

Full Length Research Paper

Removal of copper (II), iron (III) and lead (II) ions from Mono-component Simulated Waste Effluent by Adsorption on Coconut Husk

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The use of coconut husk as a low-cost natural adsorbent for the removal of Cu (II), Fe (III) and Pb (II) from simulated industrial waste effluent was studied. Batch experiments were conducted to determine the effects of varying adsorbent loadings, pH, contact time, metal ion concentration and temperature of adsorption. The adsorption of Pb (II) was found to be maximum (94%±3.2) at pH 5, temperature of 100 °C, metal ion concentration of 30 ppm and contact time of 30 min. The adsorption of Cu (II) and Fe (III) were maxima (92%±2.8 and 94%±1.4) at pH range of 5 - 7, metal ion concentration of 50 ppm, temperature of 50 °C but at different times of 30 and 90 min respectively. 1 g of the adsorbent material was found to be optimal for all the metal ions; the Freundlich isotherm was found to be suitable for the adsorption of Cu(II) and Fe(III) while the Langmuir isotherm was found to be suitable for the adsorption of Pb(II). The adsorption kinetics was also studied.

Key words: Metal ions, adsorption, simulated effluent, coconut husk.

INTRODUCTION

Increased use of metals and chemicals in process industries has resulted in generation of large quantities of effluent that contain high level of toxic heavy metals and their presence pose environmental-disposal problems due to their non-degradable and persistence nature. In addition mining, mineral processing and extractive-metallurgical operations also generate toxic liquid wastes (Goyal and Ahluwalia, 2007; Olayinka et al., 2007; Olayinka et al., 2009). The removal of toxic heavy metal contaminants from aqueous waste streams is currently one of the most important environmental issues being investigated (Igwe et al., 2005; Mondal, 2009; Suthipong and Siranee, 2009). Adsorption on low cost-adsorbent for removal of toxic metals from wastewater has been investigated extensively. These materials include thioglycolic acid modified oil-palm (Akaniwor et al., 2007), wild cocoyam biomass (Horsfall and Spiff, 2004), brewery Biomass (Kim et al., 2005), sodium hydroxide modified

Lalang (*Imperata cylindrica*) leaf powder (Hanafiah et al., 2006).

The aim of this research was to investigate the use of unmodified coconut husk in the removal of metal ions from aqueous solutions. Coconut husk is a low cost adsorbent which is a waste material from coconut. Coconut is abundant in Nigeria and has a high sorption capacity due to its high tannin content. The study involved the examination of experimental conditions such as pH of the solution, temperature, contact time and adsorbent loading on the removal of Cu (II), Fe (III) and Pb (II) from aqueous solutions. The Freundlich and Langmuir adsorption isotherms were used to investigate the adsorption process. Kinetic study was also carried out to evaluate the order of adsorption.

MATERIALS AND METHODS

Adsorbent

The adsorbent was prepared as described by Feng and Ju-Chang (2009). The coconut husk was cut into small pieces and blended, extracted with hot water several times until the supernatant was

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colourless, and dried at 70 °C. The biomaterial was sieved to obtain a particle size range of 0.15 - 0.5 mm and this was stored in clean air-tight containers. The concentrations of Cu (II), Fe (III) and Pb (II) in the adsorbent were determined by placing 1g of the adsorbent in 10 ml de-ionized water for one hour with continuous agitation, after which it was centrifuged at 2000 rpm with a Remi R-8C laboratory centrifuge. The supernatant was carefully decanted into acid cleaned polyethylene containers and analysed using a flame Atomic Absorption Spectrophotometer (FAAS) Buck Scientific 310 VGP. The pH of the absorbent used was determined according to British Standard ISO 10390 (2005), using a Mettler Toledo pH meter and found to be 6.8.

Adsorbates

The solutions of Cu(II), Fe(III) and Pb(II) metal ions were prepared from analytical grade $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, FeCl_3 and $\text{Pb}(\text{NO}_3)_2$ respectively. 1,000 mg/L aqueous solutions (stock solutions) of these salts were prepared with de-ionized water in 1% HNO_3 solution and these stock solutions were diluted with de-ionized water to obtain the working standard solutions.

Adsorption experiments

For the adsorption experiment, the effect of adsorbent loading on the adsorption of the ions was investigated. 0.2 - 1.0 g of the adsorbent was weighed respectively into conical flasks. 20 ml of 10 mg/L solution of each of the metal ion solution was added and the mixture shaken with an IKA HS 260 basic reciprocating shaker at 150 rpm for 30 min.

The mixtures were centrifuged at 2,000 rpm for 30 min, the supernatant decanted and the metal ion content was determined using a Buck Scientific VGP 210 Flame AAS. The percentage adsorption was determined by Equation (1)

$$\frac{C_0 - C_a}{C_0} \times 100 \quad (1)$$

Where; C_0 = Initial concentration of solution, C_a = Concentration of the solution after adsorption.

To determine the effect of concentration on the adsorption of the metal ions, 1.0 g of the adsorbent, being the optimum adsorbent weight in the previous experiment was added to 20 ml each of varying concentrations (between 10 - 100 mg/L) of the metal ion solutions. The mixtures were shaken, centrifuged and the concentration of the metal ions adsorbed was determined. The effect of contact time was also investigated by adding 1.0 g of the adsorbent to 20 ml of 10 mg/L of Pb(II), 50 mg/L of Fe(III) and Cu(II) ions being their respective optimum adsorption concentrations; and shaking using varying contact times (between 30 – 180 min) and the percentage of adsorbed ions determined. The effect of pH on adsorption of the metals was investigated using 1.0 g of the adsorbent and 20 ml of 10 mg/L of Pb (II), 50 mg/L of Fe (III) and Cu (II) ions. The mixture was shaken for 30 min for Cu (II) and Fe (III) and 90 min for Pb (II), centrifuged and the amount of ion adsorbed was determined.

RESULTS AND DISCUSSION

Effect of adsorbent loading

Adsorbent dose is an important parameter in the

biosorption of metal ions from aqueous solution owing to its effect on the amount of metal ions removed per unit mass of the adsorbent (Miretzky et al., 2008). Figure 1 shows that increase in adsorbent loading increased the percentage removal of Pb(II) until mass of the adsorbent reached almost 1 g; this increase in percentage adsorption could be as a result of the number of available sites as this increased with the mass of the adsorbent. However, increase in adsorbent dosage improved the removal Cu (II) until the equilibrium was reached at 0.6 g after which further increase in mass did not bring about any increase in adsorption. At this stage, almost all the metal ions might have been removed such that further increase in the adsorbent dosage will not bring about appreciable adsorption. The removal of Fe (III) also followed the same pattern observed for Pb (II).

Effect of concentration on adsorption of the metal ions

Varying concentration of Pb(II) did not have any effect on its adsorption from solution as could be observed in Figure 2, as 90% of the ions was removed at 10 mg/L. 70% of Cu(II) and Fe(III) were removed at 30 mg/L of solution such that further increase in concentration did not bring about any appreciable adsorption.

Effect of Hydrogen ion concentration

The removal of all the three ions under consideration was affected by changes in pH as observed from Figure 3. Their removal was high under acidic conditions as close to 90% of Fe(III) was removed at pH 5; further increase in pH above 5 led to decreased adsorption of Fe(III). At pH >7, removal of all the ions remained almost constant. Generally, metal ions are more soluble at lower pH values and this enhances their adsorption as observed by Olayinka et al. (2009).

Removal of metal ions at higher pH values could be attributed to the formation of their hydroxides which results in precipitates, this is consistent with the observation of Lisa et al., 2004 and Xiao and Ju-Chang, 2009. Therefore, removal of metal ions at higher pH values is due to the formation of precipitates rather than adsorption. Kim et al. (2005) concluded that adsorption experiments for Cu and Pb are better performed at low pH to avoid precipitate formation.

Effect of contact time on adsorption of the metal ions

70% of Cu (II) was removed after 30 min and further increase in time resulted in the desorption of the metal ion from the adsorbent surface. However, the removal of Pb(II) and Fe(III) increased with and reached a maximum at 45 min after which further increase in time did not bring

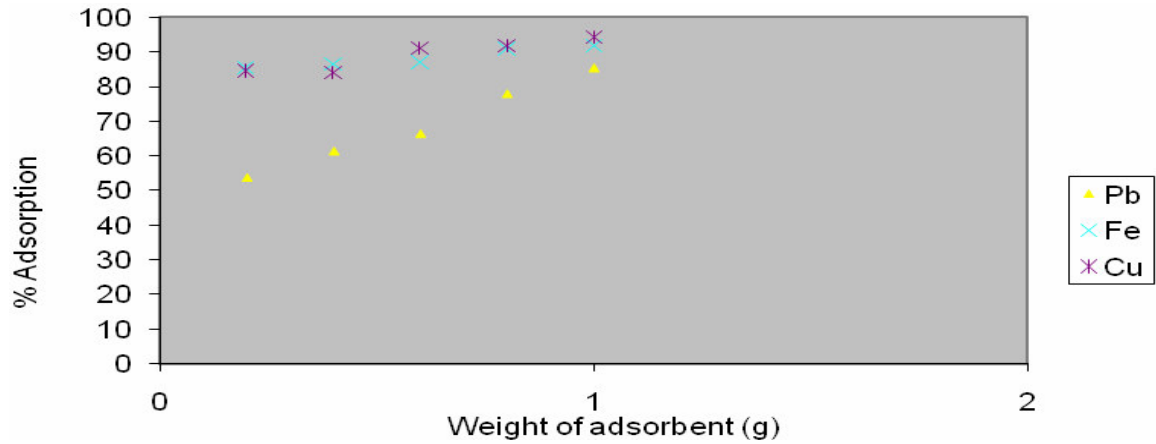


Figure 1. Effect of adsorbent loading on the adsorption of Fe, Cu and Pb.

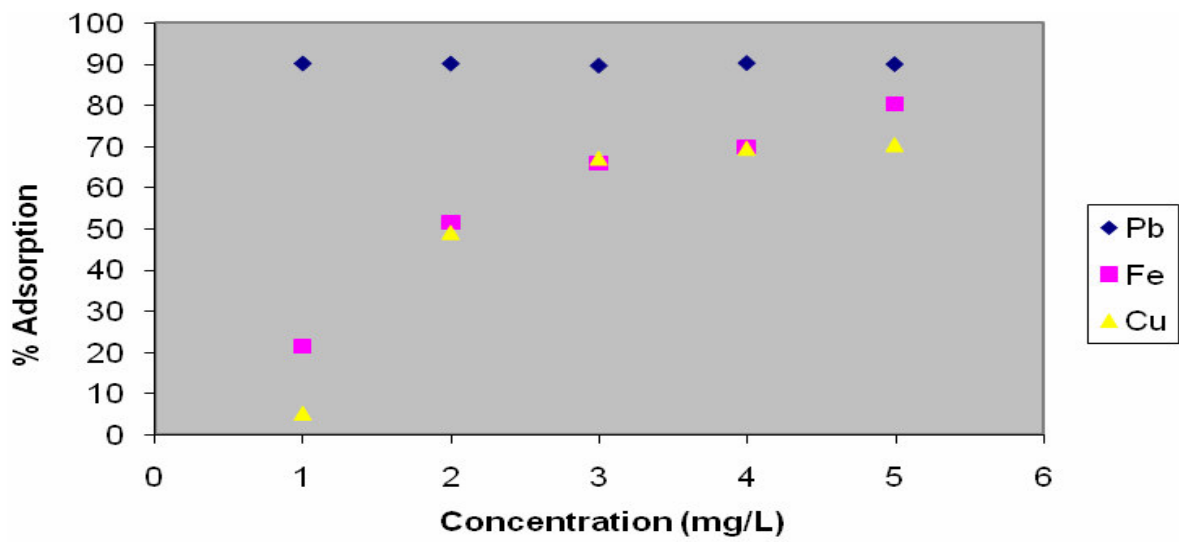


Figure 2. Effect of concentration on adsorption of Fe, Cu and Pb.

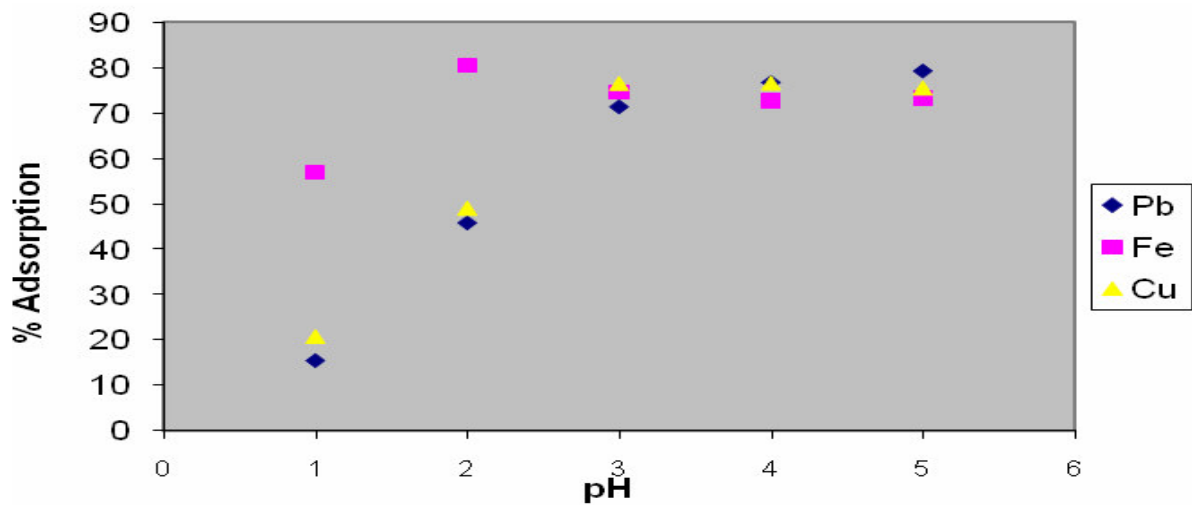


Figure 3. Effect of pH on adsorption of Fe, Cu and Pb.

Table 1. Adsorption isotherms.

Metal ions	Freundlich adsorption isotherm		Langmuir adsorption isotherm	
	Equation of graph	R ²	Equation of graph	R ²
Cu (II)	$y = 1.0018x - 0.1755$	1	$y = 1.197x - 10.68$	0.882
Fe (III)	$y = 0.9998x - 0.1762$	1	$y = 1.405x - 12.36$	0.905
Pb (III)	$y = 0.1279x - 0.4449$	0.5964	$y = 0.364x - 2.275$	0.987

about any improvement, but resulted in desorption of the ions from the adsorbent surface as shown in Figure 4.

Effect of temperature on adsorption of the metal ions

Increase in temperature did not bring about any increase in adsorption as shown in Figure 5 rather it decreased the adsorption as observed in the previous experiments. Increase in temperature leads to increase in kinetic energy of the metal ions and therefore weakening the forces of attraction between the metal ions and the adsorbent. Increase in temperature resulted in decreased adsorption for Cu(II) and Fe(III) and an increased adsorption for Pb(II) ions, indicating that the processes were exothermic and endothermic respectively (Jaman et al., 2009).

Sorption isotherms

Adsorption isotherms are important to describe the adsorption mechanism for the interaction of cations on the adsorbent surface. A variety of isotherm equations have been in use, some of which have a strong theoretical base and some being of mere empirical nature. In the present work, Langmuir and Freundlich isotherm models were tested with the experimentally obtained equilibrium data.

Langmuir isotherm

This isotherm is applicable when the extent of adsorbate coverage is limited to one molecular layer. This isotherm equation gives the fractional coverage (q) in the form of

$$Q = \frac{N_e}{Q_m} = \frac{bC_e}{1 + bC_e} \quad (2)$$

Where; b , is the adsorption equilibrium constant (1 mg^{-1}) that is related to the apparent energy of adsorption and Q_m is the quantity of adsorbate required to form a single monolayer on unit mass of the adsorbent (mg g^{-1}) and N_e is the amount adsorbed on unit mass of the adsorbent (mg g^{-1}) when the equilibrium concentration is C_e (mg L^{-1}). The equation can be linearized thus

$$\frac{C_e}{N_e} = \frac{1}{bQ_m} + \left(\frac{1}{Q_m}\right) C_e \quad (3)$$

A plot of $\left(\frac{C_e}{N_e}\right)$ vs C_e should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium (Gupta and Babu, 2009)

Freundlich isotherm

For adsorption from solution, the Freundlich isotherm is expressed by

$$q_e = K_f C_e^n \quad (4)$$

where, K_f is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent related to the bonding energy, and n is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient.

The Freundlich constants, K_f and n are obtained by plotting the graph between $\log q_e$ versus $\log C_e$. Experimental data was fitted to Langmuir and Freundlich models. From Table 1 it can be seen that the Freundlich isotherm represented the experimental data better than Langmuir for Cu (II) and Fe (III) ions adsorption with regression coefficient of 1 for each whereas in the Freundlich isotherm it was 0.882 and 0.905 respectively. The Langmuir model represents the experimental data better for Pb (II) ion with regression coefficient of 0.987 compared to 0.596 in Freundlich. This indicates that Pb (II) adsorption on coconut husk was monolayer adsorption.

Sorption kinetics

The mechanism of the adsorption of metal ions can be explained using pseudo first-order and second-order kinetic models.

Pseudo first-order kinetics

The non-linear form of pseudo first-order equation is

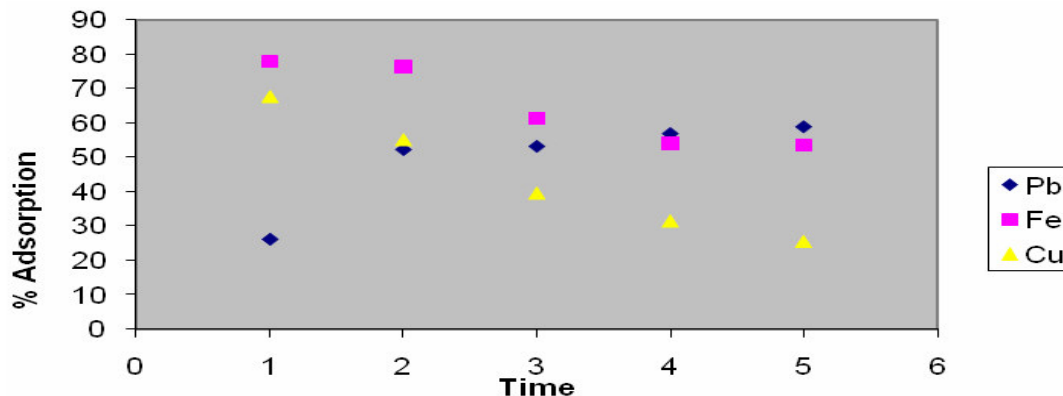


Figure 4. Effect of contact time on adsorption of Fe, Cu and Pb.

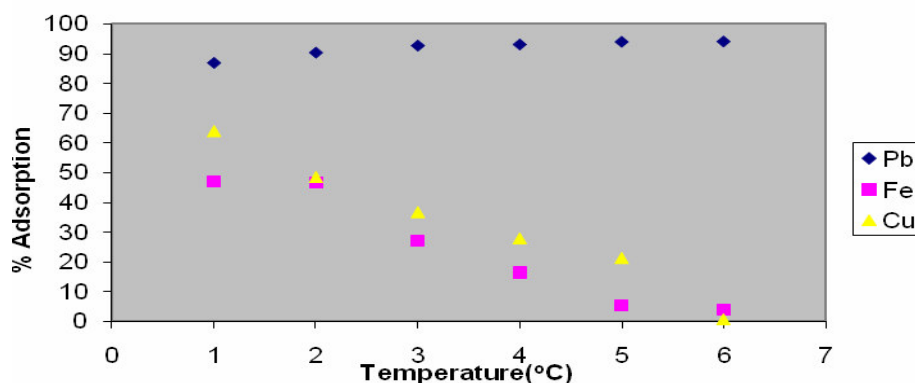


Figure 5. Effect of temperature on adsorption of Cu, Fe and Pb.

given by

$$\frac{dN_t}{dt} = k_{ad}(N_e - N_t) \quad (\text{Ho and Mckay, 1999}) \quad (5)$$

Where N_e and N_t are the amounts of metal ions adsorbed at equilibrium time and any instant of time (t) respectively. k_{ad} is the rate constant. The integrated rate law then becomes

$$\log(N_e - N_t) = \log N_e - \frac{k_{ad}t}{2.303} \quad (6)$$

Plot of $\log(N_e - N_t)$ vs t gives a straight line and the adsorption rate constant k_{ad} can then be computed.

Second-order kinetics

Applicability of the second order kinetics is tested with the rate equation

$$\frac{dN_t}{dt} = k_2(N_e - N_t)^2 \quad (7)$$

Where; k_2 is the second order rate constant. From the boundary conditions $t = 0$ to $t = t$ and $N_t = 0$ to $N_t = N_t$, the integrated rate law becomes

$$\frac{1}{(N_e - N_t)} = \frac{1}{N_e} + k_2 t \quad (8)$$

This can be written as,

$$\frac{t}{N_t} = \frac{1}{h} + \left(\frac{1}{N_e}\right)t \quad (9)$$

Where; $h = k_2 N_e^2$ and can be regarded as the initial sorption rate as $t = 0$. Under such circumstances, the plot of $\frac{t}{N_t}$ vs t should give a linear relationship, which allows computation of N_e , k_2 and h . (Ho and Mckay, 1999; Gupta and Babu, 2009).

Pseudo second order model represented the sorption of all the metal ions better than the first kinetic model as could be seen in Table 2. Copper (II) was most well fitted with regression coefficient of 1, followed by Fe (III) and Pb(II) ions with regression coefficients of 0.999 and

Table 2. Adsorption kinetics.

Metal ions	Pseudo first order kinetics	R ²	Second order kinetics	R ²
Cu (II)	$y = 0.005x - 0.337$	0.095	$0.105x - 0.121$	1
Fe (III)	$y = 17.14x - 10.00$	0.979	$0.109x - 0.216$	0.999
Pb (III)	$y = - 0.009x + 0.392$	0.253	$0.104x + 3.948$	0.910

0.910 respectively.

Conclusion

On optimizing all the conditions studied in this work, it was discovered that coconut husk can compete favorably well with known commercial adsorbents such as activated carbon and zeolite. The percentage removal of the ions was found to be 94% for Pb (II) and Fe (III) respectively and 92% for Cu (II) for 1 g of the adsorbent. The adsorbent could be recycled in acidic conditions and the feasibility of re-use possible. It can be concluded that coconut husk can be considered a low-cost alternative for removal of toxic metal ions from aqueous industrial effluents.

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