion unto RH – MP

S/ N	C _o (mg/L)	C _e (mg/L)	1/C _e	Log C _e	Ln C _e	Q _e (mg/g)	1/Q _e	Log Q _e	Ln Q _e	C _e /Q _e g/L	ε ²
1	0.00	0.00	0.000	0.000	0.000	0.00	0.00	0.00	0.00	0.00	0.00
2	10.00	1.39	0.719 4	0.143	0.329	8.61	0.116	0.935	2.153	0.161	1.80x10 ⁶
3	50.00	10.57	0.094 6	1.024	2.358	39.43	0.025	1.596	3.674	0.268	5.016x10 ⁴
4	100.00	48.78	0.021 5	1.688	3.887	51.22	0.019	1.709	3.936	0.952	2.527x10 ³
5	150.00	56.45	0.017 4	1.759	4.051	92.55	0.011	1.966	4.528	0.621	1.83x10 ³
6	200.00	56.35	0.017 7	1.751	4.031	143.65	0.007	2.157	4.967	0.392	1.89x10 ³

Table 3: Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherm constants for the adsorption of Zn(II) ion unto RH – MP

META L IONS	LANGMUIR ISOTHERM				FREUNDLICH IOSTHERM			
	Zn ²⁺	Q _o (mg/g)	k _L (L/m g)	R _L	R ²	$\frac{1}{n}$	n	k _f (mg/g)
	101.01	0.065	0.133	0.99	0.625	1.6	7.61	0.89
	TEMKIN ISOTHERM				DUBININ – RADUSHKEVICH ISOTHERM			
	A _T (L/m g)	b _T	B	R ²	q _s (mg/g)	K _{ad} (mol ² /kJ ²)	E(KJ/mol)	R ²
	1.075	97.788	25.336	0.615	70.598	1x10 ⁻⁶	0.707	0.792



IV. CONCLUSION

In this paper, investigation of the equilibrium sorption was carried out at 25°C and pH between 6.3 and 6.5. Other physico-chemical parameters were determined and four adsorption isotherm models were studied. The sorption data fitted into Langmuir, Freundlich, Temkin and Dubinin – Radushkevich isotherms out of which Langmuir Adsorption model was found to be have the highest regression value and hence the best fit. It could be concluded that rice husk modified with orthophosphoric acid (RH - MP) is a potential and active biosorbent for removal of Zinc ions from its aqueous solution and industrial waste water remediation.

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