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MODELING OF BIOSORPTION OF PB(II) AND ZN(II) IONS ONTO PAMRH: LANGMUIR, FREUNDLICH, TEMKIN, DUBININ-RADUSKEVICH, JOVANOVIC, FLORY-HUGGINS, FOWLER-GUGGENHEIM AND KISELEV COMPARATIVE ISOTHERM STUDIES

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ABSTRACT

Biosorption of Pb2+ and Zn2+ onto Phosphoric Acid Modified Rice Husk (PAMRH) was carried out. The equilibrium adsorption data of Pb2+ and Zn2+ for initial concentration ranging from 10 – 200 mg g-1 were fitted into Langmuir, Freundlich, Temkin, Dubinin-Raduskevich, Jovanovic, Flory-Huggins, Fowler-Guggenheim and Kiselev isotherm models. The comparative isotherm studies however, unraveled the adsorption capacities of PAMRH and a great affinity of the adsorbent (PAMRH) for Pb2+ than Zn2+. The studies showed that the adsorption

capacities obtained from isotherm models for Pb2+ are relatively higher than that of Zn2+. Comparatively, based on the correlation coefficients (R2) obtained from both Pb2+ and Zn2+ linear plots, the equilibrium data fitted to the isotherm models in the following order: Langmuir > Kiselev > DKR > Temkin > Freundlich > Jovanovic > Flory-Huggins > Fowler-Guggenheim. A maximum monolayer adsorption capacity of 138.89 mg g-1 was obtained from Langmuir adsorption isotherm for Pb2+ and 121.95 mgg-1 for Zn2+. Biosorption isotherm modeling shows that the uptake of these divalent heavy metals ions (Pb2+ than Zn2+) onto PAMRH took place at specific localized sites on the surface and the saturation coverage corresponds to complete occupancy of these sites. The mean adsorption free energy, E per molecule evaluated from DKR model was less than 8 kJmol-1 indicating a physisorption mechanism and electrostatic attraction. This study revealed vividly that PAMRH is a better and promising eco-friendly low cost adsorbent for both Pb2+ and Zn2+

Keywords: Biosorption, Isotherm modeling, Heavy metals, PAMRH.

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1. INTRODUCTION

Research on the utilizations of low cost adsorbent has attracted the interest of several researchers for more than a decade. Rice husks are the hard protecting coverings of grains of rice. It is an agricultural waste material obtained from the threshing of the rice and constitutes about 20% of 650 million tons of rice produced annually in the world [1]. Despite its low calorific value, rice husk is used as fuel for both industrial and household purposes as well as low cost effective adsorbent for purifying biodiesel form wastes frying oil, treatment of dyes and heavy metal ions [2, 3].

Lead and zinc which are the major heavy metal ions of interest in this paper are mainly released through anthropogenic activities. Lead could cause serious health problems, even madness and death. More recently, lead poisoning in Anka and Bukkuyum local government areas of Zamfara state resulted in the death of over 400 children and this has been identified as the worst lead poisoning in Nigeria's history [4]. Also, Zinc toxicity could result in both acute and chronic forms. Acute adverse effects of high zinc intake include nausea, vomiting, loss of appetite, abdominal cramps, diarrhea, and headaches [5]. Interest of researchers on the use of low cost method of removing heavy metal ions via cost effective adsorbents is on the increase. Of all the methods harnessed in the remove heavy metal ions, adsorption remains the most cost effective and efficient. Due to the efficacy of adsorption, Phosphoric Acid Modified Rich Husk (PAMRH) was utilized as cost effective adsorbent material to sorb lead and zinc from their aqueous solution.

Adsorption is usually modelled by isotherms which relate the relative concentration of solute adsorbed onto the solute in solution. Adsorption isotherm is an invaluable curve describing the principles governing the binding (adsorption) or release (desorption) of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH [6 – 8]. It is an expression that relates the amount of substance

adsorbed per unit mass of the adsorbent to the equilibrium concentration at constant temperature [9 – 10]. Adsorption equilibrium is established when an adsorbate-containing phase has been contacted with the adsorbent for specific time. The adsorbate concentration in the bulk solution is in a dynamic balance with the interface con-centration [11]. In this original research, a comparative study of the adsorption isotherms vis-à-vis Langmuir, Freundlich, Temkin, Dubinin–Radushkevich (D-R), Jovanovic, Flory-Huggins, Fowler-Guggenheim and Kiselev was carried out on the equilibrium adsorption of lead and zinc ions onto phosphoric acid modified rice husk (PAMRH).

2. MATERIALS AND METHODS

2.1. Chemical Reagents

All the chemicals used in this study ($Pb(NO_3)_2$, $Zn(NO_3)_2$, H_3PO_4, NaOH, HCl) were of analytical grade and were used without further purification. Stock solution containing 1000 mg L^{-1} of $Pb(NO_3)_2$ and $Zn(NO_3)_2$ was prepared by accurately weighing 0.3998 g and 0.727g respectively from their salt into 250cm^3 of Erlenmeyer flask dissolved in de-ionized water. Working concentrations for both Pb^{2+} and Zn^{2+} in the range of 10 mg L^{-1} – 200 mg L^{-1} were prepared by serial dilution. Deionized water was used throughout this experiment.

2.2. Preparation of Adsorbent

Rice husk was obtained from a local mill in Ilorin, Kwara State. It was washed, dried in the oven at 60 ^oC for 5 hours and later functionalized using 1.0 mol dm^{-3} H_3PO_4 according to the method reported by Dada *et al*.[12-13]

2.3. Equilibrium Adsorption Studies

The equilibrium adsorption of the Pb^{2+} and Zn^{2+} ions unto PAMRH was carried out by contacting 0.1 g of the adsorbent with 100 cm^3 of different concentrations from 10 mgL^{-1} – 200 mgL^{-1} in 250 cm^3 Pyrex conical flask intermittently for 120 minutes on the orbital shaker. The mixture was filtered and the residual concentration of the filtrate was analyzed using Atomic adsorption Spectrophotometer (2380 UNICAM AAS). Adsorption capacities were obtained using a mass balance equation [14]:

$$Q = \frac{(c_o - c_e)V}{W} \tag{1}$$

where Q is the equilibrium adsorption capacity per gram dry weight of PAMRH (mg g^{-1}), V is the volume of the adsorbates (L), C_o is the initial concentration of the adsorbates before adsorption (mg L^{-1}), C_e is the final concentration of the adsorbates after adsorption (mg L^{-1}), W is the dry weight in gram of the adsorbent. The removal efficiency was calculated using the formulae in Eq. (2) as reported by [15 – 16]:

$$\% \, RE = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

The data were fitted into the following isotherm models: Langmuir, Freundlich, Temkin, Dubinin-Raduskevich, Jovanovic, Flory-Huggins, Fowler-Guggenheim and Kiselev

3. RESULTS AND DISCUSSION

3.1. ADSORPTION ISOTHERMS

Adsorption of Pb^{2+} and Zn^{2+} from their solutions was modeled using the Langmuir, Freundlich, Temkin, Dubinin-Raduskevich, Jovanovic, Flory-Huggins, Fowler-Guggenheim and Kiselev isotherms with the quality of the fit assessed using the correlation coefficient, a comparison was examined. The evaluated parameters were obtained from the slopes and intercepts of the linear plots in Figs 1 (A – P)

3.1.1. 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. This model assumes a monolayer adsorption onto a homogeneous surface with a finite number of identical sites also there is a uniform energy of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface [10 – 16]. The linear form of Langmuir represents:

$$\frac{Ce}{A_e} = \frac{1}{K_L A_m} + \frac{C_e}{A_m} \tag{3}$$

A_m is the maximum monolayer coverage capacity ($mg.g^{-1}$), K_L is the Langmuir isotherm constant ($L.mg^{-1}$) related to the energy of adsorption.

$$R_L = \frac{1}{1 + K_L C_o} \tag{5}$$

R_L is the Dimensionless constant as well as the Separation factor.

From the slope and intercept of the plot of C_e/A_e versus C_e (Fig 1a & 1b) at room temperature, the Langmuir isotherm constants A_m *and* K_L were determined. Evaluated parameters presented in Table 1 show that PAMRH adsorbed Pb^{2+} better than Zn^{2+} based on correlation coefficients. The essential feature of Langmuir isotherm model as expressed in terms of the dimensionless constant (R_L) as well as the separation factor, showed that adsorption was favourable since R_L was less that unity but greater than zero ($0 < R_L < 1$) [Dada et al., 2013]

3.1.2. Freundlich Adsorption Isotherm

The Freundlich adsorption isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies

The Linear form of Freundlich equation is:

$$\log A_e = \log K_f + {}^{1}\!/\!_{n} \log C_e \tag{7}$$

Presented in Figs 1c & d are the linear plots of log A_e against log C_e. The Freundlich isotherm constants, K_f and n are parameters characteristic of the adsorbent-adsorbate system determined from the intercept and slope. If n lies between unity and ten, this indicates a favorable adsorption process [11, 16]. In this study, the value of n is greater than unity indicating a favourable adsorption and electrostatic interaction between PAMRH and the adsorbates (Pb^{2+} and Zn^{2+}). The adsorption capacity (K_f) of Pb^{2+} surpassed that of Zn^{2+} indicating that PAMRH adsorbed Pb^{2+} better than Zn^{2+}).

3.1.3. Temkin Isotherm

This isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. The model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly with the surface coverage due to adsorbent–adsorbate interactions. The linear form of the equation is given as [12, 13, 15, 17]:

$$A_e = \frac{RT}{b_T} \ln S_T + \frac{RT}{b_T} \ln Ce \,. \tag{8}$$

Where b_T is the Temkin isotherm constant related to the heat of adsorption and S_T is the Temkin isotherm equilibrium binding constant (Lg^{-1}). The heat of adsorption and the correlation coefficient of Pb^{2+} are more than that of Zn^{2+} based on the parameters presented in Table 1

3.1.4. Dubinin–Kaganer–Radushkevich (DKR) isotherm model

Dubinin– Kaganer–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [3, 6, 12, 18 - 19]. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well. The linear expression is given in Eq. (9):

$$\ell n A_e = \ell n A_m - S_{DKR} \varepsilon^2 \tag{9}$$

Where S_{DKR} is the DKR isotherm constant (mol^2/kJ^2) related to free energy and A_m is the theoretical isotherm saturation capacity (mg/g); and DKR isotherm constant determined from the appropriate linear plots presented in Figs 1 (G&F).

$$E = \left[\frac{1}{\sqrt{2A_{DR}}} \right] \tag{10}$$

Meanwhile, the parameter ε is the Polanyi potential which is computed as:

$$\varepsilon = RT\ell n\left[1 + \frac{1}{C_e}\right] \tag{10}$$

The mean free energy, E per molecule of adsorbate was computed using Eq. 10. Since the evaluated values of the E was less than 8 $kJmol^{-1}$ for adsorption of both Pb^{2+} and Zn^{2+}, it is indicated that the adsorption process is physisorption [20]. Based on evaluated parameters in Table 1, it is obvious that adsorption of Pb^{2+} is much more favourable than Zn^{2+} .

3.1.5. Jovanovic Isotherm.

This model is predicated on the assumptions contained in the Langmuir model and it takes into consideration the possibility of some mechanical contacts between the adsorbate and adsorbent. The linear function of this model is [13, 21]:

$$\ln A_e = \ell n A_{\max} - S_J C_e \tag{11}$$

Where A_e, A_m and S_J adsorbed quantity, adsorption maximum capacity in Jovanovic model (mgg^{-1}) and Jovanovic isotherm constant (Lg^{-1}) respectively. S_J and A_m were determined from the the slope and intercept of linear plot of $ln\, A_e$ versus C_e (Figs 1K&L)

3.1.6. Flory–Huggins Isotherm Model

This isotherm model describes the surface coverage of the adsorbate on the adsorbent. It is generally used to account for the surface coverage of the adsorbate on the adsorbent. The linear expression is given in Eq 12 [8, 22]:

$$Log\left(\frac{\theta}{C_o}\right) = LogK_{FH} + n_{FH}Log(1-\theta) \tag{12}$$

$$\text{Where } \theta = 1-\left(\frac{Ce}{C_o}\right) \tag{13}$$

θ is the degree of surface coverage, n_{FH} and K_{FH} are Flory-Huggin's constants defined as the number of metal ions occupying adsorption sites and the equilibrium constant of adsorption respectively. They were determined from the linear plot of log (θ/C_o) versus log (1 - θ), Figs 1 (K&L). Based on R^2 value, the equilibrium data did not fit well to this model.

3.1.7. Fowler-Guggenheim Isotherm model

Fowler-Guggenheim isotherm model accounts for the lateral interaction of the adsorption of adsorbate onto adsorbent. The linear form of the isotherm model is given in Eq. (14):

$$\ln\left[\frac{Ce\,(1-\theta)}{\theta}\right] = -\ln K_{FG} + \frac{2\omega\theta}{RT} \tag{14}$$

where K_{FG} is Fowler-Guggenheim equilibrium constant(Lmg^{-1}), Θ is fractional coverage determined by from $\Theta=A_e/A_{DKR}$, R is universal gas constant ($kJmol^{-1}K^{-1}$), T is temperature (K), and w is interaction energy between adsorbed molecules ($KJmol^{-1}$). The plot of ln[Ce (1−Θ)/Θ] versus Θ gives a straight line plot presented in Figs 1 (M&N) and the constants K_{FG} and w were obtained from the intercept and slope of the plot. The value of w being negative indicated negative is an indication of a fair interaction between Pb^{2+} and Zn^{2+} and PAMRH. This is in support of the Langmuir isotherm model that there is no interaction between molecules absorbed on neighbouring sites (23, 24Rangabhashiyam et al., 2014)

3.1.8. Kiselev Isotherm model

The Kiselev adsorption isotherm equation is a localized monomolecular layer model (Song et al., 2014). Its linearized expression is as follows Eq (15):

$$\ln\left[\frac{1}{Ce\,(1-\theta)}\right] = \frac{K_1}{\theta} + K_1K_n \tag{15}$$

where Ki is Kiselev equilibrium constant (Lmg^{-1}) and K_n is equilibrium constant of the formation of complex between adsorbed molecules determined from the linear plot of $1/Ce(1-\theta)\ versus\ 1/\theta$ presented in Figs. 1 (O &P). From this study, the surface coverage Θ > 0.68 at higher concentration indicating that the adsorption is valid and favourable at higher concentrations. The parameters in Table 1 reveal that Kiselev isotherm model fitted the equilibrium data well for adsorption of Zn^{2+} onto PAMRH than Pb^{2+} based on the correlation coefficient (R^2)

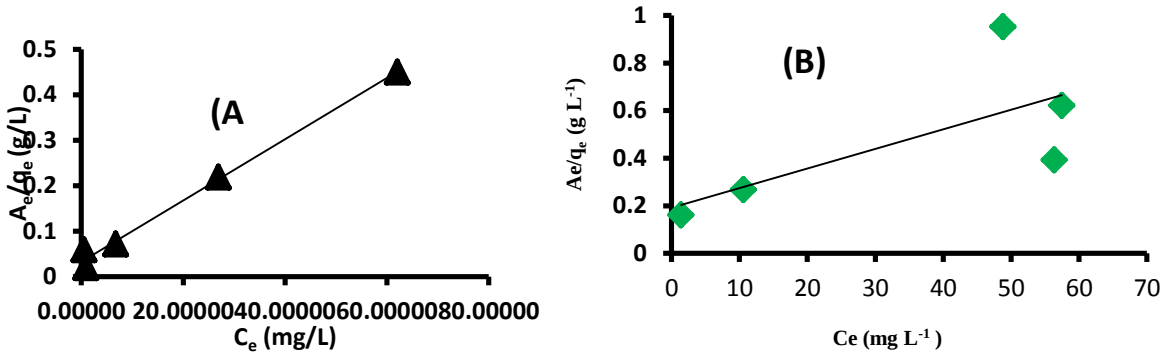

Figure 1 Langmuir isotherm model plots for adsorption of (A) Pb^{2+} and (B) Zn^{2+} onto PAMHR

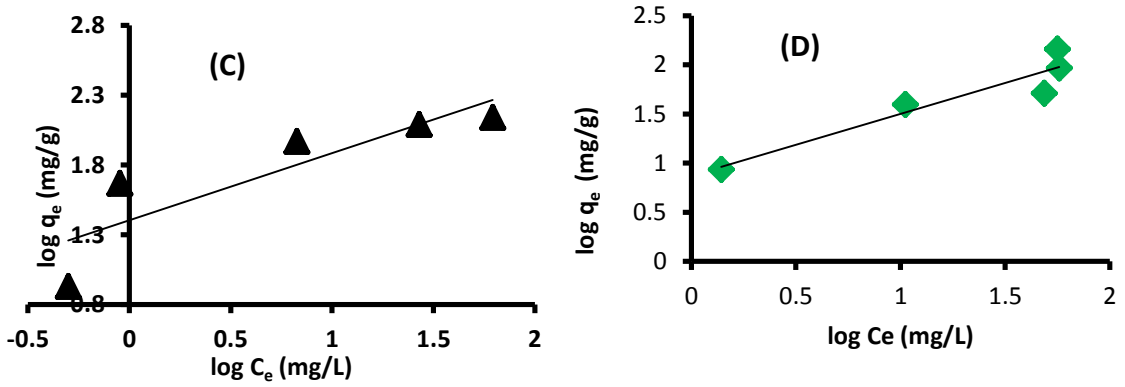

Figure 1 (C-D) Freundlich isotherm model plots for adsorption of (C) Pb^{2+} and (D) Zn^{2+} on PAMRH

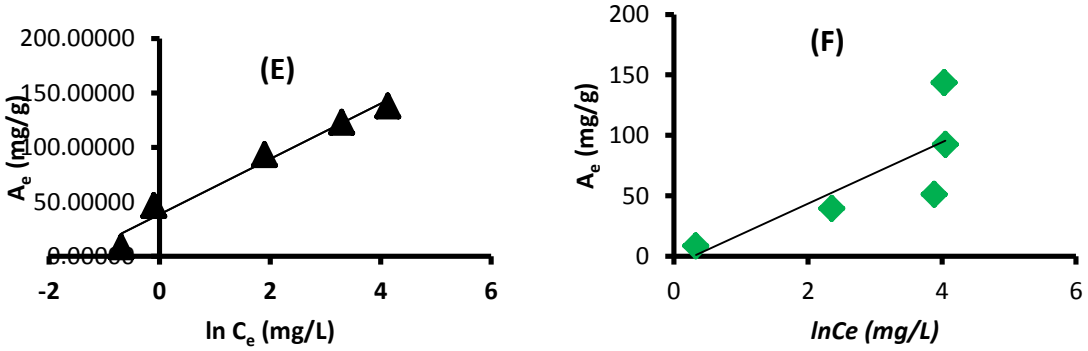

Figure 1 (E-F) Temkin isotherm model plots for adsorption of (E) Pb^{2+} and (F) Zn^{2+} on PAMRH

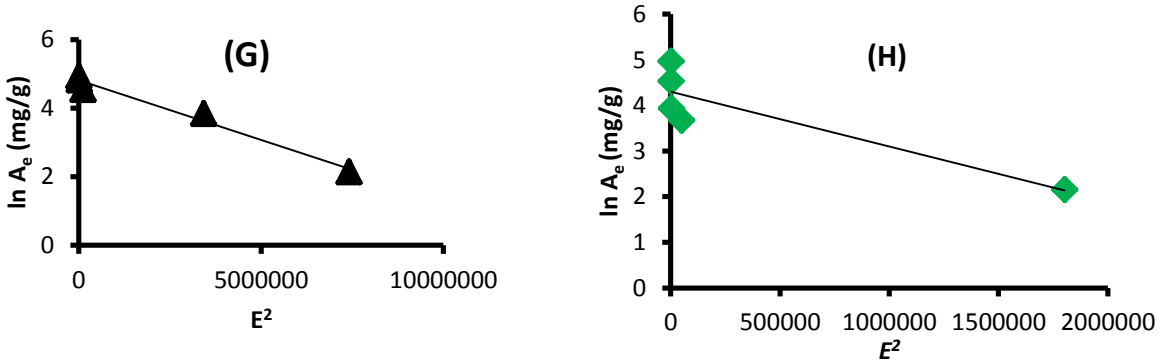

Figure 1 (G-H) DKR isotherm model plots for adsorption of (G) Pb^{2+} and (H) Zn^{2+} on PAMRH

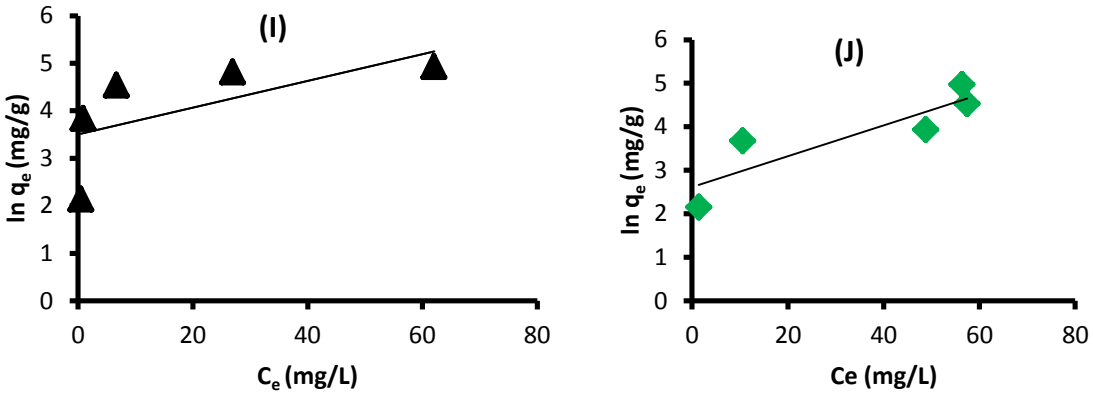

Figure 1 (I-J) Jovanovic isotherm model plots for adsorption of (I) Pb^{2+} and (J) Zn^{2+} on PAMRH

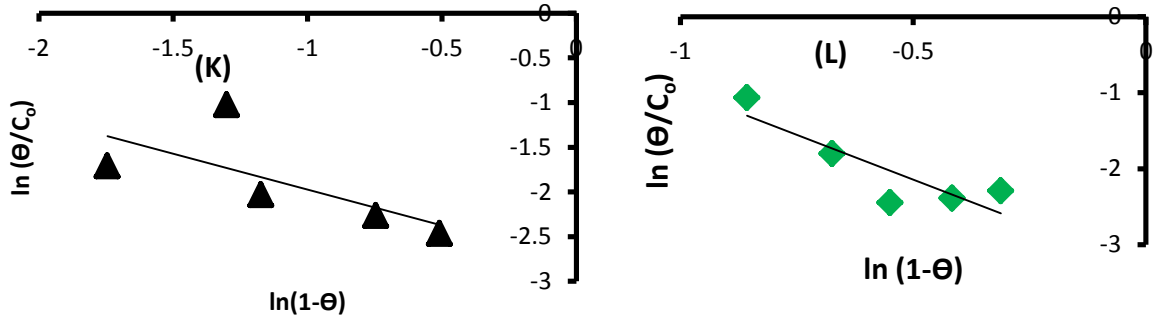

Figure 1 (K-L) Flory-Huggins isotherm model plots for adsorption of (K) Pb^{2+} and (J) Zn^{2+} on PAMRH

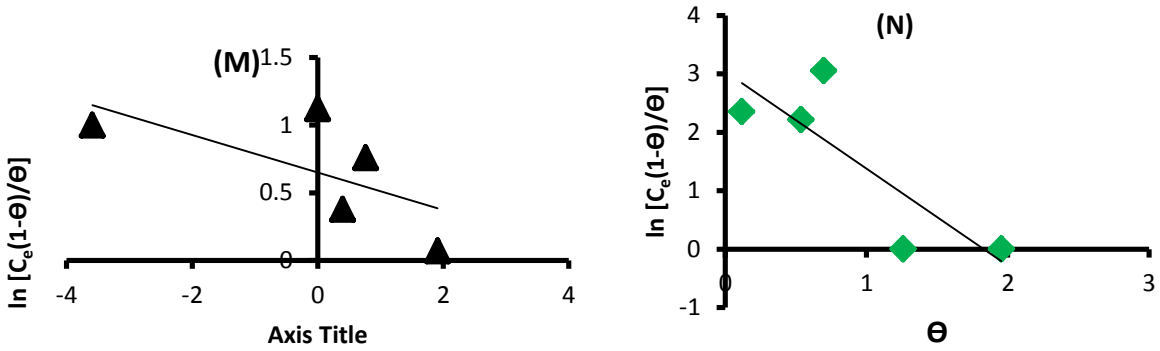

Figure 1 (M-N) Fowler-Guggenheim isotherm model plots for adsorption of (M) Pb^{2+} and (N) Zn^{2+} on PAMRH

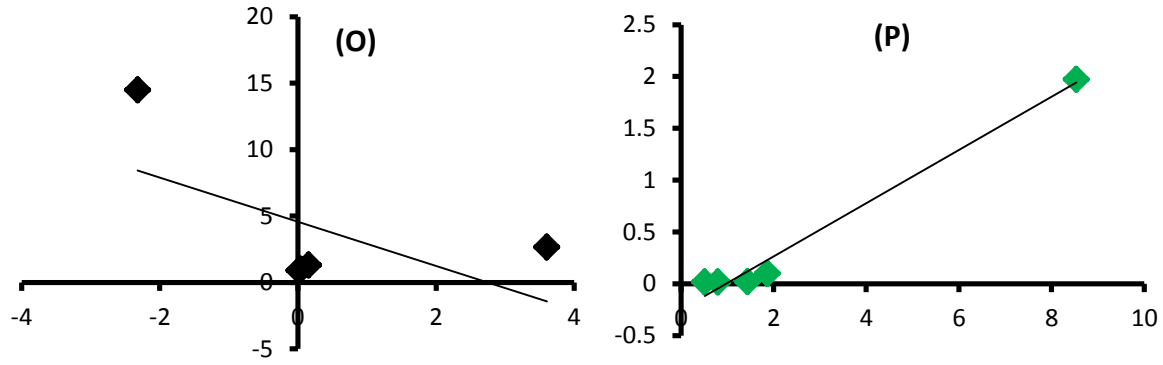

Figure 1 (O-P) Kiselev isotherm model plots for adsorption of (O) Pb^{2+} and (P) Zn^{2+} on PAMRH

Table 1 Biosorption isotherm model evaluated parameters

Langmuir	**Pb^{2+}**	**Zn^{2+}**	**Freundlich**	**Pb^{2+}**	**Zn^{2+}**	**Temkin**	**Pb^{2+}**	**Zn^{2+}**	**DKR**	**Pb^{2+}**	**Zn^{2+}**
A_{max}	138.00	121.95	K_F	25.32	7.45	B	25.405	25.35	A_{max}	123.18	73.48
K_L	0.70	0.043	1/n	0.4807	0.6289	b_T	97.523	97.73	A_{DR}	$3x10^{-7}$	$1 x 10^{-6}$
R_L	0.13-0.0079	0.70-0.10	n	2.0803	1.59	A_T	4.5606	0.7522	R^2	0.9762	0.794
R^2	0.995	0.491	R^2	0.7643	0.895	R^2	0.9708	0.62	E(J/mol)	1290	707.11
Jovanovic	Pb^{2+}	Zn^{2+}	Flory-Huggins	Pb^{2+}	Zn^{2+}	F-G	Pb^{2+}	Zn^{2+}	Kiselev	Pb^{2+}	Zn^{2+}
A_{max}	33.27	13.72	n_H	-0.803	-2.3541	K_{FG}	0.522	0.0479	K_1	-1.6653	0.2566
K_J	0.0281	0.0353	K_H	0.0623	0.0361	W	-171.2	-2054	K_n	-2.743	-0.9704
R^2	0.41	0.78	R^2	0.475	0.756	R^2	0.43	0.68	R^2	0.3615	0.9834

4. CONCLUSION

A comparison of Langmuir, Freundlich, Temkin, Dubinin-Raduskevich, Jovanovic, Flory-Huggins, Fowler-Guggenheim and Kiselev isotherms models carried out on equilibrium adsorption of Pb^{2+} and Zn^{2+} onto PAMRH unraveled the potential of PAMRH as a suitable low cost and efficient adsorbent for the removal of heavy metal ions. It is evident that chemical modification has really improved the adsorption ability of PAMRH. The evaluated parameters and the correlation coefficient showed beyond a reasonable doubt that PAMRH readily adsorbed Pb^{2+} than Zn^{2+}. The adsorption of Pb^{2+} and Zn^{2+} onto PAMRH follows the order: $Pb^{2+} > Zn^{2+}$. This is due to the charge density of cations, the exchangeable sites and pore size on the PAMRH together with the equilibrium temperature. Equilibrium data from the adsorption of Pb^{2+} onto PAMRH fitted to the models in the following order: Langmuir>DKR>Temkin>Freundlich>Flory-Huggins>Fowler-Guggenheim>Jovanovic>Kiselev isotherm models. However, in adsorption of Zn^{2+} onto PAMRH, the equilibrium data fitted the model in the following order: Kiselev>Freundlich>DKR> Jovanovic> Flory-Huggins> Fowler-Guggenheim> Temkin> Langmuir. Based on the correlation coefficient, the equilibrium data fitted best Langmuir isotherm model for adsorption of Pb^{2+} onto PAMRH indicating a monolayer adsorption at a localized site. This study showed that Phosphoric Acid Modified Rice Husk (PAMRH) is a promising low cost adsorbent for treatment of heavy metal contaminated water.

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