Biosorption of Heavy Metals from Fertilizer Industrial Waste Water Using Rice Husk (RH) and Groundnut Husk (GH) Powder in a Packed Bed Bioreactor

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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. Continuous adsorption experiment was conducted to examine the effect of adsorbent mass, pH, temperature and adsorbent combination 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 temperature dependent. The optimum adsorbent mass was 60g, optimum pH was pH 5 and pH 6 and optimum temperature was 60^{o}C for adsorption of heavy metal ions. The Langmuir biosorption isotherm provided the best fit for sorption of Mn^{2+}, Zn^{2+} and Pb^{2+} using groundnut husk as indicated by their correlation coefficient (R^2) of 0.998, 0.676 and 0.297 while the freundlich biosorption isotherm had the best fit using rice husk as indicated by their correlation coefficient (R^2) of 0.332, 0.041 and 0.556 for Mn(II), Zn(II) and Pb (II) respectively. 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+}.

Keywords: Adsorption; Isotherm; Adsorbents; Langmuir; Freundlich.

1 INTRODUCTION

Waste water from numerous industries such as paints and pigments, glass production, mining operations, metal plating, fertilizer and battery manufacturing processes are known to contain contaminants such as heavy metal [1]. Heavy metals such as Pb, Cd, Cr, Ni, Zn, Cu and Fe are present in industrial waste water, these heavy metals in waste water are not biodegradable and their existence in receiving lakes and streams causes bioaccumulation in living organisms, which leads to several health problems in animals, plants and human beings such as cancer, kidney failure, metabolic acidosis, oral ulcer, renal failure. As a result of the degree of the problems caused by heavy metals pollution, removal of heavy metals from waste water is important [5]. Investigation into new and cheap methods of metal ions removal has been on the increase lately. Recently efforts have been made to use cheap and available agricultural wastes such as coconut shell, orange peel, rice husk, peanut husk and sawdust as adsorbents to remove heavy metals from waste water [1].

The removals of these hazardous materials may be performed using various techniques, including precipitation, membrane filtration, ion exchange, sorptive flotation and adsorption [5]. The removal of heavy metals via adsorption over solid adsorbents, e.g. activated carbons and others is one of the most convenient methods used.

Biosorption is a physiochemical process that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto its cellular structure [13]. Though using biomass in environmental cleanup has been in practice for a while, scientists and engineers are hoping this phenomenon will provide an economical alternative for removing toxic heavy metals from industrial waste water and aid in environmental remediation.

Rice hulls 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. Belongs to the specie *Arachis hypogaea* L. and these materials have the potential to sequester metals from solutions[3][7].

This research was carried out from January – April 2015 at the Department of Biochemistry, Ahmadu Bello University, Zaria, Kaduna State and its focused on investigating the potential of rice husk and groundnut husk agro waste in biosorption of heavy metals from fertilizer industrial waste water.

2 MATERIALS AND METHODS

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 adsorbents were washed with Acetone to disinfect, and boiled with deionised water for 30min dried and then pulverized.

Packed Bed Bioreactor System

The reactor system used in this study consists of industrial waste water as a flowing stream and a 30cm long and 3cm internal diameter plastic column. The column was packed with a known amount of powdered rice husk and groundnut husk separately. The process was operated in a down flow mode; the industrial wastewater was fed into the reactor and emerges as stream of product. The product was then collected at the bottom of the column and quantified.

Effects of different experimental conditions

Since adsorption is affected by physical and chemical variables, the influence of adsorbent mass, pH, temperature and adsorbent combination were investigated in this study.

Effect of Adsorbent Mass

Varying masses of adsorbents (20-70g) were weighed separately and each mass was packed into the column of the same length, waste water was allowed to flow into the column at a flow rate of 5ml min^{-1}. The effluent was collected and analyzed using atomic absorption spectrophotometer (AAS).

Effect of pH

Over a pH range of 3-8, the effect of pH on adsorption of metal ions was studied. Waste water was allowed to flow into the column packed with 40g of adsorbents separately at a flow rate of 5ml min^{-1} and effluent was collected and analyzed. The pH was adjusted using Hydrochloric acid and sodium hydroxide.

Effect of Temperature

Under a temperature range of 30-70^{0}c, using a water bath to regulate the temperature, industrial waste was allowed to flow at a flow rate of 5ml min^{-1} into the column packed with 40g of rice husk and groundnut husk powder separately, effluent was then collected and analyzed using atomic absorption spectrophotometer.

Effect of Adsorbent Combination

40g of adsorbents (rice husk and groundnut husk powder) were combined in different percentages into the column separately, waste water was allowed to flow into the column at a flow rate of 5ml min^{-1} and effluent was collected and analyzed using AAS.

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.

Adsorption experiment

The continuous adsorption experiment was conducted by allowing fertilizer industrial waste water to flow into the column at a flow rate of 5ml/min^{-1} and effluent was collected and analyzed using atomic absorption spectrophotometer. All experiments were carried out in duplicate and mean values determine were presented. The percentage removal of Mn(II), Zn(II) and Pb(II) ions were calculated from the following equation:

$$R(\%) = \frac{(C_o - C_e) \times 100}{C_o} \qquad \ldots\ldots(1)$$

Where C_o and C_e are metal ions concentrations (mg/L) before and after adsorption respectively. M is the weight of the adsorbent in grams.

Statistical Analysis

The result was presented as mean ± standard deviation.

3 RESULTS AND DISCUSSION

Effect of Adsorbent Mass on Metal ions

Fig. 1 shows that increased adsorbent loading increased the metal ions percentage removal. Mn^{2+} attained maximum removal at 30g with 92.09% removal using rice husk powder as adsorbent. Increase in adsorbent dosage also increased the percentage removal of Pb^{2+} for both adsorbents. Lead attained maximum removal at 60g with 97.35% removal using rice husk powder as adsorbent. Maximum removal of Zinc (Zn) was at 60g with 96.03% removal using groundnut husk powder. 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 [6].

Effect of pH on Removal of Metal ions

From fig. 2, 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 75.62% and pH 5 with 98.82% using rice husk powder and groundnut husk powder respectively. Lead had maximum removal at pH 6 with 94.54% removal with groundnut husk powder as adsorbent. There was 100% removal of zinc at pH of 6 using rice husk powder as adsorbent. 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 [11] 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.

Effect of Temperature on removal of Metal ion

The removal of Manganese, Zinc and Lead was favored at higher temperature as shown in figure 3. The result demonstrated that an increase in temperature from 30^o-40^oc led to increase in the adsorption capacity from

91.38% to 98.28% for manganese with rice husk powder as adsorbent. Maximum adsorption for zinc was at 40^oc with 99.72% removal and at 60^oc with 99.83% removal for rice husk powder and groundnut husk powder respectively. Lead had maximum removal of 94.64% at 40^oc and 95.64% removal at 60^oc for rice husk powder and groundnut husk powder respectively. Further increase in temperature led to decrease in removal of metal ions as shown in fig 3. In general increase in temperature increases the rate of a redox reaction [14]. Using a temperature range of 30 – 70 ^oc, an increasing trend of metal ions removal with increase in temperature was observed. [4] and [7] suggested that high temperature results in creation of some new sorption sites on the adsorbent surface by increasing the rate of intra particle diffusion of sorbate ions into the pores of adsorbent at higher temperature, since diffusion is often endothermic. However at a higher temperature the trend changed as the percentage removal decreased, this may be due to damage of the physical properties of the biosorbents that interferes with binding of ionic species to it.

Effect of Adsorbent Combination on Metal ion Removal

Rice husk powder (40g) and 40g groundnut husk powder were combined in various percentages as shown in fig. 4. At 60% rice husk powder combined with 40% groundnut husk powder there was maximum adsorption of 98% for manganese, while zinc had maximum adsorption of 93.90% at 60% rice husk powder and 40% groundnut husk powder combination. Lead had maximum adsorption of 89.43% at 70% rice husk powder combined with 30% groundnut husk powder. GH and RH gave a better sorption when used in isolation than when in combination. A higher percent of GH than RH in the combination caused a decrease in sorption capacity and percentage removal. This is possibly due to aggregation/agglomeration of sorption sites, leading to a decrease in surface area; hence sorption capacity of the biosorbents may not have been fully utilised [10]. Whereas, a high percentage removal of metal ions tends to increase as more RH is combined with GH. This is possibly due to an increase in the available binding sites for metal ion [12].

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).

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 [2][3]. 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 [2].

In this work, the Langmuir and freundlich isotherm models were employed to interpret 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).

The Langmuir equation [8] is given as:

$$q_e = \frac{q_m k_a c_e}{1 + k_a c_e} \quad \text{.......(2)}$$

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:

$$\frac{c_e}{q_e} = \frac{1}{k_a q_m} + \frac{c_e}{q_m} \quad \text{......(3)}$$

A plot of $\frac{c_e}{q_e}$ versus c_e gives a straight line, with a slope of $\frac{1}{q_m}$ and intercept $\frac{1}{k_a q_m}$

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:

$$K_R = \frac{1}{1 + K_a C_o} \quad \text{.......(4)}$$

Where: K_R = Dimension less separation factor;

K_a = Langmuir constant (L/mg);

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

The shape of the isotherm is linear if $K_R = 1$, it is irreversible if $K_R < 0$, unfavourable if $K_R > 1$ and favourable 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:

$$q_e = K_f C_e^{1/n} \quad \text{.......(5)}$$

The linear form of the equation is:

$$\log q_e = \log k_f + 1/n \log c_e \quad \text{.......(6)}$$

where;

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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 favourable and the adsorption capacity increases with the occurance of new adsorption sites. But if $1/n > 1$, the adsorption bond becomes weak and unfavourable adsorption takes place, leading to a decrease in adsorption capacity.

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

Adsorbent	**Metal**	**Langmuir constant**		**Regression Coefficient**	**Freundlich constant**		**Regression Coefficient**
		q_e	**K_L**	**R^2**	**K_f**	**1/n**	**R^2**
RH	Mn	0.000	0.000	5E-05	4.709	0.822	0.332
RH	Zn	3.012	6.916	0.163	2.338	0.829	0.441
RH	Pb	5.319	2.848	0.218	5.714	0.679	0.556
GH	Mn	16.129	31.000	0.998	10.423	0.038	0.014
GH	Zn	19.607	0.485	0.676	6.194	0.682	0.842
GH	Pb	0.887	4.838	0.297	1.039	0.752	0.056

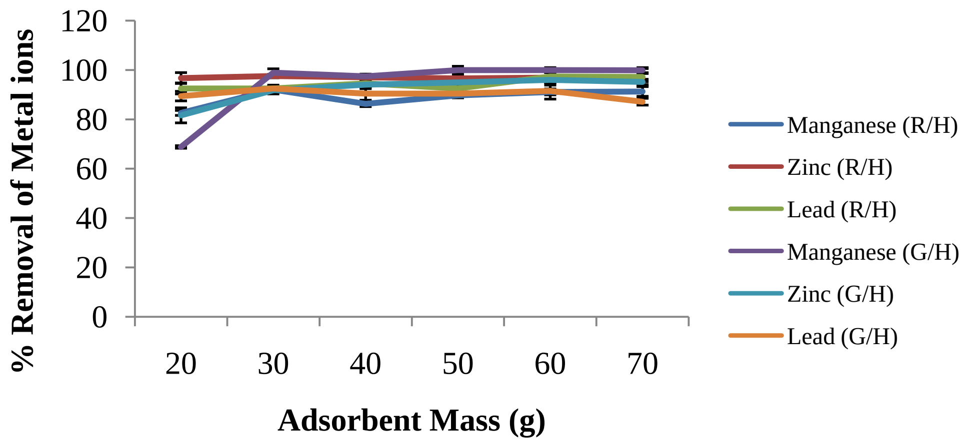

Fig. 1 Effect of Adsorbent Mass on Percentage Removal of metal ions

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

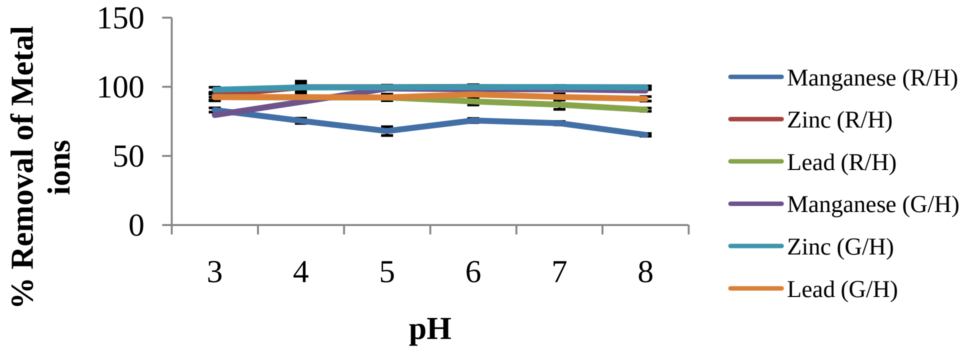

Fig. 2 Effect of pH on percentage Removal of Metal ions

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

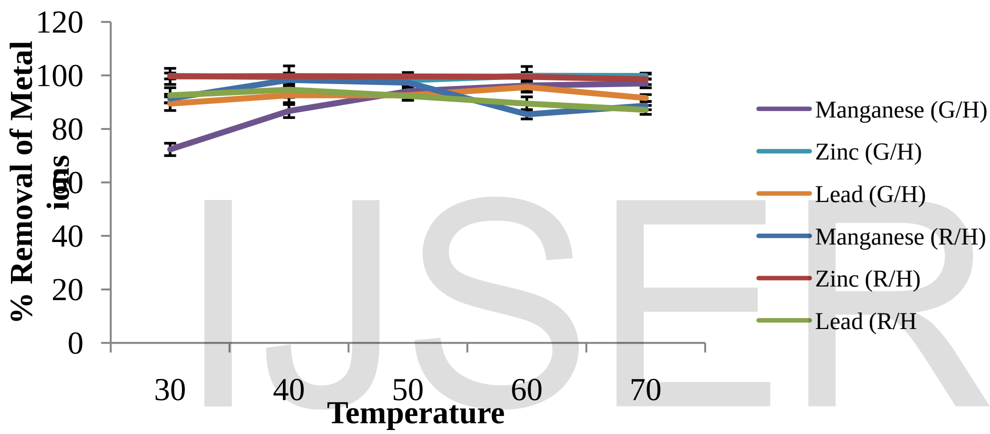

Fig. 3 Effect of Temperature on Percentage Removal of metal ions

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

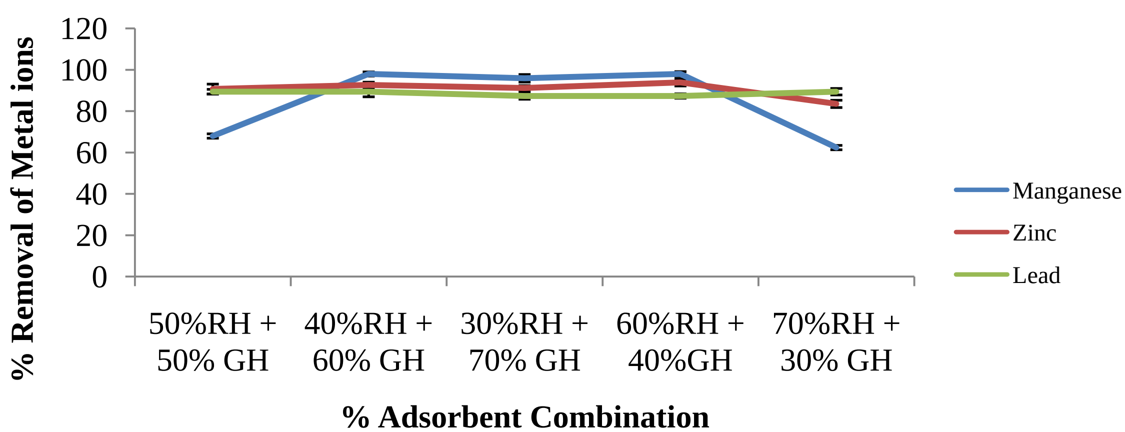

Fig. 4 Effect of Adsorbent combination on Percentage Removal of metal ions

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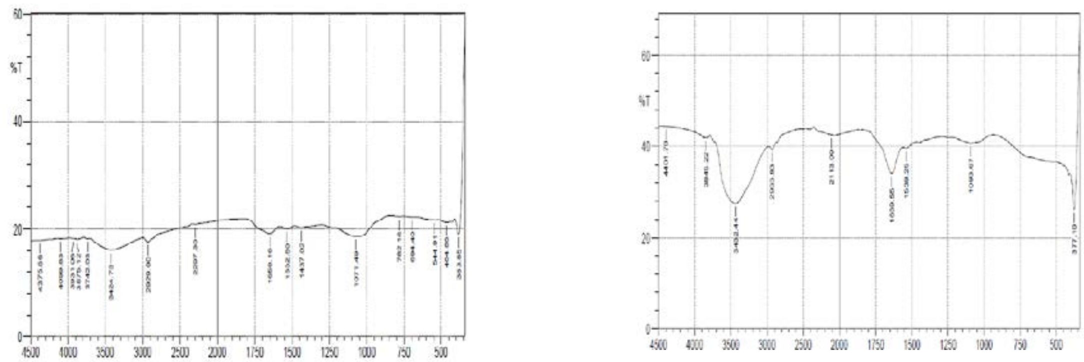
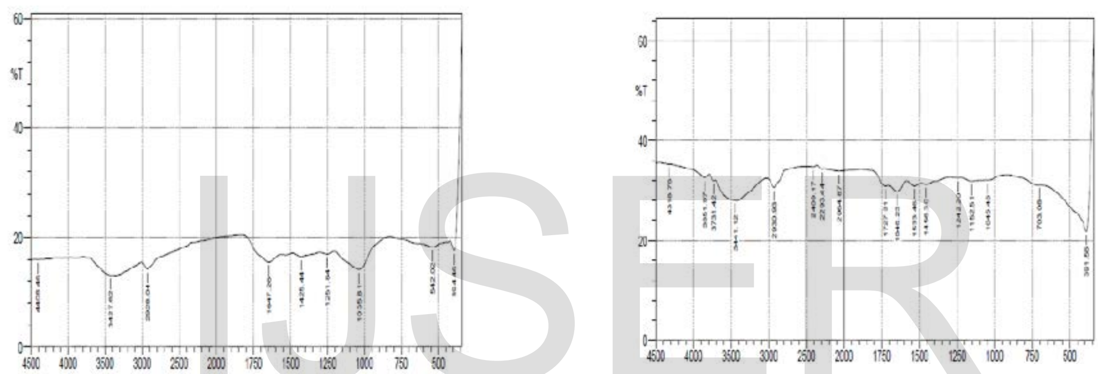
R/H = Rice Husk, G/H = Groundnut husk, g = Grams, % = Percentage



(a) Before metal ions adsorption (b) After metal ions adsorption

Fig. 5: FTIR spectrum of rice husk and used rice husk showing Fragment peaks



(a) Before metal ions adsorption (b) After metal ions adsorption

Fig. 6: FTIR spectrum of groundnut husk and used groundnut husk showing Fragment peaks

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, temperature and biosorbent dose. 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. 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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