Cu and Zn removal by adsorption using ash from palm oil factory

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Abstract

The presence of heavy metals, such as Cu and Zn, in wastewater can be hazardous to the environment. From the view point of environmental protection, it is important that their concentrations be limited to permissible levels. Technologies for heavy metals removal include ion exchange, chemical precipitation, reverse osmosis, etc. which are often ineffective or expensive. Adsorption is commonly used for the removal of heavy metals from aqueous solutions. The process would be economical if the adsorbent is easily and cheaply available in abundance and that it requires minimal or no pre-treatment; for expensive pre-treatment procedures would add to the overall treatment cost. The present study focuses on Cu and Zn removal by adsorption using ash from a palm oil factory. The effect of agitation time, pH and adsorbent mass on the removal of Cu and Zn was studied and isotherms were generated to describe the removal of the metals. The results show that the ash was an effective adsorbent for the removal of Cu and Zn.

Keywords: adsorption, copper (Cu), zinc (Zn), oil palm ash

1.0 Introduction

Heavy metals contamination is common in water and wastewater. They are generally present in the wastewaters of various industries such as electroplating, metal finishing, leather tanning, paint manufacturing, steel fabrication and battery manufacturing. Heavy metals can cause serious water pollution and threaten the environment. It is therefore, essential to control the discharge of heavy metals into the environment. Increased attention is, therefore, being paid to the development of technologies for their removal from effluents before their discharge into water bodies and/or natural streams.

Many researchers have conducted studies on various methods for the removal of heavy metals from waters and wastewaters. Traditional technologies, such as ion exchange, chemical precipitation or reverse osmosis are often ineffective or expensive, particularly for the removal of heavy metal ions at low concentrations. Efficient and environmental friendly technologies are, therefore, needed to be developed to reduce heavy metal contents in wastewaters to acceptable levels at inexpensive costs (Saeed and Iqbal, 2003).

The present study focuses on the removal of copper (Cu) and zinc (Zn) from aqueous solutions. Cu is commonly found in industrial discharges e.g. circuit boards, metal surface treatments, mining operations, etc. Cu is an essential micronutrient, but at high doses it can cause anaemia, stomach & intestinal disorder and kidney & liver damage. Zn is also an essential micronutrient. It is extensively used in various industries; these include galvanisation and brass manufacture. An excess of Zn can cause health problems such as stomach cramps, skin irritation, nausea and anaemia. Very high levels of Zn can damage the pancreas, upset protein metabolism and cause arteriosclerosis. Hence it is necessary to reduce Cu and Zn from water/wastewater to acceptable levels.

The main objective of the present study was to determine the feasibility of using easily available low cost material i.e. ash from palm oil factory, as adsorbent in the removal of Cu and Zn from aqueous solutions. Adsorption involves the separation of a substance (adsorbate) from one phase (aqueous, in the present case) accompanied by its accumulation or concentration at the surface of another (adsorbent, solid phase in the present study). For an adsorption treatment process to be truly low cost not only should the adsorbent be easily and cheaply available in abundance but it should also require minimal or no pre-treatment; for expensive pre-treatment procedures would increase the overall treatment cost.

Recently researchers have concentrated their work on low cost, unconventional adsorbents for the treatment of wastewater. Agricultural wastes or derivatives have often been used as adsorbents in these studies. Some of the recently studied low cost adsorbents include saw-dust (Zarra, 1995), apple residues (Lee et al., 1998), leaves (Gardea-Torresday et al., 2002), ash (Isa et al., 2004), etc. The abundance and availability of agricultural by-products make them good sources of adsorbents (Bansod et al., 2003). An adsorbent with no pre-treatment was sought from the palm oil industry due to its abundance in Malaysia.

The objectives of the present study were to determine the agitation time and optimum pH for the effective removal of Cu and Zn from aqueous solutions. Isotherms were generated to obtain an adsorbent-adsorbate relationship (model) that would describe the removal of Cu and Zn.

2.0 Materials and Methods

2.1 Materials

The ash used as adsorbent in the present study was collected from a local palm oil factory. It was dried at 105 °C over night before the tests. Copper sulphate ($CuSO_4.5H_2O$) and zinc sulphate ($ZnSO_4.7H_2O$)

were dissolved in distilled water to prepare the test solutions of approximately 20 mg/l adsorbate concentration. The exact concentrations of Cu and Zn in the solutions were determined before each set of adsorption tests. Different amount of adsorbents were added to the test solutions and subjected to batch adsorption tests with the help of an orbital shaker.

2.2 Test for Agitation Time

250 ml Erlenmeyer flasks with 100 ml of adsorbate (Cu or Zn) solution were prepared. Initial concentrations of samples were measured. 500 mg of adsorbent (ash) was measured and added to each of the conical flasks. The flasks were then agitated at 350 rpm using an orbital shaker. They were removed from the shaker for residual adsorbate analysis one after the other at 10, 20, 30, 40, 60, 80, 100 and 120 minutes. The samples were filtered and the final adsorbate concentrations were measured.

2.3 Test for Optimum pH

250 ml Erlenmeyer flasks with 100 ml of adsorbate (Cu or Zn) solution were used. The samples were adjusted to pH 4-9 by using 0.1 N sodium hydroxide (NaOH) or 0.1 N hydrochloric acid (HCl). 500 mg of ash was measured and added in each flask. The flasks were agitated at 350 rpm for the selected contact time. Then the samples were filtered and the final adsorbate concentrations were measured.

2.4 Isotherm Generation

250 ml Erlenmeyer flasks with 100 ml of adsorbate (Cu or Zn) solution were arranged. All samples were adjusted to the optimum pH. 100 to 1,000 mg of ash was measured and added to the samples. The conical flasks were agitated at 350 rpm for the selected contact time. The samples were filtered and the final adsorbate concentrations were measured.

2.5 Analytical Techniques

Cu and Zn concentrations of the samples were measured using a Direct Reading Spectrophotometer (DR2010) after filtration with Whatman GF/C glass fibre filters. pH was measured with a pH-meter.

3.0 Results and Discussion

3.1 Test for Agitation Time

Agitation or equilibrium time plays an important role in the adsorption process. Selvi et al. (2001) stated that the equilibrium time was independent of initial metal concentration. In this study, the agitation time was varied from 10-120 minutes in order to observe the amount of adsorbate adsorbed on 500 mg of ash from 100 ml of aqueous copper sulphate and zinc sulphate solutions. The results are shown in the following figure (Figure 1).

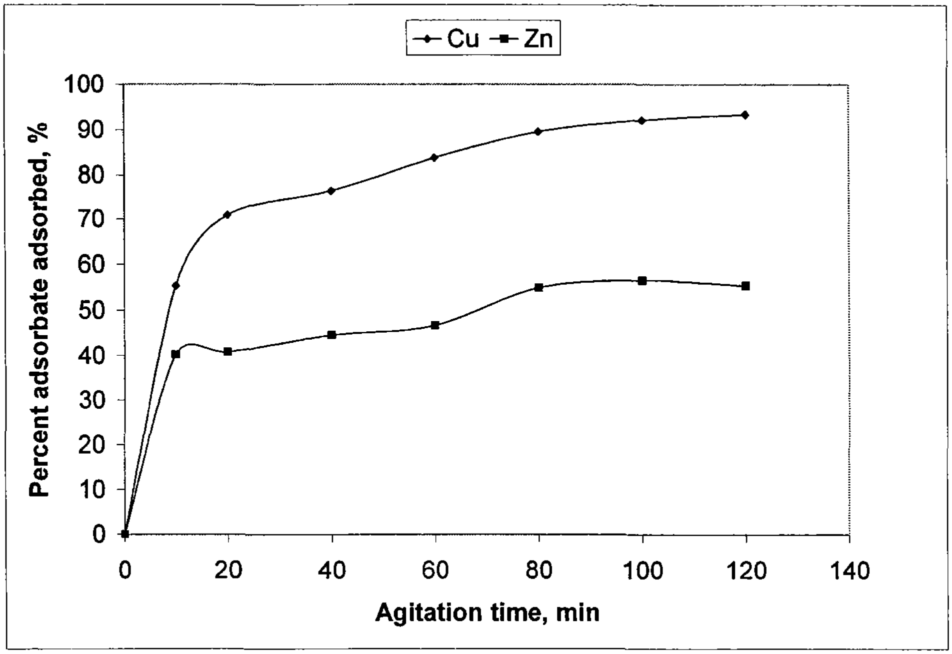


Figure 1: Agitation time

From Figure 1, it is noted that there was a sharp increase in the amount of Cu and Zn adsorbed during the first 20 minutes of agitation. Thereafter, the rate and amount of Cu and Zn adsorbed decreased. The processes were essentially complete after 120 minutes for Cu and 90 minutes for Zn. Hence for the subsequent studies the agitation times were chosen as 120 minutes and 90 minutes for Cu and Z respectively.

3.2 Test for Optimum pH

pH is also an important parameter that controls the adsorption of metal ions. Therefore, a set of experiments was conducted to determine the optimum pH for Cu and Zn removal. Various researchers have shown that different metals require different pH levels for their effective removal by adsorption using specific adsorbents. Kadirvelu and Namasivayam (2002) stated that the maximum removal of cadmium, Cd (II), using coconut coir pith was attained over the pH range 5-10. Selvaraj et al. (2003) found 93% removal of chromium, Cr (VI) by distillery sludge at pH 2-3 and that, when the pH was increased above 3 there was a reduction in adsorption. In another research, the maximum adsorption occurred at pH below 5 for chromium, Cr (VI), using rice husk activated carbon (Guo et al., 2002).

In this study, the pH was varied from 4-9 to determine the optimum values for Cu and Zn adsorption on ash. The results are shown in Figure 2. Maximum Cu adsorption occurred at pH 6 and hence this was taken as the optimum pH for subsequent Cu adsorption studies. For Zn, the removal increased rather gradually from pH 4 to 7, after which it increased sharply. As metals tend to precipitate at elevated pH levels, it was suspected that the observed sudden high removal rates may have been a result of metal precipitation as well. A separate experiment confirmed that appreciable amount of Zn was precipitated at pH above 7. Hence, pH 7 was chosen as the optimum pH for Zn adsorption in this study.

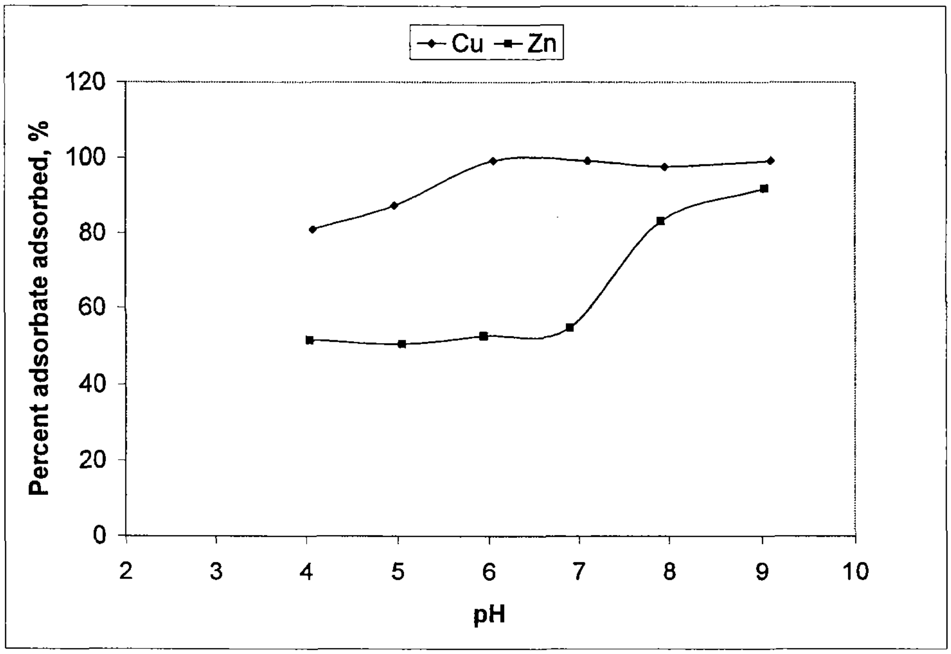


Figure 2: Optimum pH

3.3 Isotherm Generation

Isotherms are mathematical equations used to describe the adsorption behaviour of a particular adsorbent-adsorbate combination. They model the adsorption behaviour and help in calculating the adsorption capacity of materials. Three commonly used adsorption equations are the Langmuir, Freundlich, and Brunauer-Emmett-Teller (BET) isotherms. The mathematical expressions representing these isotherms and their corresponding rearranged forms to obtain linear plots are as follow:

Langmuir equation,

$$\frac{x}{m} = \frac{abC}{1+aC} \qquad (1)$$

$$\frac{1}{(x/m)} = \frac{1}{abC} + \frac{1}{b} \quad (2)$$

Freundlich equation,

$$\frac{x}{m} = KC^{1/n} \quad (3)$$

$$\log\left(\frac{x}{m}\right) = \frac{1}{n}\log C + \log K \quad (4)$$

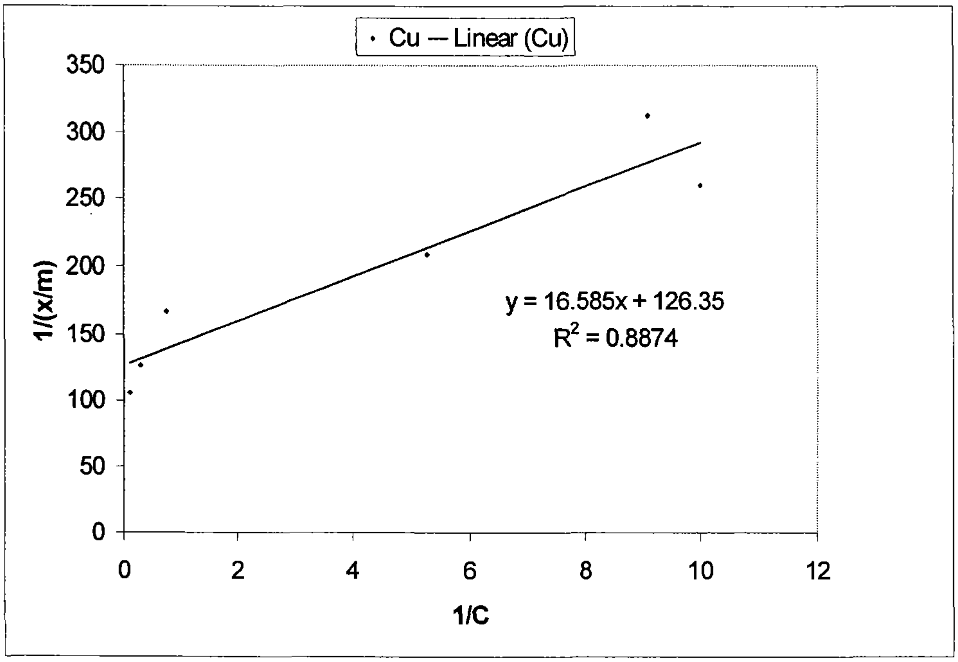
BET equation,

$$\frac{x}{m} = \frac{ACx_m}{(C_s - C)\left[1 + (A-1)\frac{C}{C_s}\right]} \quad (5)$$

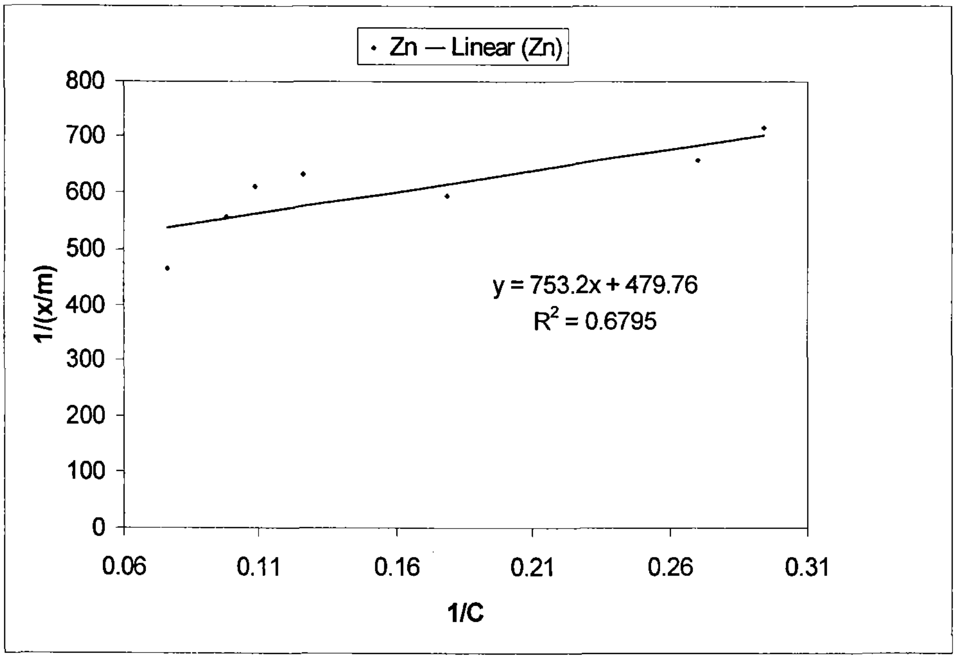
$$\frac{C}{(C_s - C)\frac{x}{m}} = \frac{1}{Ax_m} + \frac{A-1}{Ax_m}\left(\frac{C}{C_s}\right) \quad (6)$$

where x = mass of material adsorbed (mg)
m = mass of adsorbent (mg)
C = concentration of adsorbate in solution after adsorption is complete (mg/l)
C_s = saturation conc. of adsorbate (mg/l)
x_m = amount of adsorbate adsorbed in forming a complete monolayer (mg/g)
a, b, K, n and A = constants

Figures 3, 4 and 5 show the Langmuir, Freundlich and BET plots respectively as obtained in this study. It appears from the plots that Cu and Zn adsorption by the ash is best represented by the BET isotherms (highest R^2 values for both Cu and Zn). The parameter 'A' in the BET equation is a constant to describe the energy of interaction between the solute and the adsorbent surface (Benefield et al., 1982). A closer look of Figure 5 shows that the BET isotherms yielded negative values of 'A' for both Cu and Zn. The use of BET equation to represent Cu and Zn adsorption in the present study was therefore discarded. Hence it can be concluded that, for the present study, adsorption of Cu and Zn by the ash can be represented by Freundlich isotherms.

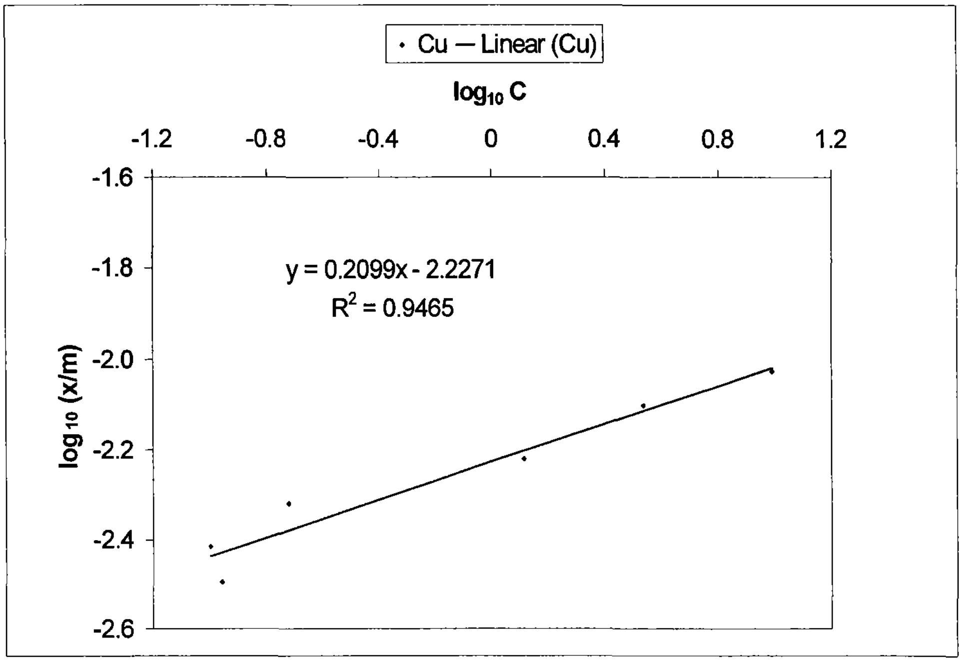


(a) Cu adsorption

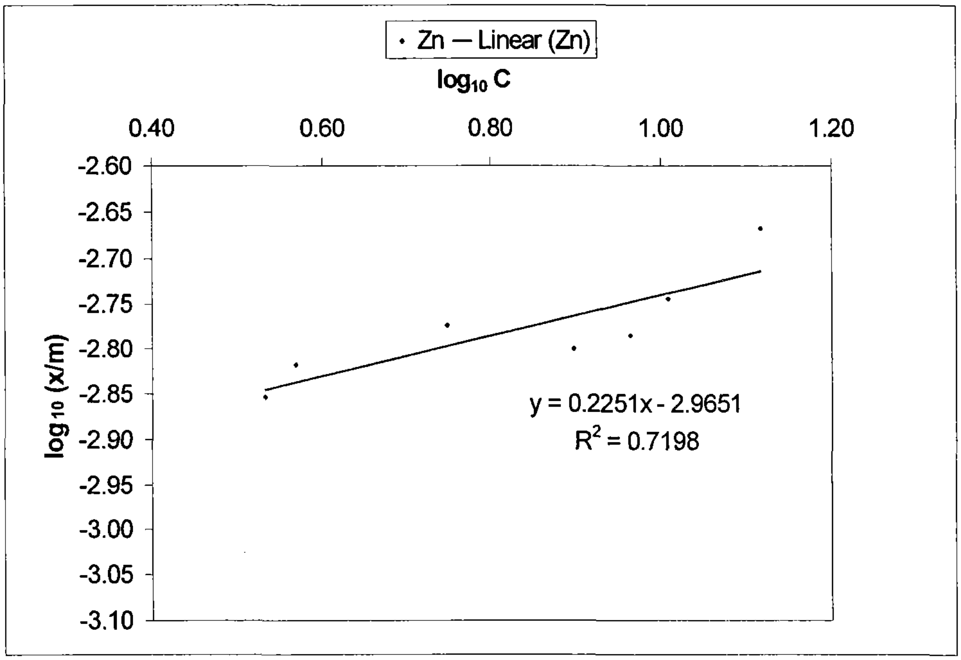


(b) Zn adsorption

Figure 3: Langmuir isotherms

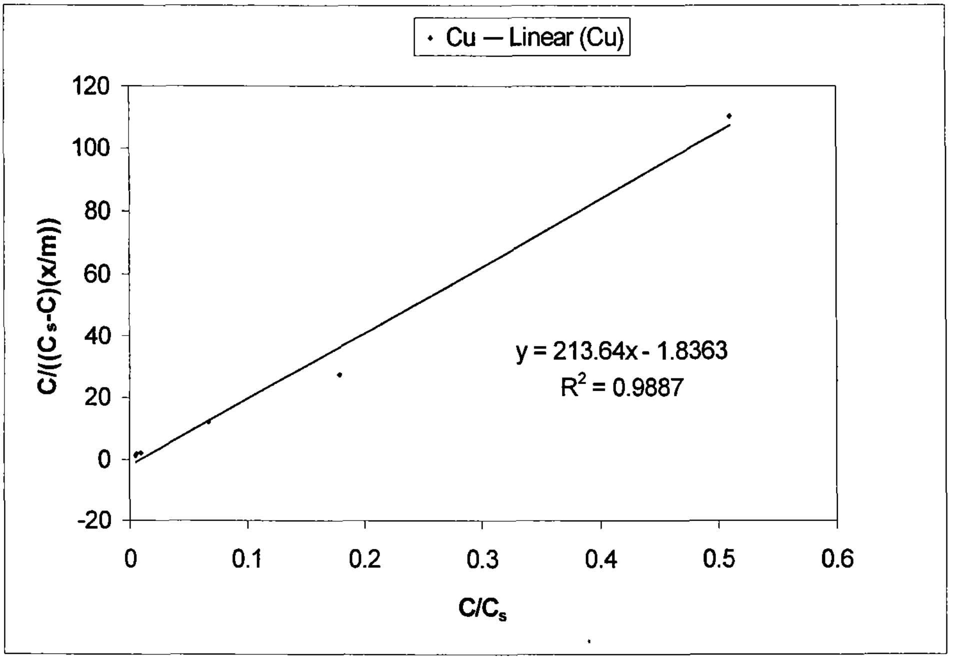


(a) Cu adsorption

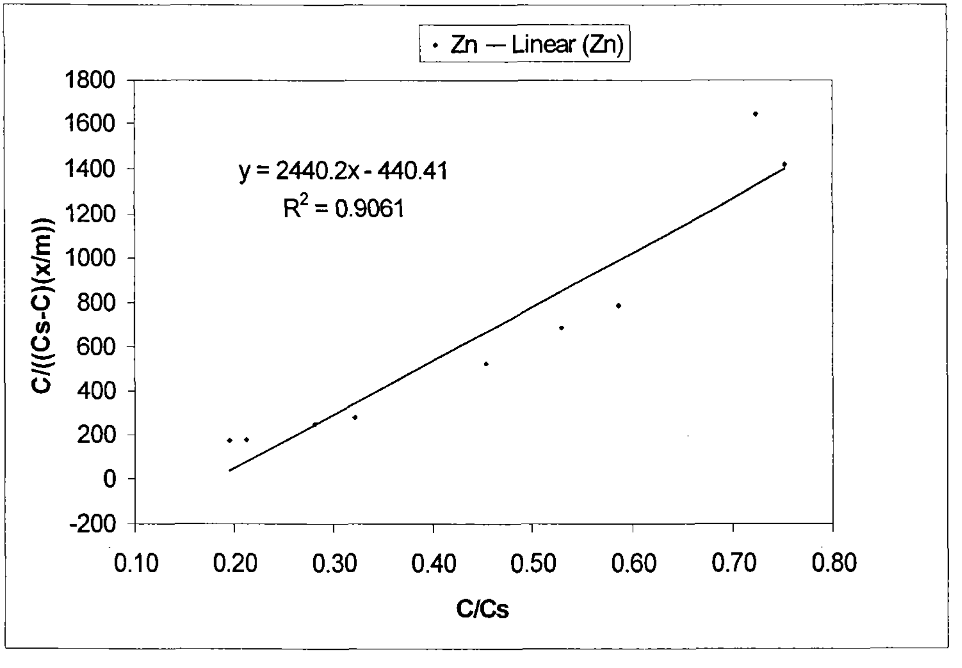


(b) Zn adsorption

Figure 4: Freundlich isotherms



(a) Cu adsorption



(b) Zn adsorption

Figure 5: Brunauer-Emmett-Teller (BET) isotherms

Comparing the equations of the best fit lines in Figure 4 with the Freundlich isotherm expression i.e. equation (4) above and solving for the constants yields:

For Cu adsorption: $n = 4.7642$ and $K = 5.9279 \times 10^{-3}$

For Zn adsorption: $n = 4.4425$ and $K = 1.0837 \times 10^{-3}$

Thus the Freundlich adsorption expressions for Cu and Zn removal under the present test conditions are given by:-

For Cu adsorption,

$$\frac{x}{m} = 5.9279 \times 10^{-3}\, C^{0.2099}$$

For Zn adsorption,

$$\frac{x}{m} = 1.0837 \times 10^{-3}\, C^{0.2251}$$

The above equations show that whereas the Freundlich intensity parameter (1/n) values are comparable for the two cases, the Freundlich capacity factor (K) is distinctly higher for Cu.

4.0 Conclusions

The following conclusions can be drawn from the present study:

- Ash from palm oil industry is an effective adsorbent for Cu and Zn. Its affinity for Cu is highe than that for Zn.
- Suitable agitation times for Cu and Zn adsorption are 120 minutes and 90 minutes respectively.
- The optimum pH for Cu and Zn adsorption are 6 and 7 respectively.
- Cu and Zn adsorption are well described by the Freundlich isotherm.

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