

EXTENDED LANGMUIR MODEL FITTING TO THE FILTER COLUMN ADSORPTION DATA OF COPPER AND ZINC

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Abstract

This study involved laboratory scale experiments to test the efficiency of washed quarry dust (WQD) in the removal of heavy metals such as zinc and copper from wastewater of electroplating industry, before their safe disposal into public sewer. The washed quarry dust collected from Aristocrust quarries in Mlolongo was prepared and characterized for various physiochemical properties. The wastewater samples were collected from Master Platers Ltd, located in Nairobi's industrial area. To determine the heavy metals' removal efficiency of WQD, samples of wastewater were treated by column adsorption experiments. The concentration (C_0) of heavy metals in the industrial effluent were analyzed and compared to that treated with the adsorbent. The heavy metals analyzed were zinc, copper, cadmium, chromium, arsenic, lead and iron. It was established that zinc and copper concentrations were high in the industrial effluents while the concentrations of other metals were within the requirements of the Kenya Standard; KS1966-2:2007. Wastewater samples of known heavy metal concentrations (C_0) were passed through the 0.5, 0.75 and 1 M columns at varying flow rates of 6, 9 and 12 ml/min. Leachate samples collected at different depths of WQD column were analyzed for concentrations of zinc and copper ions using atomic absorption spectrometer. The removal efficiency was around 94% and 92% for zinc and copper respectively using column depth of 1 M at a flow rate of 12 ml/min.

The adsorption model adopted was described by extended Langmuir adsorption isotherm since the adsorption process involved competitive adsorption in the presence of more than one heavy metal in the wastewater. The model represented the data well when adsorption density curves were plotted for model and laboratory test results. From the column experimental results, washed quarry dust filtration has a high potential to be used in the removal of heavy metals from industrial wastewater. Unlike other adsorbents, WQD is readily available, efficient and cost effective.

Key words: adsorbent, copper, heavy metals, treatment, wastewater, washed quarry dust (WQD), zinc

1.0 Introduction

A number of industrial processes especially metal processing industries, discharge effluents with high quantities of toxic metals. This leads to the contamination of freshwater and marine environment (Low *et al.*, 1995). Since most of heavy metals are non-degradable, their concentrations must be reduced to acceptable levels before discharging wastewater into the environment. According to World Health Organization (WHO) the metals of most immediate concern are chromium, zinc, iron, mercury and lead (WHO and ILO, 1995) because they are toxic to human health.

By using efficient and cheaper methods of heavy metal removal, the treated wastewater can be made available for re-use in industries. Adsorption method has been used in the removal of heavy metals from portable water and wastewater. It is an effective purification and separation technique used in the industry for the treatment of wastewater (Aksu, 2001). Adsorption is a term commonly used for several different processes involving physical as well as chemical interactions between the solid surfaces of a substance and dissolved metal ions. Thus, adsorption in general can be influenced by changes in hydro chemical parameters such as pH and flow-rate (Abdus-Salam *et al.*, 2005).

Adsorption of the heavy metals from solution has been studied using naturally occurring minerals. Pyrolusite has been used for adsorption of Pb, Zn and Mg from their aqueous solution (Ajmal *et al.*, 1995). Zeolites have been used for removal of heavy metals from wastewater (Yuan *et al.*, 1999). Another adsorbent that has been used for the removal of heavy metals is carbonaceous material developed from fertilizer waste slurry (Srivestava *et al.*, 1989).

In recent years, many low-cost adsorbents including agricultural and waste by-products such as soybean and cottonseed hulls, rice straw, timber sawdust and sugarcane bagasse have also been tested in batch and fixed bed adsorption systems (yu *et al.*, 2001, Badmus *et al.*, 2007). Other low cost adsorbents that have been used include soils (Campbell and Davies, 1995) and activated carbons from date pits (Girgis and Hendawy, 1997). Some researchers reported the adsorption of lead on oxide of silicon, manganese, aluminium (Bilinshi *et al.*, 1977), bentonite (Kozar *et al.*, 1992), hydrated titanium dioxide (Abe *et al.*, 1989), modified silica gel (Mareira *et al.*, 1990), sawdust (yu *et al.*, 2001), lateritic minerals (Ahmad *et al.*, 2002), and carbon (Qadeer and Akhtar, 2005).

The aim of this study was to find out the effectiveness of WQD in the removal of heavy metals from electroplating wastewater. WQD has large surface area and is uniform in its physical and chemical properties.

2.0 Methodology

2.1 Quarry Dust Characterization and Preparation

Samples were collected from aggregate and machine cut building stone quarries in Mlolongo, Kitengela and Juja in Kenya. The elemental analysis of the samples was done using the X-ray fluorescence (XRF). Quarry dust of size 0-3 mm sampled from aggregate quarry factory was washed to remove all impurities such as clay and silt. It was rinsed using distilled water, dried in the sunlight and then dried in the oven at 110°C for 24 hours to reduce the moisture content.

2.2 Wastewater Sampling and Analysis

Industrial effluent from electroplating factory was collected at the point of discharge into the public sewerage system. Jerrycan containers used for sample collection were pre-treated by washing them with dilute hydrochloric acid, rinsed with distilled water and allowed to dry. At the collection point, containers were rinsed with samples twice and then filled with the sample. The containers were corked tightly and samples taken to the laboratory for treatment and analysis.

The pH meter was used to determine the pH of the wastewater at the point of collection. To determine the heavy metal concentration, 50 ml of the filtered samples was digested with concentrated HNO₃ by adding HNO₃ every time the sample volume is less than 10ml till white smoke was released. Thereafter, the digested sample was topped upto 50ml with distilled water and the concentration of heavy metals; zinc, copper, cadmium, chromium, arsenic, lead and iron were determined. All the tests were done according to standard methods (APHA, 1995) and used atomic absorption spectrophotometer: model Phillip PU 9100. Three sets of samples were analyzed and mean concentration used.

2.3 Effect of Column Depth and Effluent Flow Rate

Sampling points were located at 0.5, 0.75 and 1 m of the column height. WQD was put in the column up to 1 m bed height. Once the WQD was packed inside the column, the columns were fully filled with deionised water for 24 h to 'wet' the column. This was important to ensure that all air was expelled between and within the WQD particles before the experiment began. If there was an air pocket inside the column, channeling and air entrapment would occur which would lower the bed performance. The wastewater sample pH was adjusted to 7 ± 0.2 by use of 0.1N HCL and 0.1N NaOH. After flushing the column with deionized water, the wastewater was then passed up the column by putting it into the holding tank and passing it through the inlet to the column via gate valve. This avoided channeling due to gravity and enhanced uniform distribution of solution throughout the column. Gate valve was tuned to give the correct flow rate which was maintained constant during the experiment. Periodic flow rate checks were carried out by physically collecting samples of solution at the outlet for a given time and

measuring it. The linear flow rates used on each column were varied to 1.2, 1.8 and 2.4 l/min/m² (6, 9, 12ml/min respectively).

Leachate samples of treated wastewater were collected through the outlets located at 0.5, 0.75 and 1 metre of the column. The samples were filtered through Whatman No.44 filter paper and digested with concentrated HNO₃ by adding HNO₃ every time the volume of the sample is less than 10 ml until white smoke was released. The digested samples were topped up to the initial volume using distilled water. The equilibrium concentrations (C_e) of zinc and copper were determined using AAS. The adsorption column height which gives the highest heavy metal removal efficiency at a given flow rate was selected for application in the treatment of wastewater.

2.4 Determination of Adsorption Capacity of WQD

The determination of adsorption capacity of WQD assists in the determination of the time for replacement or regeneration of WQD. WQD was put in the column up to 1 m bed height. Once the WQD was packed inside the column, the column was fully filled with deionized water for 24 hours to 'wet' the column. The wastewater sample pH was adjusted to 7±0.2 by use of 0.1N HCL and 0.1N NaOH. After flushing the column with deionized water, wastewater was then passed up the column. Flow rate of 12 ml/min was used as determined in experiment above. 50 ml leachate samples were collected through the 0.5, 0.75 and 1 metre outlets at intervals of 60 minutes. The flow of wastewater was continuous until the leachate concentration (C_e) of zinc and copper collected at the outlets was equal to wastewater concentration C₀. The samples were filtered through Whatman No.44 filter paper. The samples were then digested with concentrated HNO₃ by adding HNO₃ every time the volume of the mix is less than 10 ml until white smoke was released. The digested samples were topped up to initial volume using distilled water. The equilibrium concentrations (C_e) of zinc and copper were determined using AAS. Preference was given to testing the samples immediately after adsorption for more reliable analytical results. However in cases where the samples' heavy metal concentrations were not determined immediately, they were preserved by acidifying them with concentrated nitric acid (HNO₃) to pH less than 2. The samples were kept and tested at room temperature.

3.0 Results and Discussion

3.1 Quarry Dust Characterization

Table 1 shows the results of elemental analysis of the quarry dusts. It was observed that quarry dusts from aggregate and building stone quarries are predominantly siliceous, followed by the insoluble oxides of aluminium, iron, manganese, calcium, magnesium and alkaline salts (sodium oxide and potassium oxide). However quarry dusts from aggregate quarries have higher contents of silica and aluminum oxide.

Table 1: Characterization of washed quarry dust

| Parameters/elements | Sample from aggregate quarries | Sample from building stone quarries |
|--------------------------------|--------------------------------|-------------------------------------|
| | Contents (%) | Contents (%) |
| SiO ₂ | 53.1 | 62.5 |
| Al ₂ O ₃ | 20.4 | 11.42 |
| Na ₂ O | 8.4 | 5.8 |
| K ₂ O | 5.8 | 4.57 |
| Fe ₂ O ₃ | 5.1 | 6.22 |
| MnO | 1.9 | 0.22 |
| MgO | 0.89 | 0.46 |
| CaO | 0.85 | 0.71 |
| LOI | 4.09 | 8.65 |

Samples from machine cut building stones are grey silica whose bulk density is 1.5. Quarry dust samples from aggregate quarries have a bulk density of 2.4 g/cm³. Quarry dusts from aggregate quarry are crushed from pyroclastic type of rock and are better adsorbent than building stone quarry dusts due to higher content of alumina element. Quarry dusts from building stone quarries were not used in the treatment of industrial effluent due to their low alumina content and inability to be crushed into sizes 0-3 mm.

3.2 Industrial Effluent pH and Heavy Metal Concentration

Table 2 shows industrial effluent pH and concentrations of various heavy metals in the effluent. The test results indicate that wastewater is acidic with an average pH of 2. It was established that zinc and copper are the major polluting element in the effluent.

Table 2: Industrial effluent pH and heavy metal concentration

| Sample s | pH | Heavy metal's effluent concentration, C _o in mg/l | | | | | | |
|----------|----|--|--------|---------|----------|---------|------|------|
| | | Zinc | Copper | Cadmium | Chromium | Arsenic | Lead | Iron |
| 1 | 2 | 41.09 | 10.08 | 0.03 | 0.03 | 0.01 | 0.03 | 0.04 |
| 2 | 2 | 40.15 | 9.81 | 0.03 | 0.03 | 0.01 | 0.02 | 0.03 |
| 3 | 2 | 38.32 | 9.69 | 0.03 | 0.02 | 0.01 | 0.02 | 0.03 |
| 4 | 2 | 36.05 | 9.45 | 0.01 | 0.02 | 0.01 | 0.01 | 0.03 |
| 5 | 2 | 35.07 | 9.32 | 0.01 | 0.02 | 0.01 | 0.01 | 0.03 |

Zinc concentration varied from 41.09mg/l to 35.08mg/l while that of copper varied from 10.08mg/l to 9.32mg/l. Other elements such as cadmium, chromium, arsenic, lead and iron contributed insignificant amounts (below 0.05mg/l) which are within

the requirements of the Kenya Standard KS 1966-2:2007, Kenya Standard Specification Effluent tolerance limits, Part 2: Effluent discharged into public sewers. The variation in the concentration of zinc and copper was attributed to metals used for electroplating in the industry. Zinc and copper were selected for adsorption study due to their high concentration unlike other metals which were within the requirements of the Kenya Standard.

3.3 Calculation of Heavy Metal ions Adsorbed

The amount of metal ions adsorbed was determined using a mass balance equation:

$$q = \frac{v}{m} (C_o - C_e) \dots\dots\dots (1)$$

Where

- q is the metal uptake (mg/g).
- C_o is the initial metal concentration of the wastewater sample (mg/l)
- C_e is the equilibrium metal concentration of the wastewater leachate collected at the outlet, (mg/l).
- V is the volume (l) of the treated wastewater collected at the column outlet after sampling time interval.
- m is the mass of adsorbent used in the column (g).

The definition of removal efficiency is given by equation 2 below:

$$\text{Removal efficiency (\%)} = \left[\frac{(C_o - C_e)}{C_o} \right] * 100 \dots\dots\dots (2)$$

- C_o is the metal concentration in the wastewater sample before treatment (mg/l)
- C_e is the metal concentration in the wastewater sample after treatment (mg/l)

3.4 Effect of Adsorption Bed Depth and Effluent Flow Rate

Adsorption bed depth determines the amount of WQD used. Shorter bed depth means smaller amount of WQD thus availability of less adsorption sites.

3.5 Effect on Zinc

Table 3 shows the effect of flow rate and column depth on zinc ions removal efficiency. At bed depth of 0.5 m, the percentage removal of zinc decreases from 93.37% to 67.88% as flow rate is increased from 6 to 12 ml/min. This can be attributed to reduction in contact time from 120 minutes to 60 minutes.

Table 3: Effect of effluent flow rate and column depth on the removal efficiency of zinc ions

| Bed depth (m) | Zinc concentration (mg/l) | | | Zinc percentage removal (%) | | |
|---------------|---------------------------|------------|-------------|-----------------------------|------------|-------------|
| | 6 (ml/min) | 9 (ml/min) | 12 (ml/min) | 6 (ml/min) | 9 (ml/min) | 12 (ml/min) |
| 0.5 | 2.33 | 7.30 | 11.26 | 93.37 | 79.20 | 67.88 |
| 0.75 | 2.09 | 2.15 | 7.27 | 94.04 | 93.86 | 79.26 |
| 1 | 1.88 | 1.81 | 1.81 | 94.65 | 94.83 | 94.83 |

At bed depth of 0.75 m, the percentage removal of zinc decreased from 94.04% to 79.26% as flow rate increased from 6 to 12 ml/min. This can be attributed to reduction in contact time from 180 minutes to 90 minutes as flow rate increased from 6 to 12 ml/min.

At bed depth of 1 m, there was negligible change on the percentage removal of zinc. The change in removal efficiency increased from 94.65% to 94.83% as flow rate increased from 6 to 12 ml/min.

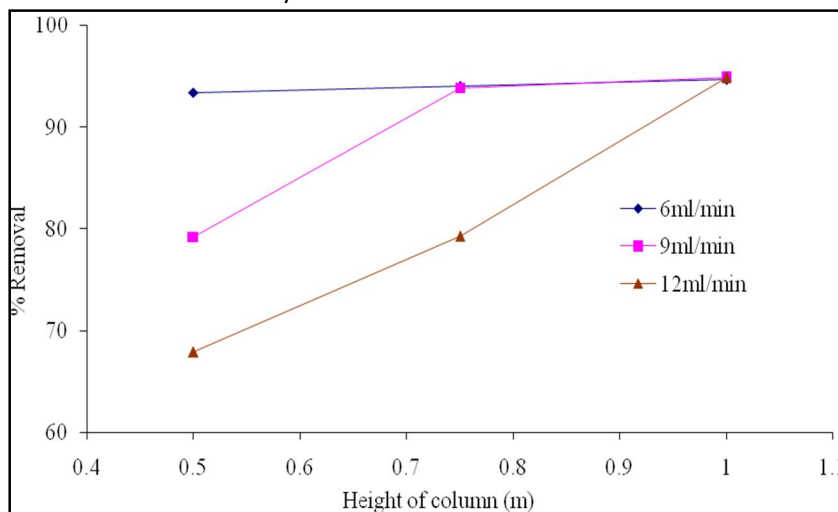


Figure 1: Effect of effluent flow rate and column depth on the removal efficiency of zinc ions

Figure 1 shows the effect of influent injection rates at various column depths. It was observed that zinc removal efficiency increased with increase in column depth at a given flow rate. At sample flow rate of 12 ml/min, the percentage removal increased from 68% to 95% as the adsorption column depth increased from 0.5 m to 1 m. The time taken to sample leachate at column depth 0.5, 0.75 and 1 m is 60, 90 and 120 minutes respectively.

At sample flow rate of 9 ml/min, the percentage removal increased from 79% to 95% as the adsorption column depth increased from 0.5 m to 1 m. The time taken to sample leachate at column depth 0.5, 0.75 and 1 m is 90, 120 and 180 minutes

respectively. At sample flow rate of 6 ml/min, there was negligible decrease on removal efficiency of zinc. The change in percentage removal increased from 94.83% to 94.65% as the adsorption column depth increased from 0.5 m to 1 m. The time taken to sample leachate at column depth 0.5, 0.75 and 1 m was 120, 180 and 240 minutes respectively.

3.6 Effect on Copper

Table 4 shows the effect of flow rate and column depth on copper ions removal efficiency. At column depth of 0.5 m, the percentage removal of copper, decreased from 90.97% to 66.29% as flow rate is increased from 6 to 12 ml/min. This can be attributed to reduction in contact time from 120 minutes to 60 minutes.

Table 4: Effect of effluent flow rate and column depth on the removal efficiency of copper ions

| Bed depth (m) | copper concentration (mg/l) | | | Copper percentage removal (%) | | |
|---------------|-----------------------------|------------|-------------|-------------------------------|------------|-------------|
| | 6 (ml/min) | 9 (ml/min) | 12 (ml/min) | 6 (ml/min) | 9 (ml/min) | 12 (ml/min) |
| 0.5 | 0.84 | 1.91 | 3.14 | 90.97 | 79.52 | 66.29 |
| 0.75 | 0.75 | 0.77 | 1.86 | 91.94 | 91.77 | 80.00 |
| 1 | 0.74 | 0.72 | 0.72 | 92.10 | 92.26 | 92.26 |

At column depth of 0.75 m, the percentage removal of copper, decreased from 91.94% to 80% as flow rate is increased from 6 to 12 ml/min. This can be attributed to reduction in contact time from 180 minutes to 90 minutes. At column depth of 1 m, there was negligible change on the removal efficiency of copper. The change in percentage removal increased from 92.1% to 92.26% as flow rate is increased from 6 to 12 ml/min.

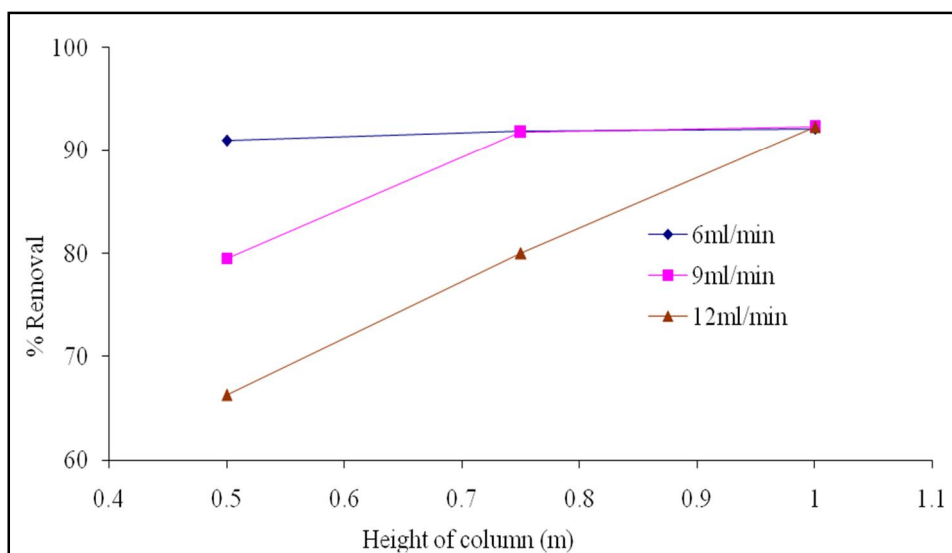


Figure 2: Effect of effluent flow rate and column depth on the removal efficiency of copper ions

Figure 2 shows the effect of influent injection rates at various column depths. It illustrates the deviation in heavy metal removal efficiency with changes in quarry dust column depth at various flow rates. The results show that copper removal efficiency increased with increase in the column depth at a given flow rate. At flow rate of 12 ml/min, the percentage removal increased from 66% to 92% as the adsorption column depth increased from 0.5 m to 1 m. The time taken to sample leachate at column depth 0.5, 0.75 and 1 m is 60, 90 and 120 minutes respectively. At sample flow rate of 9 ml/min, the percentage removal increased from 79% to 92% as the adsorption column depth increased from 0.5 m to 1 m. The time taken to sample leachate at column depth 0.5, 0.75 and 1 m is 90, 120 and 180 minutes respectively. At sample flow rate of 6 ml/min, there was negligible change on the removal efficiency of copper. The change in removal efficiency increased from 91% to 92% as the adsorption column depth increased from 0.5 m to 1 m. The time taken to sample leachate at column depth 0.5, 0.75 and 1 m was 120, 180 and 240 minutes respectively.

3.7 Adsorption Capacity of WQD

Passage of wastewater through the adsorption column cause the fill up of adsorption sites over a period of time and exhaust the removal capacity of WQD. The effect of column height on the adsorbate concentration is presented for flow rate of 12 ml/min and inlet wastewater concentration of 35.1 mg/l and 9.3 mg/l for zinc and copper respectively. The bed heights considered are 0.5, 0.75 and 1 m. Figure 3 and figure 4 shows plot of concentration ratio C/C_0 against time for Zinc and Copper respectively. It was observed that at smaller column height, the adsorbate concentration ratio approaches 1 faster than for a higher column height. The adsorption column is saturated in less time for smaller column heights than higher height. Smaller column height corresponds to less amount of adsorbent which means reduced capacity for the column to adsorb heavy metals from wastewater.

Figure 3 shows that zinc concentration ratio of 1 were attained in 360, 480 and 600 minutes at 0.5, 0.75 and 1 m adsorption depth respectively. This means that at column height of 0.5, 0.75 and 1 m, the WQD adsorption sites get filled up in 360, 420 and 600 minutes, when wastewater is passed up the column at a flow rate of 12 ml/min.

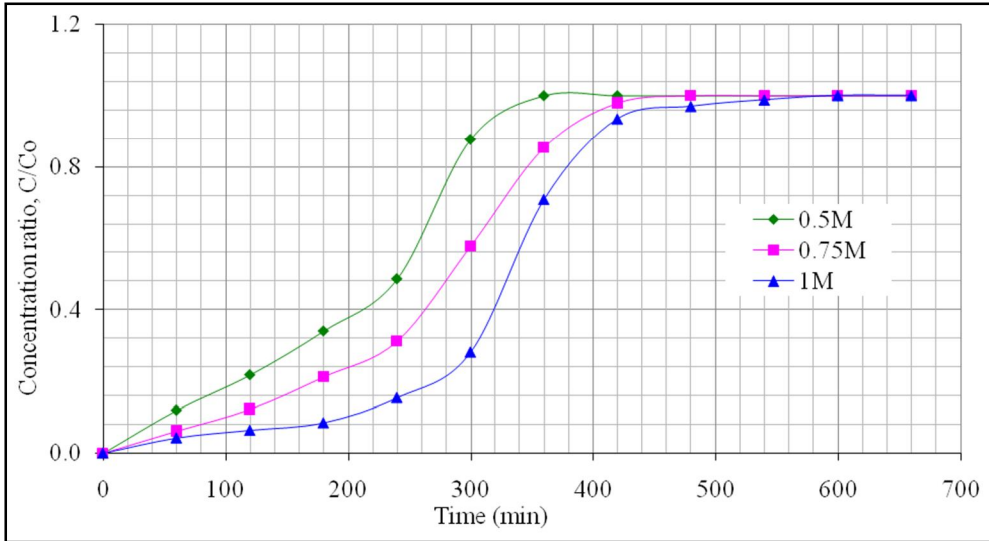


Figure 3: Effect of bed height on breakthrough curve in the adsorption of zinc ions

Figure 4 shows that copper concentration ratio of 1 were attained in 360, 480 and 580 minutes at 0.5, 0.75 and 1 m column depth respectively. This means that at column heights of 0.5, 0.75 and 1 m, the WQD adsorption sites get filled up in 360, 420 and 580 minutes respectively when wastewater is passed up the column at a flow rate of 12 ml/min.

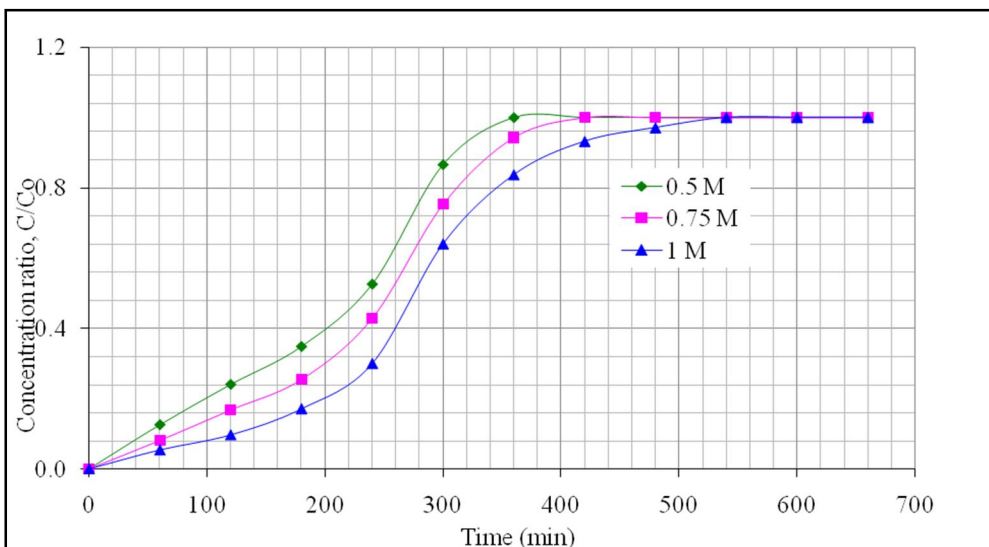


Figure 4: Effect of column height on breakthrough curve in the adsorption of copper ions

4.0 Model Development and Discussion

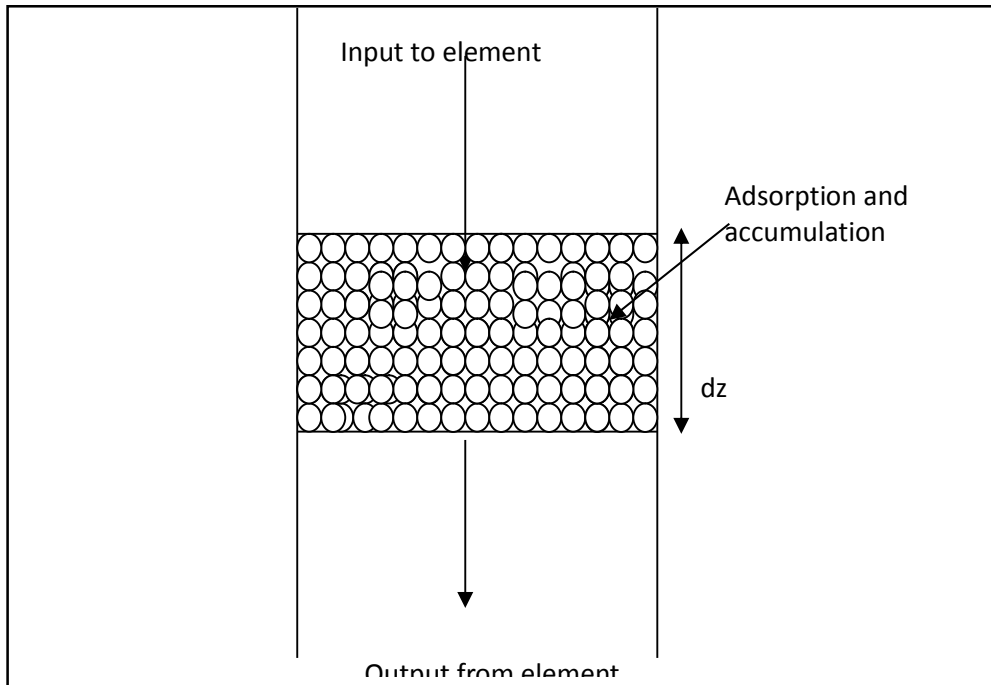


Figure 5: Mass balance in element of fixed bed

Figure 5 is an infinitesimal thickness bed of unit cross-sectional area. Using the mass balance model, the materials balance relationship for the packed bed can be expressed as:-

$$\text{Input of element} = \text{Output from element} + \text{Adsorption} + \text{Accumulation} \text{ (Yuan et al., 1999).... (3)}$$

A mathematical formulation can be expressed as

Input to element: $C \cdot U$

Output from element: $\left(C + \frac{\partial c}{\partial z} dz \right) U$

Adsorption: $\rho \left(\frac{\partial q}{\partial t} \right) dz dA$

Accumulation: $\varepsilon \left(\frac{\partial c}{\partial t} \right) dz dA$

Where

U is the wastewater sample volumetric flow rate, litres/hour.

C is the concentration of adsorbate/solute in solution, solution phase concentration of solute (mg/l).

q is the adsorption density at the equilibrium solute concentration C_e, Solid phase concentration of solute (mg of adsorbate per g of adsorbent).

z is the axial distance, cm.

t is the time in hours.

A is the cross-sectional area of the column in cm².

ϵ is the void ration or porosity, dimensionless.

ρ is the packed-bed density, g/l.

Replacing eqn.3 with mathematical expressions and assuming a unit cross-sectional area, we get eqn.4 below

$$C * U = \left(C + \frac{\partial c}{\partial z} dz \right) U + \rho \left(\frac{\partial q}{\partial t} \right) dz + \epsilon \left(\frac{\partial c}{\partial t} \right) dz$$

..... (4)

Eqn.4 can be simplified by removing the brackets and balancing the equation to become

$$U \frac{\partial c}{\partial z} + \epsilon \frac{\partial c}{\partial t} + \rho \frac{\partial q}{\partial t} = 0$$

..... (5)

The partial differential equation, Eqn.5, can be solved using adsorption equilibrium phenomena. The distribution of solute between liquid and solid phases in an adsorbent –solute-solvent system at equilibrium is commonly termed as adsorption isotherms. Adsorption equilibrium data is conventionally presented and correlated by plotting the quantity of solute adsorbed per unit weight of adsorbent, q as a function of the concentration of solute remaining in solution at equilibrium C_e.

Several mathematical formulations that describe adsorption equilibria include Freundlich, Langmuir and BET model isotherms (Yuan *et al.*, 1999). Mathematical representations of these models are for

$$q = \frac{X}{M} = KC_e^{\frac{1}{n}}$$

Freundlich (5.1)

$$q = \frac{X}{M} = \frac{X_m KC_e}{1 + KC_e}$$

Langmuir (5.2)

$$q = \frac{X}{M} = \frac{AC_e X_m}{\{C_s - C_e\} \left[1 + (A - 1) \frac{C_e}{C_s} \right]} \dots\dots\dots (5.3)$$

BET

where;

q = Adsorption density at the equilibrium solute concentration C_e (mg of adsorbate per g of adsorbent).

X = Mass of adsorbate (solute adsorbed) in milligrams

M = Mass of adsorbent in grams

C_e = Equilibrium concentration of adsorbate/solute in solution (mg/l)

In Freundlich model K and n are constants for a given adsorbate and adsorbent at a particular temperature.

X_m = Maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbent).

K = Langmuir equilibrium constant which is related to the affinity of binding sites for a given adsorbate and adsorbent at a particular temperature (constant related to energy of adsorption, litre of adsorbent per mg of adsorbate).

C_s = Saturation concentration of solute (mg/l)

A = A constant to describe the energy of interaction between the solute and the adsorbent surface.

Freundlich and BET models are limited for application in single-solute system (Qadeer and Akhtar, 2005). Only the Langmuir model has been extended to account for competitive adsorption equilibria in multiple-solute systems.

For the di-solute case involving zinc and copper ions, the extent of adsorption for zinc is given by; (yu *et al.*, 2001, Badmus *et al.*, 2007).

$$q_{Zn} = \frac{X}{M} = \frac{X_{mZn} K_{Zn} C_{eZn}}{1 + K_{Zn} C_{eZn} + K_{Cu} C_{eCu}} \dots\dots\dots (5.4)$$

The extent of adsorption for copper is given by;

$$q_{Cu} = \frac{X}{M} = \frac{X_{mCu} K_{Cu} C_{eCu}}{1 + K_{Cu} C_{eCu} + K_{Zn} C_{eZn}} \dots\dots\dots (5.5)$$

where;

q_{Zn} = Zinc ion adsorption density at the equilibrium solute concentration C_e (mg of adsorbate per g of adsorbent).

q_{Cu} = Copper ion adsorption density at the equilibrium solute concentration C_e (mg of adsorbate per g of adsorbent).

X = Mass of adsorbate (solute adsorbed) in milligrams

M = Mass of adsorbent in grams

C_{eZn} = Zinc ion equilibrium concentration of adsorbate/solute in solution (mg/l)

C_{eCu} = Copper ion equilibrium concentration of adsorbate/solute in solution (mg/l)

X_{mZn} = Zinc ions maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbent).

X_{mCu} = Copper ions maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbent).

K_{Zn} and K_{Cu} = Langmuir equilibrium constant which is related to the affinity of binding sites for a given adsorbate and adsorbent at a particular temperature (constant related to energy of adsorption, l of adsorbent per mg of adsorbate).

X_{mZn} , X_{mCu} , K_{Zn} and K_{Cu} are those that are measured in monosolute, pure solution systems.

4.1 Langmuir Model for Monosolute System

Langmuir adsorption isotherm is mathematically expressed as;

$$q = \frac{X}{M} = \frac{X_m K C_e}{1 + K C_e} \dots\dots\dots (6)$$

Where:

q = Adsorption density at the equilibrium solute concentration C_e (mg of adsorbate per g of adsorbent).

X = Mass of adsorbate (solute adsorbed) in milligrams

M = Mass of adsorbent in grams

C_e = Equilibrium concentration of adsorbate/solute in solution (mg/l)

X_m = Maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbent).

K = Langmuir equilibrium constant which is related to the affinity of binding sites for a given adsorbate and adsorbent at a particular temperature (constant related to energy of adsorption, litre of adsorbent per mg of adsorbate).

The constants K and X_m are the characteristics of the Langmuir equation and can be determined from a linerized form of the Langmuir equation Eqn.5.2, represented as (Yuan *et al.*, 1999).

$$\frac{1}{q} = \frac{1}{C_e X_m K} + \frac{1}{X_m} \dots\dots\dots (7)$$

Therefore, a plot of $\frac{1}{q}$ versus $\frac{1}{C_e}$, gives a straight line of slope $\frac{1}{KX_m}$ and intercept $\frac{1}{X_m}$. The constant K is the Langmuir equilibrium constant and gives the theoretical monolayer saturation capacity.

5.0 Zinc and Copper Monosolute Adsorption Density

Solutions of zinc and copper were prepared from standard heavy metal solutions. Concentration of heavy metal solutions 40 mg/l for zinc and 10 mg/l for copper were prepared. The solutions were treated through column adsorption method using WQD size 0-3 mm.

The experiment procedure was as shown below:-

WQD 0-3 mm was put in the column up to 1 m bed height. Once the WQD was packed inside the column, the columns were fully filled with deionised water for 24 h to 'wet' the column and remove entrapped air. The metal solution pH was adjusted to 7 ± 0.2 by use of 0.1N HCL and 0.1N NaOH. The column was flushed with deionized water and heavy metal solution was put into the holding tank and passed through the inlet to the column via gate valve at optimum flow rate of 12 ml/min. Gate valve was regulated and tuned to give the correct flow rate which was maintained constant during each experiment. Periodic flow rate checks were carried out by physically collecting samples of solution at the outlet for a given time and measuring the amount collected. 50ml leachate samples of heavy metal solution were collected through the 1 metre outlet at intervals of 60 minutes. The flow of the solution was continuous until the leachate concentrations (C_e) of zinc and copper monosolutes collected at the outlet were equal to inlet concentration C_o . The volume of the heavy metal solutions were measured at every sampling time interval. The samples were filtered through Whatman No.44 filter paper. The samples were then digested with concentrated HNO_3 by adding HNO_3 every time the volume of the mix was less than 10 ml until white smoke was released. The digested samples were topped up to initial volume using distilled water. The equilibrium concentrations (C_e) of zinc and copper were determined using AAS. The experimental procedure was repeated until the leachate concentrations (C_e) of monosolutes collected at the outlets were equal to initial concentration C_o .

Using the balance equation $q = \frac{v}{m}(C_o - C_e)$, the values of q were calculated for every value of C_e obtained from the experiment.

Where

q is the heavy metal uptake (adsorption density) (mg/g)

C_o is the initial heavy metal concentration in the heavy metal solution (mg/l)

C_e is the equilibrium metal concentration in the treated heavy metal solution (mg/l)

v is the volume of heavy metal solution treated by the adsorption column at respective sampling time interval (l)

m is the mass of adsorbent in the adsorption column (g).

q was plotted against C_e for zinc and copper solution.

5.1 Zinc Solution

Figure 6 shows a plot of adsorption density versus equilibrium concentrations for zinc. It was observed that the concentration of zinc in the treated solution increased with time. There was higher removal rate of zinc ions during the first four hours as shown in Figure 3. As the adsorption sites got filled up, the adsorption rate reduced as proved by a gentle curve in figure 6. From Figure 6, the maximum equilibrium concentration (C_e Max) and maximum equilibrium density (X_m) were 17.2 mg/l and 0.021 mg/g respectively.

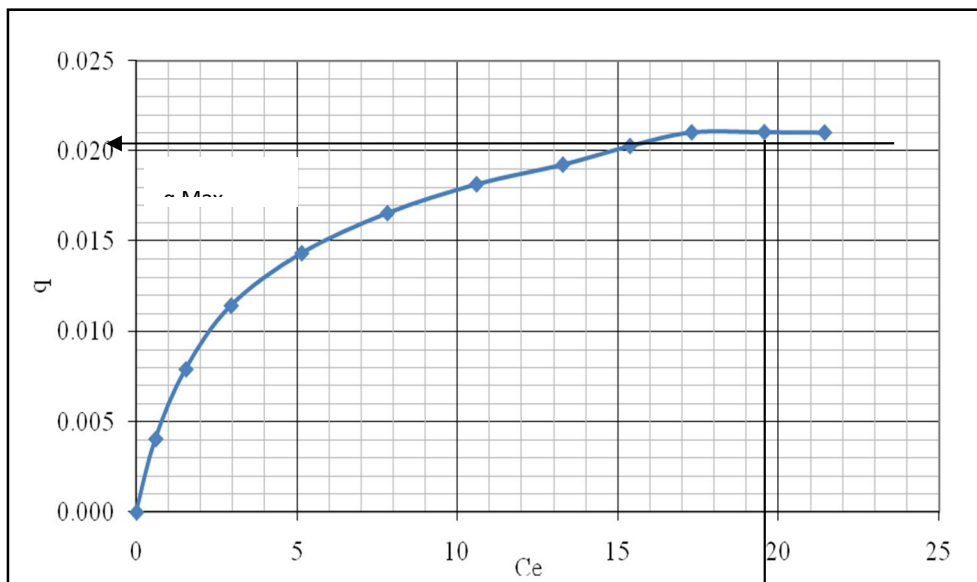


Figure 6: Adsorption curve for zinc solution

5.2 Copper Solution

Figure 7 shows a plot of adsorption density versus equilibrium concentrations for copper. It was observed that the concentration of copper in the treated solution increased with time. There was higher removal rate of copper ions during the first three hours. As the adsorption sites got filled up, the adsorption rate reduced as proved by a gentle curve in figure 7. From Figure 7, the maximum equilibrium concentration (C_e Max) and maximum equilibrium density (X_m) were 4.6 mg/l and 0.005 mg/g respectively.

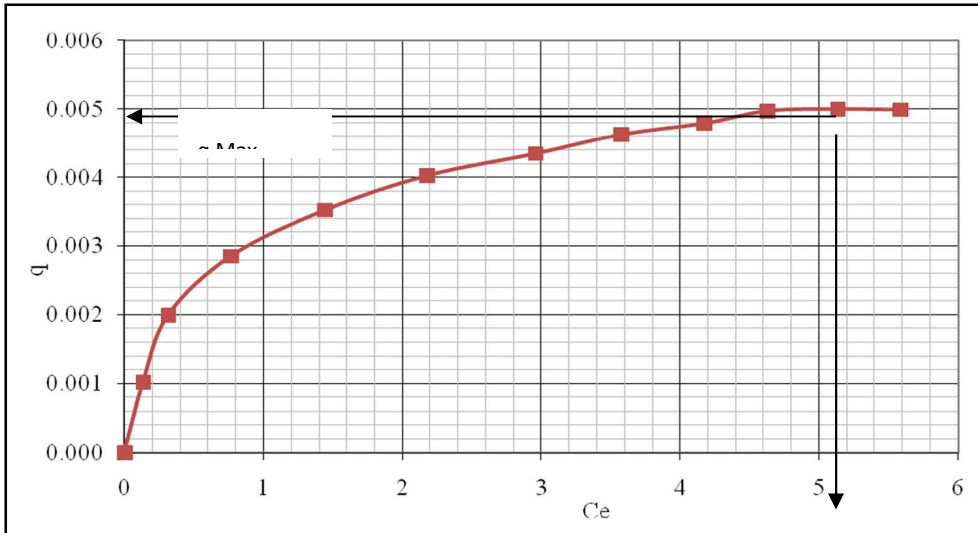


Figure 7: Adsorption curve for copper solution

5.3 Zinc and Copper Monosolute Linear Curves

Table 5 shows the volume of treated Zinc and Copper solutions, by adsorption column at given time intervals. The weight of the WQD in the adsorption column was 7000 grams. Using C_e of the solute at given time intervals and initial concentration of 40 mg/l and 10 mg/l for zinc and copper solutions respectively, q was calculated using mass balance equation.

Table 5: Volume of treated solute at a given time

| Time in min | Volume in ml |
|-------------|--------------|
| 60 | 720 |
| 120 | 140 |
| 180 | 2150 |
| 240 | 2900 |
| 300 | 3600 |
| 360 | 4300 |
| 420 | 5000 |

Figure 8 shows a linear curve $\frac{1}{q}$ versus $\frac{1}{C_e}$ for zinc adsorption. The linear curve gave regression coefficient of 0.999, indicating a good linearity. The curve's linear equation is $y = 121.1x + 45.01$. From this equation $\frac{1}{KX_m} = 121.1$ and $\frac{1}{X_m} = 45.01$.

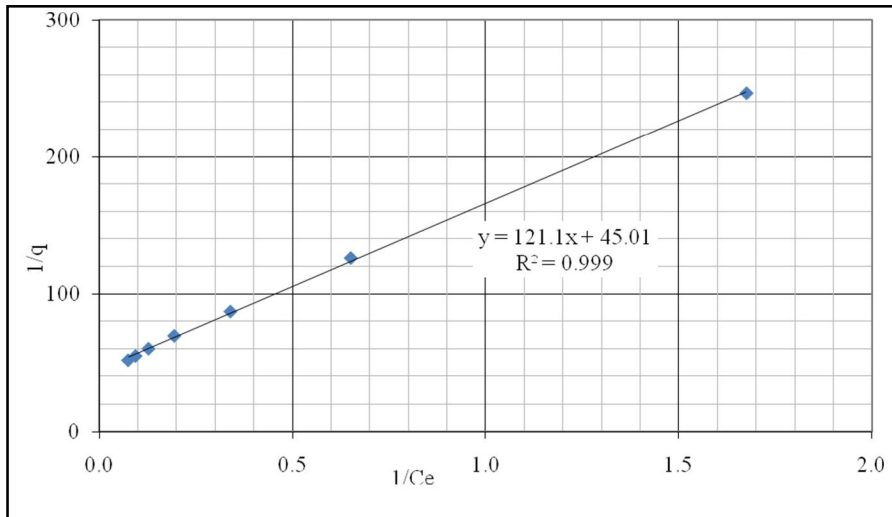


Figure 8: Langmuir plot for zinc solution

Figure 9 shows a linear curve $\frac{1}{q}$ versus $\frac{1}{C_e}$ for copper adsorption. The linear curve gave regression coefficient of 0.996, indicating a good linearity. The curve's linear equation is $y = 105.4x + 197.0$.

From this equation $\frac{1}{KX_m} = 105.4$ and $\frac{1}{X_m} = 197.0$

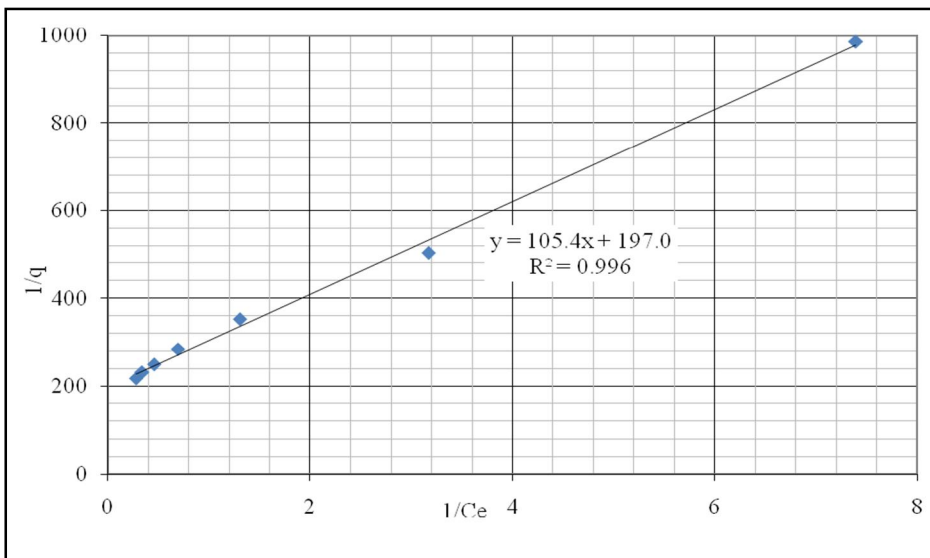


Figure 9: Langmuir plot for copper solution

The Langmuir constants X_m and K for zinc and copper ions were obtained by solving the linear equations. Table 6 shows the single solution Langmuir constant values for zinc and copper. The maximum adsorption capacity X_m for zinc and copper are 0.022 mg/g and 0.005 mg/g respectively. These values are similar to the q_{Max} (X_m) values 0.021 mg/g and 0.005 mg/g for zinc and copper as shown in figures 6 and 7 respectively.

Table 6: Langmuir isotherm equilibrium constants for Zinc and Copper

| Heavy metal | X_m (Maximum adsorption capacity in mg/g of WQD) | K (energy of adsorption in l/mg) |
|-------------|--|------------------------------------|
| Zn | 0.022 | 0.37 |
| Cu | 0.005 | 1.87 |

6.0 Langmuir Model for Competitive System

Langmuir isotherm model for the single component system cannot be straightforwardly applied for the binary system, due to the possible competitive adsorption of the two components. One of the possibilities is to use the extended Langmuir isotherm models for the binary isotherm adsorption data. Using Langmuir isotherm constants in Table 6, the extended Langmuir equations can be written as indicated in equation 8 and 9:

For Zinc

$$q = \frac{X_{mZn} K_{Zn} C_{eZn}}{1 + K_{Zn} C_{eZn} + K_{Cu} C_{eCu}} = \frac{0.008 C_{eZn}}{1 + 0.37 C_{eZn} + 1.87 C_{eCu}} \dots\dots\dots (8)$$

For Copper

$$q = \frac{X_{mCu} K_{Cu} C_{eCu}}{1 + K_{Cu} C_{eCu} + K_{Zn} C_{eZn}} = \frac{0.009 C_{eCu}}{1 + 1.87 C_{eCu} + 0.37 C_{eZn}} \dots\dots\dots (9)$$

6.1 Validation of the Extended Langmuir Model

WQD was put in the column up to 1 m bed height. Once the WQD was packed inside the column, the columns were fully filled with deionised water for 24 h to ‘wet’ the column. The wastewater sample pH was adjusted to 7±0.2 by use of 0.1N HCL and 0.1N NaOH. After flushing the column with deionized water, wastewater was then passed vertically upward inside the column by putting wastewater into the holding tank and passing it through the inlet to the column via gate valve at 12 ml/min flow rate for 120 minutes. Gate valve was regulated and tuned to give the correct flow rate which was maintained constant during each experiment. Periodic flow rate checks are carried out by physically collecting samples of solution at the outlet for a given time and measuring the amount collected. Leachate samples, 50ml, of treated wastewater were collected at intervals of 60 minutes through the

sample outlet points located 1 metre of the column. The volume of the treated sample was measured at each time interval. The samples were filtered through Whatman No.44 filter paper. The samples were digested with concentrated HNO₃ by adding HNO₃ every time the volume of the mix was less than 10 ml until white smoke was released. The digested samples were topped up to the initial volume using distilled water. The equilibrium concentrations (C_e) of zinc and copper were determined using AAS.

Using the balance equation $q = \frac{v}{m}(C_o - C_e)$, the values of q were calculated for every value of C_e obtained from the experiment.

Where

q is the heavy metal uptake (adsorption density) (mg/g)

C_o is the initial heavy metal concentration in the industrial effluent (mg/l)

C_e is the equilibrium metal concentration in the treated wastewater (mg/l)

v is the volume of treated wastewater by the adsorption column at 60 minutes interval (l)

m is the mass of adsorbent in the adsorption column (g).

q was plotted against C_e for zinc and copper solution.

Using the equilibrium concentration C_e, obtained above, the equilibrium density q_e was calculated using extended Langmuir model and compared to q_e obtained from the mass balance equation above.

Figures 10 and 11 show adsorption density verses equilibrium concentration obtained from column experiment and calculated using the extended Langmuir model. It was observed that the extended Langmuir model curve and the experimental curve were similar and equal. This means that the model can be used to calculate adsorption density given the values of C_e or vice versa.

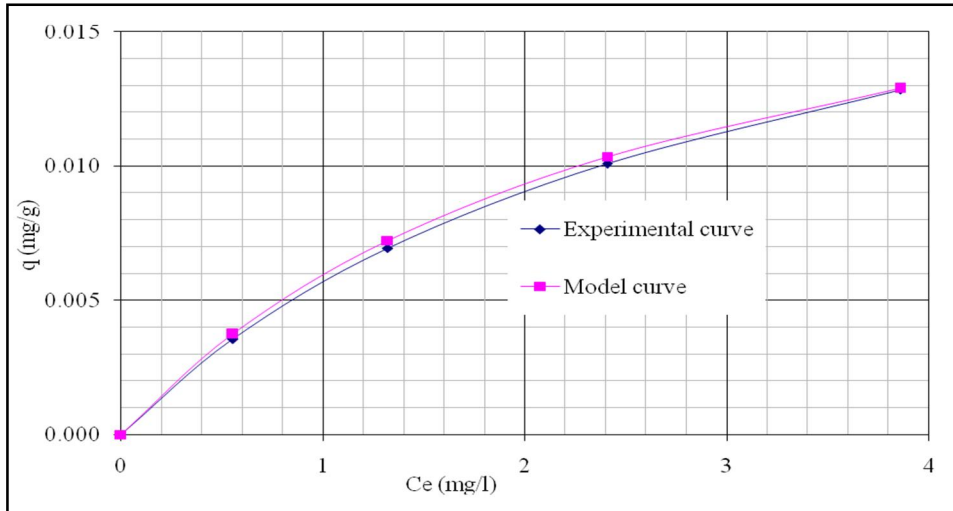


Figure 10: Experimental and model adsorption density for zinc ions

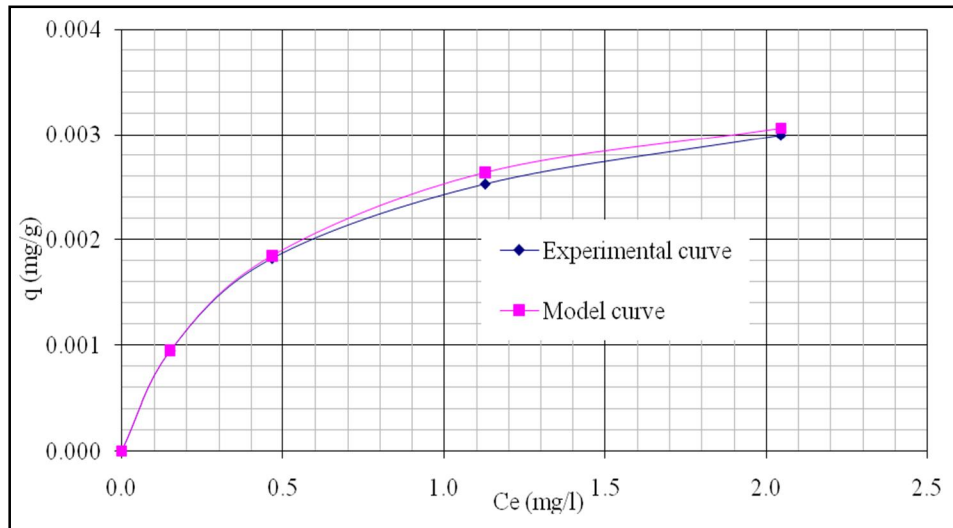


Figure 11: Experimental and model adsorption density for copper ions

6.0 Conclusion

The use of WQD in the removal of heavy metals, is technically feasible, eco-friendly and with high efficacy. It compares well with other adsorbents with 94% and 92% removal efficiency for zinc and copper respectively. Low cost adsorbents such as soybean and cottonseed hulls, rice straw, timber sawdust and sugarcane bagasse tested in batch and fixed bed adsorption systems show lower removal efficiency (yu *et al.*, 2001, Badmus *et al.*, 2007). The extended Langmuir adsorption isotherm represented the data well when adsorption density curves were plotted for model and laboratory test results.

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