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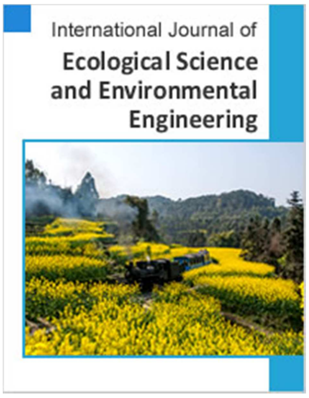

Heavy Metals Biosorption from Fertilizer Industrial Waste Water Using Rice Husk and Groundnut Husk Powder

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Abstract

Groundnut husk (GH) and Rice husk (RH) were used as adsorbents to remove Mn^{2+}, Zn^{2+} and Pb^{2+} ions from fertilizer industrial waste water. Batch adsorption experiment was conducted to examine the effect of adsorbent mass, pH, contact time, activated carbon (standard adsorbent) on adsorption of Mn^{2+}, Zn^{2+} and Pb^{2+} from fertilizer industrial waste water. The results showed that the adsorption of the metal ions was adsorbent mass, pH, and contact time dependent. The optimum adsorbent mass was 50g and 60g, optimum pH was pH 4 and pH 6 for adsorption of metal ions. The kinetic studies showed that pseudo-second order reaction model best described the adsorption process and the Langmuir biosorption isotherm provided the best fit for sorption of Mn^{2+}, and Pb^{2+} using groundnut husk as indicated by their correlation coefficient (R^2) of 0.558 and 0.441. The freundlich biosorption isotherm had the best fit using rice husk as indicated by their correlation coefficient (R^2) of 0.730 and 0.395 for Mn(II) and Pb(II). The study also showed that groundnut husk and rice husk can be efficiently used as low cost alternative for removal of Mn^{2+}, Zn^{2+} and Pb^{2+}.

1. Introduction

Industrial waste is the waste produced by industrial activity which includes any material that is rendered useless during a manufacturing process such as that of factories, mills and mines [1]. Some examples of industrial waste are chemical solvents, paints, sand paper, paper products, industrial by-products, metals, and radioactive wastes.

Biosorption is a physiochemical process that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto its cellular structure [2]. Pollution interacts naturally with biological systems; it is currently uncontrolled, seeping into any biological entity within the range of exposure. The most problematic contaminants include heavy metals, pesticides and other organic compounds which can be toxic to wildlife and humans in small concentration. There are existing methods for remediation, but they are expensive or in effective [3]. Fungi, seaweed, yeast and carrot peels [4] can efficiently remove toxic heavy metal ions from contaminated water.

Heavy metals such as zinc, copper, lead, manganese, *etc.* in wastewater are hazardous to the environment, because of their toxicity and their pollution affect the ecosystem that poses human health risk [5].

The efficient removal of toxic metals from waste water is an important matter, a number of technologies have been developed over the years to remove toxic metals from waste water such as the use of conventional adsorbents and natural adsorbents. Adsorption has been proven to be an effective and versatile method for removal of heavy metals [6].

Rice husks are the coatings of seeds, or grains of rice to protect the seed during the growing season, the hull is formed from hard materials, including opaline silica and lignin. Groundnut hull is an agricultural based waste material commonly called groundnut husk, peanut hulls, groundnut shells, peanut shells. These materials have the potential to sequester metals from solutions. Pollution of water due to the presence of certain industrial waste and metals ions is a severe socio-environmental problem. In view of their toxicity, non-biodegradability and persistent nature, their removal becomes an absolute necessity. The abundance and availability of agricultural by-products (rice husk and groundnut husk) makes them good sources of raw materials for natural sorbents [7].

This research article was focused on investigating the potential of rice husk and groundnut husk agro waste in biosorption of heavy metals from fertilizer industrial wastewater.

2. Materials and Methods

2.1. Preparation of Biosorbent

The biosorbents used were rice husk and groundnut husk, obtained from a local farm at Samaru, Zaria, Kaduna State, Nigeria. The rice husk and groundnut husk were identified at the herbarium in the Department of Biological Science Ahmadu Bello University Zaria. The husks were washed with Acetone and boiled with deionised water for 30 minutes, dried and then pulverized.

2.2. Effects of Different Experimental Conditions

2.2.1. Effect of Adsorbent Mass

Varying masses of the adsorbent (20-70g) were added in different conical flasks containing 1 liter of wastewater, corked and agitated in a magnetic stirrer for 1hr at a speed of 100 rotations per minute (rpm) at room temperature (RT). The content of each flask was filtered using Whatman filter (No.1) paper and analyzed using atomic absorption spectrophotometer.

2.2.2. Effect of pH

Exactly 1L of wastewater was measured into different conical flask and 30g of the adsorbents were added and agitated at 100 rpm for one hour over a pH range of 3-8. The pH was adjusted using Hydrochloric Acid and Sodium hydroxide.

2.2.3. Effect of Contact Time

The effect of contact time on removal of metal ions was studied. Adsorbents were added to different conical flask containing 1L of waste water; the flask was closed and placed in a magnetic stirrer, and agitated at 100 rotations per minute (rpm) for each of the contact time (20-120min). The content of each flask was then filtered and analyzed.

2.2.4. Effect of Activated Carbon

20g and 30g of activated carbon (standard synthetic adsorbent used in industries) were weighed and added in a conical flask containing 1L of waste water separately, corked and agitated in a magnetic stirrer for 1hr at a speed of 100 rpm at RT. The content of the flask was then filtered and analyzed using AAS.

2.3. Heavy Metal Determination and Analysis of Adsorbents

Zinc (Zn), Lead (Pb) and Manganese (Mn) were analyzed before and after treatment. Fourier Transformed Infrared Spectroscopy (FTIR) was carried out to identify the presence of functional groups.

2.4. Batch Adsorption Experiments

Batch adsorption experiment was conducted by mixing biosorbents with fertilizer industrial waste water containing heavy metal ions in a 1L conical flask. The conical flask was corked and agitated in a magnetic stirrer for 1hr at a speed of 100 rpm at RT. The amount of biosorption was calculated based on the difference between the initial concentration (C_e, mg/L) in every flask as follows:

$$q_e = (C_o - C_e)V/ M \quad (1)$$

$$q_t = (C_o - C_t)V/ M \quad (2)$$

$$R(\%) = (C_o - C_t) \times 100/ C_o \quad (3)$$

Where: q_e and q_t = Amount of metal ions adsorbed (mg/g) at equilibrium and at time (t) respectively;

C_o and C_t = Initial concentration (at t = 0) and its concentration at time t = t (mg/L);

M= Mass of adsorbents (g)

V= Volume of metal ions (L)

R= Percentage of metal ions removed

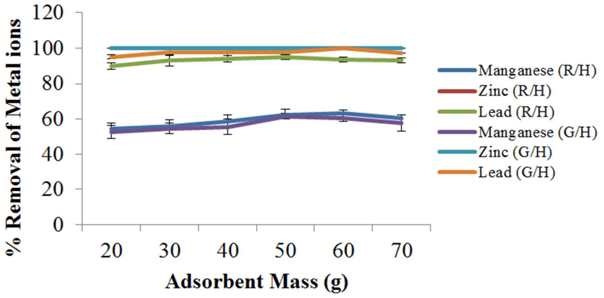
2.5. Statistical Analysis

All experiments were carried out in duplicate and the result was presented as mean ± standard deviation.

3. Results and Discussion

3.1. Effect of Adsorbent Mass on Removal of Metal Ions

Figure. 1 shows that increased adsorbent loading increased the metal ions percentage removal. Manganese attained maximum removal at 60g with 63.44% removal using rice husk powder as adsorbent and maximum removal was at 50g with 61.62% removal using groundnut husk powder as adsorbent. Lead attained maximum removal at 50g with 95.04% removal using rice husk powder as adsorbent and 60g with 99.93% removal using groundnut husk powder as adsorbent. Maximum removal of Zinc was attained at 20g with 100% removal for both adsorbents and increase in mass of adsorbents brought no change in adsorption of zinc. The percentage removal of Mn(II), Zn(II) and Pb(II) ions in this study, increased with increasing dosage due mainly to an increase in the number of available exchangeable active sites for metal ion sorption [8].

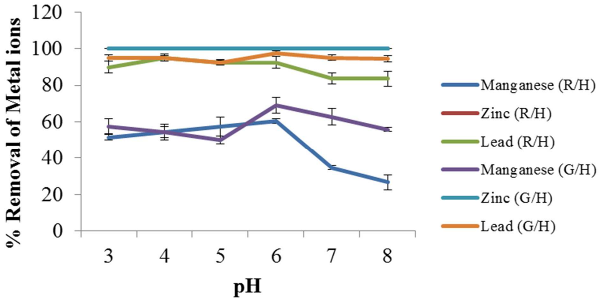


RH = Rice Husk, GH = Groundnut husk, g = Grams, % = Percentage

Figure 1. *Effect of Adsorbent Mass on Percentage Removal of metal ions.*

3.2. Effect of pH on Removal of Metal Ions

From Figure. 2, with rice husk powder and groundnut husk powder used as adsorbents, it was observed that with increase in the pH of waste water, the percentage removal of metal ions increased and attained maximum removal for Manganese at pH 6 with 69.01% using groundnut husk powder, while Lead had maximum removal of 97.66% at pH 6 with groundnut husk powder as adsorbent. There was 100% removal of zinc at low pH of 3 and no further change in zinc adsorption with increase in pH of waste water for both rice husk powder and groundnut husk powder. At pH 7 and 8 there was decrease in removal of metal ions for all the metals. At low pH, higher concentration and mobility of H^+ ions favour H^+ sorption compared to metal ions, this creates a competition between the protons and metal ions for the active sites of the biosorbent. According to [9] metal ions are more soluble in solution at lower pH values and this reduces their sorption. The low sorption at low pH was thus due to saturation of the active sites of GH and RH with hydrogen ions.

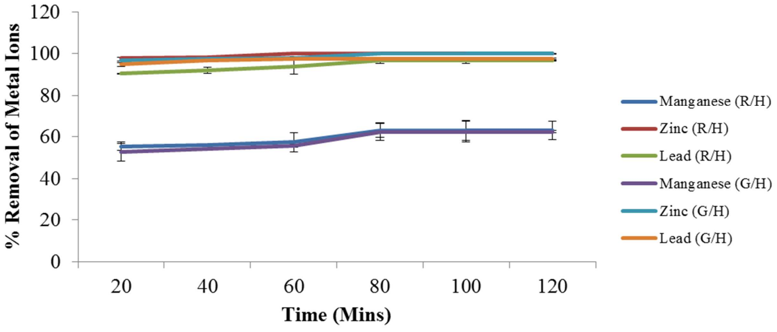


RH = Rice Husk, GH = Groundnut husk, g = Grams, % = Percentage

Figure 2. *Effect of pH on percentage Removal of Metal ions.*

3.3. Effect of Contact Time on Metal Ion Removal

The percentage metal ion removal approached equilibrium within 80 minutes for manganese, 60 minutes for zinc and 80 minutes for lead using rice husk as adsorbent, with manganese recording 63.06%, zinc 100% and lead 96.81% removal. Having a trend of $Zn^{2+} > Pb^{2+} > Mn^{2+}$. This experiment shows that different metal ions attained equilibrium at different times. The removal rate of metal ions also increases with an increase in contact time. The rate of biosorption is higher at the early stage, due to a large available surface area of the biosorbent and presence of abundant active sites on the surface. The fast initial uptake is also due to the rapid accumulation of the heavy metal ions on the surface of the biosorbent. As these sites become exhausted or saturated with time, the sorption rate also decreases [10]. The faster removal rate with Zn(II) than with Pb(II) and Mn(II) may be due to the smaller ionic radius of Zn(II) than Pb(II) and Mn(II), which makes for easier, more rapid diffusion to the surface of GH and RH [11].

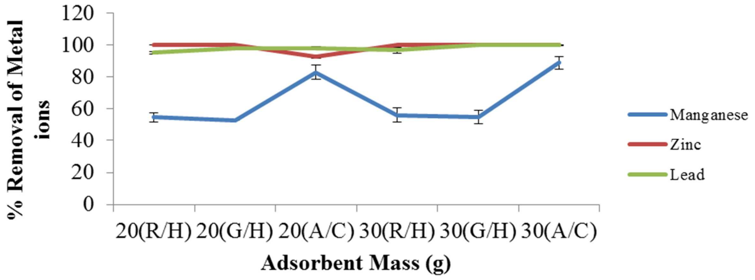


R/H = Rice Husk, G/H = Groundnut husk, g = Grams, % = Percentage

Figure 3. *Effect of Contact Time on Percentage Removal of metal ions.*

3.4. Effect of Removal of Metal Ions by Activated Carbon Vis-à-Vis Adsorbents

Figure 4 shows the percentage removal of metal ions by rice husk powder, groundnut husk powder and activated carbon (standard adsorbent used in industries). At 30g of adsorbent used, removal of lead was 96.72% with rice husk powder, 99.75% with groundnut husk powder and 99.81% with activated carbon as adsorbent, while rice husk had 100% removal for zinc at both 20g and 30g of adsorbent. Activated carbon had 92.83% and 100% removal for zinc at 20g and 30g respectively. At 20g of adsorbents used, lead removal was 95.04% with rice husk powder, 98% with activated carbon and 97.66% with groundnut husk powder as shown in figure 4. Using this industrial adsorbent Powder Activated Carbon (PAC), to reduce heavy metals from fertilizer industrial waste water, it showed that activated carbon had a better adsorption capacity for metal ions than rice husk powder and groundnut husk powder but the percentage difference was not significant. This could be due to more surface area of activated carbon, available for metal ions binding.



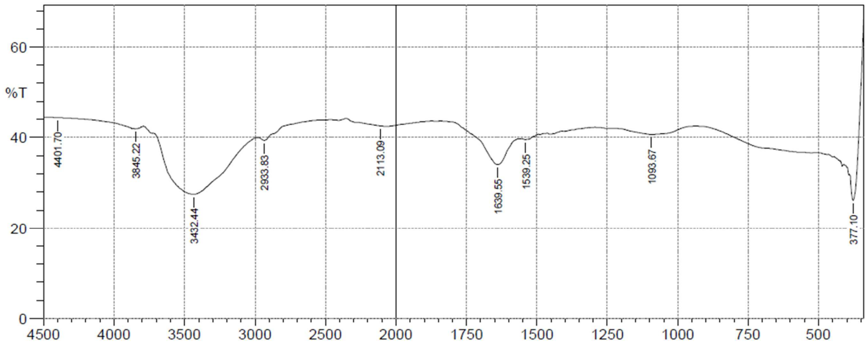
R/H = Rice Husk, G/H = Groundnut husk, g = Grams, % = Percentage

Figure 4. *Percentage Removal of metal ions by Activated Carbon a Standard Adsorbent Vis-a-Vis Adsorbents (Rice husk powder and Groundnut Husk Powder).*

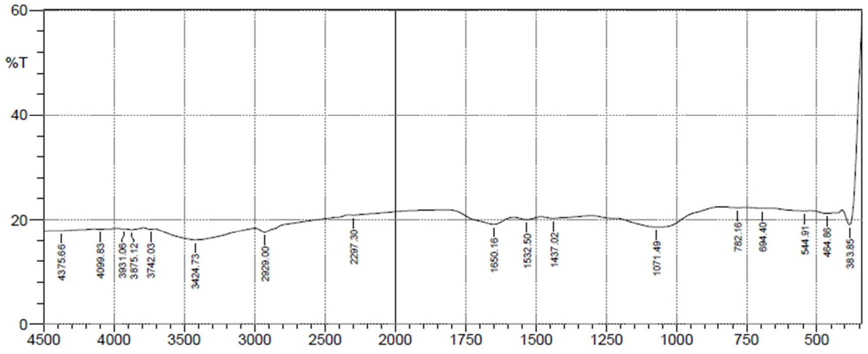
3.5. Fourier Transform Infra-Red Spectroscopy (FTIR) Analysis

The results of FTIR peak values and functional groups of rice husk powder and used rice husk powder are shown in Figure 5 below. IR-spectrum shows the presence of Alkyl halides (R-I), Alkenes (=C-H), Alkynes (≡C-H), Alkanes and Alkyls (-(CH$_2$)$_n$, Alcohols (C-O), Ethers (=C-O-C), Amides (N-H), Carboxylic acids (O-H), in rice husk powder while used rice husk powder shows the absence of Alkenes (=C-H) and Alkynes (C≡C).

Figure. 6 below also shows the peak values and functional groups of groundnut husk powder and used groundnut husk powder respectively. IR-spectrum shows the presence of Alkyl halides (R-I), Alkenes (=C-H), Aromatic compound mono substituted (C-H), Alcohols (C-O), Alkyl halides (C-F), Ethers (=C-O-C), Alkanes and Alkyls (C-H), Aromatic Compounds (C=C), Amides (N-H), Alkenes (C=C), Aldehydes (C=O), Esters (C=O), Carboxylic acids (O-H), for groundnut husk powder while the used groundnut husk powder shows the absence of Aromatic Compounds (C=C), Aldehydes (C=O), Alkenes (C=C).

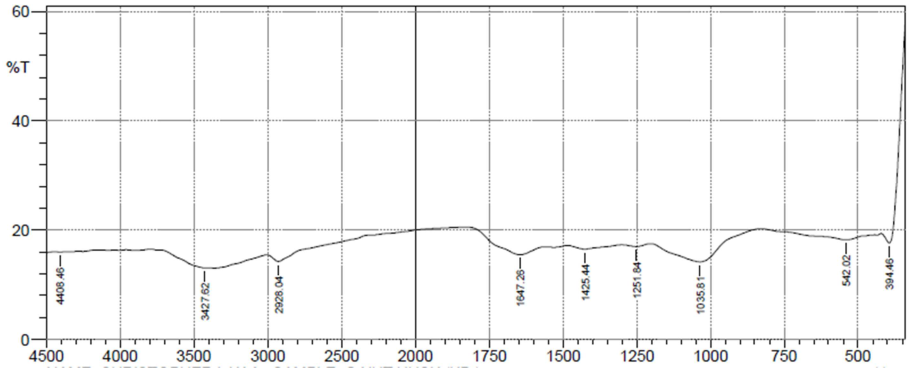


(a)Before metal ions adsorption

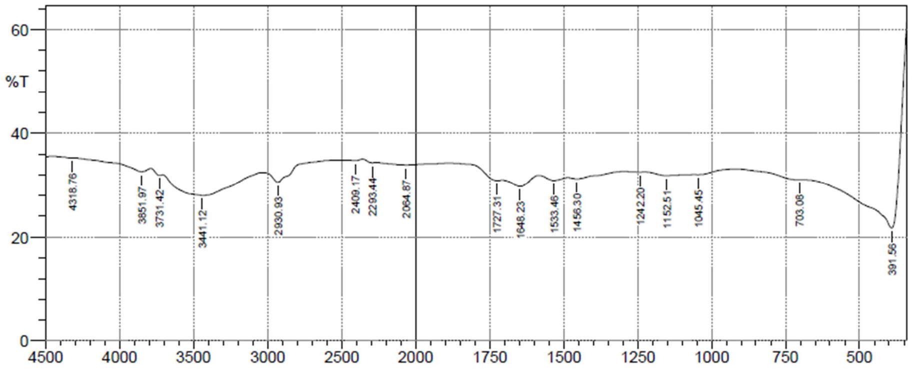


(b) After metal ions adsorption

Figure 5. *FTIR spectrum of rice husk and used rice husk showing Fragment peaks.*



(a) Before metal ions adsorption



(b) After metal ions adsorption

Figure 6. *FTIR spectrum of groundnut husk and used groundnut husk showing Fragment peaks.*

3.6. Adsorption Isotherms

An adsorption isotherm model gives the equilibrium relationship between the sorbate in the fluid phase (solution) and the sorbate sorbed on the sorbent at constant temperature [12] [13]. They are very useful for obtaining the adsorption capacity so as to facilitate the evaluation of the feasibility of the adsorption process for a given application and for selection of the most appropriate sorbent at the optimum experimental conditions [12].

In this work, the Langmuir and freundlich isotherm models were employed to interprete the sorption process in order to understand the mechanism of metal ions adsorption on rice husk and groundnut husk powder. The experimental data were fitted to the aforementioned equilibrium isotherm models. Langmuir biosorption isotherm gave the best fit for sorption of metal ions using groundnut husk as indicated by their correlation coefficient which were higher than that of the freundlich isotherm while the freundlich biosorption isotherm gave the best fit using rice husk powder as indicated by their correlation coefficient which were higher than that of the Langmuir isotherm (Table 1).

Table 1. *Isotherm model parameters for the adsorption of metal ions by RH and GH.*

Adsorbent	Metal	Langmuir constant		Correlation Coefficient	Freundlich constant		Correlation Coefficient
		q_e	K_L	R^2	K_f	1/n	R^2
GH	Mn	0.128	0.072	0.558	2.296	3.886	0.557
GH	Pb	0.000	0.235	0.441	5.741	0.143	0.289
RH	Mn	0.110	0.078	0.528	3.994	4.228	0.730
RH	Pb	0.538	0.485	0.014	2.529	1.157	0.359

The Langmuir equation (Ho, 2005) is given as:

$$q_e = q_m k_a c_e/(1 + k_a c_e) \tag{4}$$

Where q_e= Amount of metal ions adsorbed per unit mass at equilibrium (mg/g)

q_m = Maximum possible amount of metal ions that can be adsorbed per unit mass of adsorbent (mg/g)

c_e = concentration of sorbate (in solution at equilibrium (mg/l);

K_a = sorption equilibrium constant

The linearised form of equation is:

$$c_e=1/ q_e k_a+c_e/q_m q_m \tag{5}$$

A plot of c_e/q_e versus c_e gives a straight line, with a slope of $1/q_m$ and intercept $1/ k_a q_m$

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant K_R, the separation factor or equilibrium parameter, which is defined as:

$$K_R=1/(1+K_aC_o) \tag{6}$$

Where: K_R = dimension less separation factor;

K_a = Langmuir constant (L/mg);

C_o = the initial concentration of metal ions (mg/L).

The shape of the isotherm is linear if $K_R = 1$, it is irreversible if $K_R < 0$, unfavorable if $K_R > 1$ and favorable if $0 < K_R < 1$ (46, 47).

The Freundlich isotherm is an empirical model which indicates the surface heterogeneity of the adsorbent. The equation is given as:

$$q_e = K_f C_e^{1/n} \tag{7}$$

The linear form of the equation is:

$$\log q_e = \log k_f + 1/n \log c_e \tag{8}$$

where: q_e=the amount of sorbate adsorbed at equilibrium (mg/g);

k_f(L/g) and n=Freundlich constants which indicate the adsorption capacity of the adsorbent and adsorption intensity, respectively;

C_e=the equilibrium concentration of sorbate in the solution(mg/dm^3).

A plot of $\log q_e$ versus $\log c_e$ gives a straight line of slope $1/n$ and intercept log k_f from which n and k_f can be evaluated. If $1/n < 1$, then the adsorption is favorable and the adsorption capacity increases with the occurrence of new adsorption sites. But if $1/n > 1$, the adsorption bond becomes weak and unfavorable adsorption takes place, leading to a decrease in adsorption capacity.

3.7. Adsorption Kinetics

The study of the adsorption kinetics of a sorption process is very important as it describes the rate of adsorbate uptake, which in turn evidently controls the residence time of the solute uptake at the solid-solution interface or the sorption reaction [14] [15] [16]. It is an important characteristic in defining the efficiency of sorption [14]. The data obtained from the study of adsorption dynamics are necessary to understand the variables that affect the sorption of solutes, and the rate of sorption observed can also be used to develop predictive models for column experiments [16].

The most important thing when searching for an appropriate sorption mechanism, therefore, is to choose a mathematical model which not only fits the data with satisfactory accuracy but also complies with a reasonable sorption mechanism [17].

Generally, sorption of adsorbate by an adsorbent consists of several steps which include:

a Transport of sorbate (solute) from the solution to the film surrounding the sorbent particles. This is called bulk diffusion.
b Diffusion of the sorbate from the film to the external surface (external diffusion)
c Diffusion from the surface to the internal sites i.e intra-particle transport within the particle.
d Sorption of the sorbate on the interior surface of the sorbent (i.e. pore diffusion). This can involve several mechanisms including reaction kinetics at phase boundaries [15] [17] [18].

Various kinetic models have been proposed and used to study and describe the mechanism of a

Solute uptake by an adsorbent from aqueous solution [17]. In this study, however, the kinetic equations employed to investigate the mechanism of metal ions adsorption are:

The Pseudo-first order by Lagergren (1898) given as:

$$d_q/ d_t = k_1(q_e - q_t) \tag{9}$$

Where: q_e and q_t = the adsorption capacities at equilibrium and at time t (mg/g) respectively;

k_1=rate constant of pseudo-first order adsorption (min^{-1})

After integration and applying boundary conditions t = 0, to t = t, and $q_t = 0$ to $q_t = q_e$, equation (10) becomes;

$$\mathrm{Log}(q_e - q_t) = \log q_e - k_1t/2.303 \tag{10}$$

Where: q_e (mg g^{-1}) = the amount of metal ions adsorbed at equilibrium;

q_t(mg g^{-1}) = the amount of metal ions adsorbed at time t;

k_1 (min^{-1}) = the rate constant of pseudo-first order adsorption.

A plot of ($q_e - q_t$) versus t gives the slope = k_1, and intercept = log q_e

The largergren first order rate constant (k_1) and q_e determined from the model for the metals, and their respective coefficients of correlation, R^2, are shown in table 2.

Table 2. *Kinetic Parameters for the adsorption of metal ions by RH and GH.*

Adsorbent	Metal	Pseudo-first-order		Regression Coefficient	Pseudo-second-order		Regression Coefficient
		q_e	k	R^2	q_e	k_2	R^2
RH	Mn	9.506	0.006	0.972	0.677	1.166	0.999
RH	Zn	73.113	0.004	1.000	0.580	24.772	1.000
RH	Pb	44.360	0.018	0.988	0.229	3.507	0.999
GH	Mn	7.277	0.009	0.999	0.664	0.791	0.999
GH	Zn	46.025	0.009	0.981	0.581	5.253	1.000
GH	Pb	55.462	0.052	1.000	0.236	5.930	1.000

The Pseudo-second order equation [13] is given as:

$$d_q/d_t = k_2(q_e - q_t)^2 \tag{11}$$

Where k_2 is the rate constant of pseudo-second order adsorption (g mg^{-1} min^{-1}), and other symbols have their usual meanings. After integration, equation (12) becomes:

$$1/(q_e - q_t) = 1/\, q_e + k_2 \qquad (12)$$

Equation (12) is linearised to give:

$$t = 1 q_e^2 /\, q_t k_2 + (1/q_e)\, t \qquad (13)$$

If

$$k_2 qe^2 = h \qquad (14)$$

Combining equations (13) and (14) gives

$$t = 1/\, q_t\, h + (1/q_e) t \qquad (15)$$

A plot of t/q_t verses t gives a straight line.

If the sorption process follows pseudo-second order, h, is described as the initial rate constant as t approaches zero.

The correlation coefficients and adsorption capacities calculated from the kinetics models employed in the interpretation of the experimental data are given in Table 2. The pseudo-second order model gives the best description of the mechanism of metal ions adsorption on GH and RH.

4. Conclusion

The potential of modified rice husk and groundnut husk for the removal of Mn(II), Zn(II) and Pb(II) ions from aqueous solutions was dependent on biosorption process such as pH, biosorbent dose and contact time. The equilibrium data have been analyzed using Langmuir and freundlich isotherms. The characteristics parameters for each isotherm and related correlation coefficients R^2 were determined. The Langmuir biosorption isotherm were demonstrated to provide the best correlation for the biosorption of Mn(II), Zn(II) and Pb(II) ions onto GH powder while the freundlich biosorption isotherm provided the best correlation coefficient for the biosorption of Mn(II), Zn(II) and Pb(II) ions unto RH powder. The kinetics results provided the best correlation of the experimental data of biosorption of Mn(II), Zn(II) and Pb(II) onto RH and GH powder by pseudo-second order equation. It can be concluded that since the RH and GH powder is an easily, locally available, low cost adsorbent and has a considerable high biosorption capacity, it may be treated as an alternative adsorbent for the treatment of waste water containing Mn(II), Zn(II) and Pb(II) ions.

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