



REMOVAL OF Pb²⁺ FROM AQUEOUS SOLUTION USING RICE HUSK AS AN ADSORBENT



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Abstract: The adsorption of Pb²⁺ using rice husk as adsorbent was studied using batch adsorption method. The physico-chemical parameters gave values of 6.13, 42 %, 23, 5 %, 0.5 mg/L and 55.50 mg/L for pH, attrition, ash content, moisture content, bulk density and iodine number. Atomic absorption spectrophotometer was used to monitor the adsorption of Pb²⁺. The optimum values obtained were 84.45% at 20 mg/L for concentration, 99.60% at a pH of 11, 81.50 % at a contact time of 40 min and 92.44 at an adsorbent dose of 5 g, signifying that rice husk is a good adsorbent for the removal of Pb²⁺ from simulated waste water. The result fitted into Langmuir and Freundlich isotherm.

Keywords: Adsorption isotherm, batch adsorption, Langmuir, thermodynamic

Introduction

Water contamination by heavy metal has been a serious concern over the years due to environmental and safety reasons. Water pollutants mainly consist of heavy metals, microorganisms, fertilizers and thousands of toxic organic compounds (Chaitali *et al.*, 2013). Heavy metals find their way into water as a result of the discharge of effluents from textile, chemical, dye, leather, tannery, electroplating, galvanizing, pigments, metallurgical and paint industries. Metal processing and refining operations at small and industrial scale also releases considerable amount of toxic metal ions. They get into the environment through ways such as weathering of the earth's crust, mining, soil erosion, industrial discharge, urban runoff, sewage effluents, dumping of hospital wastes, pest and disease control agents applied to plants and air pollution (Shanmugapriya *et al.*, 2013; Subba *et al.*, 2003). Due to degradation problems, the presence of heavy metals in water has much effect on the micro algae which constitute the main food source for bivalve mollusc in their growth stages, zooplankton (rotifers, copepods, and borne shrimps) and for larval stages of some crustacean and fish species (Nazire *et al.*, 2015).

Several methods have been employed in the removal of heavy metals from wastewater (Habib *et al.*, 2007; Mebrahtu and Zerabruk, 2011; Wuana and Okieimen, 2011) by agricultural industries, water treatment plants and also in medicine and these include; membrane extraction, adsorption, ion-exchange, precipitation, liquid extraction or electrolysis. Most of these techniques are extremely expensive or inefficient and take too much time. Among the techniques, adsorption using a low cost adsorbent or material such as rice husk has been employed (Lata *et al.*, 2014; El-Sherif *et al.*, 2013; Vieira *et al.*, 2014; Manish *et al.*, 2015) The choice of a suitable method for removal of heavy metals is usually influenced by different factors such as the efficiency of removing the pollutant materials, availability of used chemicals and the chemistry of the contaminated material beside the process cost. The major advantages of adsorption over conventional treatment methods are; low cost, high efficiency, no additional nutrient requirement, regeneration of adsorbent and the possibility of metal recovery (Ahile *et al.*, 2015; Dabrowski *et al.*, 2001; Onidipe *et al.*, 2015; Raikar *et al.*, 2015).

Rice husk is an agro-waste which is produced as a by-product of rice milling industry and it is estimated to be more than 100 million tonnes with about 96 percent generated in developing countries. Rice husk mainly consist of crude protein (3 %), ash (including 17 % silica), lignin (20 %), hemicellulose (25

%) and cellulose (35 %) rendering it suitable for metallic cation fixation (Vieira *et al.*, 2014; Elsaidi *et al.*, 2015). Rice husk is mostly used as a fuel in the boiler of furnaces of various industries to produce energy. The ash generated after burning the rice husk in the furnace is called rice husk ash. This research is aimed at removing Pb²⁺ from aqueous solution using rice husk as an adsorbent.

Materials and Methods

Sample collection, activation and carbonization of the adsorbent

Rice husk was obtained from a local rice mill located in Makurdi, Benue State-Nigeria. The rice husk was washed with distilled water to remove all dirt after which it was air dried at room temperature and later oven dried for 24 h at 105°C. The dried sample was then grinded and sieved to obtain fine powder and stored in a plastic container for future use. The dried sample was activated by treating it with saturated solution of ammonium chloride with constant stirring and was steeped for 24 h. 250 g of the adsorbent was carbonized at 650°C for 25 min in a muffle furnace (Ney-252 model). The sample was cooled in a desiccator and washed several times with distilled water until the pH of the flushing water was between 6 and 7. The wet sample was dried and then stored in air tight bottles for further use (Yusuf *et al.*, 2012).

Characterization of the adsorbent

The adsorbent was characterized based on bulk density, pH, ash content, moisture content, iodine number and attrition.

Determination of bulk density

The adsorbent (5 g) was measured into 10 mL measuring cylinder. It was tapped on a bench until a lower volume was obtained. The density was calculated in g/mL using equation 1.

$$D_B = \frac{M_3 - M_2}{V_1} \quad 1$$

Where: D_B = Bulk density; M₂ = Mass in grams of the measuring cylinder; M₃ = Mass in grams of the measuring cylinder + sample; V₁ = volume

Determination of pH

The sample (1 g) was weighed using a weighing balance. The weighed sample was steeped in 100 mL of distilled water and was placed on a magnetic stirrer for 4 h. The sample was filtered and the pH of the filtrate was read by a pH meter and the value recorded.

Determination of ash content

The sample (2 g) was weighed on a weighing balance. The sample was placed in a muffle furnace and heated till it turned to ash. The ash sample was cooled and the weight was recorded. The ash content was calculated using equation 2 below.

$$\text{Ash content} = \frac{W_3 - W_1}{W_2 - W_1} \times 100\% \quad 2$$

Where: W₁ = Weight of the crucible; W₂ = Weight of crucible + Sample before ashing; W₃ = Weight of crucible + Sample after ashing

Determination of moisture content

The sample (3 g) was weighed using weighing balance and was heated in an oven at 105°C. This was repeated several times until a constant weight was obtained. The moisture content was calculated using equation 3.

$$\begin{aligned} \text{Moisture content} &= \frac{M_2 - M_3}{M_2 - M_1} \times 100\% \quad 3 \\ &= \frac{\text{Loss of weight}}{\text{Initial weight of sample}} \times 100\% \end{aligned}$$

Where: M₁ = Weight of crucible; M₂ = Weight of crucible + Sample before heating; M₃ = Weight of crucible + Sample after cooling

Iodine number

The standard solution (20 mL) was titrated with sodium thiosulphate which was the blank without the adsorbent. 1 g of the adsorbent was steeped in 25 mL of the standard iodine solution and was stirred for 2 h. The solution was filtered and the filtrate was titrated with 0.01M solution of sodium thiosulphate using starch as the indicator. The iodine solution was calculated using equation 4.

$$\text{Iodine Value} = \frac{Y - X}{Y \times V} \times \frac{1}{W \times M} \quad 4$$

Where: Y = Volume of thiosulphate for blank; X = Titre value; V = Volume of the iodine solution used; W = Weight of the sample; M = Molarity of iodine solution

Attrition

The sample (1 g) was steeped into 50 mL of distilled water. It was stirred with a magnetic stirrer for 2 h. The solution was filtered and the residue was dried and weighed. The attrition was calculated using equation 5.

$$\% \text{ Loss of attrition} = \frac{M_1 - M_2}{M_1} \times 100\% \quad 5$$

Where: M₁ = initial mass; M₂ = final mass

Batch adsorption studies

The adsorption of heavy metal was studied by batch technique. 0.5 g of the adsorbent was equilibrated with 1000 mL of the lead solution of known concentration of 4.0, 8.0, 12.0, 16.0 and 20.0 mg/L in stoppered borosil glass flask at a fixed temperature of 30°C in an orbital shaker for 20-60 mins. After equilibrium, 10mL sample was collected from each flask in time interval of 20, 30, 40, 50 and 60 min, the suspension of the adsorbent was separated from the solution by filtration using filter paper. The concentration of lead (II) ion in the solution was measured by atomic absorption spectrophotometer.

Effect of pH

Batch adsorption experiments were used to measure the amount of Pb adsorbed by rice husk as a function of varying pH. The experiment was performed in an orbital shaker by using 0.5 g of the adsorbent and shaking with 50 mL of lead solution for an hour. After the period of shaking, the amount of lead adsorbed per gram of material (q_{eq}) was calculated using equation 6 below.

$$Q_{eq} = (C_o - C_e) \times \frac{V}{M} \quad 6$$

Where: C_o and C_{eq} are the initial and equilibrium concentration of the solution respectively (mg/L); V = is the volume of the solution (mL), M = mass of the material (g)

Contact time

The effect of contact time was carried out at different time intervals of 10, 20, 30, 40, 50 and 60 min at room temperature using 50 mL of the solution. 1 g of the sample was measured into a beaker and placed in a thermostat water bath at 25°C, it was filtered and the absorbance was read using an atomic absorption spectrophotometer.

Concentration

A mass of 5 g of the adsorbent was measured and contacted with 50 mL of lead nitrate solution with concentration in the range of 4.0, 8.0, 12.0, 16.0 and 20.0 mg/L in a thermostat bath maintained at 30°C. The solution was filtered and the absorbance was read using an atomic absorption spectrophotometer.

Adsorbent dose

1.0, 2.0, 3.0, 4.0 and 5.0 g of the adsorbent was measured and contacted with 50 mL of lead nitrate solution on an orbital shaker for 1 hr. The solution was filtered and the residue concentration was determined using an atomic absorption spectrophotometer.

Results and Discussion

Physico-chemical characteristics were carried out on the adsorbent and are presented in Table 1. The pH of the activated rice husks was found to be 6.13. For most applications, pH of 5 – 6 is acceptable. The bulk density of the rice husk was determined to be 0.5 mg/L. The percentage moisture content was 5 %. The percentage ash content was 23 %. The percentage loss of attrition was 42 %. From the results of the physico-chemical characteristics obtained, the activated rice husks can serve as a good adsorbent for the removal of lead (II) ions from simulated wastewater.

Table 1: Physico-chemical parameters of rice husk

Parameter	Value
pH	6.13
Attrition (%)	42.00
Ash content (%)	23.00
Moisture content (%)	5.00
Bulk density (mg/L)	0.50
Iodine number (mg/L)	55.50

The removal of lead is dependent on its initial concentration. Fig. 1 shows the effect of initial lead concentration on the percent removal of lead ions. It was observed that the percentage removal efficiency increased steadily from 75.50 % to 79.92 % with an increase in initial lead concentration from 4 mg/L to 12 mg/L and takes a shorter time to reach equilibrium because of the fact that with increase in concentration, there will be increase in active adsorption sites and the process will increase. Hence, adsorption increases with increasing concentration (Amuda *et al.*, 2007; Okuman *et al.*, 1991).

The pH of solution has been identified as the most important variable governing metal adsorption. This is partly due to the fact that hydrogen ions (H⁺) themselves are strong competing ions that the pH of solution influences the chemical speciation of the functional groups on to the adsorbent surfaces. From Fig. 2, it can be observed that the removal of Pb(II) increases with increasing pH of solution and a maximum value was reached at an equilibrium pH of around 6.8 (Bernard and Jimoh, 2013). The adsorption was found to strongly dependent on the pH of the solution. it was found that the optimum pH for the adsorption Pb²⁺ ions was about 10 an alkaline pH. At lower pH, there was an excessive protonation

The Adsorption of Pb²⁺ Using Rice Husk as Adsorbent

of the active sites at rice husk surface and which often prevents the formation of links between Pb²⁺ ions and the active site. At moderate pH values of between 6-8, linked H⁺ is released from the active sites on the adsorbent, therefore the adsorbed amount of Pb ions increases. At higher pH values of above 10, the precipitation is dominant or both ion exchange and aqueous metal hydroxide formation may become significant mechanisms in the metal removal process a condition not often desirable as the metal precipitation usually lead to a misunderstanding for the adsorption capacity (Kumari *et al.*, 2009)

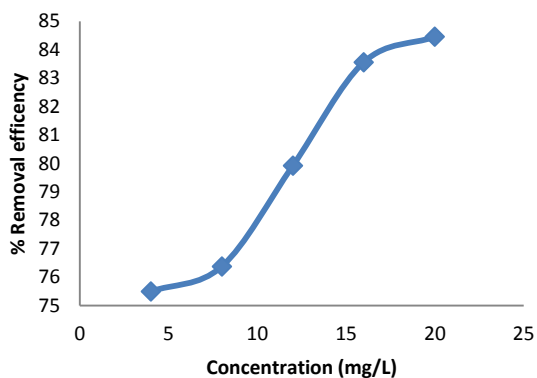


Fig. 1: Effect of concentration of the adsorbent

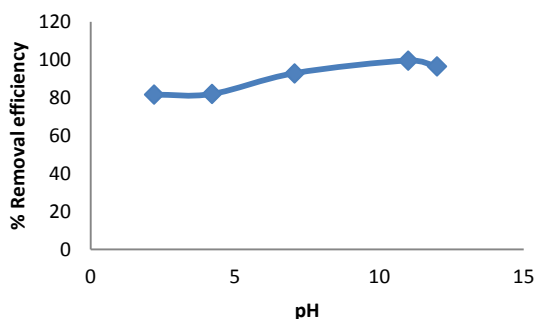


Fig. 2: Effect of pH of the adsorbent

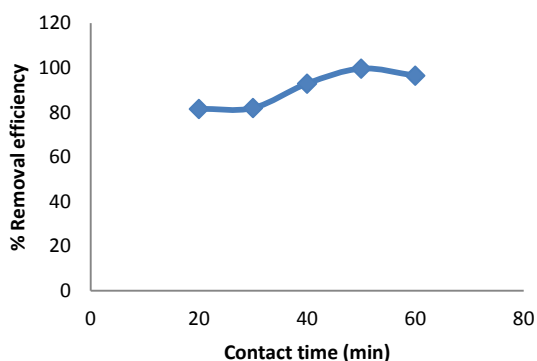


Fig. 3: Effect of Contact time of the adsorption

The variation between adsorption efficiency in terms of percentage removal of lead and contact time is shown in Fig. 3. It was observed that the percentage removal of lead is least (81.35 %) at 60 mins of contact time and highest (81.50 %) at contact period of 40 min. The adsorption of Pb(II) increased with increasing contact time from 81.47 % to 81.50 % at contact period of 20-40 min. The maximum rate of adsorption

took place within a contact time of 20-40 mins. This indicates that the rate of adsorption increases with increase in time. However, the rate of adsorption was found to be fairly constant and decreased beyond 40 min (between 50-60 min), which suggest that the adsorption process was fastest within the first 40 mins as the largest amount of Pb(II) was attached to the adsorbent within that period. Higher adsorption efficiency activated rice husks are attributed to available adsorption sites (surface functional groups) on the adsorbent surface as the time increases (Vieira *et al.*, 2014).

Dosage study was conducted at room temperature (33°C) by varying the amounts of dosage from 1 to 5 g/L. in this study, the initial concentration of Pb²⁺ ions was fixed as 50 mg/L. Fig. 4 shows that there was an increase in the uptake of Pb²⁺ as the dosage increases from 1 to 4 g/L a consequence of the limited number of the adsorbing species present for a relatively larger number of available surface sites on the adsorbent at higher dosages. It is a known fact that at higher dosages of the adsorbent there would be higher availability of exchangeable sites from metals ions uptake (Kumari *et al.*, 2009). The most significant increase (optimum) in adsorption was observed when the dose was increased from 3 to 4 g/L. further addition of the adsorbent beyond the optimum dose did not cause any significant change in the uptake, this is probably due to overlapping of adsorption sites a consequence of overcrowding of adsorbent particles. The optimum removal of Pb²⁺ (83.19%) was obtained in the adsorbent dose of 4 g/L (Dabrowski, 2001).

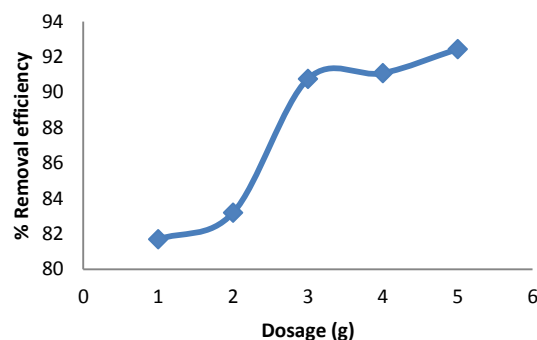


Fig. 4: Effect of dosage of the adsorbent

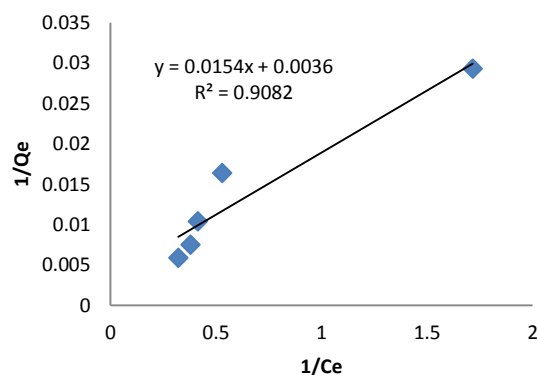


Fig. 5: Langmuir adsorption isotherm

The Langmuir and Freundlich isotherms constants are illustrated in Figs. 5 and 6, respectively. From Fig. 5 it was observed that the regression correlation coefficient (R²) of the Langmuir isotherm (R²= 0.9082) is greater than Freundlich isotherm (R²= 0.8664), thus the Langmuir isotherm is found to be the best fit isotherm (Oladoja *et al.*, 2008)

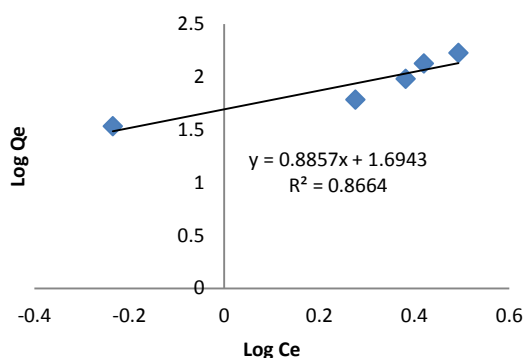


Fig. 6: Freundlich adsorption isotherm

Conclusion

In this study, batch adsorption experiment for the removal of Pb(II) ions from aqueous solution have been carried out using carbonised rice husk as a low cost, readily available adsorbent. The study shows that the activated rice husk is an effective adsorbent for the removal of Pb(II) ions from aqueous solutions. The highest percentage removal of Pb²⁺ was recorded at 84.45, 99.60, 81.50 and 92.44%. For concentration, pH, contact time, and adsorbent dose respectively, Equilibrium data was represented by Langmuir and Freundlich isotherms. The adsorption studies showed that Langmuir isotherm was found to provide the best fit of the experimental data. From this study, it can be inferred that rice husk, an abundantly available agricultural waste can be used as a low cost adsorbent. The higher adsorption capacity is favoured by higher number of active binding sites, improved ion exchange properties and enhancement of functional groups after chemical treatment. Pb(II) ions are effectively adsorbed from simulated wastewater by carbonized rice husk.

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Conflict of Interest

The Authors declare that there is no conflict of interest.

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