

Use of Washed Quarry Dust in the Treatment of Industrial
Effluents: Case Study of Electroplating Industry

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DECLARATION

This thesis is my original work and has not been presented for a degree in any other University.

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DEDICATION

My wife Eddah and our children: You all mean a lot in my life; you give me a reason to soldier on in life.

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LIST OF ABBREVIATIONS AND ACRONYMS

| | |
|----------------------|---|
| AAS | Atomic Absorption Spectrometry |
| AICAD | Africa Institute of Capacity Development |
| BDST | Bed Depth Service Time |
| C | Concentration of adsorbent |
| CCEE | Civil, Construction and Environmental Engineering |
| C_e | Equilibrium Concentration of adsorbent |
| C_o | Initial heavy metal concentration in the waste water |
| HETP | Height Equivalent to a Theoretical Plate |
| JKUAT | Jomo Kenyatta University of Agriculture and Technology |
| KEBS | Kenya Bureau of Standards |
| KS ISO | Kenya Standard Specifications/ test methods |
| NEMA | National Environment Management Authority |
| NEQS | National Environment Quality Standards |
| R² | Coefficient of correlation |
| Temp (°c) | Temperature in degree Celsius |
| WHO | World Health Organization |
| WQD | Washed quarry dust |

ABSTRACT

This study records laboratory scale experiments to test the efficiency of washed quarry dust in the removal of heavy metals such as zinc and copper from wastewater of electroplating industry, before 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 metal removal efficiency of washed quarry dust (WQD), samples of wastewater were treated by batch and column adsorption experiments. The concentration of heavy metals in the industrial effluent (C_o) 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.

Batch adsorption tests were carried out to determine the influence of process variables such pH, washed quarry dust size and contact time in the removal of heavy metals. The experimental results showed that zinc and copper ions' removal efficiency, increased with increasing wastewater pH and contact time up to pH 7 and 120 minutes respectively. After pH 7, removal efficiency decreased with increasing pH. The adsorption of zinc and copper were almost zero after optimum contact time of 120 minutes.

Thereafter, wastewater samples of known heavy metal concentrations (C_o) were passed through the 0.5, 0.75 and 1 M columns at varying flow rate of 6, 9 and 12 ml/min.

Treated 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 with monosolute correlation coefficient of 0.999 and 0.996 for zinc and copper ions respectively. Bohart-Adams equation was applied in the design of other adsorption columns using the laboratory results of three columns. The service time predicted using Bohart-Adams equation for 0.5, 0.75 and 1m column at a linear flow rate of 1.8 l/min/m² were similar to those found in the laboratory column experiment.

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.

CHAPTER ONE

1.0 INTRODUCTION

1.1 General

Industrialization has expanded industrial manufacturing processes tremendously around the globe. These industries utilize a lot of water, most of which go to the cooling process. This increased demand for water globally has put a lot of stress on a resource which is in short supply.

The major water related problems faced by industries are water accessibility, water quality, water scarcity and treatment of effluents for reuse or disposal. Lack of adequate funds in developing countries has compounded these problems further. It has become increasingly necessary that new techniques of water conservation and treatment have to be developed to combat the ever-increasing water scarcity. This will enable re-use of industrial wastewater in industrial processes and reduce environmental contamination.

A number of industrial processes especially metal processing factories such as electroplating industries discharge effluents with high quantities of toxic metals and this can lead in turn to the contamination of freshwater and marine environment (Low et al., 1995). Hence, heavy metals are major pollutants in marine, ground, and even treated wastewaters.

Removal of heavy metals from industrial wastewater is of primary importance because they are not only causing contamination of water bodies but are also toxic to many life forms (Ajmal et al., 1995). 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 treatment of water and 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 rates (Abdus-Salam and Adekola, 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). Other adsorbents that have been used for the removal of heavy metals include carbonaceous material developed from fertilizer waste slurry (Srivestava et al., 1989; Babel and Kurniawan, 2000).

In recent years, many low-cost adsorbents including agricultural and waste by-products such as soybean and cotton seed hulls, rice straw, timber sawdust and sugarcane bagasse have been tested in batch and fixed bed adsorption systems (Yu et al., 2001, Badmus et al., 2007). Tea waste has been used for the removal of Pb, Cu, Hg, Cd and Zn from wastewater at a rate of 77-85% of the dissolved heavy metals (Amir, 2005).

Other adsorbents that have been used for the removal of heavy metals solution include soils (Campbell and Davies, 1995) and activated carbons from date pits (Girgis and Hendawy, 1997). Other researchers reported the adsorption of lead on oxide of silicon, manganese, aluminum (Bilinshi et al., 1977), bentonite (Kozar et al., 1992), hydrated titanium dioxide (Abe et al., 1989), modified silica gel (Mareira et al., 1990), dithizone-

anchored poly (EDGMA-HEMA) micro beads (Salih et al., 1988), anionic micro gel (Morris et al., 1997), ZnS surface (Patrick et al., 1998), magnetite (Georgeaud et al., 1998), pedogenic oxides, ferrihydrite and leaf compost (Sebastein et al., 2000), sawdust (Yu et al., 2001), lateritic minerals (Ahmad et al., 2002), and carbon (Qadeer and Akhtar, 2005).

A research carried out at the University of Agriculture, Faisalabad in conjunction with the Ministry of Environment, Islamabad, Pakistan has shown that river sand has removal efficiency for Zinc ranging from 71-87% using adsorption column (Aslam et al., 2004).

1.2 Research rationale

Industrial manufacturing processes are fast growing in Kenya. A number of these industrial processes especially metal processing factories such as electroplating industries discharge toxic metals and this can lead in turn to the contamination of freshwater and marine environment. According to World Health Organization (WHO) the metals of most immediate concern are chromium, cadmium, zinc, iron, mercury and lead due to their toxicity (WHO and ILO, 1995). Electroplating industries are one of the most important economical sectors with regard to their application and labour force employment. Treatment of electroplating wastewater is by far the most important environmental problem faced by the steel industry (Yu et al., 2001).

The wastewater produced by electroplating industry is highly polluted in terms of copper (Cu), iron (Fe) and zinc (Zn) (Kaneco et al., 2000) and due to their non-biodegradability

and persistence, can accumulate in the environment elements such as food chain, and thus pose a significant danger to human health.

Removal of heavy metals from industrial effluents is a big challenge in developing countries. In Kenya wastewater from steel industries is rarely treated for heavy metals. This has led to release of industrial effluents with high levels of heavy metals into public sewers and rivers such as Athi-river and Nairobi-river (NEMA, 2003).

Inadequate treatment of industrial effluents could be due to high cost of conventional treatment technologies such as ion-exchange, chemical precipitation and ultra filtration.

Many physico-chemical methods have been proposed for their removal from industrial effluents. A wide range of adsorbent materials have been tested for heavy metal removal.

The most widely used adsorbents are activated carbon, silica gel and zeolites (Kaneco et al., 2000). Since cost is an important parameter for comparing the adsorbent materials, many low-cost adsorbents including agricultural and waste by-products have also been tested in batch and fixed bed adsorption systems (Bailey et al., 1999). By-products of soybean and cottonseed hulls, rice straw and sugarcane bagasse have been evaluated as metal ion adsorbents in aqueous solutions. However, the equilibrium adsorption capacities for these systems are low.

Therefore, there is a need for an alternative adsorbent which is effective and economical.

In this study the efficiency of washed quarry dust in the removal of heavy metals from wastewater through adsorption was determined. Quarry dusts are produced in large quantities. For this reason, they are cheap and easily available for use in the treatment of industrial effluents.

1.3 Objectives

Major objective

The overall objective of the study was to determine the efficiency of washed quarry dust as adsorbent for the removal of heavy metals from industrial effluents.

Specific objectives

The specific objectives were

- i. To determine the heavy metals' removal capacities of different sizes of washed quarry dust.
- ii. To evaluate the effect of wastewater pH in the adsorption of heavy metals from industrial effluents.
- iii. To evaluate the performance of the adsorption column height in the removal of heavy metals.
- iv. To evaluate the adsorption isotherms applicable in the removal of heavy metals from industrial effluents

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Electroplating

Electroplating is the process of using electrical current to coat an electrically conductive object with a relatively thin layer of metal. It involves the deposition of a thin protective layer (usually metallic) onto a prepared metal surface, using electrochemical processes. The process involves pretreatment (cleaning, degreasing, and other preparation steps), plating, rinsing, passivating, and drying. The cleaning and pretreatment stages involve a variety of solvents and surface stripping agents, including caustic soda and a range of strong acids, depending on the metal surface to be plated (World Bank group, 1998).

The primary application of electroplating is to deposit a layer of a metal having some desired property (e.g., abrasion and wear resistance, corrosion protection, lubricity, improvement of aesthetic qualities, etc.) onto a surface lacking that property. Another application uses electroplating to build up thickness on undersized parts. The process used in electroplating is called electro-deposition. It is analogous to a galvanic or electrochemical cell acting in reverse. The part to be plated is the cathode of the circuit. In one technique, the anode is made of the metal to be plated on the part. Both components are immersed in a solution containing one or more metal salts as well as other ions that permit the flow of electricity.

A rectifier supplies a direct current to the cathode causing the metal ions in solution to lose their charge and plate out on the cathode. As the electrical current flows through the circuit, the anode slowly dissolves and replenishes the ions in the bath. Other

electroplating processes may use a non-consumable anode such as lead. In these techniques, ions of the metal to be plated must be periodically replenished in the bath as they are drawn out of the solution.

2.2 Industrial wastewater

Human activities and industrial processes produce wastes which enter rivers, lakes, oceans and other surface waters thus introducing harmful or objectionable material to damage the water's quality (WHO, 1984).

Industries are creating and utilizing new chemicals each year, all of which eventually find their way to water. In high concentrations these wastes result in heavy metal contamination and excessive nutrient loading (eutrophication). Inorganic industrial wastes are much trickier to control and potentially more hazardous. Industries discharge a variety of toxic compounds and heavy metals such as copper, zinc, manganese, lead, and cadmium (Osama et al., 2006).

Sources of heavy metals in electroplating wastewater are the metals ions used for plating such as zinc, copper, cadmium, chromium, arsenic, lead and iron (Mustafiz et al., 2002).

2.3 Heavy metals

The term heavy metals refer to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations (WHO and ILO, 1995). Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As

trace elements, some heavy metals such as copper, selenium, zinc are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination, high ambient air concentrations near emission sources, or intake via the food chain.

Heavy metals are dangerous because they tend to bio-accumulate. Bio-accumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater (Qureslii et al., 2001).

2.4 Effects of heavy metals on human health

Heavy metals such as arsenic, lead, zinc, copper, cadmium and chromium are well known for their acute toxicity. For example, an ingested dose of 70-180 μg of arsenic trioxide (As_2O_3) is lethal to humans (Kortenkamp et al., 1996).

Heavy metals cause acute effects in the respiratory, gastrointestinal, cardiovascular, and nervous systems. Chronic exposure to heavy metals in drinking water has been linked to serious dermatological conditions, including Blackfoot disease (Park and Jung, 2001). Epidemiological studies have linked heavy metals in drinking water with cancer of the skin, bladder, lung, liver, and kidney. Some heavy metals adsorbed in the human body

tend to accumulate in the tissues, whereas others such as organic arsenic are rapidly and almost completely eliminated via the kidneys (Kortenkamp et al., 1996). The toxicity of each metal is as discussed below.

2.4.1 Effects of Cadmium

Cadmium derives its toxicological properties from its chemical similarity to zinc an essential micronutrient for plants, animals and humans. Cadmium is bio-persistent and, once absorbed by an organism, remains resident for many years (over decades for humans) although it is eventually excreted. In humans, long-term exposure is associated with renal dysfunction. High exposure can lead to obstructive lung disease and has been linked to lung cancer. In addition, this metal can be linked to increased blood pressure and effects on the myocardium in animals (Jarup et al., 2000).

2.4.2 Effects of Chromium

Low-level exposure can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damage. It can also damage circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium (Kortenkamp et al., 1996).

2.4.3 Effects of Copper

Copper is an essential element to human life, but in high doses it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation. People with Wilson's disease are at greater risk for health effects from over exposure to copper (Benoff et al., 2000).

2.4.4 Effects of Lead

In humans exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing foetus and infant being more sensitive than the adult. High levels of exposure may result in toxic biochemical effects in humans which in turn cause problems in the synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system.

At intermediate concentrations, lead can have small, subtle, sub clinical effects, particularly on neuropsychological developments in children (Benoff et al., 2000).

2.4.5 Effects of Arsenic

Once absorbed into the body, arsenic undergoes some accumulation in soft tissue organs such as the liver, spleen, kidneys, and lungs, but the major long-term storage site for arsenic is keratin-rich tissues, such as skin, hair, and nails. Acute arsenic poisoning is infamous for its lethality, which stems from arsenic's destruction of the integrity of blood vessels and gastrointestinal tissue and its effect on the heart and brain (Benoff et al., 2000). Chronic exposure to lower levels of arsenic results in somewhat unusual patterns

of skin hyper pigmentation, peripheral nerve damage manifesting as numbness, tingling, and weakness in the hands and feet, diabetes, and blood vessel damage resulting in a gangrenous condition affecting the extremities. Chronic arsenic exposure also causes a markedly elevated risk for developing a number of cancers, most notably skin cancer, cancers of the liver (angiosarcoma), lung, bladder, and possibly the kidney and colon (Tsai et al., 1999).

2.5 Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or, more rarely, a liquid (adsorbent), forming a molecular or atomic film (adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process (Mustafiz et al., 2002).

Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Adsorption, ion exchange and chromatography are sorption processes in which certain adsorptives are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column.

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms (Tang et al.,

1997). Thus it is energetically favourable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption (Aksu, 2001).

2.6 Fundamentals of adsorption

In discussing the fundamentals of adsorption, it is useful to distinguish between physical adsorption, involving only relatively weak intermolecular forces and chemisorption which involves essentially, the formation of a chemical bond between the sorbate molecule and the surface of the adsorbent. Although this distinction is conceptually useful there are many intermediate cases and it is not always possible to categorize a particular system unequivocally (Tang et al., 1997, Vasanth et al., 2007). The general features which distinguish physical adsorption and chemisorption are as shown in Table 2.6 (Vasanth et al., 2007).

Table 2.6: Similarities between physical adsorption and chemisorption

| Physical adsorption | Chemisorption |
|---|--|
| Low heat of adsorption (<2 or 3 times latent heat of ionization) | High heat of adsorption (>2 or 3 times latent heat of ionization) |
| Non specific | Highly specific |
| Monolayer or multilayer only No dissociation of adsorbent species Only significant at relatively low temperatures | Monolayer only May involve dissociation Possible over a wide range of temperature |
| Rapid, non activated and reversible No electron transfer although polarization of sorbate may occur | May be slow, activated and irreversible Electron transfer leading to bond formation between sorbate and surface |

2.7 Adsorbents

Adsorbents are solids or, more rarely, liquids where gases or liquids (Solute) accumulate on the surface. Any solid has some tendency to adsorb fluid medium onto their surface, however, only some solid materials have the selective adsorption capacity to adsorbate molecules (Karthikeyan et al., 2004). The adsorbents are used usually in the form of spherical pellets, rods, moldings or monoliths with hydrodynamic diameter between 0.5 and 10 mm. They must have high abrasion resistance, high thermal stability and small

micropore diameter, which result in higher exposed surface area and hence high capacity for adsorption. Different types of industrial adsorbents used are: silica gel, hydrophilic zeolites, activated carbon, activated alumina, char bones, clay minerals and sand (Badmus et al., 2007).

2.8 Washed quarry dust as adsorbent

The internal pore characteristics are very important properties of washed quarry dust. The size, the number, and the continuity of the pores of aggregate particles enhance the adsorption properties of the quarry dust, abrasion resistance, surface texture and specific gravity (Vallejo et al., 1999). Washed quarry dust is very porous. Properties such as specific surface area and average pore radius determine the adsorption rate.

The porous quarry dust surface may be considered to consist of a number of chemically active sites. The attachment of sorbate species occurs at these sites. So, the sorption capacity of sorbent for a specific sorbate is a function of available active sites. The available sites can vary for the same sorbate–sorbent system under different environmental conditions such as pH, temperature, and particle size.

The attachment of heavy metal ions from aqueous phase to available active sites is considered to occur in two steps:-

- (i) Transfer of sorbate from the aqueous phase to the available active sites on the sorbent.
- (ii) Chemical complexation/ion-exchange at these chemically active sites.

The assumption made in the development of this thesis is that both physisorption and chemisorption occur simultaneously.

2.9 Adsorption isotherms

Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid).

These isotherms are:-

2.9.1 Freundlich isotherm

Freundlich isotherm is an empirical mathematical formula expressed as shown in Eqn.2.9.1.1

$$q = \frac{X}{M} = KC_e^{\frac{1}{n}} \dots\dots\dots \text{Eqn.2.9.1.1}$$

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).

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

By taking the logarithm of both sides, the above Eqn.2.9.1.1 equation can be written as in Eqn.2.9.1.2

$$\text{Log} \left[\frac{X}{M} \right] = \log K + \frac{1}{n} \log C_e \dots\dots\dots \text{Eqn.2.9.1.2}$$

Thus, a plot of $\log \left[\frac{X}{M} \right]$ against $\log C_e$ gives a straight line of slope $\frac{1}{n}$ and intercept

$\log K$, for adsorption data that follow the Freundlich theory.

Values of the constants n and k can be determined from the graph plot.

2.9.2 Langmuir isotherm

Langmuir isotherm is an empirical isotherm derived from a proposed kinetic mechanism.

It is based on four hypotheses, namely:-

- a. The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.
- b. Adsorbed molecules do not interact.
- c. All adsorption occurs through the same mechanism.
- d. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

These four points are seldom true: there are always imperfections on the surface, adsorbed molecules are not necessarily inert, and the mechanism is clearly not the same for the very first molecules as for the last to adsorb. The fourth condition is the most troublesome, as often more molecules can adsorb on the monolayer, but this problem is solved by the Brunauer-Emmett-Teller (BET) isotherm.

Langmuir adsorption isotherm is mathematically expressed as in Eqn.2.9.2.1

$$q = \frac{X}{M} = \frac{X_m K C_e}{1 + K C_e} \dots\dots\dots \text{Eqn.2.9.2.1}$$

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, L 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 linearized form of the Langmuir equation Eqn.2.9.2.1, represented as in Eqn.2.9.2.2.

$$\frac{C_e}{X/M} = \frac{1}{X_m K} + \frac{C_e}{X_m} \dots\dots\dots \text{Eqn.2.9.2.2}$$

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

2.9.3 Brunauer-Emmett-Teller (B.E.T) Isotherm

Often molecules do form a multilayer, that is, some are adsorbed on already adsorbed molecules and the Langmuir isotherm is not valid. Brunauer-Emmett-Teller (BET) isotherm is applicable in this situation and is mathematically expressed as shown Eqn.2.9.3.1.

$$q = \frac{X}{M} = \frac{AC_e X_m}{\{C_s - C_e\} \left[1 + (A-1) \frac{C_e}{C_s} \right]} \dots\dots\dots \text{Eqn.2.9.3.1}$$

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 = Amount of solute adsorbed in forming a complete monolayer (mg/l).

C_s = Saturation concentration of solute (mg/l).

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

Equation Eqn.2.9.3.1 can be rearranged to give a linear Equation 2.9.3.2

$$\frac{C_e}{(C_s - C_e) \frac{X}{M}} = \frac{1}{AX_m} + \frac{[A-1]C_e}{AX_m C_s} \dots\dots\dots \text{Eqn.2.9.3.2}$$

Data from adsorption process that conform to the BET equation will yield a straight line

when $\frac{C_e}{(C_s - C_e) \frac{X}{M}}$ is plotted against $\frac{C_e}{C_s}$.

The resulting graph plot will have a slope of $\frac{[A-1]}{AX_m}$ and an intercept of $\frac{1}{AX_m}$.

Usually the isotherm equation that yields a linear graph plot of the data is selected for use (Benfield et al., 1982).

CHAPTER THREE

3.0 METHODOLOGY

3.1 Introduction

The study was carried out using effluent from Insteel Ltd, Tononoka Steel Ltd and Master Platers Electroplating Factory, situated in Nairobi's industrial area.

Quarry dusts were sampled from aggregate quarries in Mlolongo and Kitengela. Also samples of quarry dust were picked from machine cut building stones in Juja for elemental analysis using XRF.

The electroplating industry coats metallic items mainly with copper and zinc. The wastewater generated after rinsing the plated items is discharged into public sewer. The factories generate over 5000 litres of effluent daily.

The aggregate quarries manufacture concrete and road aggregates by crushing the stones. The aggregates are sieved into various sizes ranging from size 25 mm to quarry dust (0-6 mm). The quarry dust is used to manufacture paving blocks, masonry units and other general construction works. The companies produce over 100000 tonnes of quarry dust daily.

The building stone quarries cut stones for building using powered machines. The broken pieces are used as hardcore in building construction. Crushing and sieving is not done.

In this study, batch and column experiments were performed to determine heavy metals' removal efficiency for washed quarry dust.



Figure 3.1: Quarry dust at a ballast factory in Kitengela

3.2 Washed quarry dust characterization

Quarry dust samples were collected from ballast and machine cut building stone quarries in Mlolongo, Kitengela and Juja. The samples were picked randomly from the factory using sisal bags. The elemental analysis of the washed quarry dust was done using the X-ray fluorescence (XRF). The test procedure for XRF is as follows:-

- Samples from the quarries were crushed into powder form using Sicrotechnik pulveriser (Figure 3.2a).
- 5 grams of fine stone powder samples were mixed with 10 grams of potato starch which acts as a binder.
- The sample mixtures were compacted to form pellets using a pellet machine (Figure 3.2b).

- The pellets were exposed to X-rays using X-Ray Fluoresces (XRF): Minipal2 model (Figure 3.2c) machine to analyze the stones elemental composition.



Figure 3.2a: Sicrotechnik Pulveriser

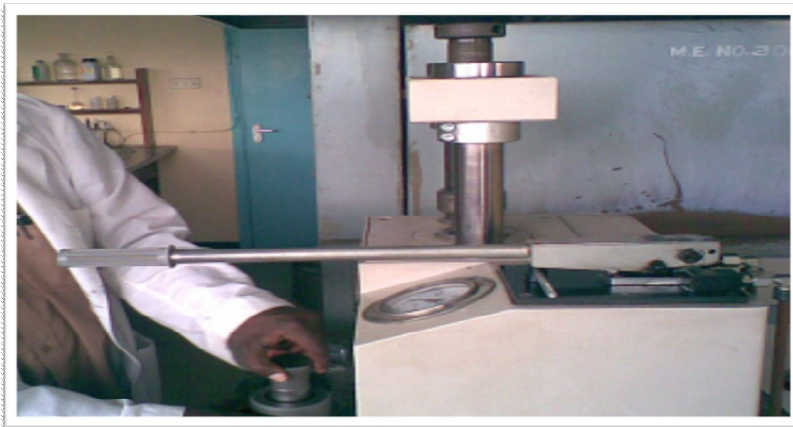


Figure 3.2b: Pellet machine



Figure 3.2c: X-Ray Fluoresces

3.3 Preparation of washed quarry dust

Quarry dust from stone quarry factory was washed with distilled water to remove all impurities such as clay and silt particles and then sun dried for 24 hours. Two sizes, 0-3 mm and 3-6 mm of quarry dust were separated by grading through sieve analysis using sieve sizes 6 mm, 3 mm and pan. These quarry dust sizes were rinsed using distilled water then dried in the sunlight before drying in the oven at 110°C for 24 hours to reduce the moisture content.

3.4 Determination of washed quarry dust (WQD) porosity

The quarry dust sizes 0-3 mm and 3-6 mm were put into two beakers. Water was slowly poured into the beakers until the quarry dust was covered. The amount of water used was recorded as W_1 . Water was then drained after 30 minutes and volume recorded as W_2 . This

was repeated five times using different samples of the same WQD size. Then the porosity

was calculated using the equation, $Porosity = \frac{W_1 - W_2}{W_1} \times 100$.

3.5 Wastewater sample collection, preparation 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 up. At the collection point (the point where wastewater is discharged into the public sewer), 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 secondary wastewater effluent was collected from electroplating steel industry as stipulated in Annex A of Kenya Standard KS 1966-2:2007 and used as influent in the experiment.

The pH meter was used to determine the pH of the wastewater samples. The samples were filtered with Whatman No. 44 filter paper. To determine the heavy metals' concentration, 50 ml of the wastewater samples was digested with concentrated Nitric acid (HNO₃) by adding Nitric acid (HNO₃) every time the volume of the mix is less than 10 ml until white smoke was released. Thereafter, the digested sample was topped up to initial volume (50 ml) with distilled water.

The concentration of heavy metals; zinc, copper, cadmium, chromium, arsenic, lead and iron were determined using Atomic Adsorption Spectrophotometer (AAS): model Phillip PU 9100. Triplicate samples were analyzed and mean concentration taken.

3.6 Batch adsorption tests

Batch experiments were carried out at room temperature, to assess the effect of various process variables in the removal efficiency of heavy metals from wastewater by WQD. All the tests were conducted according to standard methods APHA, 1995 for each parameter.

3.6.1 Efficiency of WQD sizes 0-3 and 3-6 mm

Two sizes of washed quarry dust, 0-3 mm and 3-6 mm, were used to remove heavy metals in industrial effluent. This was done to determine the size that could remove heavy metals more efficiently through batch equilibrium experiments.

The test procedure was as indicated below.

- 10 g of washed quarry dust size 0-3 mm and 3-6 mm, each was put in six conical flasks containing 200 ml of industrial effluent of known heavy metal concentration. The concentration of the adsorbent was therefore 50g/l in each of the twelve flasks.
- The wastewater pH was adjusted to 7 ± 0.2 using dilute sodium hydroxide (NaOH) and hydrochloric acid (HCl) solutions.

- The twelve conical flasks were capped and shaken in the flask shaker at 200 rpm. Samples from a set of two conical flasks, one with quarry dust size 0-3 mm and another one with size 3-6 mm were sampled for analysis at time intervals of 30, 60, 90, 120, 150 and 180 minutes.
- The samples were filtered, digested and their equilibrium concentration determined as indicated in section 3.5.

3.6.2 Optimum contact time

Optimum contact time for washed quarry dust was tested through batch adsorption.

The test procedure was as indicated below.

- 10 g of washed quarry dust size 0-3 mm was put in six conical flasks containing 200 ml of industrial effluent of known heavy metal concentration.
- The wastewater pH was adjusted to 7 ± 0.2 using dilute sodium hydroxide (NaOH) and hydrochloric acid (HCl) solutions.
- The six conical flasks were capped and shaken in the flask shaker at 200 rpm. Samples from the conical flasks were collected by removing one conical flask at a time from the shaker after contact time intervals of 30, 60, 90, 120, 150 and 180 minutes.
- The samples were filtered, digested and their equilibrium concentration determined as indicated in section 3.5.

3.6.3 Optimum pH

To examine the effect of pH on the heavy metal removal efficiency the procedure below was used.

- The effluent of known heavy metal concentration was divided into seven equal volumes of 200 ml and 10 g of washed quarry dust size 0-3 mm was added to each conical flask.
- Samples in the seven conical flasks had pH varied from 4, 5, 6, 7, 8, 9 and 10, ± 0.2 . The pH was maintained at the desired value with ± 0.2 by adding drops of 0.1 N HCL or 0.1 N NaOH solutions.
- The seven conical flasks were capped and shaken in the flask shaker at 200 rpm for optimum contact time of 120 minutes.
- The samples were filtered, digested and their equilibrium concentration determined as indicated in section 3.5.

3.7 Column adsorption tests

3.7.1 Adsorption column

The design and sizing of the adsorption column, Height Equivalent to a Theoretical Plate (HETP) was adopted from a book entitled Distillation Design by Kister (1992). Distillation Design contains an exhaustive list of HETP values based on the components of the system and the type of packing used. As for preliminary estimates, the following HETP values were used: circular cross section with a diameter of 80 millimetres and a

height of 1.2 metres. The head and the bottom of column are closed using aluminium plates with inlet for the influent at the bottom.

A holding (regulating tank), 30 cm diameter and 50 cm height, was placed at a height of 1.5 m from the column inlet to enable wastewater flow upwards. A gate valve was put at the holding tank's outlet to regulate the effluent flow rate. The column and holding tank were made of aluminium sheets while the stands were made of steel bars. A schematic diagram of adsorption column set-up is as shown in Figure 3.7.

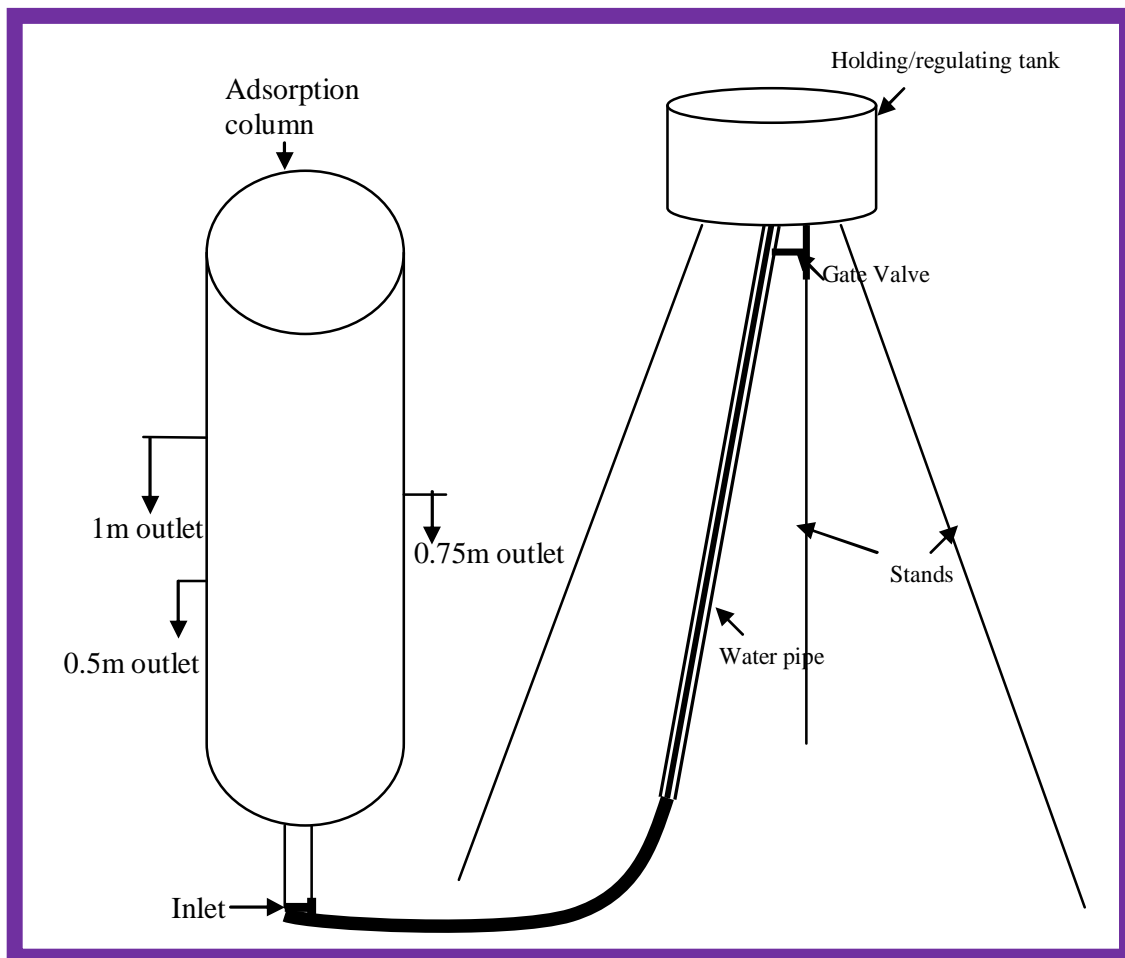


Figure 3.7: Schematic diagram of adsorption column

Washed quarry dust was placed in the column to form a bed depth at column height of 0.5 m, 0.75 m and 1 m. The treated water was sampled at 0.5, 0.75 and 1 metre bed depth outlets as indicated in Figure 3.7.

3.7.2 Column flow rates

Using optimum contact time obtained from batch experiment, the quarry dust porosity and bed depth capacity, the flow rate can be determined from the Eqn. 3.7b.

The volume of wastewater at a column bed depth h can be calculated using Eqn 3.7a.

$$V = 1000 * \frac{\Pi}{4} \rho h D^2 \dots\dots\dots \text{Eqn 3.7a}$$

Where

V is the volume of wastewater at a column bed depth h (litres).

h is the washed quarry dust bed depth in the column (metres).

D is the column diameter (metres).

ρ is the washed quarry dust porosity (Percentage).

The flow rate, v is determined by dividing Eq.3.7a by optimum contact time, t.

$$v = \frac{V}{t} \dots\dots\dots \text{Eqn 3.7b}$$

Where

v is the wastewater sample flow rate in litres per minute (l/min).

V is the volume of wastewater at a column bed depth h (litres).

t is the optimum contact time (minutes).

Table 3.7.1 shows the flow rates at different bed depth. Using contact time of 120 minutes and quarry dust porosity of 30%, flow rates used were 6 ml/min, 9 ml/min and 12 ml/min. These were the flow rate, which would take 120 minutes for the effluent to travel through upward flow up the column to height 0.5 m, 0.75 m and 1 m respectively.

Table 3.7.1: Wastewater flow rate

| h (m) | D (m) | V (ml) | v(ml/min) |
|-------|-------|--------|-----------|
| 0.50 | 0.08 | 754 | 6 |
| 0.75 | 0.08 | 1131 | 9 |
| 1.00 | 0.08 | 1508 | 12 |

Using 6 ml/min flow rate, wastewater samples travelled up the adsorption bed depth 0.5 m, 0.75 m and 1 m within 120, 180 and 240 minutes respectively. When 9 ml/min flow rate was used, leachate were collected at adsorption bed depth 0.5 m, 0.75 m and 1 m after 90, 120 and 180 minutes respectively. However when 12 ml/min flow rate was used, leachate were collected at adsorption bed depth 0.5 m, 0.75 m and 1 m after 60, 90 and 120 minutes respectively.

The flow rate was measured using volumetric method, with the help of a beaker and stopwatch. After several trials, the average flow rate was determined and then the wastewater pipe connected to the adsorption column.

3.7.3 Effect of adsorption column depth and effluent flow rate

To evaluate the effects of WQD adsorption column depth, sampling points were located at 0.5, 0.75 and 1 m of the column height.

The treatment procedure was as indicated below:-

- 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, channelling and air entrapment would occur which would lower the bed performance.
- The wastewater sample pH was adjusted to 7 ± 0.2 using dilute sodium hydroxide (NaOH) and hydrochloric acid (HCl) solutions.
- After flushing the column with deionized water, wastewater was then passed up the column by putting wastewater into the holding tank and passing it through the inlet to the column via gate valve. This avoided channelling due to gravity and enhanced uniform distribution of solution throughout the column. 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 collecting samples of solution at the outlet for a given time and measuring the amount collected.
- Step 1, 2 and 3 above were repeated for 6, 9, 12 ml/min flow rates.

- 50 ml leachate samples of treated wastewater were collected through the sample outlet points located at 0.5, 0.75 and 1 metre of the column.
- The leachate samples were filtered digested and their equilibrium concentrations (C_e) of zinc and copper were determined as indicated in Section 3.5.

The adsorption column height which gave the highest heavy metal removal efficiency at a given flow rate was selected for application in the treatment of wastewater.

3.7.4 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. To estimate the time of regeneration of WQD, wastewater samples were passed through the adsorption column.

The treatment procedure was as follows:-

- WQD was put in the column up to 1 m bed height and wastewater treated as discussed in steps 1, 2 and 3 of section 3.7.3 using optimum flow rate of 12ml/min as determine in experiment 3.7.3.
- 50 ml leachate samples of treated wastewater were collected through the 0.5, 0.75 and 1 metre outlets. The samples were collected at intervals of 60 minutes at each outlet. The flow of wastewater was continuous until the leachate concentrations (C_e) of zinc and copper collected at the outlets was equal to wastewater concentration C_o .
- The leachate samples were filtered digested and their equilibrium concentrations (C_e) of zinc and copper were determined as indicated in Section 3.5.

3.7.5 Determination of zinc and copper monosolute adsorption density

Solutions of zinc and copper were prepared from standard metal solutions. Concentration of 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 was put in the column up to 1 m bed height and wastewater treated as discussed in steps 1, 2 and 3 of section 3.7.3 using optimum flow rate of 12ml/min.
- 50 ml leachate samples of heavy 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 volumes of the metal solutions were measured at every sampling time interval.
- The leachate samples were filtered digested and their equilibrium concentrations (C_e) of zinc and copper were determined as indicated in Section 3.5.

3.7.6 Determination of validation data for the extended Langmuir model

The determination of adsorption of zinc and copper by WQD over a given time assists in the determination equilibrium concentration C_e . The C_e determined would assist in calculating for adsorption density q from extended Langmuir model and the column experiment. The similarity between the two adsorption densities would assist in determination of the applicability of the model.

The experiment procedure was as follows:

- WQD was put in the column up to 1 m bed height and wastewater treated as discussed in steps 1, and 2 of section 3.7.3.
- Wastewater was treated as discussed in steps 3 of section 3.7.3 at a flow rate of 12 ml/min.
- 50 ml leachate samples 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 leachate samples were filtered, digested and their equilibrium concentrations (C_e) of zinc and copper were determined as indicated in Section 3.5.

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 (HNO_3) to pH less than 2. The samples were kept and tested at room temperature.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Quarry dust characterization

Table 4.1 shows the results of elemental analysis of the quarry dusts. These are mean results of five experimental trials done. It was observed that the 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).

Samples from machine cut building stone are grey silica whose specific gravity is 1.0. The samples were highly soluble in water which made it unsuitable for use as a column adsorbent.

Samples from aggregate quarries were insoluble in water with a bulk density of 2.4 g/cm³. This pyroclastic type of rock is a better adsorbent than building stone quarry dust due to higher content of alumina elements.

The metal salt in the quarry dust hydrolyses in the presence of natural alkalinity to form metal hydroxides. The multivalent cations present can reduce the zeta potential while the metal hydroxides are good adsorbent.

Quarry dust from building stone quarry was not used in the treatment of industrial effluent due to its high solubility, low alumina content and inability to be crushed into sizes 0-6 mm.

Table 4.1: Characterization of washed quarry dust

| Parameters/Elements | Sample from Aggregate quarries | Sample from building stone quarries |
|--------------------------------|-----------------------------------|--|
| | Contents (%) | Contents (%) |
| SiO ₂ | 53.10 | 62.50 |
| Al ₂ O ₃ | 20.40 | 11.42 |
| Na ₂ O | 8.40 | 5.80 |
| K ₂ O | 5.80 | 4.57 |
| Fe ₂ O ₃ | 5.10 | 6.22 |
| MnO | 1.90 | 0.22 |
| MgO | 0.89 | 0.46 |
| CaO | 0.85 | 0.71 |
| LOI | 4.09 | 8.65 |

4.2 Washed quarry dust porosity

Table 4.2 shows porosity results of washed quarry dust (WQD) sampled from aggregate crushing factories in Mlolongo and Kitengela. Quarry dust from machine cut stones in Juja could not be tested for porosity since it was not possible to crush them to sizes 0-6 mm for sieve analysis. The result shows the quarry dust size 3-6 mm and 0-3 mm have an average porosity of 43% and 30% respectively. It was established that quarry dust size 3-6 mm has a higher porosity.

Table 4.2: Quarry dust porosity

| Trials | 3-6 mm size | | 0-3 mm size | |
|-------------------------|--|---|--|---|
| | Volume of water used (W ₁ -W ₂) in ml | Porosity (%) $= \frac{W_1 - W_2}{W_1}$ | Volume of water used (W ₁ -W ₂) in ml | Porosity (%) $= \frac{W_1 - W_2}{W_1}$ |
| 1 | 148 | 42 | 105 | 30 |
| 2 | 150 | 43 | 106 | 30 |
| 3 | 150 | 43 | 105 | 30 |
| 4 | 148 | 42 | 104 | 30 |
| 5 | 150 | 43 | 105 | 30 |
| Average Porosity | | 43 | | 30 |

4.3 Industrial effluent pH and heavy metal concentration

Table 4.3 shows the industrial effluent characteristics. The mean test results indicate that wastewater is acidic with an average pH of 2. From the metal content analysis, it was established that zinc and copper are the major polluting element in the effluent. Zinc concentration varied from 41.09 mg/l to 35.08 mg/l while that of copper varied from 10.08 mg/l to 9.32 mg/l. Other elements such as cadmium, chromium, arsenic, lead and iron contributed trace amounts. Their concentrations were below 0.05 mg/l, thus they were within the requirements of the Kenya Standard KS 1966-2:2007. Hence the metals,

zinc and copper. Hence, 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.

Table 4.3: Industrial effluent pH and heavy metal concentration

| Samples | pH | Heavy metal's effluent mean concentration, C_0 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 |

4.4 Calculation of heavy metal ions adsorbed

Two important physiochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibria of the adsorption and the kinetics.

Equilibrium studies give the capacity of the adsorbent (Ho and McKay, 1999). The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms. Adsorption isotherm is the ratio between amounts of solute adsorbed per unit

amount of adsorbent (solid phase concentration) and equilibrium concentration of solute in the wastewater at a fixed temperature.

The amount of metal ion adsorbed during the series of batch investigations was determined using a mass balance equation 4.4,

$$q = \frac{v}{m} (C_o - C_e) \dots\dots\dots \text{Eqn. 4.4}$$

Where

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).

q is the metal uptake (mg/g).

v is the wastewater sample volume (l).

m is the mass of adsorbent used (g).

The definition of removal efficiency is calculated using Equation 4.5.

$$\text{Removal efficiency (\%)} = \left[\frac{(C_o - C_e)}{C_o} \right] * 100 \dots\dots\dots \text{Eqn. 4.5}$$

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).

4.5 Batch experiments

4.5.1 Effect of WQD particle size

Table 4.5.1 shows average heavy metal removal efficiency of washed quarry sand size 0-3 and 3-6 mm. Removal efficiency for the two sizes increased with increase in the contact time up to 120 minutes.

Table 4.5.1: Effect of adsorbent particle size on adsorption of zinc and copper

| Contact time (min) | Washed quarry dust size 0-3 mm | | | | Washed quarry dust size 3-6 mm | | | |
|--------------------|--------------------------------|----------------|-------------|----------------|--------------------------------|----------------|-------------|----------------|
| | [Zn] (mg/l) | [Zn] % Removal | [Cu] (mg/l) | [Cu] % Removal | [Zn] (mg/l) | [Zn] % Removal | [Cu] (mg/l) | [Cu] % Removal |
| 0 (Effluent) | 35.07 | | 9.32 | | 35.07 | | 9.32 | |
| 30 | 14.93 | 57.42 | 4.21 | 54.84 | 15.36 | 56.20 | 4.51 | 51.61 |
| 60 | 11.11 | 68.31 | 3.10 | 66.77 | 11.44 | 67.40 | 3.35 | 64.03 |
| 90 | 7.21 | 79.44 | 1.80 | 80.65 | 7.49 | 78.65 | 2.12 | 77.26 |
| 120 | 1.32 | 96.23 | 0.50 | 94.68 | 2.07 | 94.10 | 0.78 | 91.61 |
| 150 | 1.39 | 96.05 | 0.51 | 94.52 | 2.07 | 94.10 | 0.78 | 91.61 |
| 180 | 1.37 | 96.11 | 0.53 | 94.35 | 2.10 | 94.04 | 0.80 | 91.45 |

Maximum removal efficiency of zinc was 96.23% and 94.1% using WQD size 0-3 and 3-6 mm respectively. Removal efficiency for the two sizes increased with increase in the

contact time up to 120 minutes. Maximum removal efficiency of copper was 94.68% and 91.61% using WQD size 0-3 and 3-6 mm respectively.

Figure 4.5.1a and Figure 4.5.1b shows the effect of WQD particle size on the adsorption of zinc and copper respectively.

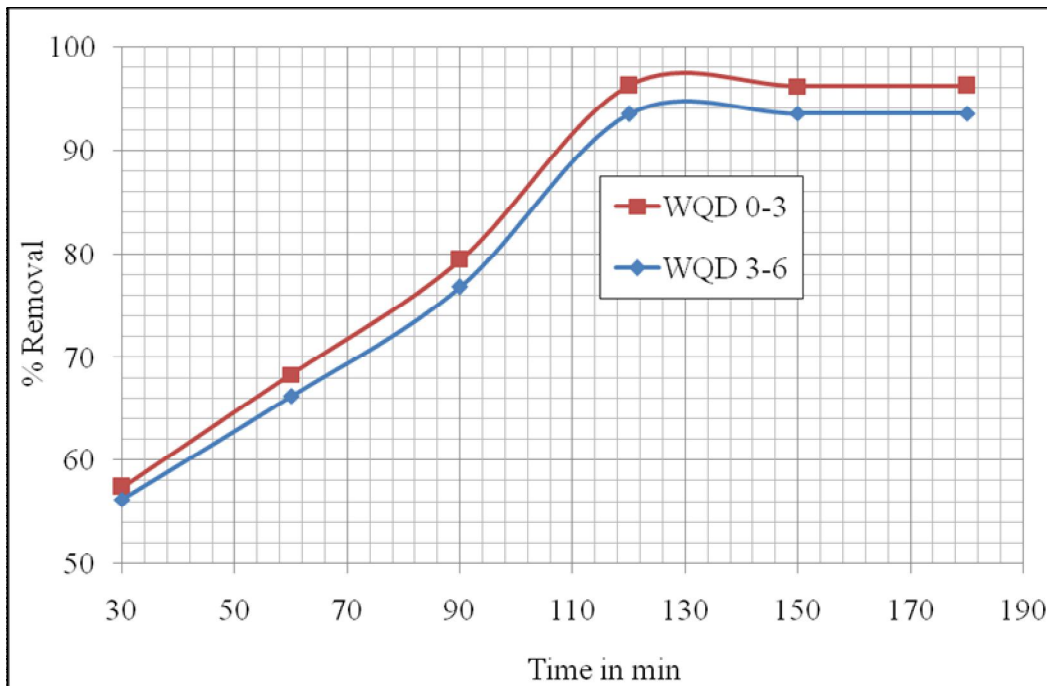


Figure 4.5.1a: Effect of WQD particle size on adsorption of zinc

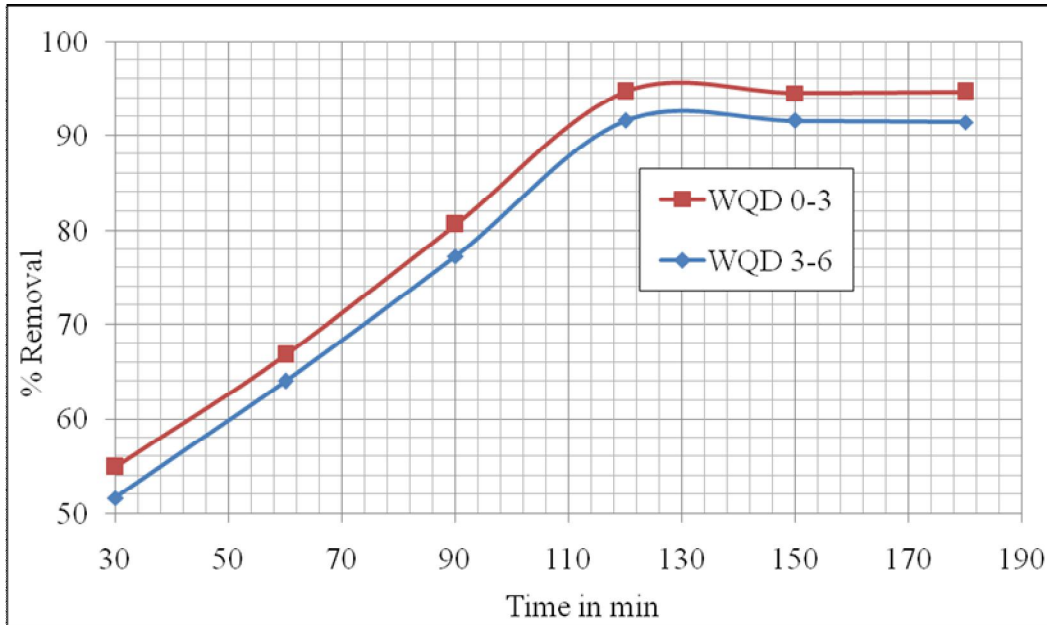


Figure 4.5.1b: Effect of WQD particle size on adsorption of copper

The removal efficiency for zinc and copper increased with increase in contact time for both sizes up to 120 minutes. Between 30 and 120 minutes contact time, removal efficiency for zinc increased from 57% to 96% using WQD size 0-3 mm and from 56% to 94% using size 3-6 mm. Over the same period, copper removal efficiency increased from 54% to 94% using WQD size 0-3 mm and from 51% to 91% using size 3-6 mm. From these results, WQD particle size 0-3 mm had slightly higher removal percentage of zinc and copper. This was most probably due to the increase in the total surface area, which provided more adsorption sites for the metal ion. The breaking of larger particles tends to open tiny cracks and channels on the particle surface of the quarry dust, resulting in more accessibility to better diffusion, owing to the smaller particle size (Karthikeyan et al., 2004). The enhanced removal of sorbate by smaller particles has been noted previously

during a study into the removal of colour by silica (McKay et al., 1980) and during study on the use of sago waste for the sorption of lead and copper (Quek et al., 1998).

Since washed quarry dust size 0-3 mm was found to be more efficient, it was used in the subsequent batch and column experiment covered by this report.

4.5.2 Effect of contact time

Figure 4.5.2 shows percentage removal of zinc and copper ion from wastewater using WQD size 0-3 mm as a function of contact time. The result shows that the zinc and copper removal rate was rapid at the beginning thereafter slowing down before being complete in 120 min. Equilibrium concentration was attained in 120 min since percentage removal of heavy metals remained constant after contact time of 120 min. Hence optimum contact time was found to be 120 minutes.

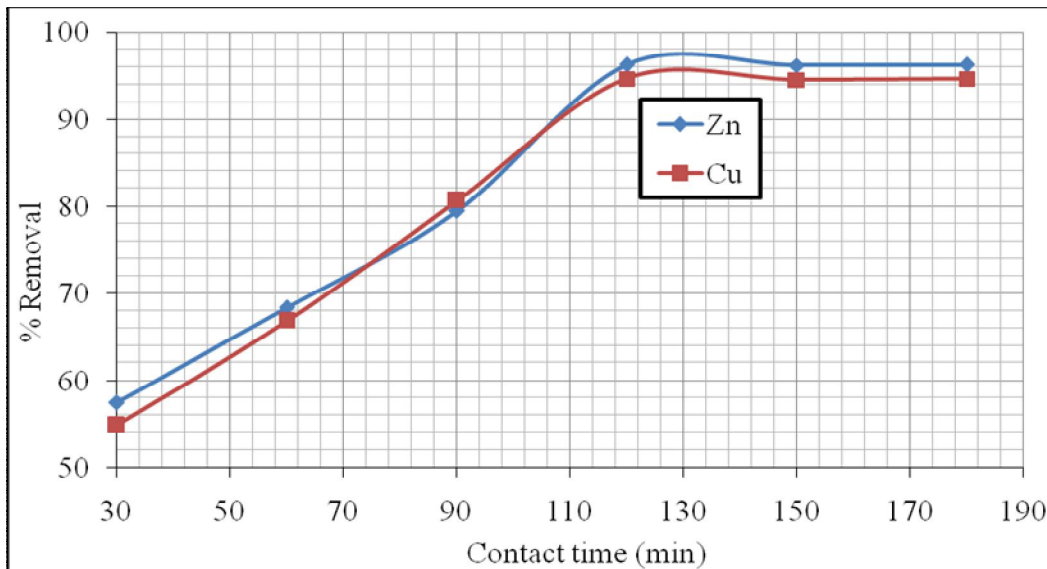


Figure 4.5.2: Effect of contact time on the adsorption of zinc and copper

The initial faster rate may be due to the availability of the uncovered surface area of the adsorbents, since the adsorption kinetics depends on the surface area of the adsorbents. Zinc and copper adsorption takes place at the more reactive sites. As these sites are progressively filled the sorption of these metals becomes slow. This is the general characteristic of adsorption of these metal ions (Appel and Lena, 2002; Abdus-Salam and Adekola, 2005; Qadeer and Akhtar, 2005). These changes and differences in metal ion uptake rate could be attributed to two different adsorption processes. These processes could be as a result of fast ion exchange followed by chemisorption (Low, 1960).

4.5.3 Effect of pH

Table 4.5.3 shows mean concentrations of zinc and copper when adsorption was done at different pH. It was established that the percentage removal of zinc and copper had an increasing trend from pH 4 to pH 7 but decreased after pH 7.

pH is an important parameter for adsorption of metal ions because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. The removal of metal ions from wastewater sample by adsorption is related to the pH of the sample, as the latter affects the surface charge of adsorbents and the degree of ionization of adsorbate.

The pH of the aqueous solution is an important controlling parameter in the adsorption process (Baes and Mesmer, 1976) and thus the role of Hydrogen ions concentration was

examined from samples at different pH covering a range of 4-10 as shown in Table 4.5.3 and Figure 4.5.3.

The variation in removal efficiency due to the wastewater sample pH is attributed to the precipitation of zinc hydroxide ($Zn(OH)_2$) and copper hydroxide ($Cu(OH)_2$) at a higher pH. As the pH increases, there is increasing trend in concentration of hydroxide ions (OH^-) in the sample thus causing disturbance of equilibrium. Therefore, the system adjusts to terminate this effect (Le Chatelier principle) by more precipitation of hydroxide out of the wastewater sample.

Table 4.5.3: Effect of pH on the adsorption of zinc and copper

| Sample pH | [Zn] (mg/l) | [Cu] (mg/l) | [Zn] % Removal | [Cu] % Removal |
|--------------|----------------|----------------|-------------------|-------------------|
| 2 | 35.07 | 9.32 | 0 | 0 |
| 4 | 6.72 | 2.07 | 80.84 | 77.74 |
| 5 | 5.08 | 1.76 | 85.52 | 81.13 |
| 6 | 2.60 | 0.77 | 92.58 | 91.77 |
| 7 | 1.32 | 0.50 | 96.23 | 94.68 |
| 8 | 2.24 | 0.90 | 93.61 | 90.32 |
| 9 | 3.24 | 1.08 | 90.75 | 88.39 |
| 10 | 4.33 | 1.29 | 87.65 | 86.13 |

Figure 4.5.3 depicts the effect of pH on percent removal of heavy metals. The result shows that maximum removal occurs at pH of 7, with zinc reduced from 35.07 to 1.32

mg/l (96.23% removal) and copper from 9.32 to 0.5 mg/l (94.68%). The result shows that with the increase in the pH of the wastewater sample, the extent of removal increases. But after pH 7, there is a decrease in the removal of metal ions. According to Baes and Mesmer (1976), as the sample pH increases, the onset of the metal hydrolysis and the precipitation began at pH greater than 6. The hydrolysis of cations occurs by the replacement of metal ligands in the inner co-ordination sphere with the hydroxyl groups (Badmus et al., 2007).

This replacement occurs after the removal of the outer hydration of metal cations. At low pH values the surface of the adsorbent would be closely associated with hydroxonium ions (H_3O^+), by repulsive forces, to the surface functional groups, consequently decreasing the percentage removal of metal (Low et al., 1995).

When the wastewater pH was increased from 4 to 7, there was a corresponding increase in deprotonation of the adsorbent surface, leading to a decrease in hydrogen ion on the adsorbent surface. This creates more negative charges on the adsorbent surface, which favours adsorption of positively charge species and the positive sites on the adsorbent surface (Kadirvelu and Namasivayam, 2003; Abdus-Salam and Adekola, 2005).

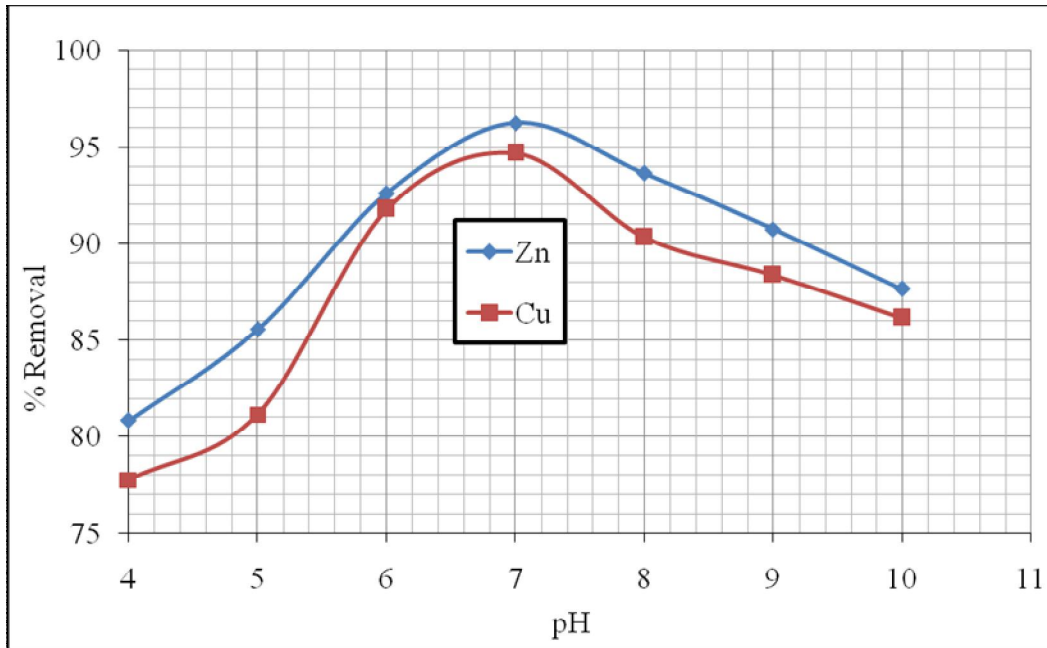


Figure 4.5.3: Effect of pH on the adsorption of zinc and copper

It was observed that the dependence of metal ion adsorption on pH over a wider range of pH (4-10) has an S-like adsorption curve (Bruce, 2000; Glover et al., 2002). The solubility of metals is known to be lowered at higher pH ($\text{pH} > 8$) values (Abdus-Salam and Adekola, 2005) due to the likelihood of precipitation of the hydroxide forms of the adsorbate species.

Thus, results that gave the S-like curve were a reflection of adsorption and precipitation processes on adsorbents rather than adsorption only. The removal of zinc and copper from wastewater samples by adsorbents involves a complex mechanism that is partly controlled by adsorption and partly by chemical precipitation at the solid wastewater sample interface and also by the pore filling mechanism.

Precipitates are not permanently adsorbed by the quarry dust particles. Therefore washing of quarry dust will remove the hydroxide and bring the metals into direct contact with the external environment.

4.6 Adsorption mechanism

To investigate the mechanism of zinc and copper adsorption by WQD and the potential rate controlling steps, such as diffusion mass transport and chemical reaction processes, it is necessary to characterize the main adsorption mechanisms.

The diffusion process can be controlled by:-

- Film or external boundary layer diffusion.
- Diffusion in the liquid filled-pores of adsorbents.
- Surface diffusion of adsorbed-soluble molecules that migrate along the surface of the adsorbent.

The rate controlling mechanism may be one diffusion mass transfer resistance or a combination of 2 or 3 of these processes.

When the water sample is shaken, the adsorbate species, zinc and copper, are transported to the solid phase by the intraparticle transport phenomenon. The intraparticle transport is supposed to be the rate controlling step. The rate of particle transport through this mechanism is slower than adsorption on the exterior surface site of the adsorbent. Before optimum contact time, the amount of adsorbed species, zinc and copper, varies proportionately with a function of contact time.

The equation can be expressed as shown in Eqn 4.6 :-

$$X = Kt^n \dots\dots\dots\text{Eqn 4.6}$$

Where

X is the percentage (%) reduction.

t is the contact time in minutes.

n is the slope of the linear plot.

K is the constant coefficient.

By taking the natural logarithm of both sides, Eqn.4.6 equation can be written as shown in Eqn 4.6.1.

$$\ln X = \ln K + n \ln t \dots\dots\dots\text{Eqn.4.6.1}$$

Thus, a plot of $\ln X$ against $\ln t$ gives a straight line of slope n and intercepts $\ln K$.

Values of the constants n and k can be determined from the graph plot.

The deviation of the line from the origin shows that intraparticle transport is not the only rate limiting factor (Badmus et al., 2007). Probably, the transport of the water sample through the particle-sample interface into the pores of the particles, as well as the adsorption on the available surface of the adsorbents, is responsible for adsorption.

The study of the adsorption kinetics is the main factor for designing an appropriate adsorption system and quantifying the changes in adsorption with time requires that an appropriate kinetic model is used.

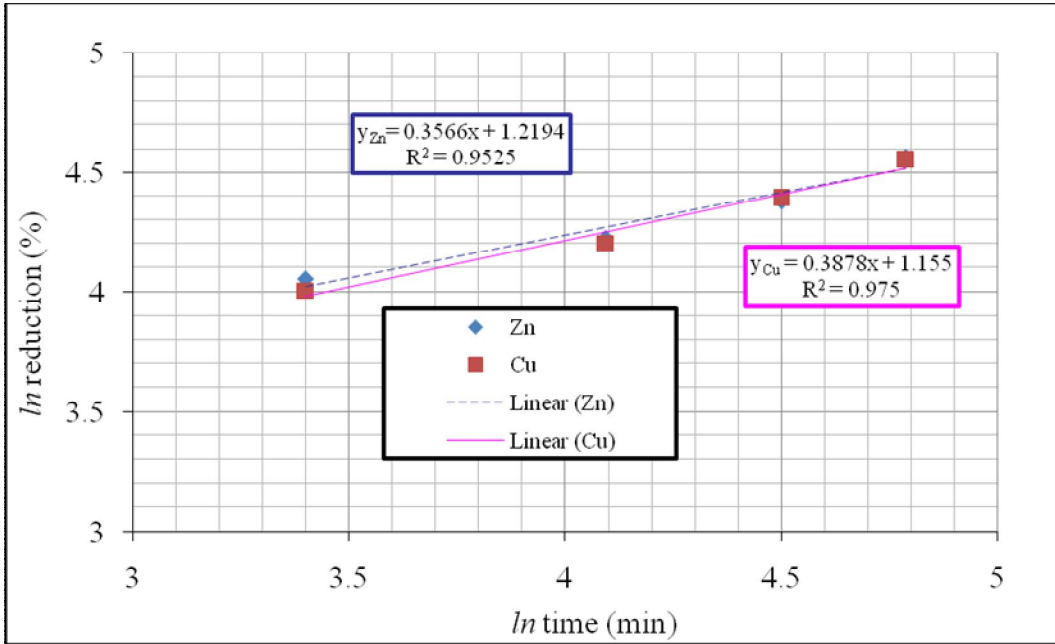


Figure 4.6: *ln* percentage reduction verses *ln* time

4.6.1 Elovich equation

The Elovich equation was developed to describe the kinetics of chemisorption of a gas onto solids (Low, 1960), and its differential form is represented in Eqn.4.6.1a.

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \dots\dots\dots \text{Eqn.4.6.1a}$$

Where

q_t is the amount adsorbed at time t.

α is a constant representing the rate of chemisorption at zero coverage.

β is a constant related to the extent of surface coverage and the activation energy of chemisorption.

The constant α can be regarded as the initial rate since $\frac{dq_t}{dt} \rightarrow \alpha$ as $q_t \rightarrow 0$

The application of the Elovich equation is rapidly gaining popularity (Sparks, 1986). Taylor et al. (1995) successfully used the Elovich equation for the sorption of zinc ions onto solids. Juang and Chen (1997) studied the sorption kinetics of metal ions from sulphate solutions onto solvent impregnated resins. Other applications include work on radioisotopes (Mishra and Singh, 1995; Mishra et al., 1996; Raouf and Daifullah, 1997).

Integration of Elovich equation, Eqn. 4.6.1a, assuming the initial boundary conditions, $q_t = 0$ at $t = 0$ yields Eqn 4.6.1b

$$q_t = \left(\frac{1}{\beta}\right) \ln(1 + \alpha\beta t) \dots\dots\dots \text{Eqn. 4.6.1b}$$

To simplify the Elovich equation, Chien and Clayton (1980) assumed $\alpha\beta t > 1$ and applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$.

Eqn. 4.6.1b yields eqn.4.6.1c (Sparks, 1986).

$$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln(t) \dots\dots\dots \text{Eqn. 4.6.1c}$$

Hence, the constants can be obtained from the slope and intercept of the linearised plots of q_t against $\ln(t)$. Equation 4.6.1c was used to test the applicability of the Elovich equation to the kinetics of zinc and copper adsorption.

Figure 4.6.1 shows linear plots of natural logarithms of adsorption density time verses natural logarithms of contact time. The figure shows a good correlation.

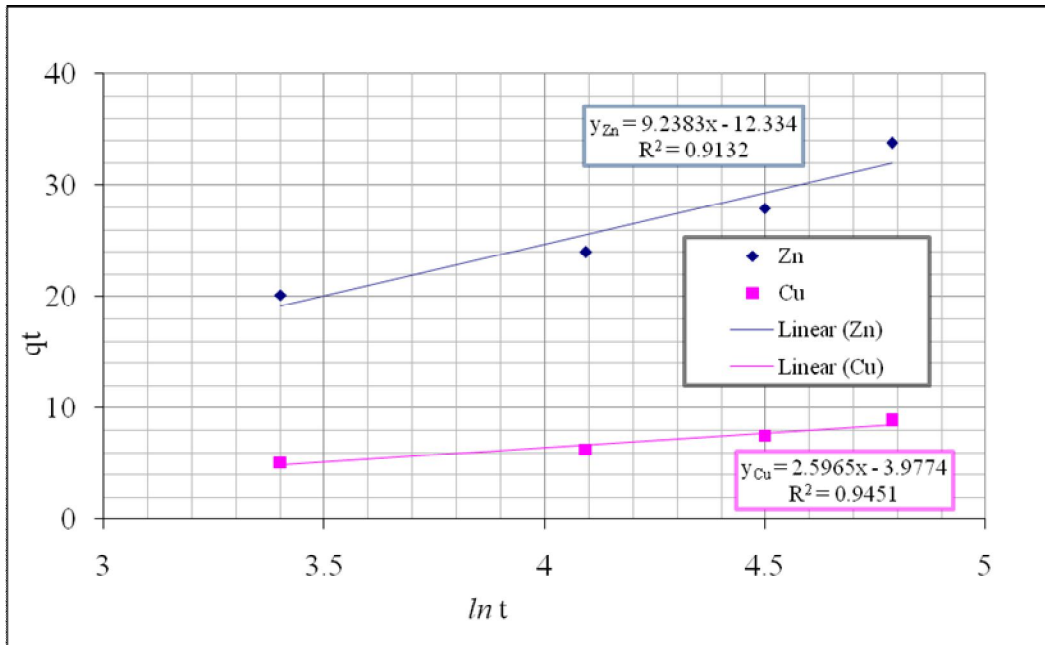


Figure 4.6.1: Plot of Elovich equation for zinc and copper

Table 4.6.1 shows Elovich equation parameters and coefficients. Data shows good compliance with the Elovich equation. The regression coefficients (R^2) for the linear plots were 0.9132 and 0.9451 for zinc and copper respectively.

Table 4.6.1: Elovich equation parameters and coefficient

| Heavy metal | Elovich equation | | |
|-------------|------------------|----------|--------|
| | β | α | R^2 |
| Zinc | 0.11 | 2.4 | 0.9132 |
| Copper | 0.39 | 0.55 | 0.9451 |

4.6.2 Pseudo-second-order

The rate constant of the pseudo-second-order chemical adsorption process is expressed in Eqn 4.6.2a,

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \dots\dots\dots \text{Eqn. 4.6.2a}$$

Where

q_e is the amount of heavy metal adsorbed on the adsorbent at equilibrium, (mg/g).

q_t is the amount of heavy metal adsorbed on the adsorbent at time t, (mg/g).

k is the equilibrium rate constant of pseudo-second-order adsorption, g/mg min.

Assuming that $q_t = 0$ at $t = 0$ the integrated form of Eqn. 4.6.2a becomes Eqn 4.6.2b,

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \dots\dots\dots \text{Eqn. 4.6.2b}$$

Eqn. 4.6.2b can be rearranged to give Eqn 4.6.2c,

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \dots\dots\dots \text{Eqn. 4.6.2c}$$

If,

$$h = kq_e^2 \dots\dots\dots \text{Eqn. 4.6.2d}$$

Where h is regarded as the initial adsorption rate.

Then Eqn. 4.6.2c becomes Eqn 4.6.2e and Eqn 4.6.2f

$$q_t = \frac{t}{\frac{1}{h} + \frac{t}{q_e}} \dots\dots\dots \text{Eqn. 4.6.2e}$$

And $\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t$ Eqn. 4.6.2f

Thus, a plot of $\frac{t}{q_t}$ against t would yield a linear relationship with the slope of $\frac{1}{q_e}$ and

intercept of $\frac{1}{h}$ or $\frac{1}{kq_e^2}$.

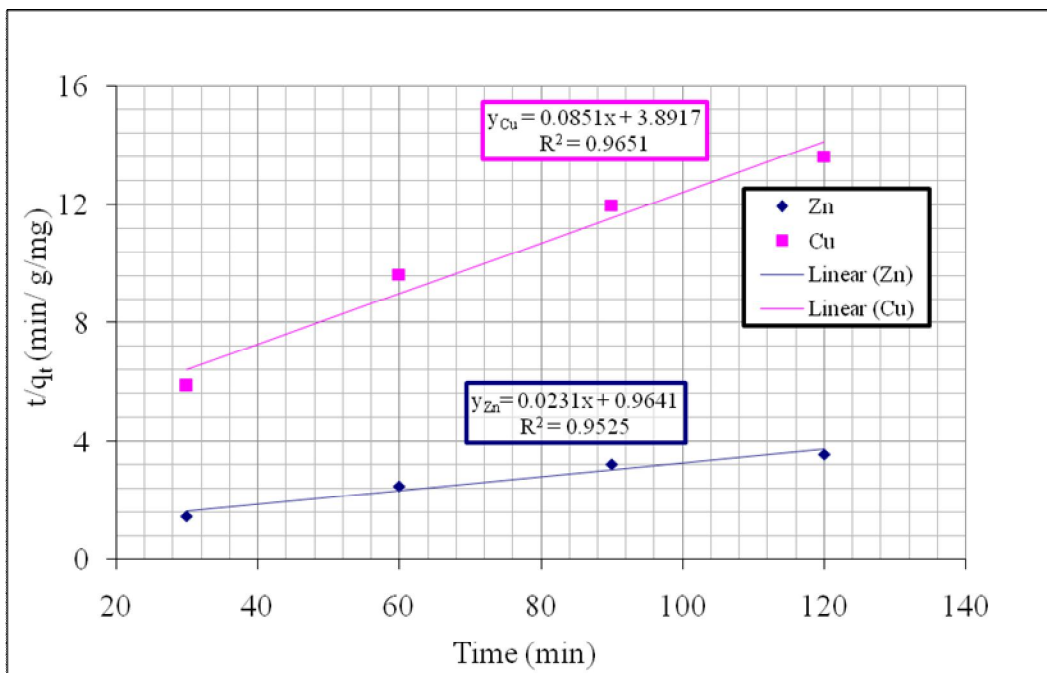


Figure 4.6.2: Pseudo-second-order adsorption kinetics of zinc and copper

Figure 4.6.2 shows the linearised form of the pseudo-second-order model for the adsorption of zinc and copper on WQD. The correlation coefficients, R^2 , and the pseudo-second-order rate parameters are shown in Table 4.6.2. The regression coefficients for the linear plots were 0.9525 and 0.9651 for zinc and copper respectively. The results indicate a good compliance with the pseudo-second-order equation.

Table 4.6.2: Pseudo-second-order parameters and coefficient

| Heavy metal | Pseudo-second-order equation | | | |
|-------------|------------------------------|-------------|--------|--------|
| | q_e (mg/g) | h (mg/g) | K | R^2 |
| Zinc | 43.29 | 1.04 | 0.0006 | 0.9525 |
| Copper | 11.75 | 0.26 | 0.0019 | 0.9651 |

Comparison of the two models reveals that the R^2 for both pseudo-second-order and the Elovich equations show that the results can be better represented by the pseudo-second-order model which has R^2 greater than 0.95 as opposed to Elovich whose R^2 was less than 0.95. The result shows that adsorption of zinc and copper by WQD is by physisorption and chemisorption reaction which occurred simultaneously.

4.7 Column experiment

4.7.1 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 lesser adsorption sites. This indicates less removal efficiency of heavy metals while increase on bed depth means more adsorption sites thus greater efficiency.

a) Effect on zinc

Table 4.7.1a 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 4.7.1a: Effect of effluent flow rate and column depth on the removal efficiency of zinc ions

| Column 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. This phenomenon is confirmed by batch experiment results which showed that adsorption equilibrium was reached at the optimum contact time of 120 minutes.

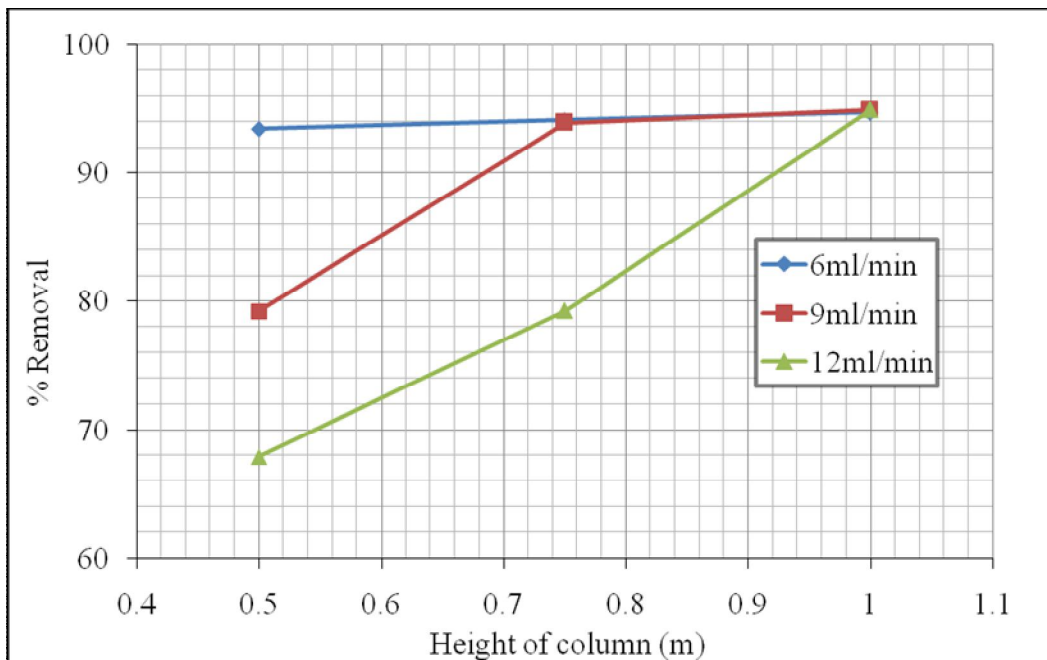


Figure 4.7.1a: Effect of effluent flow rate and column depth on the removal efficiency of zinc ions

Figure 4.7.1a 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 bed depth increased from 0.5 m to 1 m. The time taken to sample leachate at bed 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 bed depth increased from 0.5 m to 1 m. The time taken to sample leachate at bed 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 bed depth increased from 0.5 m to 1 m. The time taken to sample leachate at bed depth 0.5, 0.75 and 1 m was 120, 180 and 240 minutes respectively.

This phenomenon is confirmed by batch experiment results which showed that adsorption equilibrium was reached at optimum contact time of 120 minutes.

b) Effect on copper

Table 4.7.1b shows the effect of flow rate and column depth on copper ions removal efficiency. At bed 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 4.7.1b: Effect of effluent flow rate and column depth on the removal efficiency of copper ions

| Column 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 bed 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 bed 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.

This phenomenon is confirmed by batch experiment results which showed that adsorption equilibrium was reached at optimum contact time of 120 minutes.

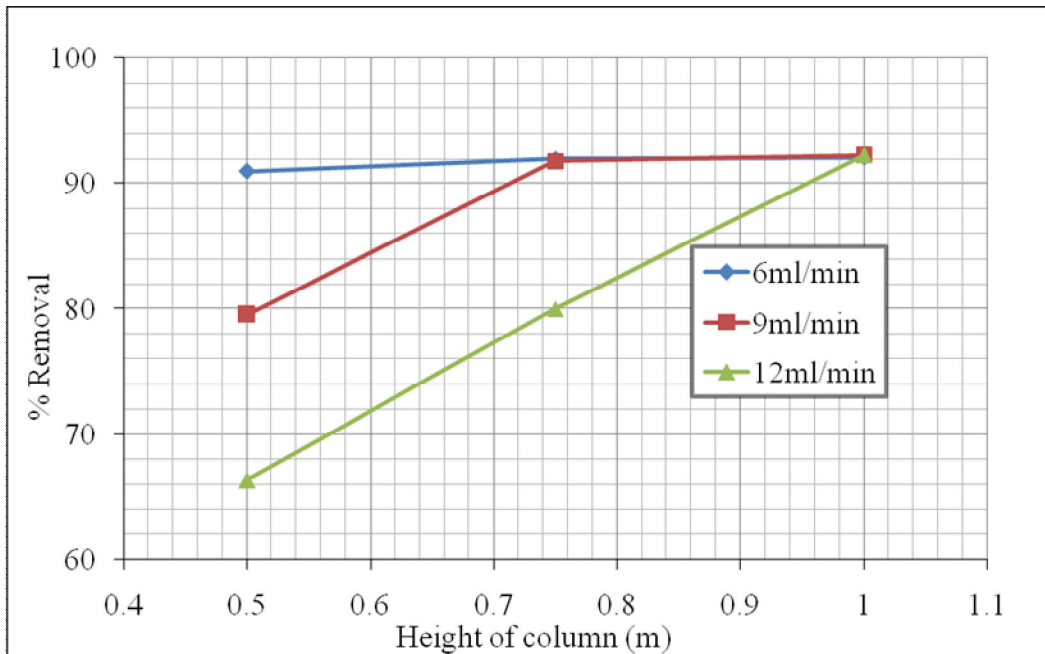


Figure 4.7.1b: Effect of effluent flow rate and column depth on the removal efficiency of copper ions

Figure 4.7.1b shows the effect of influent injection rates at various column depths. It illustrates the deviation in metal removal efficiency with changes in column depth at various flow rates. The results show that copper ions' 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 bed depth increased from 0.5 m to 1 m. The time taken to sample leachate at bed depth of 0.5m, 0.75m and 1 m was 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 bed depth increased from 0.5 m to 1 m. The time taken to sample leachate at bed depth of 0.5m, 0.75m and 1 m was 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 bed depth increased from 0.5 m to 1 m. The time taken to sample leachate at bed depth 0.5, 0.75 and 1 m was 120, 180 and 240 minutes respectively.

This phenomenon is confirmed by batch experiment results which showed that adsorption equilibrium was reached at optimum contact time of 120 minutes.

4.8 Adsorption capacity of WQD

Passage of wastewater through the adsorption column causes the fill up of adsorption sites over a period of time and exhausts the removal capacity of WQD.

The effect of bed height on the effluent adsorbate concentration is presented for flow rate of 12 ml/min and inlet adsorbate concentration of 35.1 and 9.3 mg/ml for zinc and copper respectively. The bed heights considered are 0.5, 0.75 and 1 m.

Figure 4.8a and figure 4.8b shows plot of concentration ratio C_e/C_o against time. It was observed that at smaller bed height, the effluent adsorbate concentration ratio approaches 1 faster than for a higher bed height. The WQD bed is saturated in less time for smaller bed heights than higher bed height. Smaller bed height corresponds to less amount of adsorbent which means, a smaller capacity for the bed to adsorb adsorbate from wastewater.

Figure 4.8a shows that zinc concentration ratio of 1 were attained in 360, 480 and 600 minutes at 0.5m, 0.75m and 1m adsorption depth respectively. This means that at bed

height of 0.5m, 0.75m and 1m, the WQD adsorption sites get filled up in 360, 480 and 600 minutes, when wastewater is passed up the column at a flow rate of 12 ml/min.

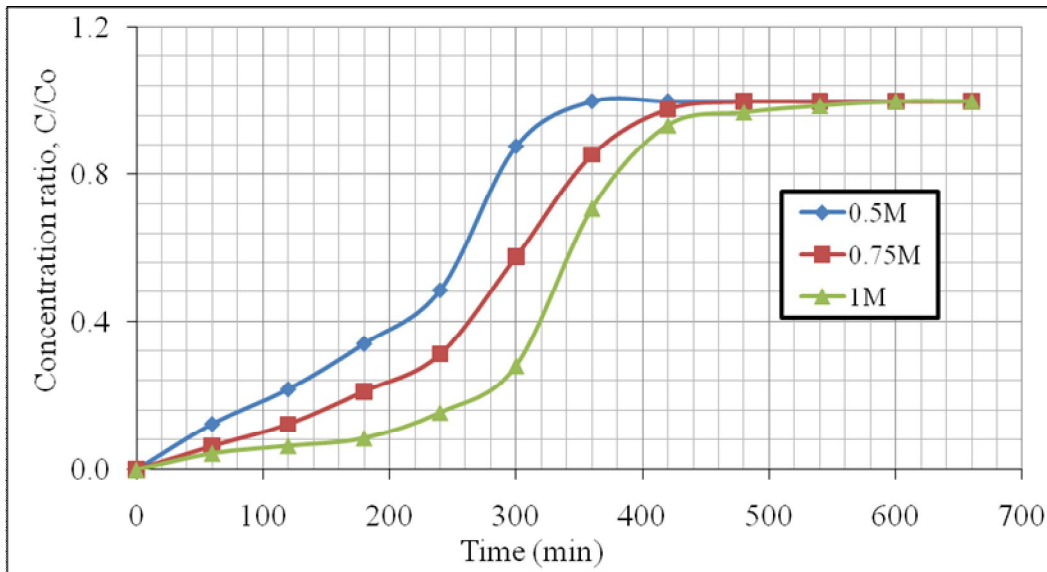


Figure 4.8a: Effect of bed height on breakthrough curve in the adsorption of zinc ions

Figure 4.8b shows that copper concentration ratio of 1 were attained in 360, 420 and 580 minutes at 0.5m, 0.75m and 1m adsorption depth respectively.

This means that at bed height of 0.5, 0.75 and 1 m, the WQD adsorption sites get filled up in 360, 420 and 580 minutes, when wastewater is passed up the column at a flow rate of 12 ml/min.

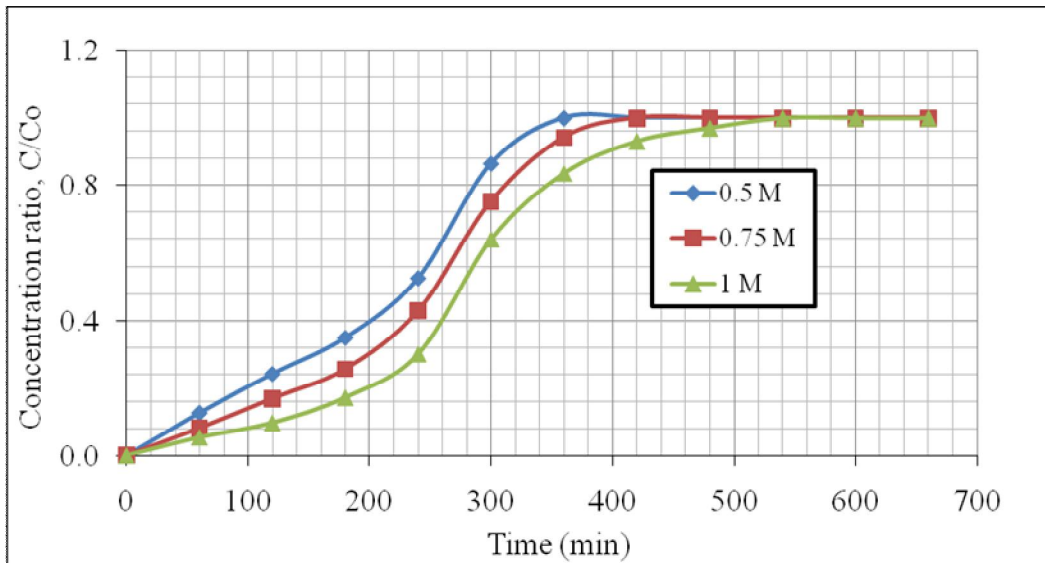


Figure 4.8b: Effect of bed height on breakthrough curve in the adsorption of copper ions

CHAPTER FIVE

5.0 MODELLING

5.1 Background

To examine the relationship between adsorbed, q and aqueous concentration C_e at equilibrium, adsorption isotherm models are widely employed for fitting the data, of which the Langmuir, Freundlich and BET equations are most widely used.

The WQD adsorption column has a columnar configuration and, therefore has concentration profiles in the axial direction. For this reason it is necessary to conduct a mass balance over an infinitesimal thickness of bed at a given cross-section. The resultant conservation of mass equation expresses the fact that any loss of solute by the wastewater sample passing through that section must be equal to the gain of solute by the adsorbent contained within that section.

In this study it was assumed that axial dispersion in the bed is negligible compared to bulk flow and that concentration gradients in the radial direction are minor.

5.2 Model development and discussion

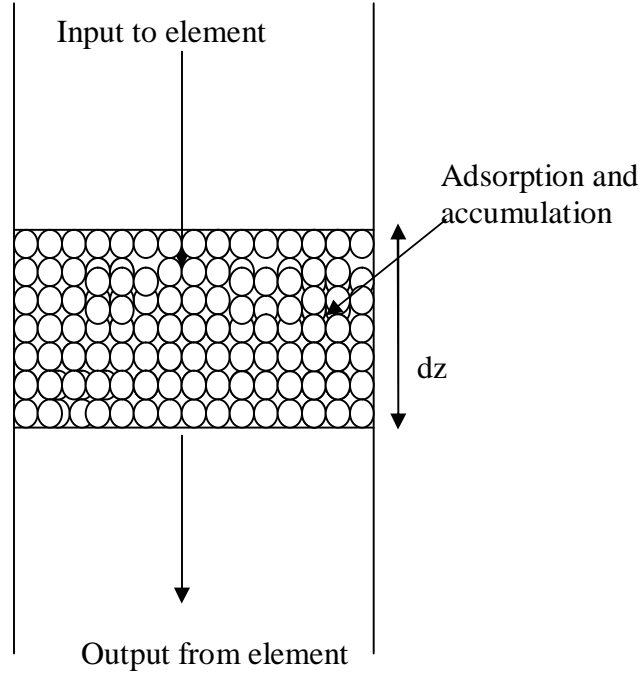


Figure 5.2a: Mass balance in element of fixed bed

Figure 5.2a 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 shown in Eqn 5.1:-

$$\text{Input of element} = \text{Output from element} + \text{Adsorption} + \text{Accumulation} \dots \dots \dots \text{Eqn5.1}$$

A mathematical formulation can be expressed as:-

Input to element: $C*U$

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: $\varepsilon \left(\frac{\partial c}{\partial t} \right) dzdA$

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 cm^2 .

ε is the void ration or porosity, dimensionless.

ρ is the packed-bed density, g/l.

Replacing Eqn5.1 with mathematical expressions and assuming a unit cross-sectional area, we get Eqn.5.2:-

$$C * U = \left(C + \frac{\partial c}{\partial z} dz \right) U + \rho \left(\frac{\partial q}{\partial t} \right) dz + \varepsilon \left(\frac{\partial c}{\partial t} \right) dz \dots\dots\dots\text{Eqn.5.2}$$

Eqn.5.2 can be simplified to become Eqn. 5.3,

$$U \frac{\partial c}{\partial z} + \varepsilon \frac{\partial c}{\partial t} + \rho \frac{\partial q}{\partial t} = 0 \dots\dots\dots\text{Eqn.5.3}$$

The partial differential equation, Eqn.5.3, 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 .

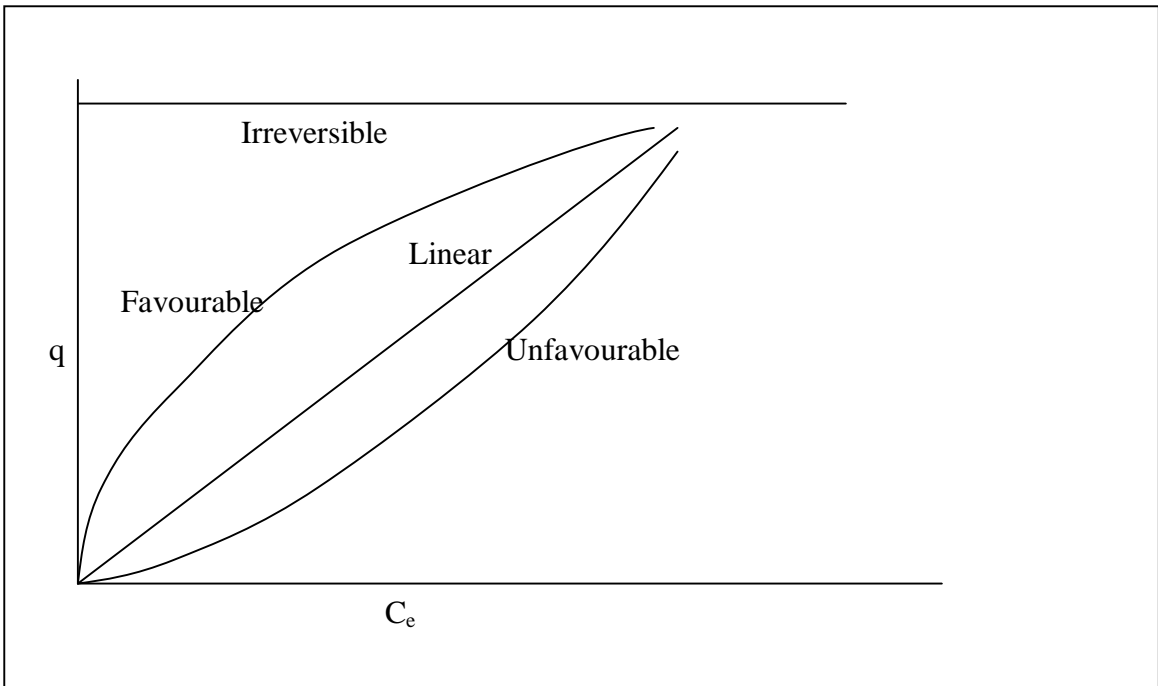


Figure 5.2b: Basic types of adsorption distributions

Figure 5.2b shows several types of distributions between phases that are possible. These distributions include the irreversible, favourable, linear and unfavourable cases.

Several mathematical formulations that describe adsorption equilibria include Freundlich, Langmuir and BET model isotherms. Mathematical representations of these models are

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

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

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

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. 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,

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

The extent of adsorption for copper is given by,

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

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 for zinc and copper ions which are 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).

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

5.3 Langmuir model for monosolute system

Langmuir adsorption isotherm is mathematically expressed by Eqn. 5.3.1;

$$q = \frac{X}{M} = \frac{X_m K C_e}{1 + K C_e} \dots\dots\dots \text{Eqn.5.3.1}$$

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 linearized form of the Langmuir equation Eqn.5.3.1, represented by Eqn.5.3.2:-

$$\frac{1}{q} = \frac{1}{C_e X_m K} + \frac{1}{X_m} \dots\dots\dots \text{Eqn.5.3.2}$$

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 X_m gives the theoretical monolayer saturation capacity.

5.4 Zinc and copper monosolute adsorption density

a) Zinc solution

Figure 5.4a shows a plot of adsorption density verses 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 the adsorption sites got filled up, the adsorption rate reduced as proved by a gentle curve in Figure 5.4a. Maximum equilibrium concentration (C_e Max) was 17.2mg/l and maximum equilibrium density (X_m) was 0.021mg/g.

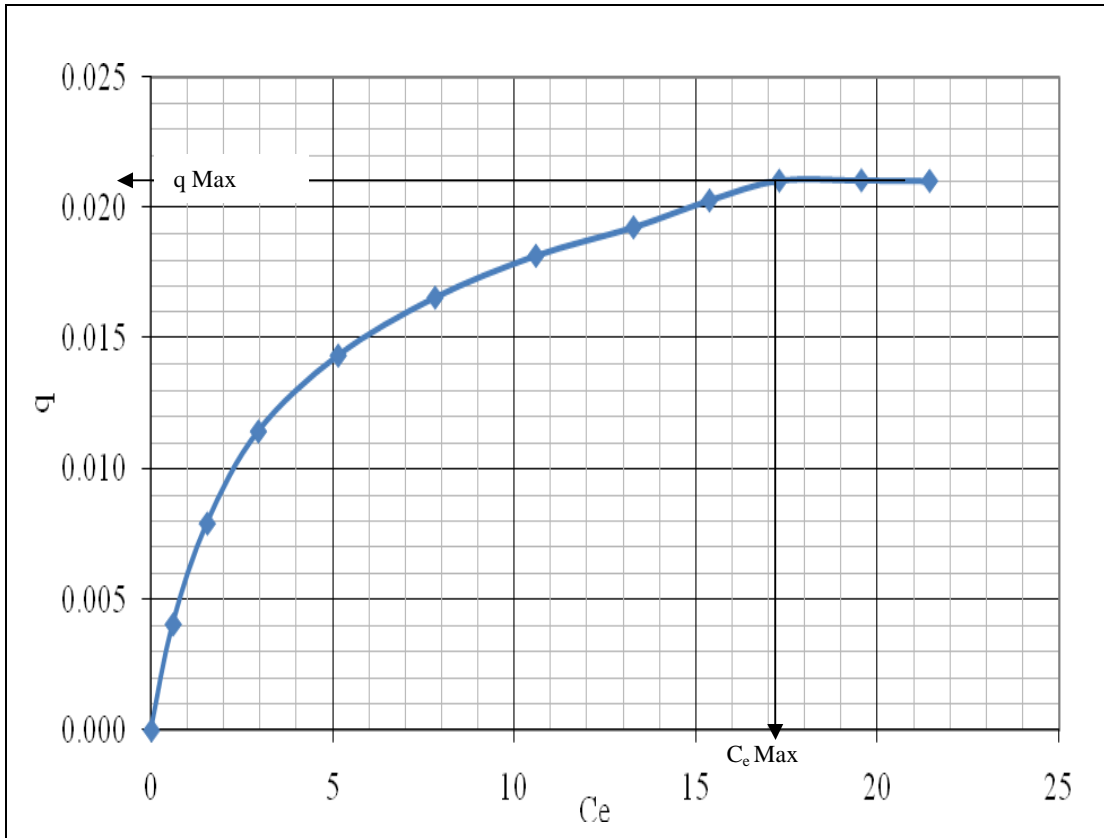


Figure 5.4a: Adsorption curve for zinc solution

b) Copper solution

Figure 5.4b 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 5.4b. Maximum equilibrium concentration (C_e Max) and maximum equilibrium density (X_m) were 4.6 mg/l and 0.005 mg/g respectively.

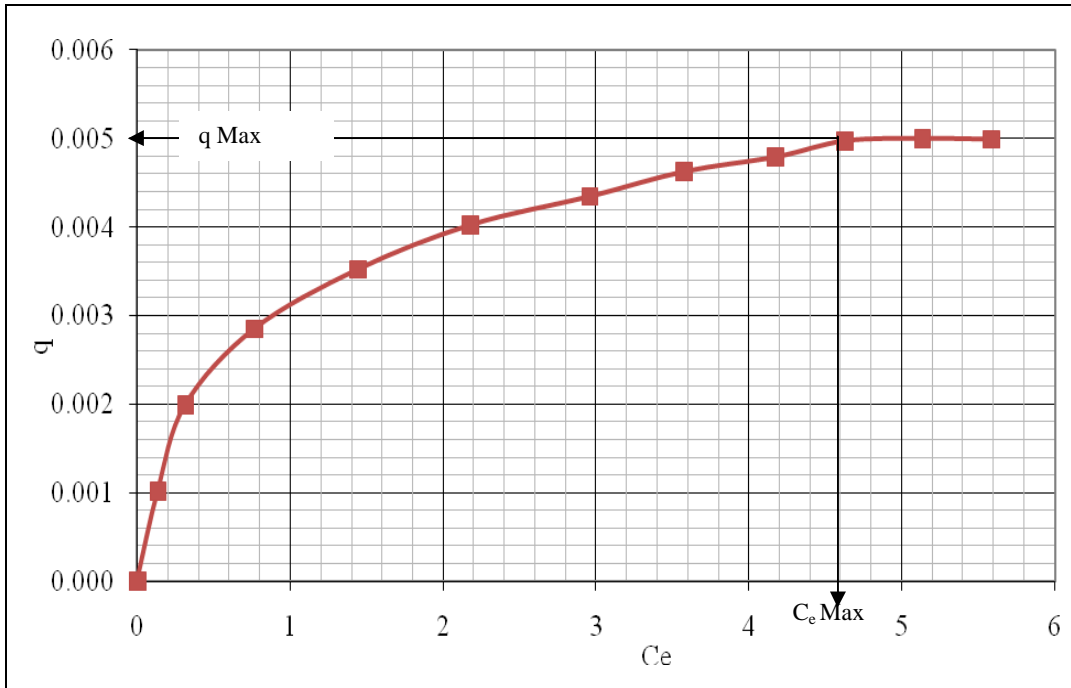


Figure 5.4b: Adsorption curve for copper solution

5.5 Zinc and copper monosolute linear curves

Table 5.5 shows the volume of treated heavy solution by adsorption column at given time intervals. The weight of the WQD in the adsorption column was 7000 grams. Using volume in Table 5.5 and 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 4.4.

Metal solutions linear curves $\frac{1}{q}$ versus $\frac{1}{C_e}$ for zinc and copper were plotted as shown

in Figure 5.5a and Figure 5.5b.

Table 5.5: Volume of treated solute at a given time

| Time in min | Volume in ml |
|-------------|--------------|
| 60 | 720 |
| 120 | 1440 |
| 180 | 2150 |
| 240 | 2900 |
| 300 | 3600 |
| 360 | 4300 |
| 420 | 5000 |

Figure 5.5a shows a linear curve 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 $\frac{1}{X_m} = 45.01$.

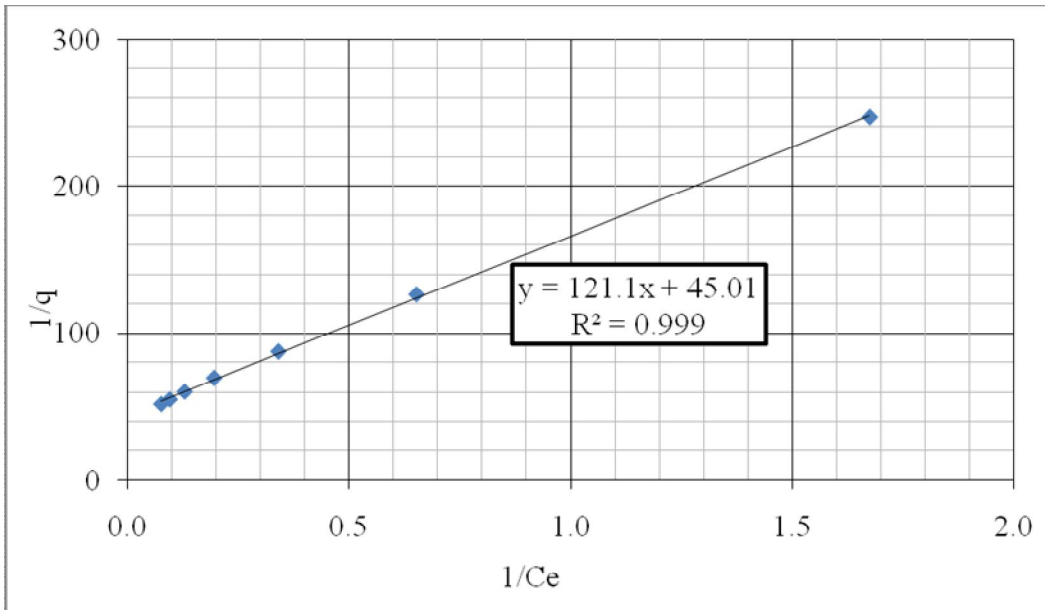


Figure 5.5a: Langmuir plot for zinc solution

Figure 5.5b shows a linear curve 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 $\frac{1}{X_m} = 197.0$.

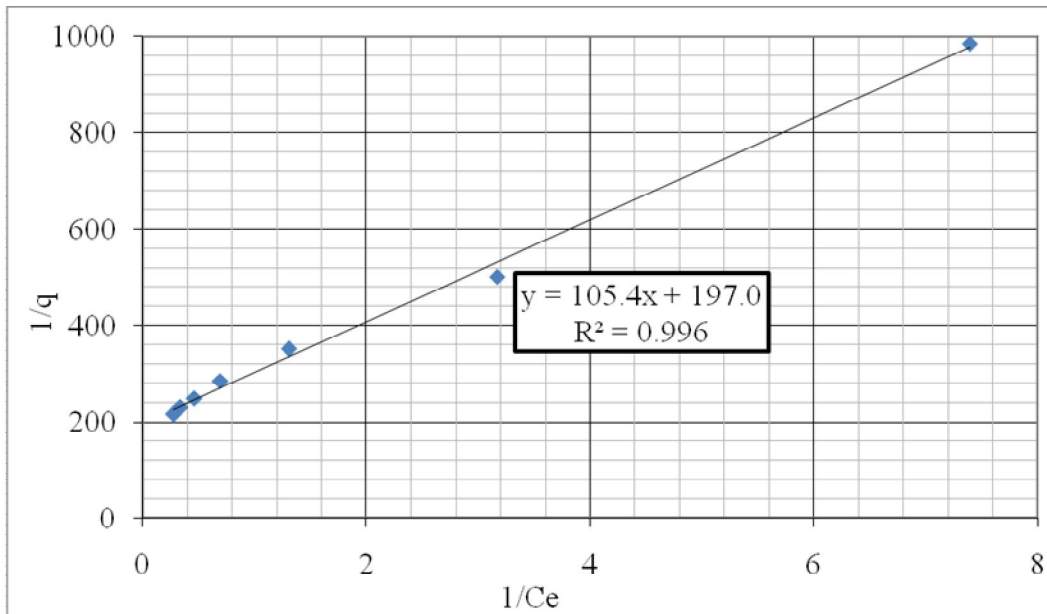


Figure 5.5b: Langmuir plot for copper solution

The Langmuir constants X_m and K for zinc and copper ions were obtained by solving the linear equations. Table 5.5 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 5.4a and 5.4b respectively.

Table 5.5: Langmuir isotherm equilibrium constants

| 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 |

5.6 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 5.5, the extended Langmuir equations can be written as indicated by Eqn. 5.6a and Eqn. 5.6b:

For Zinc

$$q = \frac{X_{mZn} K_{Zn} C_{eZn}}{1 + K_{Zn} C_{eZn} + K_{Cu} C_{eCu}} = \frac{0.008 C_{eZn}}{1 + 0.37 C_{eZn} + 1.87 C_{eCu}} \dots \text{Eqn. 5.6a}$$

For Copper

$$q = \frac{X_{mCu} K_{Cu} C_{eCu}}{1 + K_{Cu} C_{eCu} + K_{Zn} C_{eZn}} = \frac{0.009 C_{eCu}}{1 + 1.87 C_{eCu} + 0.37 C_{eZn}} \dots \text{Eqn 5.6b}$$

5.7 Validation of the extended Langmuir model

Figure 5.7a and 5.7b shows a plot of adsorption density (q) verses equilibrium concentration (C_e) obtained from adsorption column experiments and model equation.

Using the balance equation $q = \frac{v}{m} (C_o - C_e)$, the values of q was calculated for every

value of C_e obtained from the experiment.

Where

q is the heavy metal uptake (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).

Using the equilibrium concentration C_e , obtained above, the equilibrium density q was calculated using Extended Langmuir model and compared to q obtained from the mass balance equation above. Figures 5.7a and 5.7b shows 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.

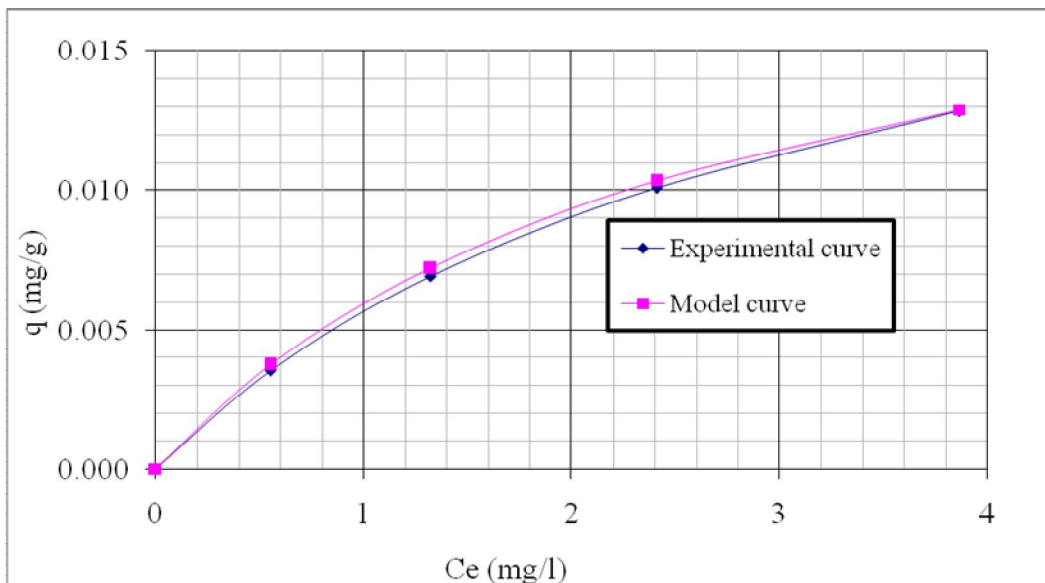


Figure 5.7a: Experimental and model adsorption density for zinc ions

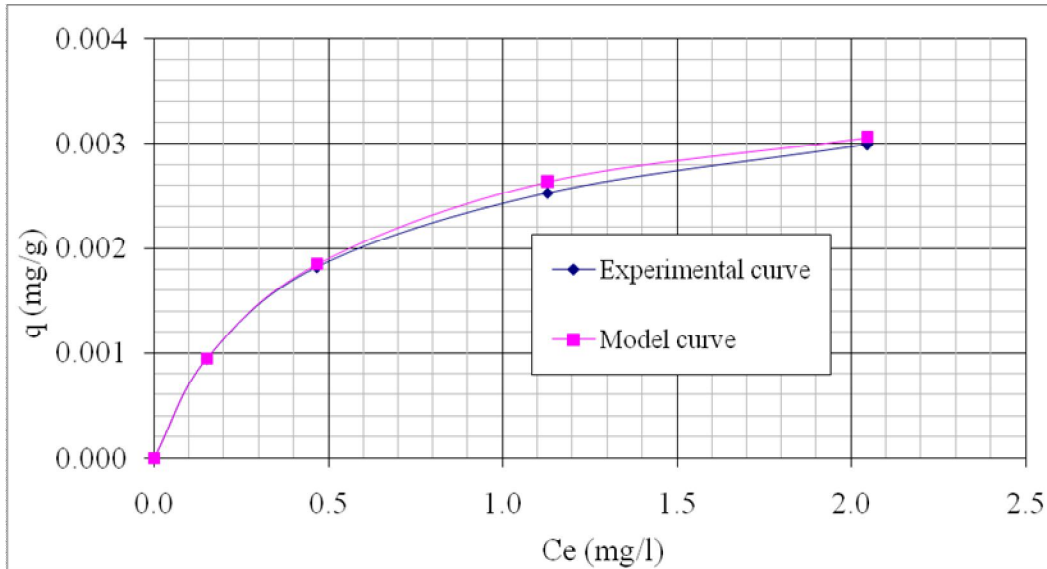


Figure 5.7b: Experimental and model adsorption density for copper ions

5.8 Design of adsorption columns based on Bohart-Adams equation

Hutchins (1973) presented a technique that requires three columns to collect data for design of adsorption column which can be used under given parameters. This technique uses the bed depth service time (BDST) approach. In this technique, the Bohart-Adams equation (Bohart and Adams, 1920) can be expressed by Eqn. 5.8a:-

$$t = ax + b \dots\dots\dots \text{Eqn.5.8a}$$

$$a = \text{Slope} = \frac{N_o}{C_o(V)} \dots\dots\dots \text{Eqn.5.8b}$$

$$b = \text{Intercept} = \frac{1}{K(C_o)} \ln\left(\frac{C_o}{C_B} - 1\right) \dots\dots\dots \text{Eqn.5.8c}$$

Where;

N_o = adsorptive capacity of WQD in mg/l.

C_o = initial concentration of solute in mg/l.

C_B = desired concentration of solute at breakthrough in mg/l.

V = Linear flow velocity of feed to bed in l/min/m².

= Flow velocity of feed to column v in ml/min divide by cross-section area. That

$$\text{is } V = \frac{v}{1000 * \pi D^2 / 4}$$

K = rate constant in l/mg-min.

If a value of a is determined for one flow, values for other flow rates can be calculated by multiplying the original slope a by the ratio of the original and new flow rates. However it is not necessary to adjust the value of b since it is insignificantly affected by changing the flow rates.

Laboratory test is conducted at solute concentration C_1 , to yield an Eqn.5.8d of the form

$$t = a_1 x + b_1 \dots\dots\dots \text{Eqn.5.8d}$$

To predict the equation for concentration C_2 can be done as follows,

$$a_2 = a_1 \frac{C_1}{C_2} \dots\dots\dots \text{Eqn.5.8e}$$

$$b_2 = b_1 \left(\frac{C_1}{C_2} \right) \frac{\ln \left(\frac{C_2}{C_F} - 1 \right)}{\ln \left(\frac{C_1}{C_B} - 1 \right)} \dots\dots\dots \text{Eqn.5.8f}$$

Where;

a_1 = Slope at concentration C_1 .

a_2 = Slope at concentration C_2 .

b_1 = Intercept at concentration C_1 .

b_2 = Intercept at concentration C_2 .

C_F = Effluent concentration at influent concentration C_2 .

C_B = Effluent concentration at influent concentration C_1 .

N_0 = adsorptive capacity of WQD in mg/l.

C_0 = initial concentration of solute in mg/l.

C_B = desired concentration of solute at breakthrough in mg/l.

V = Linear flow velocity of feed to bed in l/min/m².

V = Flow velocity, v in ml/min divided by column cross-sectional area = $\frac{v}{\pi r^2}$.

$$V = \frac{v}{\pi^2 * 1000} = \frac{v}{\pi * 0.04^2 * 1000} = \frac{v}{5} \text{ l/min/m}^2$$

K = rate constant in l/mg-min.

5.9 Validation of the Bohart-Adams equation

From the adsorption column data operating at a flow rate of 12 ml/min (linear flow rate = 2.4 l/min/m²) which was used to study the removal of heavy metals from wastewater, other adsorption columns operating under different parameters can be designed. For

example, zinc concentration was reduced from 35.1 mg/l to 1.8 mg/l with laboratory column bed depths and service times as tabulated in Table 5.8 below.

Table 5.8: Laboratory service time data for zinc

| Bed depth (m) | Time to breakthrough (min) |
|---------------|----------------------------|
| 0.5 | 360 |
| 0.75 | 480 |
| 1 | 600 |

Bohart-Adams equation can be used to predict the operating time for a 0.75 metre deep bed operating at a flow rate of 9 ml/min (linear flow rate = 1.8 l/min/m²). Moreover, the operating time (regeneration time) for this column can be predicted, if the influent concentration of zinc increased from 35.1 mg/l to 50 mg/l at a linear flow rate of 1.8 l/min/m².

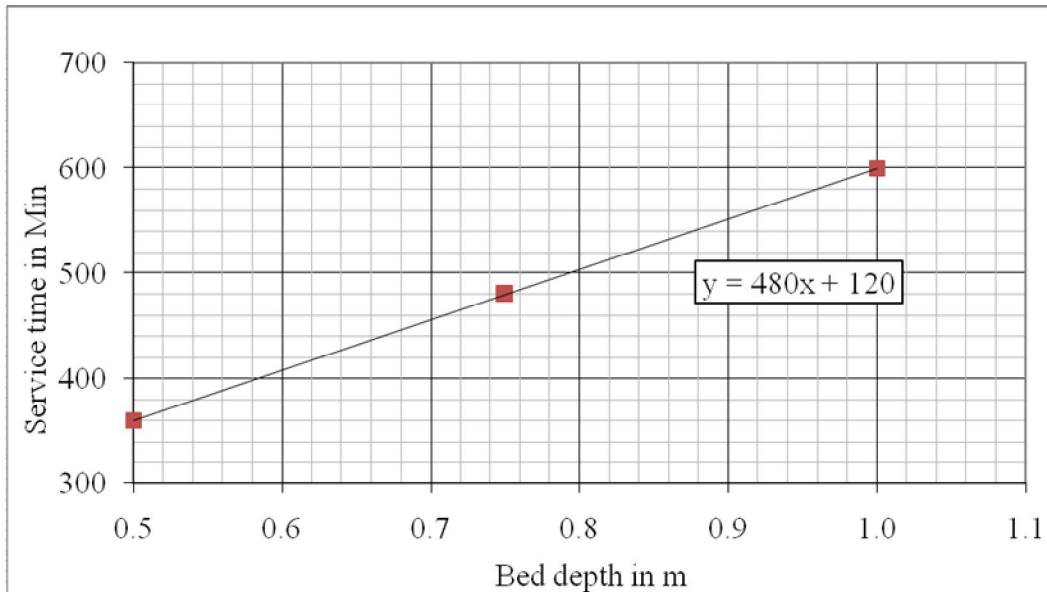


Figure 5.8: Bed depth service time plot

Figure 5.8 shows a plot of bed depth verses service time using the data in Table 5.8. The constants for the line equation $t = ax + b$, are $a = 480$ min/m and $b = 120$.

Thus, for a linear flow rate of 2.4 l/min/m² the equation for the line is $t = 480x + 120$

To determine the equation for a linear flow rate of 1.8 l/min/m², slope term a need to be adjusted without necessarily adjusting b .

$$a_1 = a \frac{V}{V_1}$$

Where;

a = Slope of the line at the original linear flow rate (V).

V = Original linear flow rate in l/min/m².

V_1 = Revised linear flow rate in l/min/m².

a_1 = Revised slope for new linear flow rate in (V_1).

$$a_1 = 480 * \frac{2.4}{1.8} = 640$$

Hence the predicted equation at $V_1 = 1.8$ l/min/m² is as shown by Eqn. 5.8g

$$t = 640x + 120 \dots\dots\dots \text{Eqn. 5.8g}$$

Equation 5.8 g can be used to predict the service time (regeneration time) for a 0.5, 0.75 and 1 m deep bed operating at a linear flow rate of 1.8 l/min/m² with an influent zinc concentration of 35.1 mg/l.

For 0.5 m adsorption column depth, regeneration time

$$t = 640 x + 120 = 640 (0.5) + 120 = 440 \text{ min}$$

For 0.75 m adsorption column depth, regeneration time

$$t = 640 x + 120 = 640 (0.75) + 120 = 600 \text{ min}$$

For 1 m adsorption column depth, regeneration time

$$t = 640 x + 120 = 640 (1) + 120 = 760 \text{ min}$$

The above regeneration time are similar to the ones found in the laboratory as shown in figure 5.9.

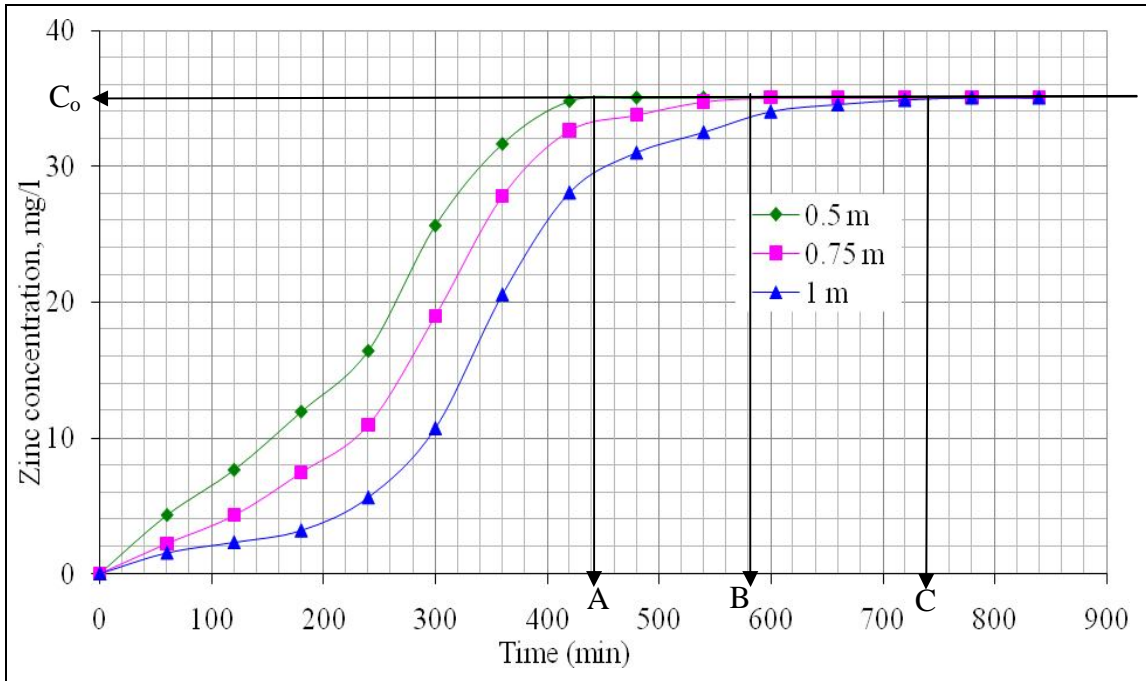


Figure 5.9: Service time curve for 9 ml/min flow rate

Figure 5.9 shows the service times for various adsorption bed depths when wastewater is passed through the column at a linear flow rate 1.8 l/min/m². C₀ is the zinc concentration of the effluent which was 35.1 mg/l. letters A, B and C indicates the service time at various bed depths. Wastewater was continuously passed through the column and

leachate samples collected at respective outlets for analysis until the inlet concentration (C_0) and outlet concentration (C) were equal. The service time for the respective adsorption bed depth were recorded in Table 5.9. The table shows service time for adsorption bed depths 0.5, 0.75 and 1 metre when water is passed up the column at a linear flow rate of 1.8 l/min/m².

Table 5.9: Laboratory and Bohart-Adams equation service time

| Adsorption bed depth in metres | Laboratory column service time in minutes | service time using BDST approach in minutes |
|--------------------------------|---|---|
| 0.5 | 440 | 440 |
| 0.75 | 580 | 600 |
| 1 | 740 | 760 |

It was observed that when Bohart-Adams equation was used to predict the service time, results were very similar to those found in the laboratory tests. Therefore it was concluded that Bohart-Adams equation can be used to predict the service time for a given column at a given flow rate using the data generated in the laboratory experiments. If zinc concentration changes at a given flow rate, both a and b must be corrected. For example if zinc concentration changes from 35.1 mg/l to 50 mg/l at a linear flow rate of 1.8 l/min/m²,

$$a_2 = a_1 \frac{C_1}{C_2}$$

Where;

a_1 = Slope value for 2.4 l/min/m² corrected to a linear flow rate of 1.8 l/min/m².

C_1 = old influent concentration in mg/l.

C_2 = new influent concentration in mg/l.

$$\text{Thus } a_2 = a_1 \frac{C_1}{C_2} = 640 * \frac{35.1}{50} = 4493$$

$$\text{Intercept for an influent concentration of 50 mg/l, } b_2 = b_1 \left(\frac{C_1}{C_2} \right) \frac{\ln\left(\frac{C_2}{C_F} - 1\right)}{\ln\left(\frac{C_1}{C_B} - 1\right)}$$

Where;

b_1 = Intercept at influent concentration C_1 .

C_1 = Influent concentration of 35.1 mg/l.

C_2 = Influent concentration of 50 mg/l.

C_B = Effluent concentration at influent concentration C_1 .

C_F = Effluent concentration at influent concentration C_2 .

C_B = Effluent concentration at influent concentration C_1 .

$$C_B = C_F = 1.8 \text{ mg/l.}$$

Hence,

b_2 = slope corrected for change in influent solute concentration.

$$b_2 = b_1 \left(\frac{C_1}{C_2} \right) \frac{\ln\left(\frac{C_2}{C_F} - 1\right)}{\ln\left(\frac{C_1}{C_B} - 1\right)} = 120 \left(\frac{35.1}{50} \right) \frac{\ln\left(\frac{50}{1.8} - 1\right)}{\ln\left(\frac{35.1}{1.8} - 1\right)} = 120(0.702) \frac{\ln 26.8}{\ln 18.5} = 84.24 * \frac{3.29}{2.9} = 95.6$$

Thus the new equation corrected for flow rate and influent concentration is

$$t = 449.3x + 95.6$$

The operating time for a 0.75 metre deep bed under these conditions is

$$t = 449.3x + 95.6 = 449.3 * 0.75 + 95.6 = 432 \text{ Minutes.}$$

CHAPTER SIX

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The following are conclusions made from this study:-

1. The use of WQD column in the removal of heavy metals, is technically feasible and with high efficacy. It compares well with other adsorbents with 96% and 94% removal efficiency for zinc and copper respectively.
2. When removing metal by adsorption, contact time, pH, column height and flow rate are important.
3. The heavy metal concentrations of the industrial effluent meet the requirements of KS 1966-2:2007, Kenya Standard Specification for Effluent tolerance limits, Part 2: Effluent discharged into public sewers.
4. The extended langmuir isotherm model adopted compared well with the adsorption data as the laboratory and model adsorption density curves were equal and similar for zinc and copper.
5. It was observed that adsorption columns can be designed based on Bohart-Adams equation. The service time predicted using Bohart-Adams equation for 0.5, 0.75 and 1m column at a linear flow rate of 1.8 l/min/m^2 were similar to those found in the laboratory column experiments.

6.2 Recommendations

The following are recommendations made from this study:-

1. Further research can be done to evaluate the effect of variation of temperature in the heavy metal removal using WQD.
2. Different heavy metal pollutants from industrial effluents can be investigated to have a conclusive fact about competitive adsorption using WQD as adsorbent.
3. Further research can be done to evaluate methods of heavy metal recovery after adsorption.
4. Further research can be done to evaluate the re-use of WQD or environmental friendly disposal methods.

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RESEARCH PAPERS

1. Mungathia, K.J., Thumbi, G.M. and Njenga, J.W. (2009). *Removal of Heavy Metals Using Quarry Dust Adsorption Column*. Journal of Kenya Bureau of Standards-the Bechmark, 32(2).
2. *Removal of Heavy Metals from Industrial Wastewater Using Washed Quarry Dust (WQD)*. This paper was presented in the CE International Conference on 24th Sept. 2008.
3. *Extended Langmuir Model Fitting to the Filter Column Adsorption Data of Heavy Metals*. This paper is ready and is in the process of being sent to journals for publication.
4. *Design of Heavy Metals Adsorption Column Based on Bohart-Adams Equation*. This paper is ready and is in the process of being sent to journals for publication.