

Thermodynamics and Kinetic Studies of Metal Adsorption on Coal Fly Ash Based on a Binary Mixture of Copper and Nickel

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A Dissertation Submitted to the Faculty of Engineering and Technology in Fulfilment of the Requirements for the Award of the Degree of Master of Engineering in Chemical Engineering of BIUST

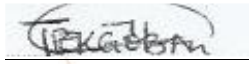
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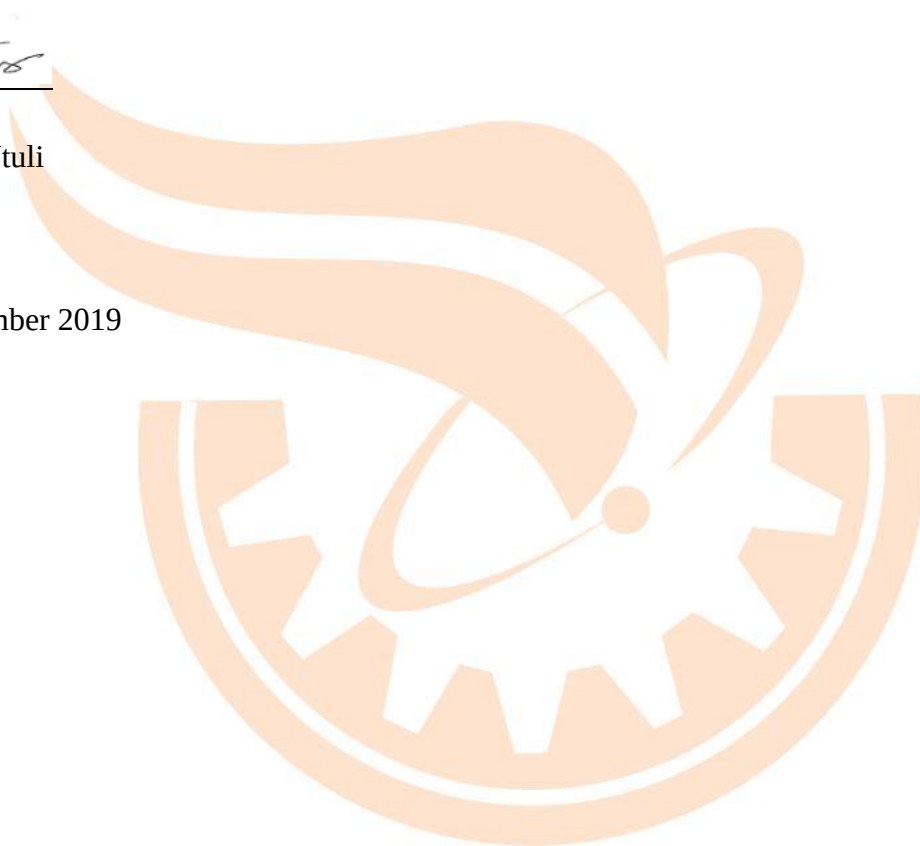
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Prof Freeman Ntuli

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ABSTRACT

The main purpose of this investigation was to study the potential application of Morupule fly ash for the removal of copper and nickel in wastewater. Batch and column study experiments were carried out by varying parameters such as pH, adsorbent dosage, contact time, temperature, bed height and flow rate. The data was fitted into the kinetic models, kinetic isotherms and the thermodynamic parameters to determine the nature of the process. Batch experiments showed a more energetically favourable adsorption process with a negative ΔG° , and positive values of ΔH° and ΔS° , indicating that the process was endothermic with a random solid – liquid interface. The pseudo first order and pseudo second order models were compared and the single metal system showed a better fit for the pseudo first order at 298 K and pseudo second order at 338K while for the binary metal system, the pseudo second order was predominant at both 293 and 313K. The results obtained were also fitted into the modified Langmuir and Freundlich kinetic isotherms and the modified Langmuir isotherm gave the best fit indicating a homogeneous and monolayer approach without interaction between the adsorbed molecules. Breakthrough curves were obtained for the fixed bed column study and the breakthrough time increased with an increase in bed height for copper while for nickel it decreased. As for the flowrate, the breakthrough time was similar at 10 and 20 ml/min for both metal ions but was slightly higher at 15 ml/min for copper and lower for nickel. The data from the column studies followed the Thomas model indicating that the process fits the Langmuir isotherm and is second order, controlled by mass transfer at the interface, which is in agreement with the models in the batch study. This generally indicates that the main mechanism of adsorption was chemisorption.

Keywords: *Adsorption, Adsorption kinetics, Batch and Column Study, Coal fly ash, Copper and Nickel*

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Chapter 1 : INTRODUCTION

1.1. Background and Motivation

Water is a very important and useful natural resource to every living thing i.e. it is a source of survival for human beings, fauna and flora. In recent years, Botswana has been facing a serious challenge of water scarcity because the country has always relied on rainfall and underground water. Reliance on rainfall and underground water to provide enough water is no longer sustainable due to changes in the weather patterns that have led to the country experiencing low rainfall hence the water scarcity situation. In light of this situation, it is imperative to embark on research to find more sustainable ways to ensure the continuous availability of water. Treatment of industrial wastewater has drawn the attention of many researchers in recent years as a way of remedying the problem of water scarcity but they have discovered that industrial wastewater contains borderline metals such as copper (Cu) and nickel (Ni) that need to be removed before the water can be suitable for use. Though these metals are used to produce some goods that are important to human life e.g. copper and nickel are used to make corrosion-resistant alloys, they bear some characteristics that make them adverse to living organisms at certain concentrations. These metals are non-biodegradable and consumption or long term exposure to them may cause serious health issues like damage to the liver and kidneys, mental retardation, central nervous system problems, hepatic and renal damage and even death (Demirbas *et al.*, 2009). Researchers have therefore developed several techniques to treat the industrial wastewater for removal of borderline metals like chemical precipitation, membrane filtration, ion exchange and adsorption (Srivastava *et al.*, 2006). Of all these techniques, adsorption has proven to be cost effective, less time consuming and requires less resource usage hence it has been given much priority than other techniques. This process requires the use of an adsorbent and some low cost adsorbents have been found that are generated from industrial processes as by-products such as blast furnace slag, sludge, fly ash, lignin and red mud and are utilised for the removal of toxic heavy metal from wastewater (Ahmed and Ahmaruzzaman, 2016). In Botswana, coal fly ash is generated in large quantities from coal firing at Morupule Power Station for power generation therefore it is best to consider studying its effectiveness as an adsorbent in the removal of borderline metals in industrial wastewater as it is available locally and will be cheaper to obtain and use. It is currently being produced at a rate of more than 600 000 tons per annum and almost 95% of this ash is disposed-off as waste with only about 5% being used in making cement. The continued increase in the production of coal fly ash, a powdered coal residue which has been considered a waste material

has driven the motivation to seek for possible industrial applications (Sočo and Kalemekiewicz, 2013). The use of coal fly ash also addresses the issue of environmental management because disposing it off in large quantities poses a threat to the environment. It poses a threat of air pollution because living things utilise air for respiration which if contaminated with ash dust becomes a hazard and water pollution when the metal contents are leached into water sources, therefore utilizing it as an adsorbent solves two problems: water quality and waste management (Xiyili *et al.*, 2017). Most research has focused on single metal adsorption from aqueous solutions but it is important to note that copper and nickel are often found together in industrial wastewaters (e.g. mine drainage systems, plating plants, paint and ink formulation units and porcelain enamelling) (Srivastava *et al.*, 2006). It is important to carry out a binary component adsorption as both metals are normally found in industrial effluents. This study will focus on removing copper and nickel from binary solutions containing both metal ions which will contribute to the recycling of treated wastewater thus remedying the problem of water scarcity in Botswana. It will also contribute to the protection of the environment by reducing air and water pollution caused by coal fly ash.

1.2. Aim and Objectives

1.2.1. Aim

To investigate the use of coal fly ash in the adsorption of copper and nickel ions from binary aqueous solutions.

1.2.2. Objectives

- a. To determine the effect of process parameters (solution pH, contact time, temperature and adsorbent dosage) on the adsorption of copper and nickel.
- b. To run both batch and column studies to determine the rate of adsorption of copper and nickel.
- c. To analyse the kinetic models and adsorption isotherms of the process.
- d. To determine the spontaneity and energy requirements of the process through thermodynamic studies.
- e. To determine the mechanism of metal removal using coal fly ash as an adsorbent.

1.3. Research Questions

The key research questions outlined are meant to address the main and specific objectives of the dissertation and the key questions are as follows;

- What is the uptake of copper and nickel in their adsorption as single component and as binary components?
- Which kinetic model and kinetic isotherm best fit the experimental data or conforms to this process?
- What are the effects of process parameters (solution pH, contact time, temperature and adsorbent dosage) on the adsorption of copper and nickel metal ions in industrial effluents?
- Is the thermodynamic study showing an endothermic or an exothermic reaction?

1.4. Hypothesis

Fly ash produced from the burning of coal is a more reasonable adsorbent for the removal of metal ions in waste water due to its hydrophilic surface and porous structure. The hydrophilic surface will allow the adsorbent to be wetted by water and the highly porous structure allows for the metal ions to be adsorbed. It is expected that the use of fly ash to remove metal ions is a more sustainable way to decontaminate water and a viable environmental management option.

1.5. References

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Chapter 2 : LITERATURE REVIEW

2.1. General Overview

The presence of metal ions in water is a cause for great concern such that they must be removed because of their effects to the population that is human and aquatic life. This chapter seeks to explore knowledge on known techniques that remove metal ions in water together with the involved adsorbents. In this chapter, a review of the characterisation techniques of fly ash will be conducted and the methods of analysis such as batch and column studies will play a critical role in justifying this research.

2.2. Wastewater

Wastewater typically contains high levels of organic materials, suspended solids, oils, grease and borderline metals. It is produced largely as either domestic wastewater or industrial wastewater depending entirely on the sector from which it comes from. There are many ways in which water gets contaminated ([Kapur and Mondal, 2014](#)) and a number of organic, inorganic and metallic species enter the water bodies or sources and become lethal/toxic after reaching a certain limit in the metabolic system. Borderline metals are among the most important pollutants in source or treated water considering the volume discharged as effluent in the industry in particular ([Wang *et al.*, 2006](#)). In industrial wastewater, borderline metals of greater concern include chromium (Cr), Cadmium (Cd), Lead (Pb), Zinc (Zn), Copper (Cu), Nickel (Ni), Arsenic (As) and Mercury (Hg) ([Ahmed and Ahmaruzzaman, 2016](#)). Their concentrations in wastewater vary from 0.5 to a high of 1000 mg/l and the international standard acceptable limit for copper and nickel in drinking water are 0.05 mg/l and 0.02 mg/l respectively ([Kapur and Mondal, 2014](#)). Wastewater treatment has been identified as the potential important step to take in most countries to address issues of water scarcity. The purpose of wastewater treatment is to remove pollutants that harm the aquatic environment and also to make drinking water safe. Researchers have shown interest in treating such effluents by applying some techniques and a variety of parameters are considered when choosing the best method such as cost, time needed for purification, chemical inputs, flexibility and design simplicity.

2.2.1. Techniques/Technologies Available for Wastewater Treatment

Numerous techniques are available for waste water treatment such as microbial system, electrochemical process, chemical precipitation, coagulation, photo catalytic degradation, ion exchange, adsorption and membrane filtration. As much as these numerous techniques have been developed to treat borderline

metal laden waste water, they have their inherent advantages and disadvantages (Varma *et al.*, 2013). Table 2.1 presents the advantages and disadvantages of these techniques.

Table 2.1: Treatment Technologies/Techniques for Borderline Metal Loaded Wastewater (Ahmed and Ahmaruzzaman, 2016)s

Treatment Technology	Advantages	Disadvantages
Biological Treatment	Removes only a few metals	Establishment and commercialisation of technology needs to be done
Electrochemical Treatment	Rapid process but effective for particular metal ions	High energy cost and generation of by-products
Coagulation/Flocculation	Economically achievable	High sludge formation
Photochemical Degradation	Forms no sludge	Generates some by-products
Ion Exchange	Good at removing a wide range of borderline metals	Adsorbent material requires regeneration and poses some disposal problems
Adsorption	Flexible and simple to design, easy to operate and insensitivity to toxic pollutants	Adsorbent often need regeneration after the process
Membrane Filtration	Good removal of borderline metals	Produces sludge and is expensive to utilise

2.3. Adsorption

Adsorption is a separation process in which certain components of a fluid phase are transferred to the surface of a solid adsorbent. Performance depends on a solid – fluid equilibrium and on mass transfer rates. Adsorption is applicable for most separations that have proved impractical by conventional methods such as distillation, absorption and membrane based systems (McCabe, *et al.*, 1993). The major application of adsorption in liquid phase systems is in the removal of relatively small amounts of impurities in water treatment, sugar refineries and other processes. In batch processes, a slurry is created by contacting a powdered adsorbent with a liquid body and the two phases are separated by filtration (Couper, *et al.*, 2005). The process of adsorption involves three processes which are surface ionisation,

complex formation and the formation of an electrostatic double layer that is adjacent to the adsorbent surface. Adsorption can be categorised into two types which are physical (physisorption) and chemical (chemisorption) adsorption. Physical adsorption results from the influence of intermolecular forces (Van Der Waals) mainly because the forces are weak and easily reversible. Chemical adsorption is where forces bind together adsorbed molecules to the solid surface and they involve the sharing or exchange of electrons (Coulson, *et al.*, 2002). Due to the binded molecules, chemisorption is less easily reversible compared to physisorption hence it is not well suited where adsorbent regeneration is required. Chemisorption forms a unimolecular (monolayer) and it may be followed by additional layers of physical adsorbed molecules because physisorption can be both monolayer and multilayer. Both types of adsorption are exothermic therefore raising the temperature generally decreases the equilibrium quantity of the adsorbate and their rate strongly depends on pressure (Chorkendorff *et al.*, 2003). Table 2.2 compares the two types of adsorption.

Table 2.2: Comparison of Physisorption and Chemisorption (Chorkendorff *et al.*, 2003)

	Physisorption	Chemisorption
Cause	Weak van der Waals forces with no electron transfer	Has strong electrostatic/covalent forces with electron transfer
Adsorbents	All solids	Some solids
Adsorbates	Gases operating below critical point and have intact molecules	Some chemically reactive gases that dissociate into atoms, ions and radicals
Temperature Range	Operates at low temperatures	Operates at high temperatures
Heat of Adsorption	Low heats of adsorption (heat of fusion at about 10 kJ/mol) hence always exothermic	Has high heats of adsorption (heat of reaction at about 80 – 200 kJ/mol) hence usually endothermic

Rate	Very fast and reaches equilibrium rapidly	Depends strongly on the temperature to be rapid.
Activation Energy	Requires low to no activation energy	Requires high activation energy
Surface Coverage	Forms multimolecular layers	Forms mono/unimolecular layers
Reversibility	Process is highly reversible	Process is often reversible
Applications	Determines the surface area and pore size of adsorbent	Determines the surface concentrations and kinetics, rates of adsorption and desorption. Determines active centres.

2.4. Adsorbents

Adsorption is a process that requires the use of an adsorbent. An adsorbent is a solid substance that has the ability to extract substances from gases, liquids or solids by causing them to adhere to its surface.

2.4.1. Nature of Adsorbents

A number of features are considered in an adsorbent for it to be commercially attractive and these include:

- Having a large internal surface area.
- Big enough pores to allow the molecules to be adsorbed.
- Easy regeneration of adsorbent.
- Having an adsorptive capacity that is able to withstand continuous recycling.
- Should be mechanically strong enough to endure handling and vibrations from any industrial unit (Coulson, *et al.*, 2002)

Commercially manufactured adsorbents such as zeolites, activated alumina, silica gel and activated carbon have been used for waste water treatment for many years (Kapur and Mondal, 2014). A growth in environmental concerns and high costs of these adsorbents arose and research has in recent years

focused on developing more environmental friendly and low cost or more economical adsorbents ([Kapur and Mondal, 2014](#)). By-products in industrial processes which are considered as industrial wastes such as blast furnace slag, sludge, fly ash, lignin and red mud have been given much attention owing to their high adsorptive capacities and abundant local availabilities ([Ahmed and Ahmaruzzaman, 2016](#)). Many adsorbents have been developed and are classified according to the materials they are derived from. [Table 2.3](#) shows the classification of commonly used adsorbents.

Table 2.3: Classification of commonly used adsorbents

Commercially Manufactured	Industrial Wastes	Natural Materials	Zeolites	Agriculture Residues
Activated Carbon	Blast furnace Slag	Bentonite	Clinoptilolite	Saw dust
Chitosan Beads	Fly ash	Attapulgit	Kaolinite	Bagasse

The removal of borderline metals from waste water is dependent on the effectiveness of these adsorbents but choosing the best adsorbent for a process centres around key parameters such as removal capacity, efficiency, cost, dosage requirements, and time taken to reach equilibrium.

2.4.2. Adsorbent Attributes

Many adsorbents can be used in the removal of borderline metals but the most important attributes of an adsorbent for any application include capacity, selectivity, regenerability, kinetics, compatibility and cost. It is very rare to find a single adsorbent optimal in all these attributes but the choice of adsorbent can be made from them ([Knaebel, 2003](#)).

Adsorption loading (capacity) is the most important characteristic of an adsorbent. This is the adsorbate amount an adsorbent can take up per unit mass (or volume) of adsorbent. It is dependent on the fluid phase concentration, temperature and the initial condition of the adsorbent. Adsorption capacity is of principal importance to the capital cost because it prescribes the amount of adsorbent required ([Knaebel, 2003](#)).

Another important characteristic is selectivity, which is the ratio at a given fluid concentration of the capacity of one component to that of other component. This ratio approaches a constant value as concentration drops to zero. A large selectivity (ideal situation) occurs when much of the major component is not adsorbed (Knaebel, 2003).

For an adsorbent to operate in a sequential cycle with uniform performance, it must be regenerable because all cyclic adsorption applications are reliant on regenerability. The heat of adsorption provides a measure of the energy required for regeneration and the adsorbable component must be weakly adsorbed. Regenerability of an adsorbent affects the fraction of the original capacity that is retained, the time and the energy required for regeneration. The life of an adsorbent is characterised by gradual decay which occurs due to ageing and poisoning which are governed by the number of cycles an adsorbent has been subjected to (Knaebel, 2003).

Kinetics is a mass transfer term that is related to intra particle mass transfer resistance. It is important because it controls the cycle time of a fixed bed adsorption process. A sharp breakthrough curve is provided for by fast kinetics and an expanded breakthrough curve is yielded by slow kinetics. The throughput per unit mass of adsorbent reduces with an increase in the cycle time and in turn this helps overcome the expended breakthrough curve (Knaebel, 2003).

Another attribute is compatibility which covers numerous possible modes of chemical and physical attack that could reduce the life expectancy of the adsorbent such as biological fouling or attrition. It is important for operating conditions such as velocity, temperature, pressure and vibration not to cause undue disintegration of the adsorbent particles (Knaebel, 2003).

Cost varies from time to time and from company to company for the same material making it the most subtle characteristic to understand (Knaebel, 2003).

2.5. Fly ash

Fly ash is an amorphous mixture of ferroaluminosilicate minerals generated by combustion of ground and powdered coal. Approximately 70% of the combustion by products is fly ash collected in electrostatic precipitators. The mineralogy, physical and chemical properties of fly ash depend on nature of the parent coal (Malarvizhi and Santhi, 2013). Physical properties such as its porosity, particle size distribution and surface area enhances the potential of fly ash for use in waste water treatment (Sočo and Kalembkiewicz, 2013). The major constituents of fly ash are silica (SiO_2), alumina (Al_2O_3), ferrous

oxide (Fe_2O_3), calcium oxide (CaO) and varying amounts of carbon (Xiyili *et al.*, 2017). Fly ash is generally classified into two classes and this is based on the amount of calcium oxide (lime) with Class F containing less than (7wt %) CaO and Class C (5 – 30wt %) CaO . Class F is normally produced from anthracite, bituminous or sub-bituminous coals while Class C is produced from lignite coals (Wang and Wu, 2006). Every year, there is a large amount of fly ash produced during combustion of coal all over the world, which requires large dumping sites for safe disposal or investigation for reuse and recycling of those fly ash waste. The utilisation rate of fly ash is still in a relatively low level and the major use of fly ash has been as an additive to cement concrete and other building materials and also as soil amendments (Luo *et al.*, 2011). Ash resulting from burning of coal to create energy of a thermal power plant may be considered a reasonable adsorbent for metal ions in diluted aqueous solutions because it has a hydrophilic surface and a porous structure suggesting that ash adsorption is a progression towards a prospective method especially at acid mine sites (Wang and Wu, 2006; Yucel and Baba, 2015). Table 2.4 shows chemical composition of some metal oxides in coal fly ash.

Table 2.4: Chemical Composition of Metal Oxides in "Class C" and "Class F" Fly Ash (Hemalatha and Ramaswamy, 2017)

Metal Oxide	Weight %	
	Class C	Class F
CaO	15.1 – 54.8	0.50 – 14.0
SiO_2	11.8 – 46.4	37.0 – 62.1
Al_2O_3	2.6 – 20.5	16.6 – 35.6
Fe_2O_3	1.4 – 15.6	2.6 – 21.2
MgO	0.1 – 6.7	0.3 – 5.2
K_2O	0.3 – 9.3	0.1 – 4.1
Na_2O	0.2 – 2.8	0.1 – 3.6
SO_3	1.4 – 12.9	0.02 – 4.7
P_2O_5	0.2 – 0.4	0.1 – 1.7

TiO ₂	0.6 – 1.0	0.5 – 2.6
MnO	0.03 – 0.2	0.03 – 0.1
LOI	0.3 – 11.7	0.1 – 32.8

2.5.1. Fly ash application for borderline metals removal

Parameters such as pH, contact time, agitation speed, adsorbent dosage and temperature play an important role in influencing the removal of heavy ions by the process of adsorption. These parameters are therefore studied to determine the effectiveness of fly ash in removing the borderline metals. Fly ash has been known to be an effective and low cost adsorbent in the removal of copper and nickel ions in waste water. For copper, it has a removal capacity of about 0.048 mg/g (Mohan and Gandhimathi, 2009; Ahmed and Ahmaruzzaman, 2016) and a removal percentage of 98 (Bayat, 2002; Gor *et al.*, 2007) with an equilibrium time of 60 minutes (Pehlivan and Cetin, 2008; Sočo and Kalembkiewicz, 2013; Kapur and Mondal, 2014). A similar trend in terms of equilibrium time was observed for nickel as it reaches equilibrium in 60 minutes (Pehlivan and Cetin, 2008; Sočo and Kalembkiewicz, 2013; Kapur and Mondal, 2014) but has a removal capacity of 4.50 mg/g (Sočo and Kalembkiewicz, 2013; Ahmed and Ahmaruzzaman, 2016) while its removal percentage ranges between 95 to 99.9 (Bayat, 2002; Rao *et al.*, 2002; Koshy and Singh, 2016). The research on the use of fly ash for adsorption has been carried out elsewhere and very little research has been done on the use of Morupule fly ash for waste water treatment in Botswana. This research therefore seeks to understand the response of Morupule fly ash in Botswana in its application to the removal of borderline metals such as Copper and Nickel in waste water.

2.5.2. Fly Ash Characterization

Characterization of the fly ash before and after adsorption helps to determine the changes in the elemental composition, mineral identification, surface morphology and the functional groups present as may be affected by metal ions occupying the sites in the adsorbent.

2.5.2.1. X – Ray Fluorescence (XRF)

Energy dispersive X-ray fluorescence technology (ED-XRF) determines the chemical composition of different types of materials and is simple, accurate and the most economic analytical method. Solid, liquid and powdered samples are suitable for ED-XRF analysis because it is a non – destructive, reliable

and requires little to no sample preparation. It detects sub-ppm level limits for a wide range of elements from sodium (11) to uranium (92) and measures concentrations of up to 100% easily and simultaneously.

2.5.2.2. X – Ray Diffractometer (XRD)

The crystallinity, mineral and phase compositions of the adsorbent are examined with an x-ray diffractometer. Sharp peaks show that the sample is crystalline while broad peaks signify the amorphous nature of the sample (Kapur and Mondal, 2014; Zhang *et al.*, 2016). Bragg's law is applied to discover the basal interlayer distance ($n\lambda = 2d\sin\theta$) (Freitas *et al.*, 2017).

2.5.2.3. Fourier Transform Infrared Spectroscopy (FTIR)

The presence of functional groups is detected on the adsorbent surface with the help of spectral bands using FTIR spectroscopy at room temperature (Kapur and Mondal, 2014; Malarvizhi and Santhi, 2013). IR spectrum can be splitted into two groups of vibration: one is internal vibration of the frame work units (SiO_4^-) or (AlO_4^-) and the other group of vibrations indicate the links between the framework units in the structure of adsorbent (Visa *et al.*, 2012).

2.5.2.4. Scanning Electron Microscope (SEM)

Surface morphology of the adsorbent is imaged using a scanning electron microscope (Wang *et al.*, 2017). Very fine pencils of electrons are used to illuminate in this microscope thereby scanning the surface of the adsorbent, much as a screen in a television tube (Swayampakula *et al.*, 2009). Morphological structure of the adsorbent is obtained using the electron microscope (WANG *et al.*, 2009). The majority of particles in raw fly ash are expected to be spherical in shape and have smooth surfaces (Kumar and Kumar, 2011; Sharma *et al.*, 2012; Xiyili *et al.*, 2017). Ash sample is characterised for constituents and morphology using the scanning electron microscope (Elouear *et al.*, 2009).

2.6. Adsorption Models

Adsorption models give the best mathematical description of the adsorption equilibrium of the metal ion onto the adsorbent (Sočo and Kalemekiewicz, 2013). The transfer of the adsorbate is characterised by either external mass transfer (boundary later diffusion) or intra –particle diffusion or both in a solid – liquid adsorption process. According to (Wang and Wu, 2006), the three consecutive steps for sorption dynamics include:

1. Transport of the solute from the bulk solution through liquid film to the adsorbent exterior surface.

2. Solute diffusion into the pore of adsorbent except for a small quantity of sorption on the external surface; parallel to this is the intra – particle transport mechanism of the surface diffusion.
3. Sorption of solute on the interior surfaces of the pores and capillary spaces of the adsorbent is considered to be an equilibrium reaction and is considered negligible.

2.6.1. Adsorption Kinetics

Adsorption kinetics explains the adsorption progress and they are a means to understand the dynamics of the adsorption process. Adsorption kinetics are generally described by the kinetic models which will give the order of the reaction at which the reaction is occurring. The pseudo first order, pseudo second order and the intra-particle diffusion are often compared in investigating the controlling mechanism of the adsorption process.

2.6.1.1. Pseudo First Order Kinetic Model

Proposed by Lagergren, the general expression is given by equation 4:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad [1]$$

The linear equation is obtained by applying the boundary equations $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ and it is given by equation 5:

$$\log (q_e - q_t) = \log q_e - \frac{(k_1)t}{2.303} \quad [2]$$

where q_e and q_t are the amounts of metal adsorbed (mg/g) at equilibrium time and at any time t respectively; k_1 (min^{-1}) is the first order rate constant (Kapur and Mondal, 2014).

2.6.1.2. Pseudo Second Order Kinetic Model

The model is expressed as:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad [3]$$

Simplified linear equation obtained after the integration under boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad [4]$$

where k_2 (g/mg.min) is the second order rate constant (Kapur and Mondal, 2014)

2.6.1.3. Error Analysis

Non-linear models are often linearized and errors are incurred as the predicted values depend on a correlation coefficient. The linearization creates a difference between the modelled or predicted values and the experimental values thus an error analysis is employed to get the fraction error incurred. The root mean square error (RMSE) is calculated by:

$$RMSE = \sqrt{\frac{\sum (q_{e,exp} - q_{e,model})^2}{n}} \quad [5]$$

2.6.1.4. Intra-particle Diffusion Kinetic Model

Proposed by Weber and Morris and it is expressed by:

$$q_t = k_{id} t^{1/2} \quad [6]$$

where k_{id} (mg/g.min^{1/2}) is the intra-particle diffusion rate constant. A plot of q_t versus $t^{1/2}$ is done and if the result is a linear graph passing through the origin, then the model is followed (Kapur and Mondal, 2014).

2.6.2. Adsorption Isotherms

Adsorption isotherms analyse the adsorbate concentration in the solution and the amount adsorbed by a specific mass of adsorbent. This is important in optimising the adsorption mechanism pathways, expression of surface properties, capacity of adsorbents and effective design of adsorption systems (Foo and Hameed, 2010). They depend upon the nature and type of system (Sočo and Kalemekiewicz, 2013). In determining the adsorption capacity of the adsorbent, the Langmuir, Freundlich and the Redlich-Peterson models are compared.

2.6.2.1. Langmuir Isotherm model

Langmuir Isotherm model works on the basis that adsorption occurs at specific homogenous sites within the adsorbent (Kapur and Mondal, 2014). It assumes the following conditions:

- ✓ Uniform surface of the adsorbent with equivalent adsorption sites.
- ✓ A monomolecular layer is formed at maximum adsorption.
- ✓ There is no transmigration of the adsorbate in the plane of the surface.
- ✓ There is no interaction between adsorbed molecules (Foo and Hameed, 2010).

The mathematical expression of the Langmuir Isotherm model is described by equations 7 and 8 for non-linear and linear forms.

$$q_e = \frac{q_o b C_e}{1 + b C_e} \text{ (Non-linear form)} \quad [7]$$

$$\frac{C_e}{q_e} = \frac{1}{b q_o} + \frac{C_e}{q_o} \text{ (Linear form)} \quad [8]$$

where C_e is the equilibrium concentration (mg/l), q_e is the amount adsorbed per unit mass of adsorbent at equilibrium (mg/g). q_o and b are the Langmuir constants related to the adsorption capacity and energy of adsorption obtained from the intercept and slope of the plot of C_e/q_e vs C_e , respectively (Kapur and Mondal, 2014).

A modified version of the Langmuir isotherm for adsorption in liquid phase was developed in 2018 by Azizian, Eris and Wilson. The modification was meant to correct the Langmuir constant related to energy of adsorption b or K_L which in the original equation has dimensions. In its modification, a dimensionless parameter K_{ML} was developed and the parameter can be used for the calculation of ΔG_{ad}° and other adsorption thermodynamic parameters.

The adsorption – desorption process in this case is described by four limiting conditions and these are:

- ✓ $C < C_s$ and $\theta = 1$ describing that desorption takes place as the system reaches equilibrium and is predominant.
- ✓ $C = C_s$ and $\theta < 1$ – adsorption is predominant and occurs until the system reaches equilibrium.
- ✓ $C = C_s$ and $\theta = 1$ – the system is in a state of dynamic equilibrium therefore there is no tendency for adsorption and desorption to take place.
- ✓ $C < C_s$ and $\theta < 1$ – describes the usual case with the occurrence of adsorption and desorption depending on the chemical potential of a species in the adsorbed phase.

The mathematical expression of the Langmuir Isotherm model is described by equations 9 and 10 for non-linear and linear forms.

$$q_e = \frac{q_m K_{ML} C_e}{(C_s - C_e) + b C_e} \text{ (Non-linear form)} \quad [9]$$

$$\frac{C_e}{q_e} = \frac{C_s}{K_{ML} q_m} + \frac{(K_{ML} - 1) C_e}{K_{ML} q_m} \text{ (Linear form)} \quad [10]$$

where C_e is the equilibrium concentration (mg/l), C_s is the saturated concentration of solutes (mg/l), q_e is the amount adsorbed per unit mass of adsorbent at equilibrium (mg/g). q_m and K_{ML} are the Langmuir constants related to the monolayer adsorption capacity and energy of the adsorption obtained from the intercept and slope of the plot of C_e/q_e vs C_e , respectively (Azizian *et al.*, 2018).

2.6.2.2. *Freundlich Isotherm model*

The Freundlich Isotherm Model is applied on heterogeneous systems and describes the non-ideal and reversible adsorption. The model is not restricted to the formation of a monolayer but can be applied to multilayer adsorption. It assumes the heterogeneity in the surface binding process (Foo and Hameed, 2010). The linear mathematical expression of the Freundlich model is shown by equation 11:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad [11]$$

where K_f and n are Freundlich constants related to adsorption capacity and intensity respectively (Foo and Hameed, 2010; Kapur and Mondal, 2014).

2.6.2.3. *Redlich-Peterson Isotherm model*

The Redlich-Peterson isotherm model is applicable to both homogeneous and heterogeneous systems due to its versatility and it features both the Langmuir and the Freundlich models (Foo and Hameed, 2010; Kapur and Mondal, 2014).

The non-linear form equation is given by equation 12:

$$q_e = \frac{K_R C_e}{1 + a_R C^\beta_e} \quad [12]$$

where K_R is the R – P isotherm constant (L/g), a_R is R – P isotherm constant (mg^{-1}) and β is the exponent ($0 < \beta < 1$), C_e is the equilibrium concentration (mg/l). In the limit, it approaches the Freundlich isotherm model at high concentrations (as the exponential β tends to zero) and it approaches the Langmuir isotherm model at low concentrations (as the β values are all close to one) (Foo and Hameed, 2010; Kapur and Mondal, 2014).

The linear form expression is given by equation 13:

$$\ln \left(K_R \frac{C_e}{q_e} - 1 \right) = \ln a_R + \beta \ln C_e \quad [13]$$

2.7. Thermodynamic Studies

Thermodynamic parameters such as change in standard free energy (ΔG°), change in enthalpy (ΔH°) and change in entropy (ΔS°) are meant to identify the energy requirements, spontaneity and degrees of freedom/ randomness of the solid/liquid interface in a process. The equilibrium constant K_c is defined by equation 14:

$$K_c = \frac{C_{Ae}}{C_s} \quad [14]$$

where C_{Ae} and C_s are the equilibrium concentrations of adsorbate on the adsorbent and in the solution respectively.

The adsorption standard free energy change is given by equation 15:

$$\Delta G^\circ = -RT \ln K_c \quad [15]$$

where R is the universal gas constant (8.314 J/mol.K) and T is the temperature in Kelvin.

The change in enthalpy obtained from the Van't Hoff Equation is calculated from:

$$\ln K_c(T_2) - \ln K_c(T_1) = \frac{-\Delta H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad [16]$$

where T_2 and T_1 are different temperatures

The standard entropy change can be obtained by equation 17:

$$\Delta S^\circ = -\frac{\Delta G^\circ - \Delta H^\circ}{T} \quad [17]$$

Activation energy determined through the Arrhenius equation shows the nature of the process and the equation is given by equation 18:

$$k = Ae^{-E_a/RT} \quad [18]$$

which in linear form can be written as:

$$\ln k = \ln A - \frac{E_a}{RT} \quad [19]$$

where E_a is the activation energy (kJ/mol), A is the frequency factor (min^{-1}) and T is the temperature in Kelvin (Li *et al.*, 2010; Kapur and Mondal, 2014)

2.8. Column Studies

Column studies experiments are suitable for large scale operations and the successful design of a column adsorption process requires prediction of the concentration – time profile or breakthrough curve for the effluent (Öztürk and Kavak, 2005). It helps determine the sorption capacity of a sorbent per unit time which gives an understanding on the transport phenomena of the system. It also determines the sorbent quantity and density of packing (Koshy and Singh, 2016). Figure 2.1 shows a typical lab scale column study schematic diagram.

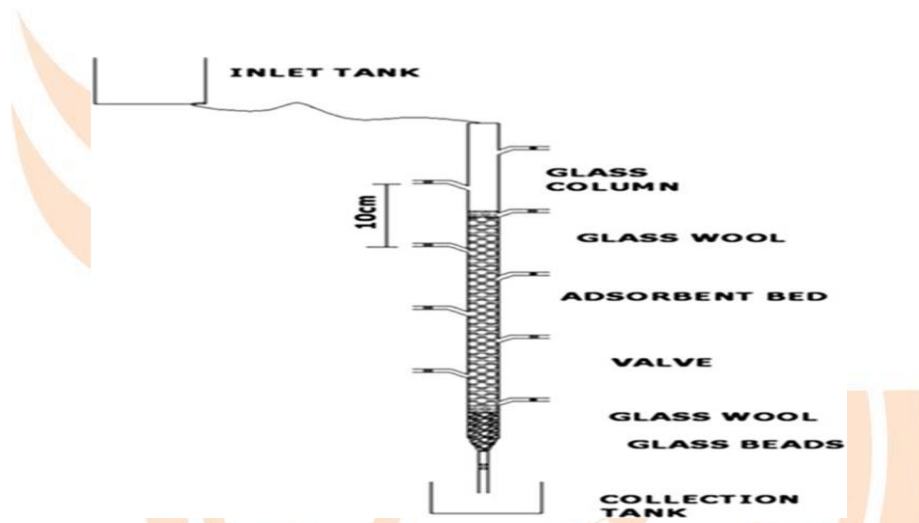


Figure 2.1: Typical Lab Scale Column Study Schematic Diagram (Bharathi et al., 2013)

2.8.1. Column Studies Models

The prediction of breakthrough curves and the determination of characteristic parameters of a column can be done by the use of three (3) models.

2.8.1.1. Bed Depth Service Time (BDST) model

The model predicts the relationship between bed depths, X and service time, t and it states that bed height and service time of a column have a linear relationship. The model assumes that forces like intra – particle diffusion and external mass transfer resistances are negligible and that the adsorbate is adsorbed onto the adsorbent surface directly. Characteristic parameters such as kinetic constant and maximum adsorption capacity are estimated by this model (Bharathi et al., 2013). Original BDST model was developed by Bohart and Adams and is given by:

$$\ln\left(\frac{C_o}{C_B} - 1\right) = \ln\left(\exp\left[\frac{KXN_o}{v}\right] - 1\right) - KC_o t \quad [20]$$

The linear relationship between the bed depth and service time is given by:

$$t = \frac{N_o}{vC_o}X - \frac{1}{KC_o} \ln \left(\frac{C_o}{C_B} - 1 \right) \ln C_o C_B - \ln(eKXvN_o - 1 - KC) \quad [21]$$

where C_o is the initial concentration of the solute (mg/L), C_B is the desired concentration of solute at breakthrough (mg/L), K is the adsorption rate constant ($L^{-1}mg^{-1}hr$), N_o is the adsorption capacity (mg/L), X is the bed depth of column (cm), v is the linear velocity of feed to bed (cm/hr) and t is the service time of column (hr).

The linear/straight line form of the equation is given by:

$$t = aX - b \quad [22]$$

where a is the slope of the BDST line ($a = \frac{N_o}{vC_o}$) and b is the intercept shown by ($b = \frac{N_o}{KC_o} \ln \left(\frac{C_o}{C_B} - 1 \right)$)

N_o and K can be calculated from the slope (a) and the intercept (b) of the plot of t versus X respectively. The critical bed depth (X_o) – theoretical depth of adsorbent sufficient to ensure that the outlet solute concentration does not exceed the breakthrough concentration (C_B) value at time $t = 0$, X_o can be calculated as:

$$X_o = \frac{v}{KN_o} \ln \left(\frac{C_o}{C_B} - 1 \right) \quad [23]$$

2.8.1.2. Thomas model

Thomas model is the most general and widely used model to describe the behaviour of sorption process in fixed bed columns. The model assumes that the process follows the Langmuir kinetics with no axial distribution. Its main drawback is that it is derived based on second order kinetics and considers that sorption process is controlled by mass transfer at interface and not limited by chemical reaction. The errors in the model are bred by the inconsistencies when it is used to model the process in specific conditions (Hasan *et al.*, 2010; Bharathi *et al.*, 2013). The model has the following form:

$$\frac{C_e}{C_o} = \frac{1}{\left[1 + \exp \frac{K_T(q_m - C_oV)}{\theta} \right]} \quad [24]$$

where K_T is the Thomas Rate Constant ($L/min.mg$) and θ is the Volumetric Flowrate (L/min).

Linearised form of the Thomas model is as follows:

$$\ln \left(\frac{C_o}{C_e} - 1 \right) = \frac{K_T q_o m}{\theta} - \frac{K_T C_o V}{\theta} \quad [25]$$

The Kinetic coefficient K_T and the adsorption capacity of the bed q_o can be determined from a plot of $\ln \frac{C_e}{C_o} - 1$ versus sampling time t at a given flowrate (Öztürk and Kavak, 2005).

2.8.1.3. Yoon – Nelson Model

The model is mathematically equivalent to Thomas model and has been applied to a range of concentrations in the effluent between the breakthrough and saturation time of the column (Bharathi *et al.*, 2013). The model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and probability of adsorbate breakthrough on the adsorbent (Öztürk and Kavak, 2005; Bharathi *et al.*, 2013). The model does not require detailed data on the features of the adsorbate, type of adsorbent and the physical properties of adsorption bed (Öztürk and Kavak, 2005).

Yoon – Nelson model regarding a single component system is given by:

$$\frac{C_e}{C_o} = \frac{1}{1 + \exp[k(\tau - t)]} \quad [26]$$

where τ is the time required for 50% sorbate breakthrough (min) and t is the breakthrough (sampling) time and k is the rate constant (min^{-1}).

The linearised form of the Yoon – Nelson Model is given by:

$$t = \tau + \frac{1}{k} \ln \frac{C_e}{C_o - C_e} \quad [27]$$

In order to calculate the breakthrough curves for single component systems, it is important to determine the parameters k and τ for the adsorbate of interest (Öztürk and Kavak, 2005). The parameters k and τ are determined by plotting $\ln \frac{C_e}{C_o - C_e}$ versus sampling time t and the 50% breakthrough occurs at $t = \tau$ (Bharathi *et al.*, 2013).

2.9. References

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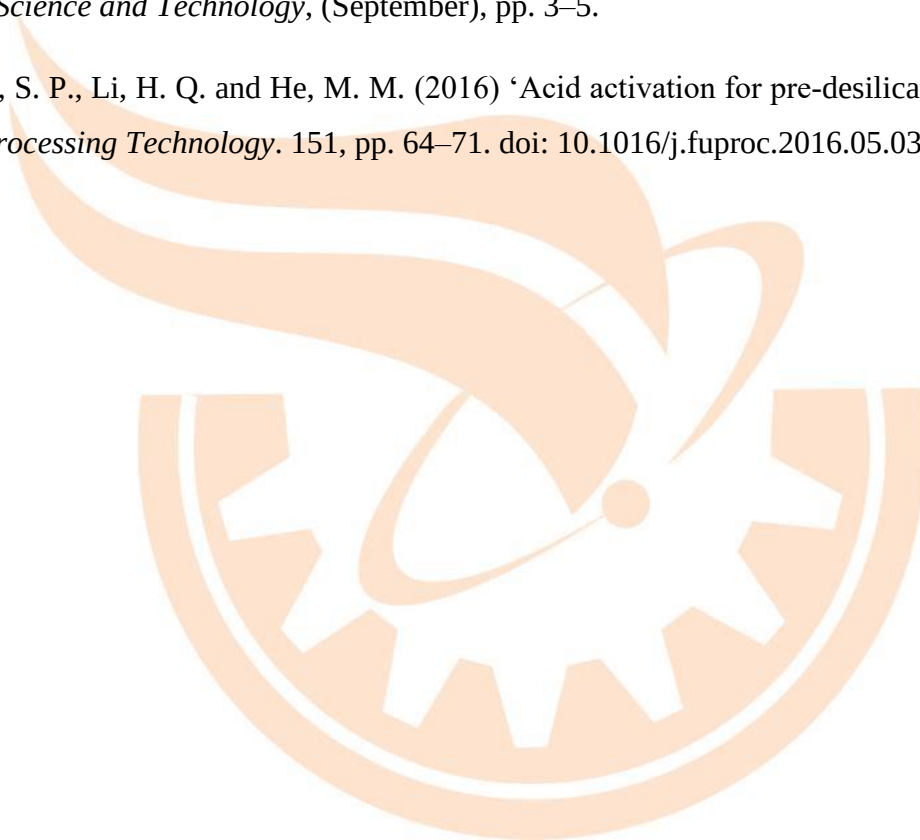
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Chapter 3 : METHODOLOGY

3.1. General Overview

This chapter outlines the experimental processes followed in carrying out the batch and column adsorption studies for the treatment of simulated waste water containing copper and nickel metal ions using raw coal fly ash as an adsorbent.

3.2. Batch Adsorption

3.2.1. Materials and Chemicals

Copper Sulphate Pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and Nickel Sulphate Hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) analytical grade chemicals supplied by Sigma Aldrich were used to prepare the synthetic/simulated wastewater. The pH of the solution was adjusted using 32% hydrochloric acid (HCl) to lower the pH of the system to the required acidic range (pH 4 – 6) upon addition of the strong alkaline ash (pH 11 – 13). 2 drops of 55% Nitric Acid (HNO_3) was used to preserve the samples before analysis to keep a low pH on the filtrates which minimizes adsorption to container wall and prevents metal ion precipitation. Coal fly ash obtained from Morupule B Power Station was used as an adsorbent.

3.2.2. Instrumentation

A Metler Toledo dual meter (Seven Duo pH/Conductivity meter with a Metler Toledo InLab Pro ISM pH electrode) was used to measure the pH of the solution. Atomic Absorption Spectrophotometer (Thermo scientific ICE 3000 Series) was used to measure the concentration of Cu^{2+} and Ni^{2+} in the filtrates and an OSD-20 overhead stirrer (fitted with a four blade propeller and a rotational speed of 500 rpm) was used to stir the samples ensuring good contact between the coal fly ash and aqueous solution. Characterization of the Morupule fly ash before and after the adsorption experiments was done using the following equipments: An X-ray Fluorescence (Rigaku ZSX Primus II) was used to determine the elemental compositions while a Fourier transform infrared spectroscopy (Thermoscientific Nicolet IS10) was used to help identify the functional groups present. Particle/surface morphology was analysed by a 40 Scanning Electron Microscope (SEM model Tescan Vega 3 XMU) while the mineral identification and crystallinity were analysed by an X-Ray Diffractometer (Rigaku Ultima IV). The thermal behaviour of the sample was characterized by a Thermo-Gravimetric Analyser (Leco TGA 701) and the particle size distribution was measured using a Malvern Mastersizer 300E – Hydro laser particle analyser.

3.2.3. Instrument Operating Parameters

Table 3.1 to Table 3.5 present the operating parameters for an AAS, FTIR, XRF, XRD and TGA respectively. The specifications or operating parameters of the listed instruments was given in the operating manual of the individual instruments. The standards for AAS provides a calibration curve that is used to understand the instrumental response to changes with the concentration of the analyte and predict the concentration of the unknown sample.

Table 3.1: AAS operating parameters

Element	Lamp	Lamp Current	Lamp Wavelength	Flame
Cu	Cu Hollow Cathode	15 mA	324.7 nm	Oxy-Acetylene
Ni	Ni Hollow Cathode	25 mA	232 nm	Oxy-Acetylene
Standards for AAS				
Metal ion	Concentration (ppm)			
Cu ²⁺	22, 44, 100			
Ni ²⁺	20, 50, 100			

Table 3.2: FTIR operating parameters

Parameter	Specification
Detector	DTGS KBr
Beam Splitter	KBr
Range	800 – 4000 cm ⁻¹
Optical velocity	0.6329

Table 3.3: XRF operating parameters

XRF specifications		
X-ray Source	X-ray Tube	End window type Rh Target 4 kW or 3 kW
	High Voltage Generator	High Frequency Inverter Type Maximum Rating 4 kW, 60 kV-150 mA
Optics	Maximum sample size	Ø51mmx30mm (H)
	Primary Beam Filter	4 filters (Al, Al-2, Cu, Zr)
	Diaphragm	6 position automatic exchanger (Ø 35, 30, 20, 10, 1.0, 0.5 mm)
	Crystal Exchanger	10 position automatic exchanger
Counting	Detector	Light Elements: F-PC
		Heavy Elements: SC

Table 3.4: XRD operating parameters

Parameter	Specification
X-Ray	40 kV, 30 mA
Scan speed/ Duration time	1.0000 deg./min
Step width	0.0100 deg.
Scan axis	2 theta/theta
Scan range	3.000 – 90.0000 deg.

Table 3.5 : TGA operating parameters

Step	Ramp Rate (°C/min)	Ramp Time (mins)	Hold Time (mins)	Total Time (mins)	Atmosphere	Flowrate (L/min)
1 - Moisture	6	14	15	29	Nitrogen	High – 10
2 - Volatiles	50	16	7	23	Nitrogen	Medium – 7
3 - Ash	15	10	0	10	Oxygen	Medium – 7

3.2.4. Single Component Studies

1.98 g of Copper Sulphate Pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and 2.26 g of Nickel Sulphate Hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) were separately dissolved in 1000 ml of deionised water to make a 500 mg/l solution of Cu^{2+} and Ni^{2+} metal ions respectively. 32% hydrochloric acid was added drop by drop to adjust the pH of each solution to 2 for the same reason given in [section 3.2.1](#).

3.2.4.1. *Determination of the effect of adsorbent dosage*

Different doses were investigated to test the effect of adsorbent dosage on Cu^{2+} and Ni^{2+} removal and this was done by stirring 1000 ml of solutions of Cu^{2+} and Ni^{2+} ions containing different doses of adsorbent with a constant stirring speed of 300 rpm. Adsorbent doses used for copper removal were 2 and 3% (i.e. 2 or 3 g/100 ml respectively) while for nickel they were 4 and 5% (4 or 5 g/100 ml respectively). Sampling was done every 15 minutes for a period of 120 minutes by sampling 10 ml sample aliquots. Samples were filtered and a drop of 55% Nitric Acid (HNO_3) was added to preserve the sample before analysis, thereafter samples were analysed using an atomic absorption spectrophotometer (AAS).

3.2.4.2. *Determination of the influence of solution pH*

The effect of pH on Cu^{2+} and Ni^{2+} removal was studied by stirring 1000 ml of solutions each containing Cu^{2+} and Ni^{2+} ions and 3% solid loading (3 g fly ash/100 ml) for a copper solution and 5% solid loading (5 g fly ash/100 ml) for a nickel solution. A 10 ml sample of each solution was drawn every 15 minutes and this was done for a period of 120 minutes totalling 8 samples for each solution. Each sample was filtered and a drop of 55% Nitric Acid (HNO_3) was added to preserve the sample before analysis. Samples were then analysed using the atomic absorption spectrophotometer (AAS).

3.2.4.3. *Determination of the effect of Contact time*

A maximum time of 120 minutes was used when testing the effect of contact time on Cu^{2+} and Ni^{2+} ions adsorption at predetermined time interval (of 15 minutes). A 1000 ml solution of copper and nickel were each agitated at 300 rpm with 3% solid loading of fly ash used for a copper solution and 5% solid loading was used for a nickel solution. Samples collected every 15 minutes were then filtered and a drop of 55% Nitric Acid (HNO_3) was added to preserve the sample before analysis thereafter samples were analysed using an atomic absorption spectrophotometer (AAS).

3.2.4.4. *Determination of the effect of Temperature*

Two (2) temperatures for both copper and nickel solutions were tested to check the effect of temperature on Cu^{2+} and Ni^{2+} ions adsorption. A 1000 ml solution of copper and nickel were each agitated at 300 rpm with 3% solid loading of fly ash used for a copper solution and 5% solid loading was used for a nickel solution. The temperatures were 25°C and 65°C and 10 ml samples were taken every 15 minutes for a period of 120 minutes. Samples were then filtered and a drop of 55% Nitric Acid (HNO_3) was added to preserve the sample before analysis then samples were analysed using an atomic absorption spectrophotometer (AAS).

3.2.5. Binary Mixture Studies (Simultaneous Cation Removal)

A 500 ppm solution of simulated wastewater was prepared by dissolving 1.98g of Copper Sulphate Pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and 2.26g of Nickel Sulphate Hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) in 1000 ml of deionised water to make a 1000 ml of 500 ppm solution of the metal ions. 32% hydrochloric acid was added drop by drop to adjust the pH of each solution to 2.

3.2.5.1. *Determination of the Process Parameters (dosage, pH and contact time)*

With reference to the single component batch studies results, binary mixture studies of copper and nickel removal were investigated by conducting a simultaneous cation removal (i.e removal of copper and nickel in the same water body at the same time). In the first test, a 3 g/100 ml dose of fly ash was used as an adsorbent in a 1000 ml solution containing Cu^{2+} and Ni^{2+} ions with a constant stirring speed of 300 rpm. 10 ml samples were taken every 15 minutes for a period of 120 minutes and at each time interval the pH of the collected sample was measured. Samples were filtered and a drop of 55% Nitric Acid (HNO_3) was added to preserve the sample before analysis then samples were analysed using an atomic absorption spectrophotometer (AAS). The experiment was repeated in the second test at a dose of 5 g/100 ml and all the preceding steps were followed.

3.2.6. Binary Mixture Studies (2-Stage Process Removal)

Based on the results obtained in the simultaneous cation removal binary mixture, a 2 stage process was carried out. A 500 ppm solution of simulated wastewater was prepared as in [section 3.2.5](#).

A solution containing 500 ppm of copper and nickel respectively was agitated at 300 rpm with a 3% solid loading load of fly ash in the first stage for the removal of copper. 10 ml samples were collected every 10 minutes for a period of 60 minutes for this stage and the pH of each sample was measured. After 60 minutes, the agitation was stopped and the mixture was filtered to remove the already used fly ash. The removal of nickel was done in the second stage by agitating a 5% solid loading of fly ash with the filtered solution in stage 1 at 300 rpm. 10 ml samples were taken every 20 minutes for a period of 120 minutes and the pH of each sample was also measured. Samples in each stage were then filtered and a drop of 55% Nitric Acid (HNO₃) was added to preserve the sample before analysis then samples were analysed using an atomic absorption spectrophotometer (AAS). This experiment was done at 20°C and it was repeated by following all the preceding steps at 40°C.

3.2.7. Data Analysis for Batch Studies

The adsorption capacity in (mg/g) and percentage removal was calculated by:

$$q_e = \frac{(C_o - C_e)}{m} * V \quad [28]$$

$$\text{Removal}(\%) = \frac{(C_o - C_e)}{C_o} * 100 \quad [29]$$

where C_o is the initial concentration (mg/l) of Ni(II) and Cu(II) ions, V is the volume of the solution (ml), m is the mass of fly ash (g) and C_e is the residual/equilibrium concentrations (mg/l) of the ions at any time (t).

The sorption data was fitted to the kinetic models and the best fit model indicates the most probable adsorption mechanism. The kinetic models considered in this study were the Pseudo First Order Model, Pseudo Second Order Model and Intra Particle Diffusion.

For adsorption isotherms analysis, the modified Langmuir and Freundlich models were compared. These models were used to investigate how Cu(II) and Ni(II) ions interact with the adsorbent, and are applied to describe the isotherm data obtained at varying temperatures.

Thermodynamic parameters such as change in standard free energy (ΔG°), change in enthalpy (ΔH°) and change in entropy (ΔS°) were calculated to determine the spontaneity of the system.

3.3. Column Adsorption Studies (Binary Mixture)

A 500 ppm solution of simulated wastewater was prepared as in [section 3.2.5](#). Materials and chemicals used in [section 3.2.1](#) were also used in this section of the experiments.

3.3.1. Instrumentation

A Jenco pH 6810 – Handheld pH/mV/Temperature meter was used to measure the pH of the solution. Microwave Plasma - Atomic Emission Spectroscopy (Agilent Technologies 4200 MP-AES) was used to measure the concentration of Cu^{2+} and Ni^{2+} in the filtrates and an Elettronica Veneta Ion Exchange Unit (mod. IEU/EV) (with borosilicate glass of ID: 16mm, glass length: 450mm) was used as an adsorption column for this study.

3.3.1.1. Instrument Operating Parameters

[Table 3.6](#) presents the operating parameters for an MP – AES

Table 3.6: MP-AES Operating Parameters

Element	Wavelength (nm)	Nebulizer flow (L/min)	Pump Speed (rpm)
Cu	324.754	1	15
Ni	352.524	0.3	15
Standards for MP – AES			
Metal ion	Concentration (ppm)		
Cu^{2+}	10, 20, 50, 100		
Ni^{2+}	10, 20, 50, 100		

3.3.2. Effect of flow rate

A 1000 ml solution containing 500 ppm of Cu^{2+} and Ni^{2+} ions was pumped from a test tank to a column loaded with fly ash. In the first stage, a 3 g/100 ml load of fly ash was used and the process was run at 10 ml/min with samples collected every 15 minutes for a period of 120 minutes to remove all the copper. After all the copper has been removed in the first stage, the filtrate was then put back in the test tank for second stage processing and 5 g/100 ml of fly ash was loaded into the column to remove the nickel. The process was run at the same flow rate as in the first stage for a period of 120 minutes with samples collected every 15 minutes. The second and third runs were performed at 15 and 20 ml/min following the same procedure as in the first run.

3.3.3. Effect of Bed Height

A 1000 ml solution containing 500 ppm of Cu^{2+} and Ni^{2+} ions was pumped from a test tank to a column loaded with fly ash. In the first run, a 3 g/ 100 ml load of fly ash was used and the process was run at 15 ml/min with samples collected every 10 minutes for a period of 60 minutes. After all the copper has been removed in the first stage, the filtrate was then put back in the test tank for second stage processing and 5 g/100 ml of fly ash was loaded into the column to remove the nickel. The process was run at the same flow rate as in the first stage for a period of 90 minutes this time with samples collected every 15 minutes. All the steps in the first run were repeated but this time the first stage solid loading was increased to 4 g/ 100 ml.

3.3.4. Data Analysis for Column Studies

The adsorption capacity in (mg/g) and percentage removal were calculated using equations 28 and 29 presented in [section 3.2.7](#).

The experimental data was fitted in the column studies models to predict the breakthrough time and the characteristic parameters of the column. The Thomas model and the Yoon – Nelson model were fitted into the data for this process.

Chapter 4 : BATCH SINGLE COMPONENT STUDIES

4.1. General Overview

This chapter shows the results obtained in carrying out the batch single component studies experiments for the treatment of simulated waste water containing copper and nickel metal ions using Morupule coal fly ash. Single component studies is the study on the adsorption of the individual ions in a solution where copper is adsorbed in the absence of nickel and nickel is adsorbed in the absence of copper. The results are also discussed in detail in this chapter.

4.2. Single Component Batch Studies

4.2.1. Effect of solution pH on adsorption

The pH of the solution has a significant impact on the uptake of metal ions, since it determines the surface charge of the adsorbent, and the degree of ionization and speciation of the adsorbate (Elouear *et al.*, 2009). SiO₂ in fly ash can adsorb either positive or negative contaminants depending on the pH of the solution. As a result, at low pH the silica surface is positively charged and at high pH values it is negatively charged. The CaO content of the fly ash is more effective in determining the alkalinity of the solution than its total basic constituent's content (Pehlivan and Cetin, 2008). Morupule fly ash was found to be at a pH of 11 in water due to its high lime content hence the solutions were reduced to a pH of 2 to neutralise the fly ash upon its addition to the solution to prevent precipitation from occurring because under the strong alkaline condition, precipitation could occur which may inhibit the adsorption process (Luo *et al.*, 2011). Figure 4.1 shows that the maximum pH for copper is 6.6 for maximum removal capacity while for nickel is 7.8. There was a sharp increase in the removal of copper at 298 K from pH 5.4 to pH 6.0 where a 99.3% removal was achieved after 120 minutes while the removal of nickel was very slow between pH 7.2 and pH 7.5 with a sharp increase from pH 7.5 to pH 7.7 at the same temperature and a maximum removal of 65.1% was attained after 120 minutes. Both copper and nickel showed a sharp increase for 45 minutes and a steady increase for the remaining time at 338 K. Proceeding beyond the maximum pH levels, precipitation could occur with copper forming ions such as Cu(OH)₂ (Demirbas *et al.*, 2009) with nickel possibly forming Ni(OH)₂.

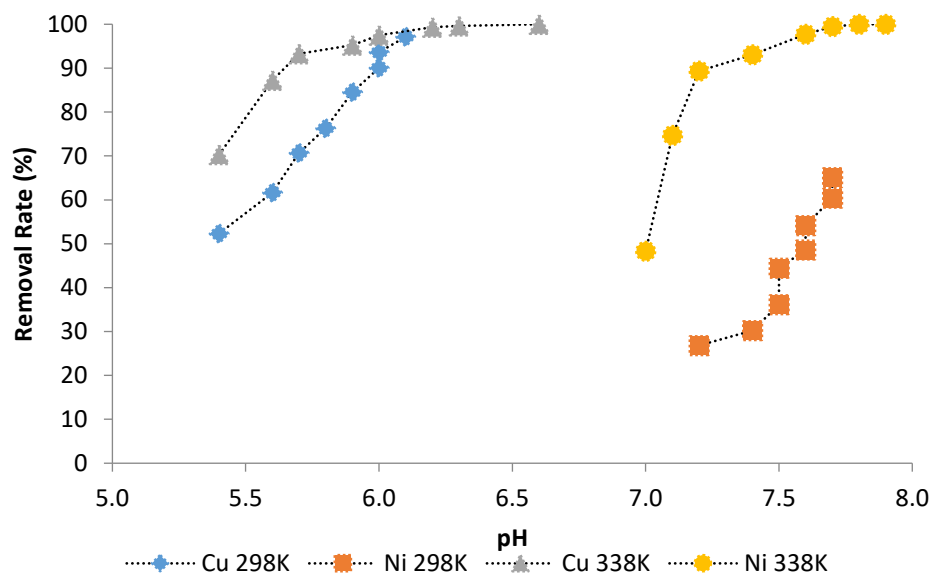


Figure 4.1: Effect of pH on Cu and Ni removal by Morupule fly ash; $C_0 = 500$ mg/l; Media load = (3% Cu and 5% Ni); Run time = 120 mins; Stirring rate = 300 rpm

4.2.2. Effect of adsorbent dosage on adsorption

An increase in the adsorption capacity on increasing the adsorbent dosage is attributed to the fact that the number of sites available for adsorption increases until it reaches a point where removal is maximum and further increase on dosage has no effect (Kapur and Mondal, 2014). The number of adsorbent particles increase and more of the adsorbate ions are attached to their surfaces (Acharya *et al.*, 2009). At 2% solid loading, copper reached a maximum removal percentage of 56.3 after 120 minutes run time while at 3% loading, the maximum removal for copper was 97.1%. Nickel was tested at 4 and 5% solid loading and the results indicate that the removal percentage reached a high of 58.8 and 65.1 respectively. The temperature of the system was kept constant at 298 K and the pH of the solution was tested for every sample that was collected every 15 minutes. For Copper, at both dosages (2 and 3% solid loading) the pH was showing a similar increase that is from 5.4 to about 6.5 and for Nickel at both doses a similar trend to that of Copper is observed where the pH increased from 7.0 to about 7.7 at both 4 and 5% solid loading. This results affirm what Li *et al.* (2010) noted that, an increase in adsorbent dosage avails a greater surface area and pore volume providing more functional groups and active adsorption sites hence increasing the adsorption capacity.

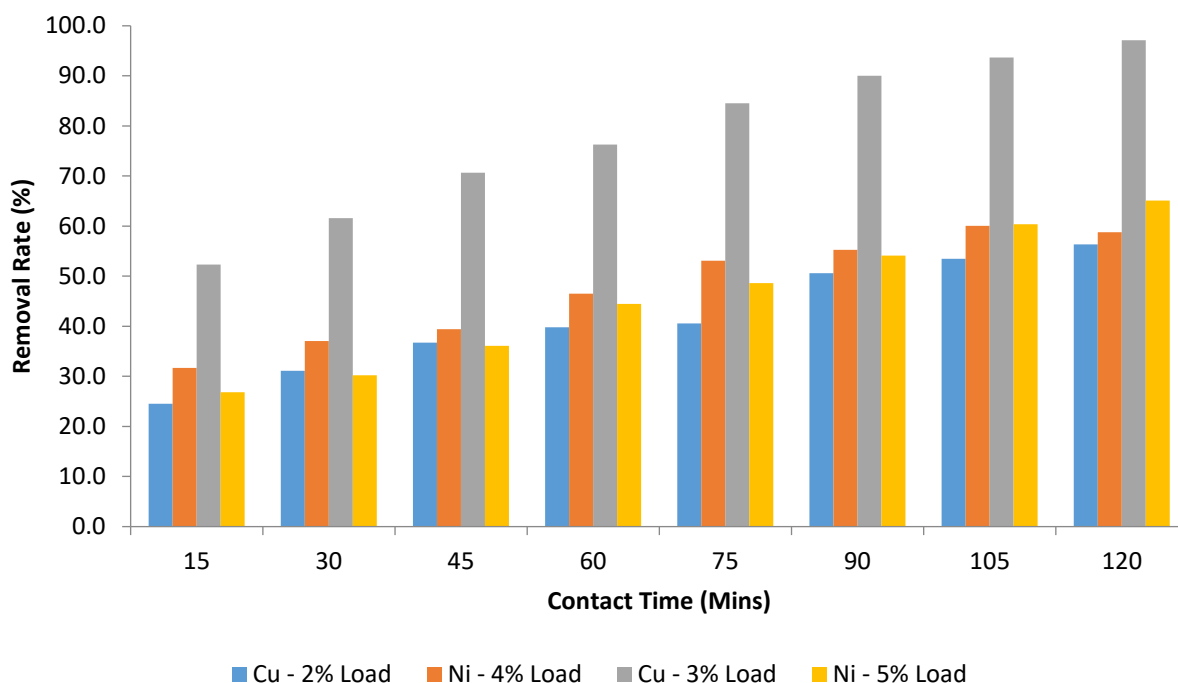


Figure 4.2: Effect of Adsorbent Dosage on Cu and Ni removal by Morupule fly ash; $C_0 = 500$ mg/l; Run time = 120 mins; Stirring rate = 300 rpm; Temperature = 298 K

4.2.3. Effect of contact time on adsorption

The process of adsorption is influenced by the length of time that the fly ash is in contact with the contaminant in the aqueous solution. Increasing contact time allows greater amounts of contaminant to be removed from the aqueous solution (Pehlivan and Cetin, 2008). The rapidity of the process is measured based on the length of time it takes to occupy the vacant adsorptive sites in the adsorbent and after maximum adsorption is reached a repulsive force is encountered between ionic species of the solution and the sites already occupied (Kapur and Mondal, 2014). Figure 4.3 shows the relationship of contact time with the percentage removal, at 338K, both copper and nickel reach equilibrium after 105 minutes while at 298K equilibrium is not reached even after the 120 minutes run time. A higher driving force enhances the metal ion transfer to the surface of the adsorbent particles at the initial stages of adsorption hence a rapid uptake (Li *et al.*, 2010).

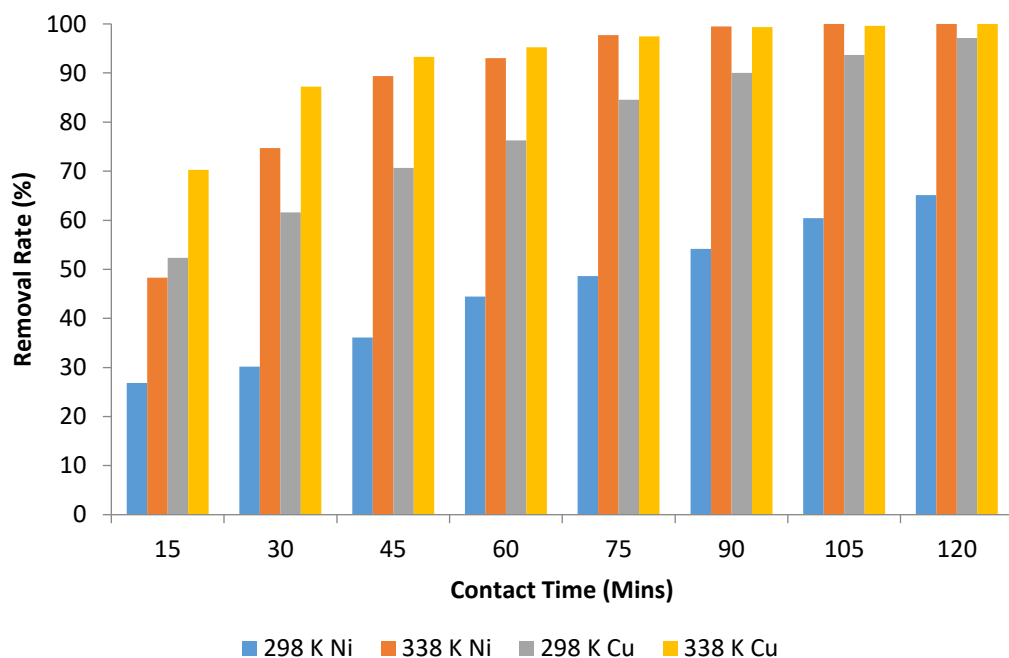


Figure 4.3: Effect of contact time on Cu and Ni removal by Morupule fly ash; $C_o = 500\text{mg/l}$; Adsorbent load = (3% Cu and 5% Ni); Run time = 120 mins; Stirring rate = 300rpm

4.2.4. Effect of temperature on adsorption

An increase in temperature helps increase removal rate and adsorption ability for an endothermic process (Luo *et al.*, 2011). Two different temperatures were studied in order to determine the effect of temperature on the adsorption process. As presented in Figure 4.4 an increase in temperature results in an increase in the adsorption capacity with time for both copper and nickel, this may be due to the increase in diffusion rate of copper and nickel ions (Wang *et al.*, 2010). Temperature is important in the diffusion rate of a process because increasing the temperature increases the movement of molecules hence increasing the rate of diffusion (Li *et al.*, 2010). Due to the porous nature of the sorbent, the increase in temperature favours the metal ions transport within the pores of the adsorbent. The endothermic nature of this process is generated by the breakage of some internal bonds near the edge of active surface sites of the adsorbent (Acharya *et al.*, 2009). According to (Özc, 2009), when the temperature exceeds the maximum allowable, agglomeration occurs and desorption takes place which lowers the rate of adsorption with time. Figure 4.4 shows that copper and nickel both reach 100% removal at 338K in a run time of 120 minutes while at 298K both metals could not reach maximum removal with copper at 97.1% and nickel at 65.1% within the same run time.

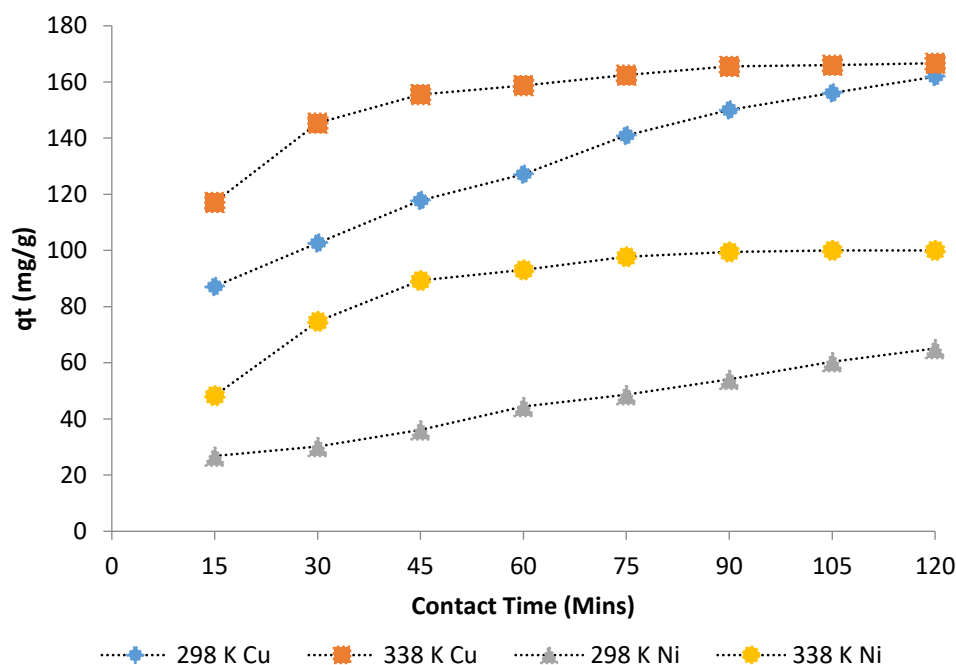


Figure 4.4: Effect of Temperature on Cu and Ni removal by Morupule fly ash; $C_o = 500\text{mg/l}$; Adsorbent load = (3% Cu and 5% Ni); Run time = 120 mins; Stirring rate = 300rpm

4.3. Kinetic Studies

In investigating the model that best fits the process, it was found that the pseudo second order model is followed by both copper and nickel at 338K while at 298K they follow the pseudo first order model based on their root mean square error (RMSE values). The process follows the pseudo first order at the lower temperature because there is low to no activation energy required. Predominance of the pseudo second order model at higher temperatures implies that adsorption process is controlled by chemisorption, which involves sharing of electrons between the adsorbate and the surface of the adsorbent (Bouhamed, Elouear and Bouzid, 2012). The unfitting of the pseudo first order model maybe due to a boundary layer controlling the beginning of the adsorption process (Wang, Lin and Wu, 2010). As for intra particle diffusion which is a rate limiting step, $I_D > 0$, indicates that both external mass transfer and intra particle diffusion are considered and an increase in I_D shows a higher resistance to ions by particles of the adsorbent (Foo and Hameed, 2010). Figure 4.5 to Figure 4.7 show the plots of the pseudo first order, pseudo second order and intra-particle diffusion models respectively while Table 4.1 summarizes the kinetic models.

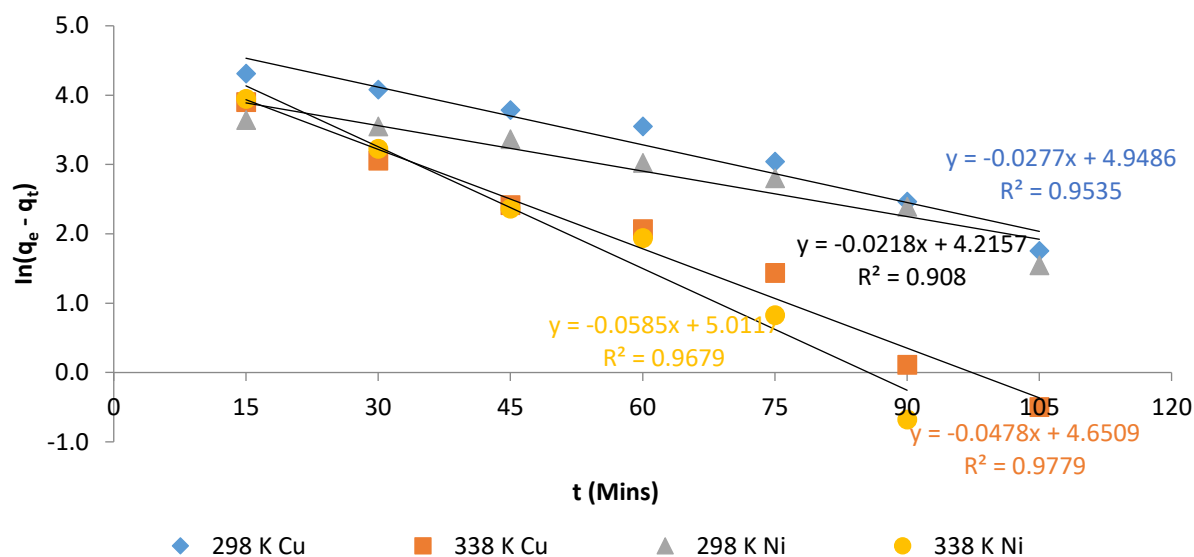


Figure 4.5: Pseudo First Order Plot for Cu and Ni

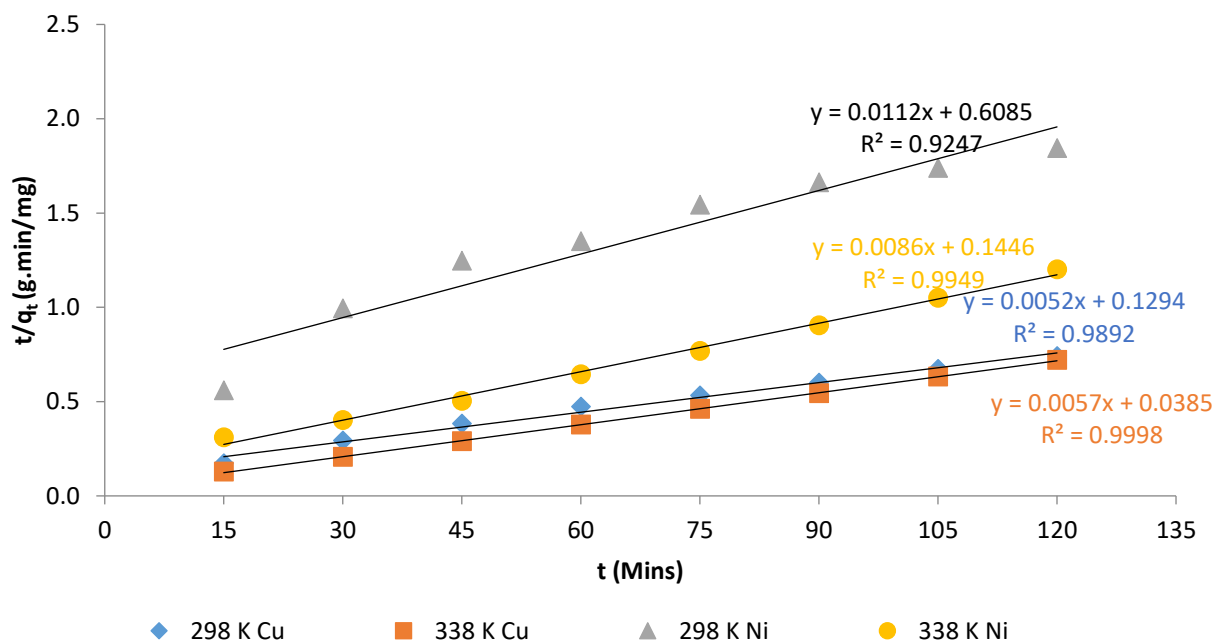


Figure 4.6: Pseudo Second Order Plot for Cu and Ni

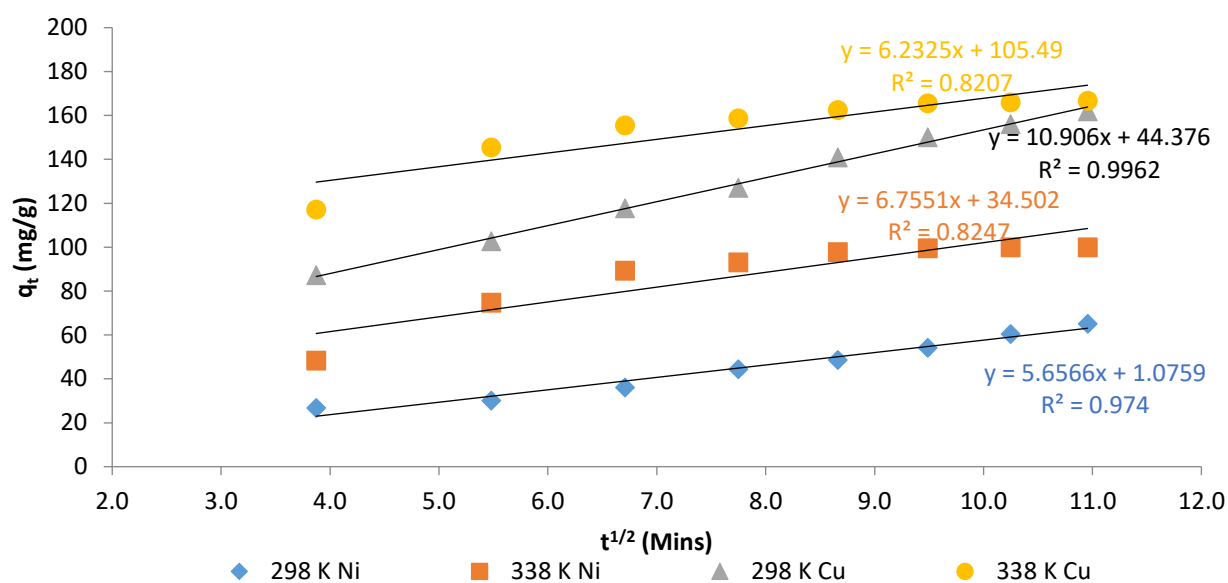


Figure 4.7: Intra - Particle Diffusion Plot for Cu and Ni

Table 4.1: Parameters for the kinetic models

Species		Cu ²⁺		Ni ²⁺	
Temperature (K)		298	338	298	338
Pseudo First Order	q _{e,model} (mg/g)	140.98	104.68	67.74	150.16
	q _{e,exp} (mg/g)	130.47	154.69	45.73	87.83
	K ₁ (min ⁻¹)	0.0638	0.1100	0.0502	0.1347
	R ²	0.9535	0.9779	0.9080	0.9679
	RMSE	0.0056	0.2283	0.0117	0.1116
Pseudo Second Order	q _{e,model} (mg/g)	192.31	175.44	89.29	116.28
	q _{e,exp} (mg/g)	130.47	154.69	45.73	87.83
	K ₂ (g/mg.min)	0.000209	0.000844	0.000206	0.000571
	R ²	0.9892	0.9998	0.9247	0.9949
	RMSE	0.1034	0.0140	0.1047	0.0196
Intra particle diffusion	K _{id} (mg/g.min ^{1/2})	10.91	6.23	5.66	6.76
	R ²	0.9962	0.8207	0.9740	0.8247
	I _D	44.376	105.49	1.0759	34.502

4.4. Kinetic Isotherms

The view of how the metal ions interact with the adsorbent is given by the adsorption isotherms and it is important in optimising the adsorption mechanism pathways, expression of surface properties, capacity of adsorbents and effective design of adsorption systems (Foo and Hameed, 2010). The modified Langmuir and the Freundlich kinetic isotherms were studied and Figure 4.8 and Figure 4.9 show the plots of the modified Langmuir and Freundlich isotherm models respectively. Table 4.2 summarises their isotherm parameters and the table shows that both metal ions follow the modified Langmuir models indicating they are taking a homogenous and monolayer approach.

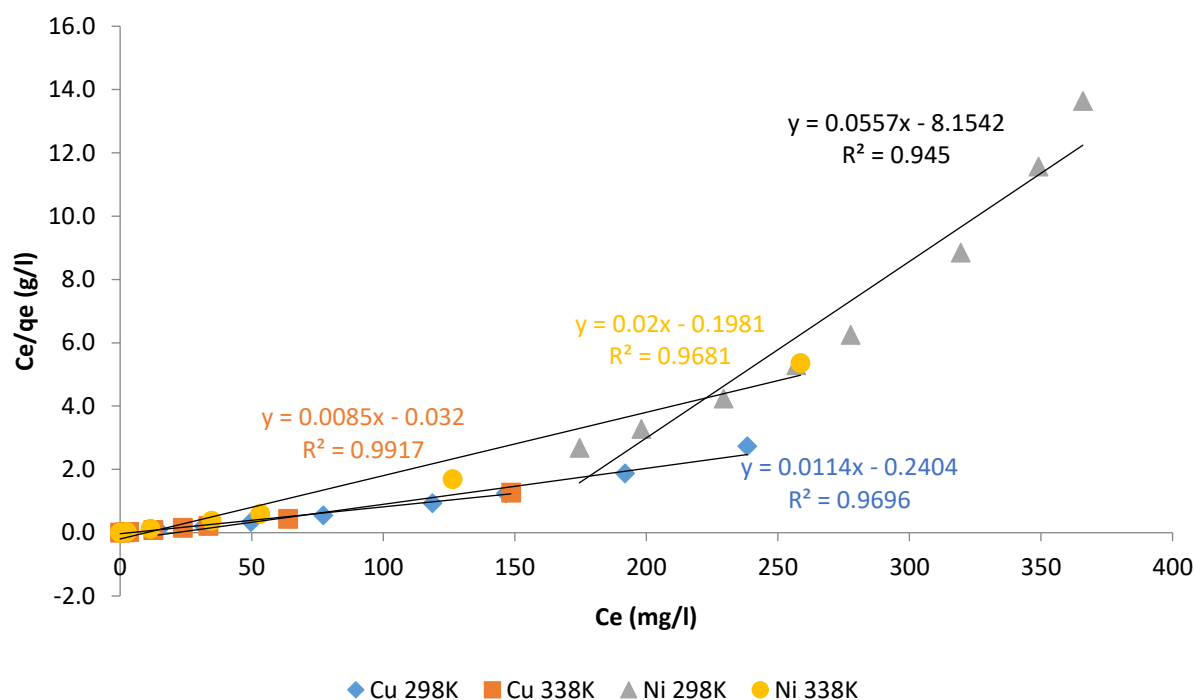


Figure 4.8: Modified Langmuir plot for Cu and Ni

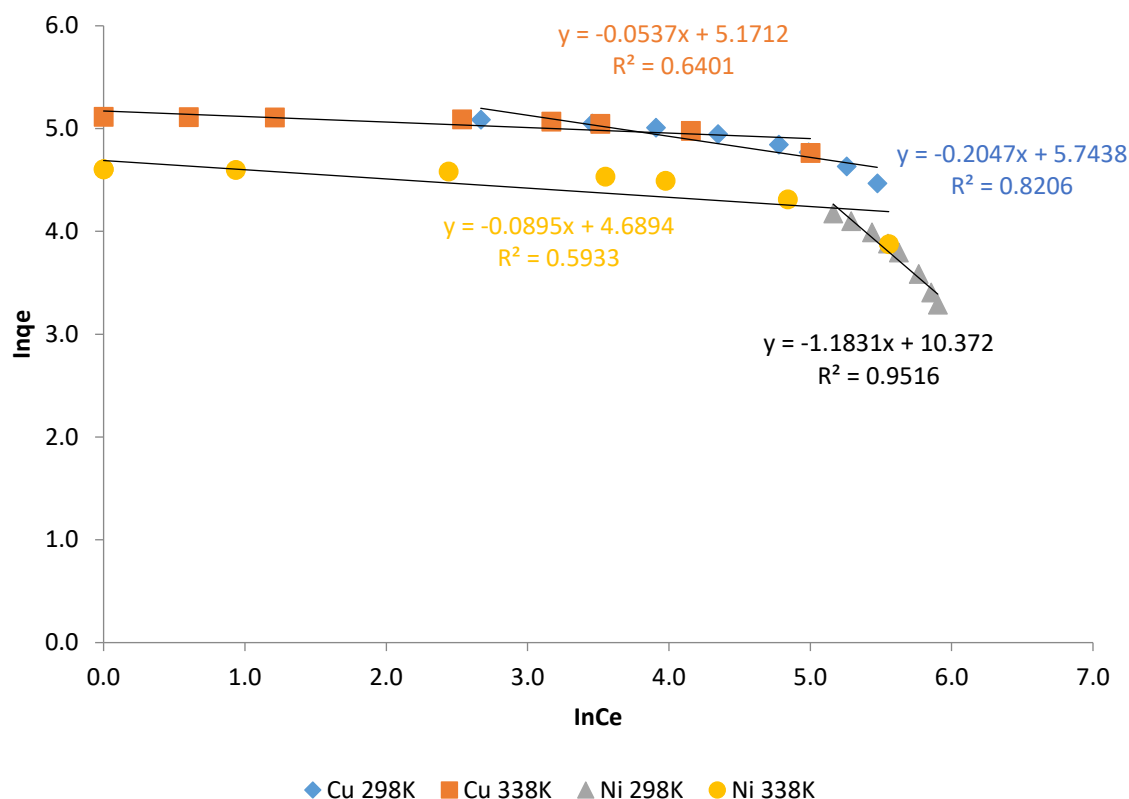


Figure 4.9: Freundlich plot for Cu and Ni

Table 4.2: Kinetic Isotherm Parameters for Cu and Ni

Species		Cu ²⁺		Ni ²⁺	
Temperature (K)		298	338	298	338
Langmuir Isotherm	$q_m(\text{mg/g})$	87.72	117.65	17.95	50.00
	K_{ML}	16548.92	181487.28	3107.03	58795.06
	R^2	0.9696	0.9917	0.9450	0.9681
Freundlich Isotherm	n	4.8828	18.622	0.845	11.173
	K_f	312.248	176.126	31952.3	108.788
	R^2	0.8206	0.6401	0.9516	0.5933

4.5. Thermodynamic Studies

Table 4.3 shows the thermodynamic parameters for the adsorption of Cu²⁺ and Ni²⁺ ions and it shows that the Gibbs free energy values are negative whereas the enthalpy and entropy values are positive. Negative values of ΔG° indicate the spontaneity of the sorption process and the high negative values

reflect a more energetically favourable sorption. Positive values of ΔH° shows that the sorption process was endothermic in nature and positive values of ΔS° show that there is a higher degree of freedom or randomness at solid-liquid interface during the reaction (Bouhamed, Elouear and Bouzid, 2012). The endothermic nature of the process implies that both copper and nickel ions require energy for their mobility.

Table 4.3: Thermodynamic Parameters for Cu and Ni

	Temp (K)	Kc	ΔG° (J/mol)	ΔH° (J/mol)	ΔS° (J/mol.K)
Cu²⁺	298	33.676	-8713.061	43814.439	176.267
	338	273.036	-15763.732		
Ni²⁺	298	1.865	-1543.908	97375.774	331.945
	338	195.270	-14821.718		

4.6. Conclusion

Copper and nickel removal by Morupule were studied by varying the different process parameters on a single component basis. Morupule fly ash shows a great potential in removing heavy metal ions from aqueous solutions. The study shows that a 100% removal percentage for both Cu²⁺ and Ni²⁺ is achieved at pH of 6.6 and 7.8 respectively for doses of 3 and 5 % solid loading respectively. The process has shown to be endothermic because the removal capacity increased with an increase in temperature over time. Both metal ions showed a better fit for the pseudo first order model at 298 K and a better fit for the pseudo second order model at 338 K. The modified Langmuir has shown predominance over the Freundlich and this implies that the process follows a homogeneous and monolayer approach. Thermodynamic studies revealed a more energetically favourable process, endothermic in nature with higher degrees of freedom and randomness at solid – liquid interface.

4.7. References

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Chapter 5 : BATCH BINARY MIXTURES STUDIES

5.1. General Overview

This chapter discusses the results obtained in carrying out batch binary mixtures adsorption studies experiments for the treatment of simulated waste water containing copper and nickel metal ions using Morupule coal fly ash. A batch binary mixture study is where copper and nickel are in the same solution and the adsorption process occurs simultaneously. Included in this chapter are the characterisation results of both raw fly ash and loaded fly ash from binary mixture studies.

5.2. Binary Mixture Studies (Simultaneous Cation Removal)

In this study, copper and nickel ions were removed simultaneously in order to investigate the ability of Morupule fly ash to adsorb both metal ions at the same time under the same conditions. The investigation was centred on determining the effect of contact time, solution pH and adsorbent dosage.

5.2.1. Effect of contact time and adsorbent dosage

Contact time and adsorbent dose are important parameters to consider in running adsorption experiments. The first experiment was conducted at an adsorbent load of 3% and [Figure 5.1](#) shows that a 100% removal of copper was achieved after 105 minutes while nickel reached a maximum of 7.5% after 120 minutes. On the second experiment at an adsorbent load of 5%, all the copper was removed after 60 minutes of the run time while only a maximum of 19.2% of nickel was removed after 120 minutes. The low removal of nickel is attributed to the fact that copper has a larger ionic radius as shown in Table 5.1 thus making it easily removed. According to ([Osińska, 2017](#)), metal ions diffuse easily through the pores when the ionic diameter becomes small whereas a larger ionic radius will cause a quick saturation of adsorption sites because of overcrowding on the surface of the adsorbent. Copper will occupy almost all the sites leaving the nickel to occupy only a few hence most of the nickel remains in the solution. At 5% load there are more sites available for adsorption hence more of the nickel was able to be removed as compared to the 3% load.

Table 5.1: Chemical characteristics of copper and nickel ([Bohli, 2013](#))

Ion	Atomic Weight	Ionic Radius (Å)	Hydrated Radius (Å)	Electronegativity
Cu ²⁺	63.5	0.69	4.19	2.00
Ni ²⁺	58.7	0.72	4.04	1.91

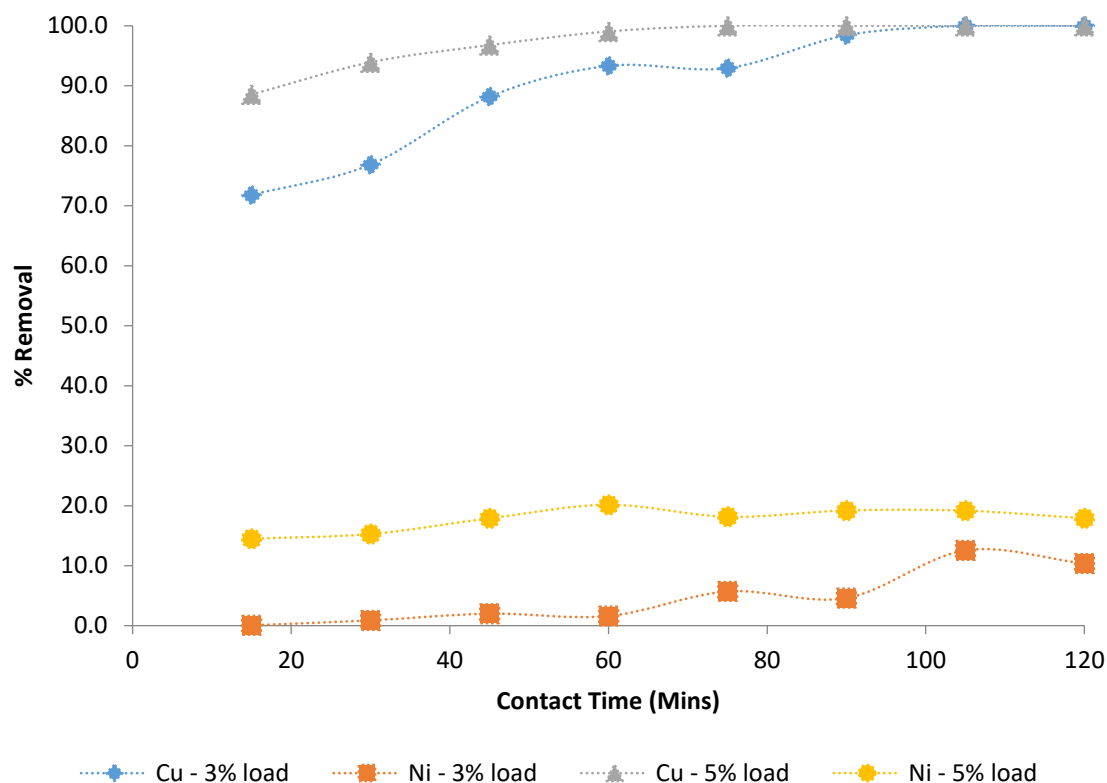


Figure 5.1: Effect of contact time and adsorbent dosage on Cu^{2+} and Ni^{2+} removal by Morupule fly ash; $\text{Co} = 500\text{g/ml}$, Run time = 120 mins; Stirring Speed = 300rpm

5.2.2. Effect of solution pH on Cu^{2+} and Ni^{2+} Removal

In order to determine how the pH of the solution changes with time in the removal of copper and nickel ions, the pH was measured for every sample and Figure 5.2 shows the trend. Morupule fly ash has a high CaO content because the coal it is produced from is treated with limestone for desulphurisation purposes therefore its pH is about 11.55 in potassium chloride. Due to its high alkalinity, the solution pH was reduced to 2 and Figure 5.2 shows that upon addition of 3% load of fly ash the pH rose steadily from 5.4 to 6.2 with a similar trend observed for the 5% load. The 5% load showed a slightly higher increase from 5.8 to 7.2 because an increase in the dose constitutes a larger amount of CaO resulting in a higher pH. At low pH, the surface of the adsorbent gets protonated and the hydrogen ion will hinder the metal ions to be removed but at pH above 4, the fly ash surface will become negatively charged allowing it to bind the cationic species (Kapur and Mondal, 2014). According to (Sočo and Kalembkiewicz, 2013), adsorption experiments for Cu^{2+} and Ni^{2+} , must be conducted at pH's below 10 to avoid precipitation, therefore the maximum pH attained in the experiment is well within what this literature suggests.

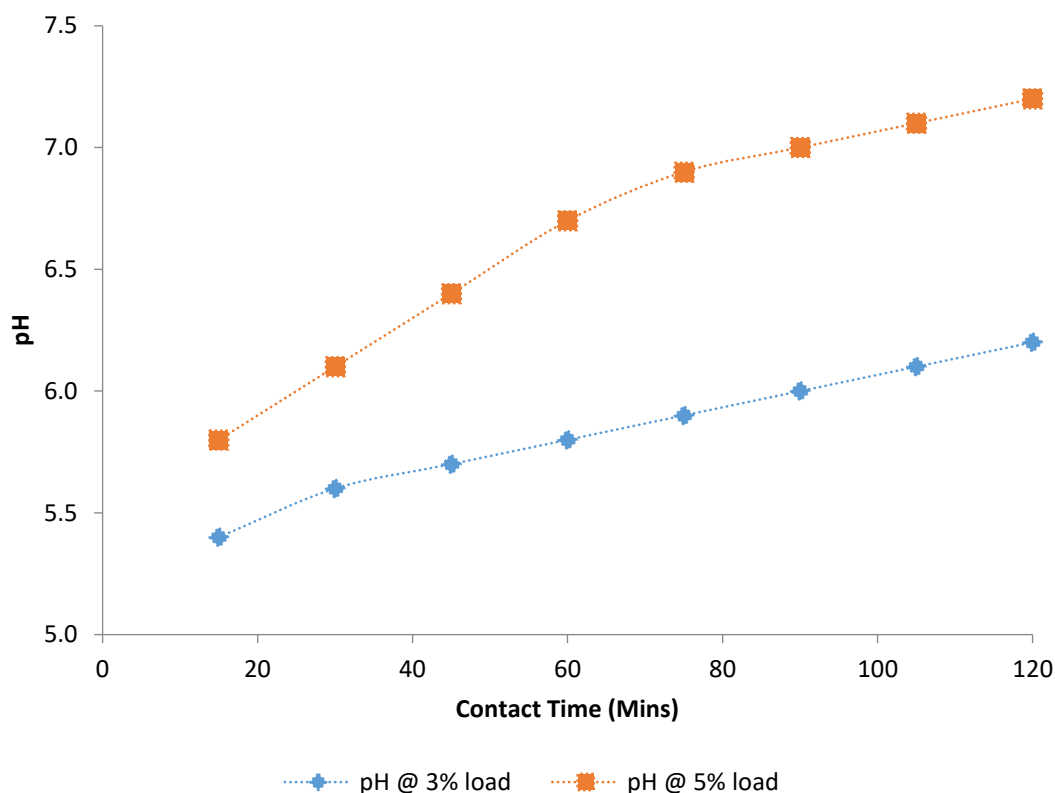


Figure 5.2: Effect of pH on Cu^{2+} and Ni^{2+} removal by Morupule fly ash: $\text{Co} = 50\text{mg/l}$; Run Time = 120 mins; Stirring Speed = 300rpm

5.3. Batch Mixtures Studies (2-Stage Removal Process)

The results in section 5.2 show that copper achieves a 100% removal while nickel shows a lower removal rate of less than 20% because copper has a small atomic radius thus making it easily removed than nickel as explained in section 5.2.1. The purpose of the study was to remove both metal ions in simulated waste water therefore a two (2) stage removal process becomes the more appropriate solution to achieve the objective so that nickel can also be removed. In a 2 stage removal process, all the copper is removed in the first stage, then the solution is filtered to remove the fly ash loaded with copper then a new load of fly ash is used to process the filtered solution in order to remove the nickel. The investigation is centred in determining the effect of temperature and pH variations as the other parameters were determined in section 5.2.

5.3.1. Effect of temperature on removal rate

The effect of temperature variation on Cu^{2+} and Ni^{2+} ions adsorption was studied at 20°C and 40°C to help determine the adsorption thermodynamic parameters of the process. Figure 5.3 shows that an increase in temperature resulted in an increase in the percentage removal of both copper and nickel over time. At 20°C, the removal percentages were 78.6 and 58.9% for Cu^{2+} and Ni^{2+} respectively while at 40°C it was 100 and 91.8% for Cu^{2+} and Ni^{2+} respectively clearly showing a rise after 120 minutes. The results showed that an increase in removal capacity with an increase in temperature implies that the mobility of ions is dependent on increases with temperature. As explained in Chapter 4, due to the porous nature of the adsorbent, an increase in temperature facilitates an easy movement of the metal ions within the pores of the adsorbent. This strong reliance on temperature by the process indicates that the process is endothermic in nature.

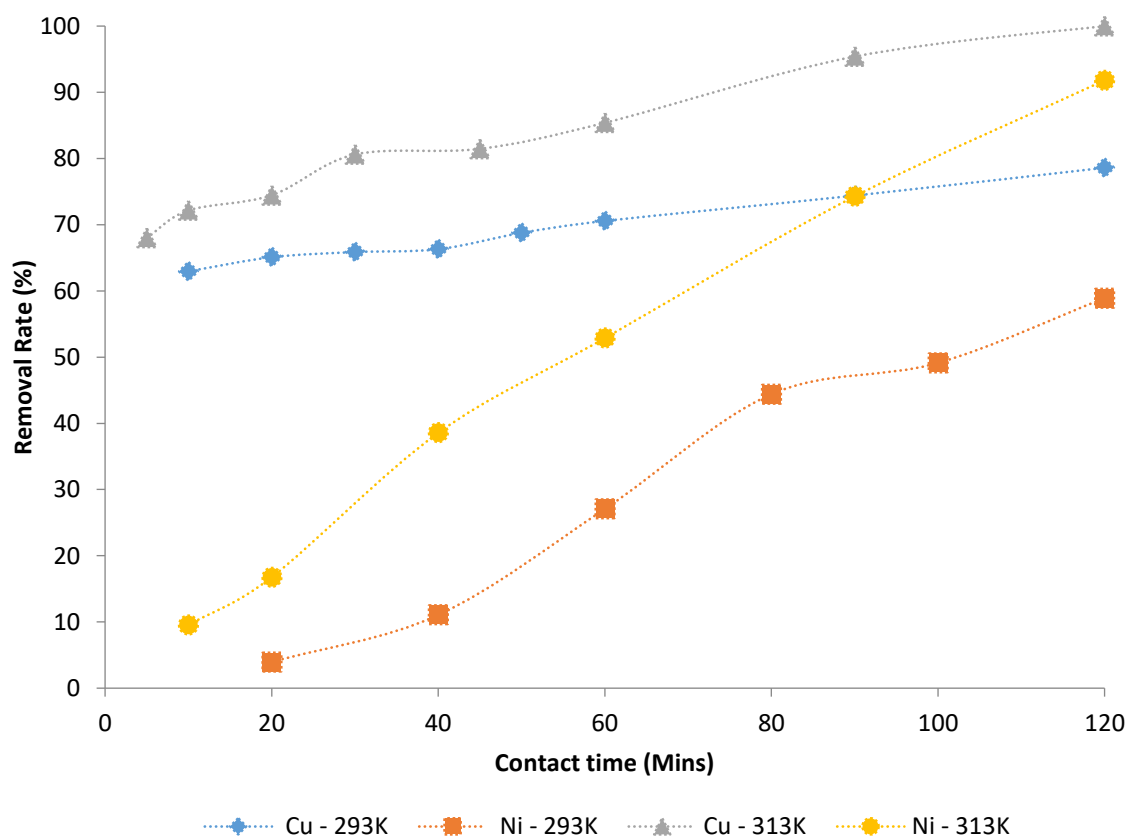


Figure 5.3: Effect of Temperature on Cu^{2+} and Ni^{2+} removal by Morupule fly ash: $\text{Co} = 500\text{mg/l}$; Adsorbent load (Stage 1 = 3%, Stage 2 = 5%), Run time = 120 mins; Stirring speed 300rpm

5.3.2. Effect of pH on the removal of Cu^{2+} and Ni^{2+}

For each sample that was taken during the study on the effect of temperature, the pH of each sample was also measured to study its behaviour in a 2 stage removal process. As discussed in section 5.2.2, the pH increases with increase in time due to the dissolution of the alkaline constituents. What is important to note is that, the pH also shows an increase with an increase in temperature but the doses for both were maintained at 3% load for copper and 5% for nickel. The pH of copper increased from 4.48 to 4.95 at 20°C and from 5.08 to 5.46 at 40°C while it increased for nickel from 6.48 to 7.07 at 20°C and from 6.43 to 7.15 at 40°C. Temperature affects pH when weak acids are involved and if the temperature is increased the equilibrium shifts to the endothermic direction and that will mean protons are consumed rendering an increase in pH.

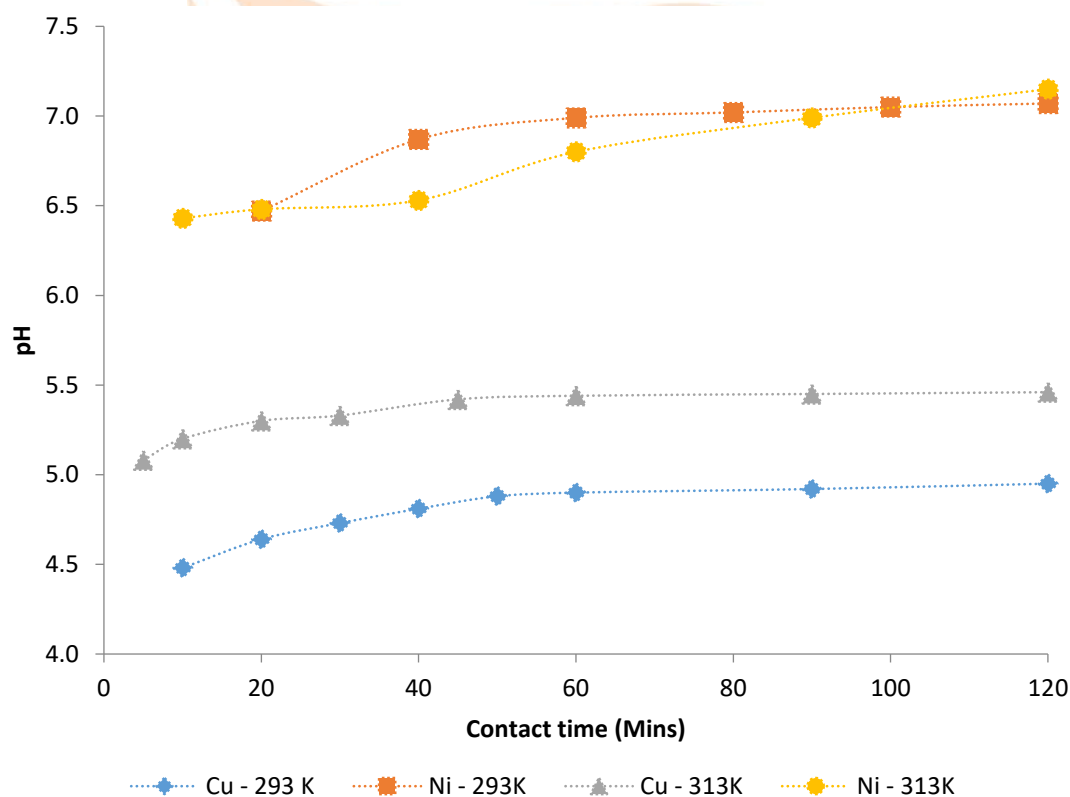


Figure 5.4: Effect of pH on Cu^{2+} and Ni^{2+} removal by Morupule fly ash: $\text{Co} = 500\text{mg/l}$; Adsorbent load (Stage 1 = 3%, Stage 2 = 5%); Run time = 120 mins; Stirring speed = 300rpm

5.4. Kinetic Studies

The pseudo first order and the pseudo second order kinetic models describe the dynamics of the sorption process while intra particle diffusion describes the rate controlling mechanism of the adsorption process.

Figure 5.5 to Figure 5.7 show the plots for the pseudo first order, pseudo second order and intra particle diffusion model respectively while Table 5.2 shows the kinetic parameters of these models. Table 5.2 shows that the root mean square errors (RMSE) for both metal ions are lower in the pseudo second order model which implies the adsorption process follows this model and is controlled by chemisorption. To identify the rate controlling mechanism, intra particle diffusion was tested and Figure 5.7 shows that all the plots did not pass through the origin indicating that the process is controlled by both film and intra particle diffusion (Kapur and Mondal, 2014).

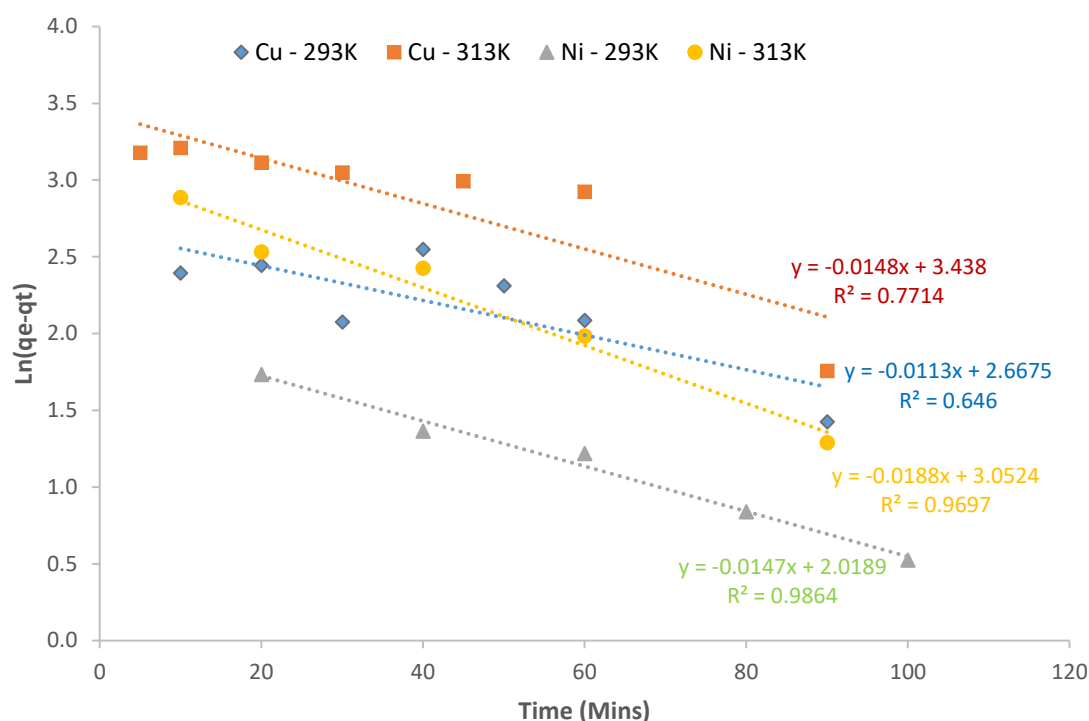


Figure 5.5: Pseudo First Order Plot for Cu^{2+} and Ni^{2+}

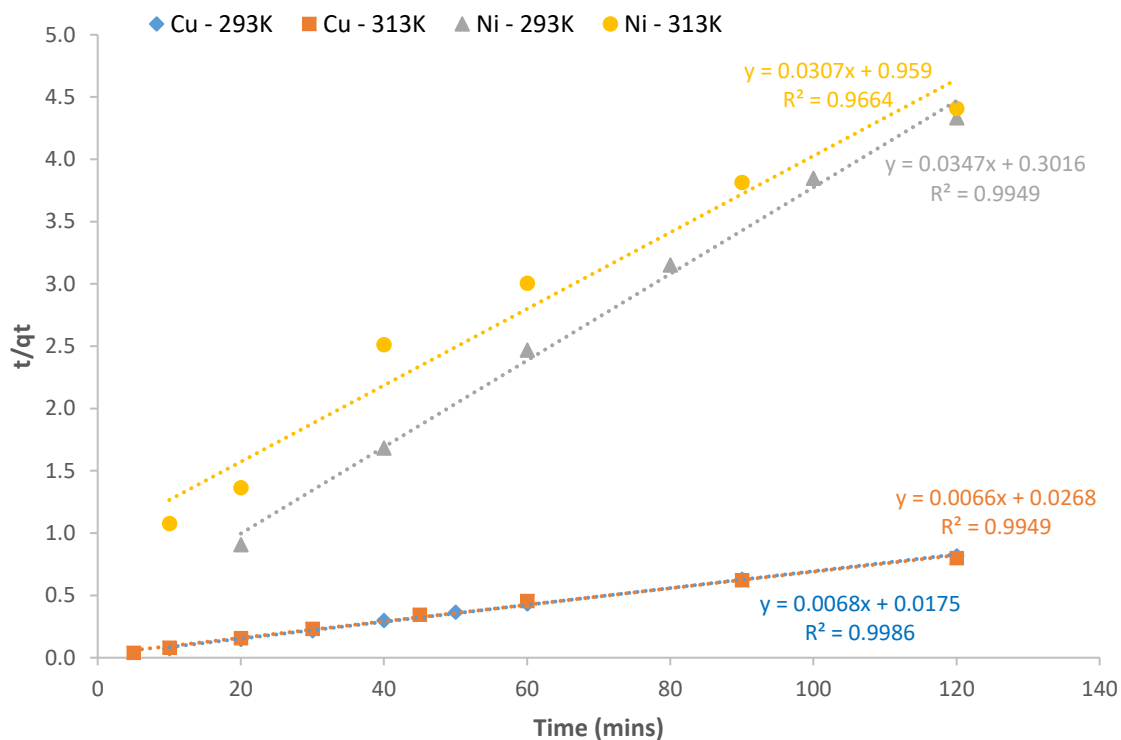


Figure 5.6: Pseudo Second Order Plot for Cu^{2+} and Ni^{2+}

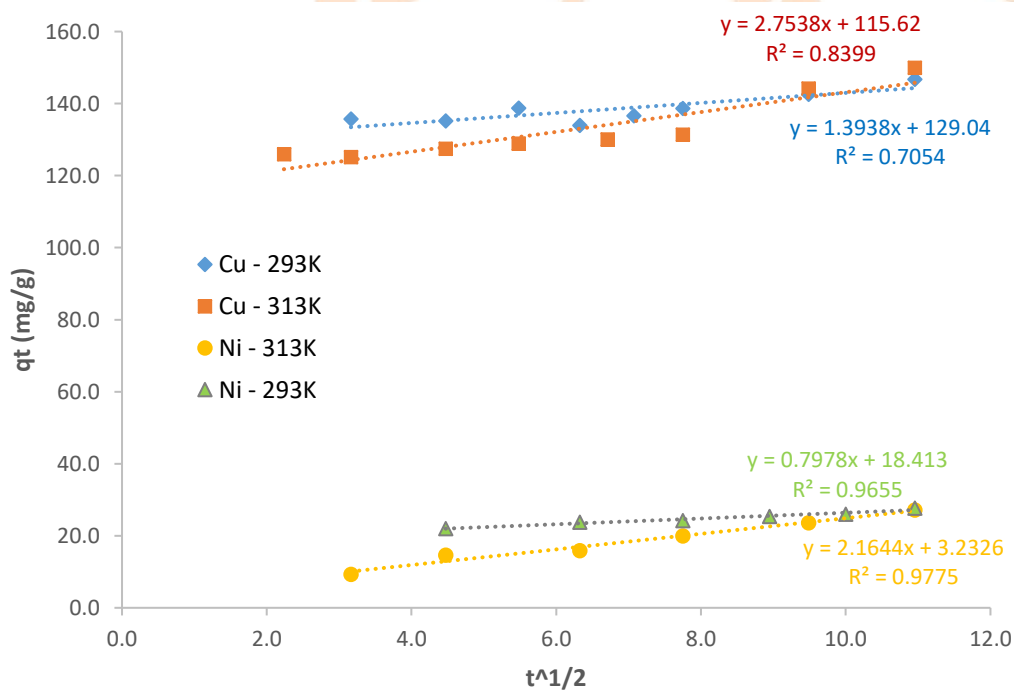


Figure 5.7: Intra-Particle Diffusion Plot for Cu^{2+} and Ni^{2+}

Table 5.2: Parameters for the Kinetic Models

Species		Cu ²⁺		Ni ²⁺	
Temperature (K)		293	313	293	313
Pseudo First Order	q _{e,model} (mg/g)	14.40	31.12	7.53	21.17
	q _{e,exp} (mg/g)	138.57	132.91	24.85	18.44
	K ₁ (min ⁻¹)	0.0113	0.0148	0.0147	0.0188
	R ²	0.6460	0.7714	0.9864	0.9697
	RMSE	74.311	10.695	5.2928	0.0166
Pseudo Second Order	q _{e,model} (mg/g)	147.06	151.52	28.82	32.57
	q _{e,exp} (mg/g)	138.57	132.91	24.85	18.44
	K ₂ (g/mg.min)	0.00264	0.00163	0.00399	0.000983
	R ²	0.9986	0.9949	0.9949	0.9664
	RMSE	0.00333	0.0151	0.0189	0.1884
Intra particle diffusion	K _{id} (mg/g.min ^{1/2})	1.3938	2.7538	0.7978	2.1644
	R ²	0.7054	0.8399	0.9655	0.9775
	I _D	129.04	115.62	18.413	3.2326

5.5. Kinetic Isotherms

The two most common isotherm models were fitted in this chapter to determine the model that best fits the process of Cu²⁺ and Ni²⁺ removal by fly ash. [Figure 5.8](#) and [Figure 5.9](#) show the modified Langmuir and Freundlich plots while [Table 5.3](#) summarises the isotherm parameters of the two models. [Table 5.3](#) shows that both metal ions follow the modified Langmuir kinetic isotherm as they have a higher coefficient of determination (R²) value for this model and this indicates that the process follows a unimolecular layer approach which may also mean that there is no interaction between the adsorbed species. According to ([Foo and Hameed, 2010](#)), the Freundlich model describes a favourable adsorption when 1 < n < 10 but from [Table 5.3](#), both Cu²⁺ and Ni²⁺ show a negative n therefore showing the process does not follow the model.

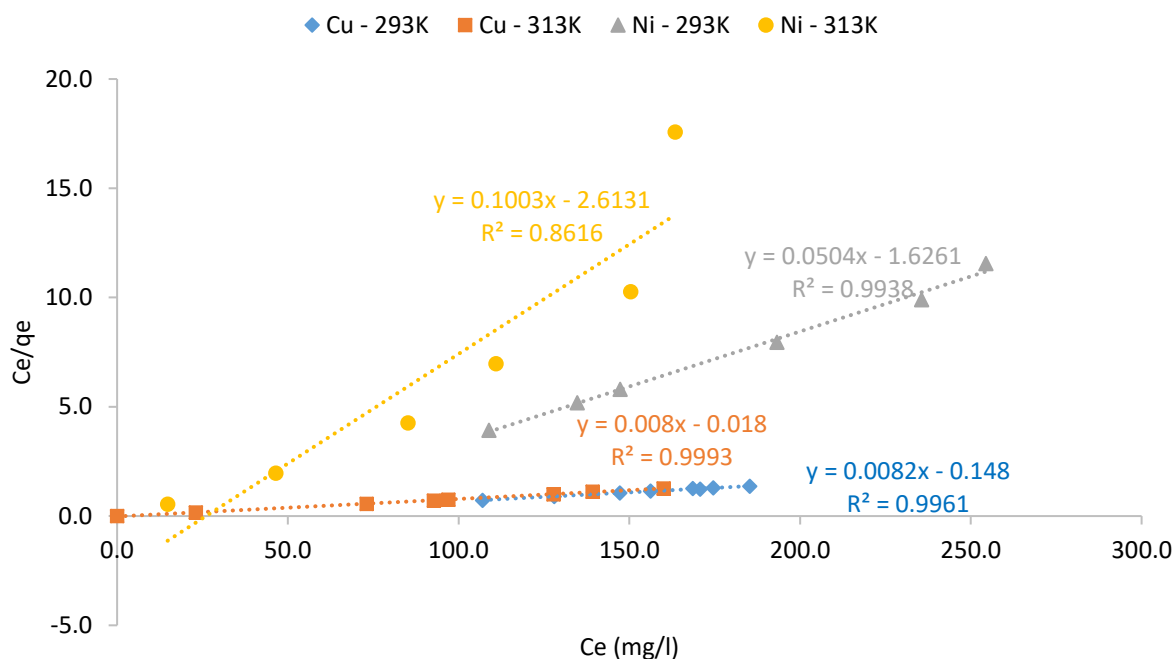


Figure 5.8: Modified Langmuir Kinetic Isotherm Plot for Cu^{2+} and Ni^{2+}

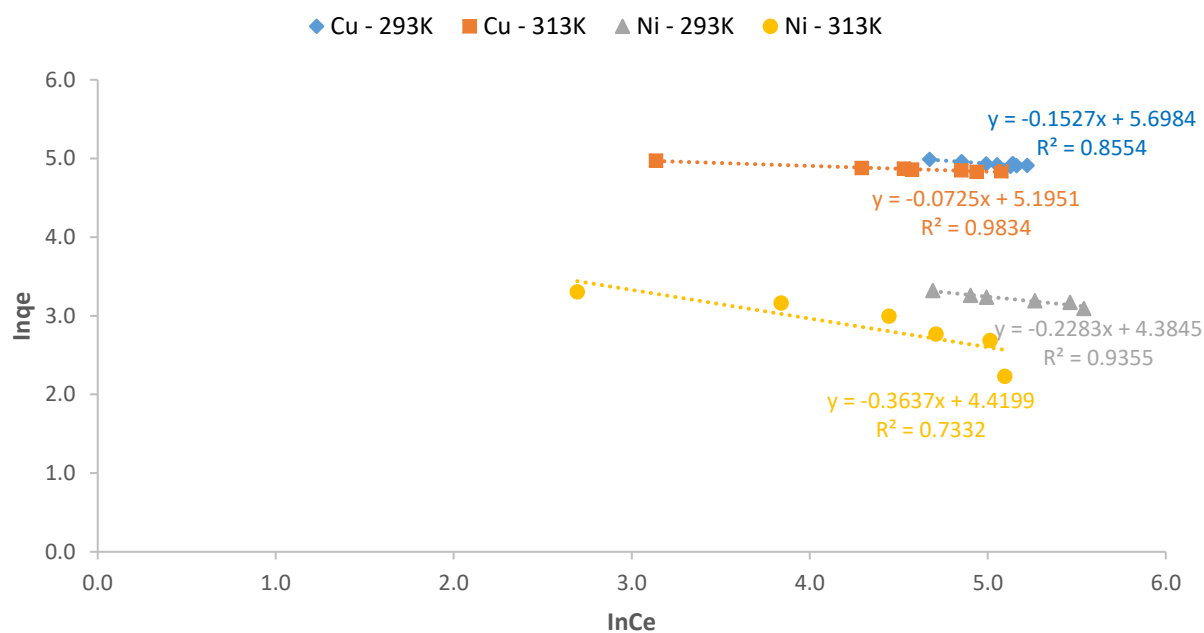


Figure 5.9: Freundlich Kinetic Isotherm Plot for Cu^{2+} and Ni^{2+}

Table 5.3: Kinetic Isotherm Parameters for Cu^{2+} and Ni^{2+}

Species		Cu^{2+}		Ni^{2+}	
Temperature (K)		293	313	293	313
Langmuir Isotherm	q_m (mg/g)	121.96	125.00	19.84	9.97
	K_{ML}	17728.73	203554.56	13760.52	19037.23
	R^2	0.9961	0.9993	0.9938	0.8616
Freundlich Isotherm	n	6.549	13.793	4.380	2.750
	K_f	298.390	180.386	80.198	83.088
	R^2	0.8554	0.9834	0.9355	0.7332

5.6. Thermodynamic Studies

Thermodynamic studies deals with the determination of heat requirements for physical and chemical processes, equilibrium conditions for chemical reactions and the transfer of chemical species between species. In this study, two metal ions (Cu^{2+} and Ni^{2+}) were transferred from waste water to a solid phase substance (fly ash) by the process of adsorption. Table 5.4 shows the thermodynamic parameters that were calculated and the higher heating values shown by the positive change in enthalpy ($+\Delta H^\circ$) indicate that the process highly depends on temperature and that the process is endothermic. The positive values of change in entropy ($+\Delta S^\circ$) imply that there are higher degrees of freedom of the system and this may be attributed to the lack of interaction between the adsorbed species as earlier shown by the Langmuir isotherm. A process is considered spontaneous and energetically when the change in Gibbs free energy (ΔG°) values are negative and the values shown in Table 5.4 support the suggested view, the ΔG° values are negative.

Table 5.4: Thermodynamic Parameters for Cu^{2+} and Ni^{2+}

	Temp (K)	Kc	ΔG° (J/mol)	ΔH° (J/mol)	ΔS° (J/mol.K)
Cu^{2+}	293	3.673	-3169.192	65993.242	236.049
	313	20.739	-7890.177		
Ni^{2+}	293	1.433	-876.656	78409.282	270.600
	313	11.208	-6288.666		

5.7. Characterisation of the Raw and Loaded Fly Ash

Characterisation of raw fly ash and loaded fly ash from binary studies experiments was carried out to identify the changes that have occurred in the composition, mineralogy, functional groups and the decomposition rate during the adsorption of copper and nickel. Raw/fresh ash is the ash that has not been utilised for adsorption while loaded ash is the ash that contains the adsorbed metals.

5.7.1. X-ray Fluorescence (XRF)

Elemental composition of the Morupule coal fly ash was determined by using the XRF vacuum spectroscopy. Table 5.5 presents the composition and characteristic analysis of Morupule coal fly ash and it shows that silica is the main constituent followed by calcium oxide. The high lime (CaO) content in Morupule fly ash is attributed to the treatment of the parent coal with limestone (CaCO_3) during combustion for desulphurisation purposes and this is also confirmed by the high pH values. The sum of silica, aluminium and iron oxides determine the class of fly ash and according to Ibrahim (2016), a Class C fly ash contains a sum of between 50 and 70% while Class F contains a sum greater than 70%. From Table 5.5, the sum of silica, aluminium and iron oxides from the raw fly ash is 65% making the fly ash a Class C which is obtained from burning sub-bituminous or lignite coals. Sub-bituminous and lignite coals are generally characterised by higher lime contents which is about 5 -30wt%. During the adsorption of copper and nickel, minor changes were noticed in the main constituents of the fly ash but the lime content was reduced from 24.7% to 18.7% because the solution was acidified to neutralise the lime content in the adsorbent. Another significant change was noticed in the sulphur content which increased from 4.76% to 9.34%, this may be because the aqueous solution was prepared from the sulphate salts of copper and nickel.

Table 5.5: Morupule coal fly ash composition and characteristics

	Fresh Ash	Loaded Ash	Differences
Component	Mass %	Mass %	
Si - Silicon	28.8	28.2	-0.53
Ca - Calcium	24.7	18.7	-5.99
Al - Aluminium	21.7	21.5	-0.19
Fe - Iron	14.7	15.3	0.67
S - Sulphur	4.76	9.34	4.58
Ti - Titanium	3.24	3.35	0.104
K - Potassium	0.443	0.421	-0.022
Mn - Manganese	0.412	0.424	0.012
Ba - Barium	0.354	0.352	-0.002
Zr - Zirconium	0.124	0.133	0.0088
Sr - Strontium	0.039	0.0042	-0.0348
Ni - Nickel	0.0080	0.010	0.002
Rb - Rubidium	0.0053	0.0056	0.0003
Cr - Chromium	0.0045	0.0078	0.0033
Cu - Copper	0.0034	0.0089	0.0055
Zn - Zinc	0.0010	0.0030	0.0020
Na - Sodium	0.0008	0.0006	-0.0002
	pH	Temp (°C)	EC (mS/m)
H₂O	11.46	21.1	6.47
KCl	11.55	21.0	-

5.7.2. X-ray Diffraction (XRD)

An X-ray diffraction analysis was conducted to identify the minerals and the crystallinity of the adsorbent. Sharp peaks will show that the sample is crystalline while broad peaks will show the amorphous nature of the adsorbent (Kapur and Mondal, 2014).

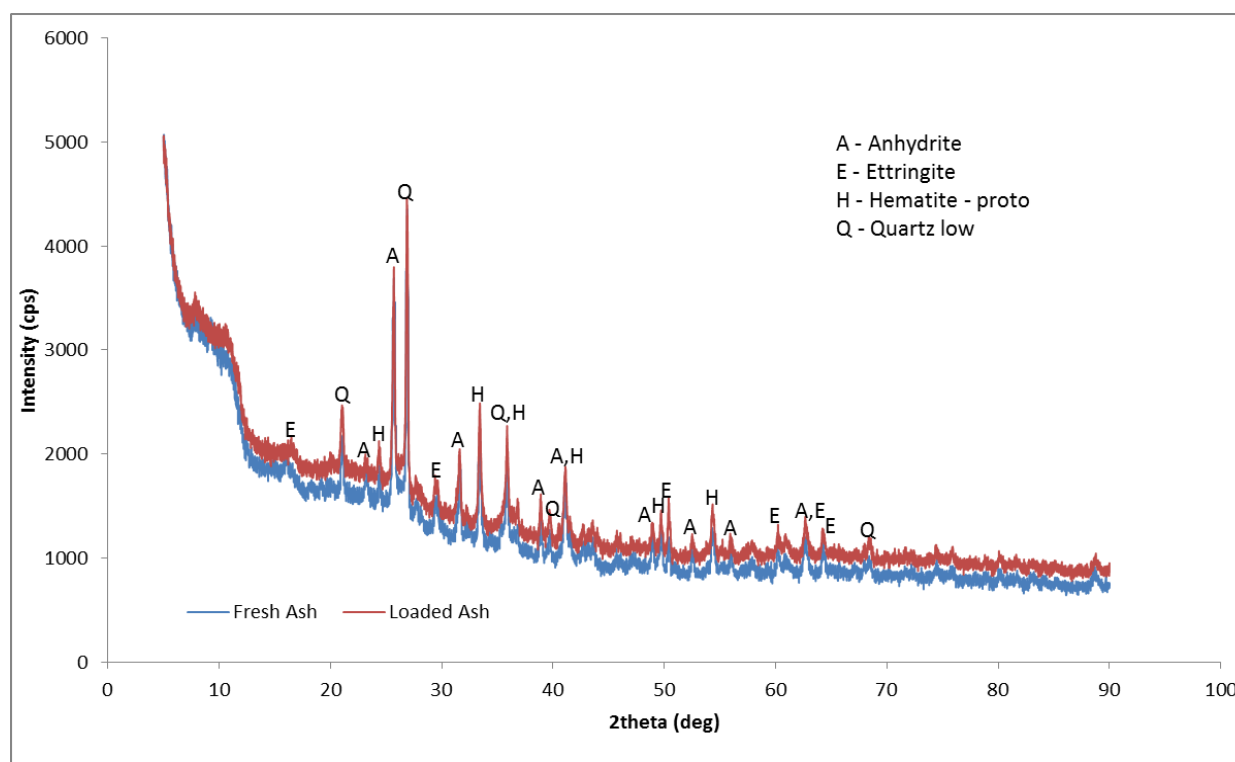


Figure 5.10: XRD plot for fresh and loaded Morupule coal fly ash (fresh-before adsorption; loaded-after adsorption)

The peaks in the x-ray diffraction pattern (Figure 5.10) represent four (4) possible mineral matches. The pattern shows the presence of Anhydrite (anhydrous Calcium Sulphate, $[\text{CaSO}_4]$) at 31.7%, Low Quartz (also known as α -quartz, $[\text{SiO}_2]$) at 29.0%, Ettringite (Hydrous Calcium Aluminium Sulphate, $[\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}]$) at 21.2% and Hematite-proto $[\text{Fe}_{1.9}\text{H}_{0.06}\text{O}_3]$ at 18.1% minerals. The two main peaks are for Anhydrite (25.47°) and Quartz – low (26.63°). Fly ash is a glassy material which usually contains about 50 – 90% amorphous phases and the remaining portion contains the crystalline phases (Ibáñez *et al.*, 2013). The diffraction pattern of Morupule fly ash is dominated by a broad lump at $26.63^\circ \approx 2\theta$ which suggests a large amount of amorphous material (Chancey *et al.*, 2010). Both raw fly ash and loaded fly ash show a similar pattern suggesting that the adsorption of copper and nickel did not impact much on the amorphicity and crystallinity of the fly ash.

5.7.3. Fourier Transform Infrared Spectroscopy (FTIR)

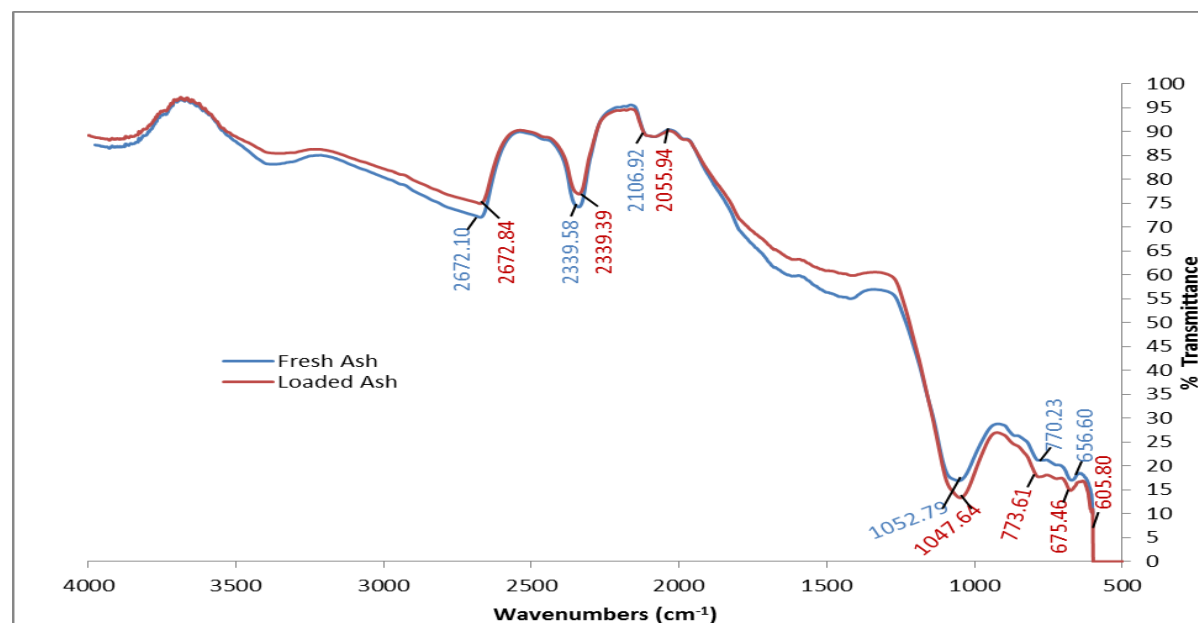


Figure 5.11: FTIR plot for fresh and loaded Morupule coal fly ash (fresh-before adsorption; loaded-after adsorption)

Table 5.6: Spectral analysis of coal fly ash before and after adsorption of Cu(II) and Ni(II)

Band position cm^{-1}			Functional Group Assigned
Before Adsorption	After Adsorption	Differences	
2672.10	2672.84	-0.74	O-H Stretch
2339.58	2339.39	+0.19	$\text{C}\equiv\text{N}$ Stretch
2106.92	2055.94	+50.98	$\text{C}\equiv\text{C}$ Stretch
1052.79	1047.64	+5.15	C-O Stretch/C-N Stretch
773.61	770.23	+3.38	C-X Stretch/Alkene sp^2 C-H Bend
675.46	656.60	+18.86	C-X Stretch/Alkene sp^2 C-H Bend
	605.80		C-X Stretch/Alkene sp^2 C-H Bend

The spectral bands of the FTIR spectroscopy in (Figure 5.11 and Table 5.6) indicate the functional groups present in the coal fly ash. The wavenumbers 2672.10 and 2672.84 cm^{-1} shows carboxylic acid group (hydrogen bonded O-H variable) with stretching vibrations. Peaks at wavenumbers 2339.58 and 2339.39 cm^{-1} are for nitriles ($\text{C}\equiv\text{N}$ stretch) while the band range 2106.92 and 2055.94 cm^{-1} shows the presence of alkynes ($\text{C}\equiv\text{C}$) stretching weak vibrations. The band range 1500 – 500 cm^{-1} represents the fingerprint region which contains complex set of absorptions unique to each compound. Comparison of these bands allows for the identification of specific compounds but is usually difficult to interpret them visually. The presence of alkoxy (C-O stretch – esters and ethers) and aliphatic (C-N stretch) groups is seen at the spectral bands 1052.79 and 1047.64 cm^{-1} . Sp^2 C-H bend from alkenes is shown by the band range of 1000 – 650 cm^{-1} and the C-X group (alkyl halides) stretches in the spectral bands 850-515 cm^{-1} .

5.7.4. Particle Size Distribution (PSD)

The results of the particle size distribution measured using a laser diffraction technique is shown in Figure 5.12. The volume distribution is characterised by a bimodal distribution with median sizes of 27.4 μm and 0.276 μm for larger and smaller particles respectively. The distribution shows that majority of particles are found in the 1 – 100 μm and this may be attributed to the aggregation of finer particles hence the bimodal pattern. A unimodal distribution characterised the number distribution with a median size of 0.113 μm and this means there is a majority of finer particles. The external surface area was calculated from the second moment (m_2) and was found as 11843.83 m^2/kg .

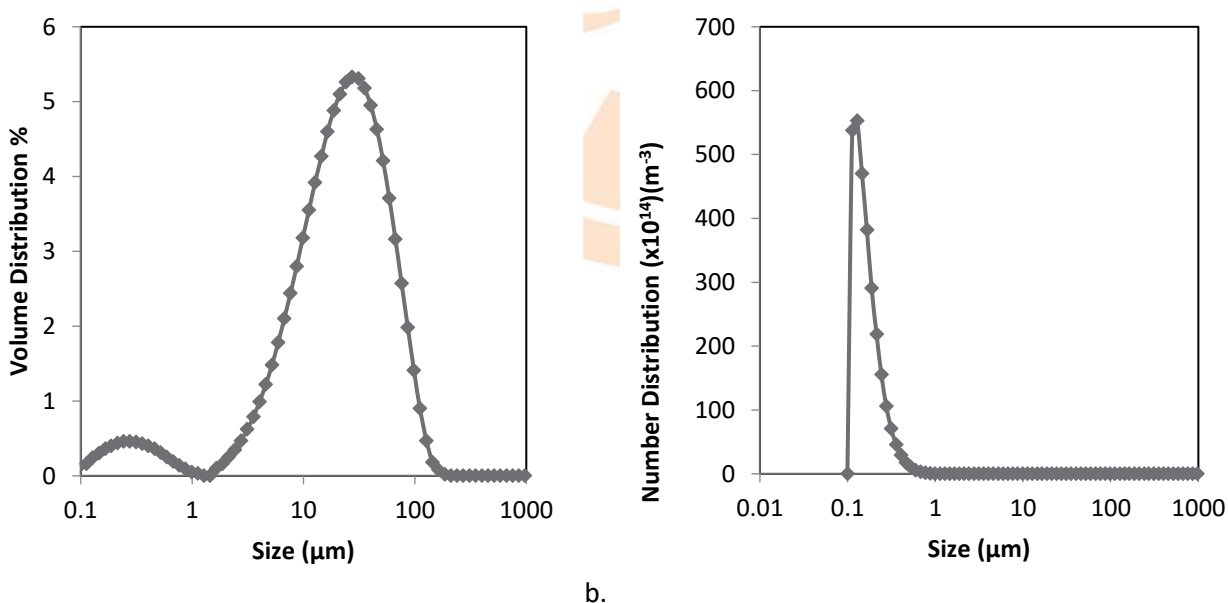


Figure 5.12: PSD Analysis (a) Volume distribution variation (b) Number distribution variation

5.7.5. Thermo-Gravimetric Analyser (TGA)

Figure 5.13 presents the results of a TGA analysis that was conducted on both fresh and loaded ash to compare their weight change patterns. Both samples show a similar trend or pattern of weight loss indicating that precipitation did not occur. Copper and nickel hydroxides usually decompose at about 200 °C and the absence of a weight loss deep at that temperature suggests that hydroxides were not formed during the adsorption of copper and nickel. The weight loss occurs across all the 3 stages and a significant loss occurs between 110 and 950 °C in the second stage where thermal decomposition of the samples was taking place in a nitrogen filled atmosphere. The breaking apart of chemical bonds occurs in this stage with fresh ash losing weight from 1.000 to 0.8229 g and loaded ash from 1.0661 to 0.9185 g.

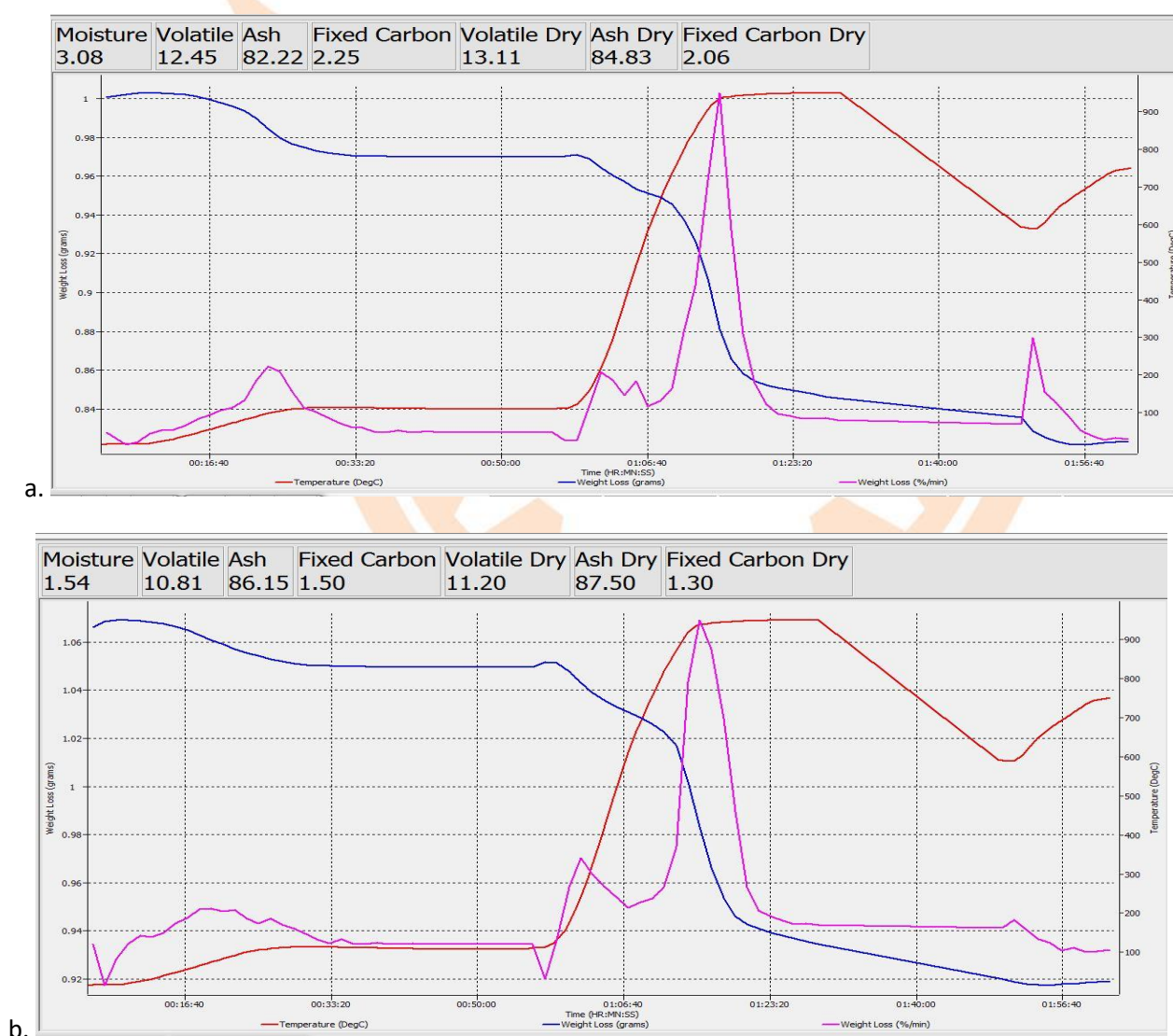


Figure 5.13: TGA Graphs (a) Fresh Ash (b) Loaded Ash

5.8. Conclusion

Process parameters such as pH, adsorbent dosage, contact time and temperature are key in determining the effectiveness of an adsorbent. The study shows that Morupule fly ash proves to be an effective adsorbent in its application to adsorption process because of its ability to remove binary mixtures of metal ions in waste water. A two stage process removal has proven a more viable approach for the removal of binary mixtures than a simultaneous cation removal because of the differences in atomic radius between the metal ions. The importance of process parameters is shown by the positive trend for which an increase in all the parameters shows that there was an increase in the removal capacity. The process shows that the best fit models are the Pseudo Second Order kinetic model and the modified Langmuir kinetic isotherm and both models imply that a monolayer and homogenous approach is favoured which defines a chemisorption process. The higher heating values in the thermodynamic studies also imply a chemisorption process as this process strongly depends on temperature to reach equilibrium.

5.9. References

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Chapter 6 : COLUMN STUDIES

6.1. General Overview

This chapter shows the results obtained by carrying out column adsorption studies experiments for the treatment of simulated waste water containing copper and nickel metal ions using Morupule fly ash. The results are discussed in detail in this chapter.

6.2. Effect of Bed Height

Figure 6.1 shows the effect of bed height on the removal of copper and nickel ions using Morupule fly ash. Increasing the bed height should result in an increase in the adsorption efficiency due to the availability of more adsorption sites (Nwabanne and Igbokwe, 2012). This test was done in a two stage system in which the first stage was meant to remove all the copper and the second stage to remove the nickel as per the results from the batch experiments in Chapter 5. Copper has a small atomic radius thus making it to be easily adsorbed than nickel therefore in the first stage it occupies all the active sites preventing the nickel from occupying any sites. Copper was best removed at a bed height of 210 mm (3 g/100 ml) while nickel was best removed at 360 mm (5 g/100 ml). This may mean that the adsorbate concentration ratio increases more rapidly in small bed heights as compared to higher bed heights hence the bed was saturated in a short time (Nwabanne and Igbokwe, 2012).

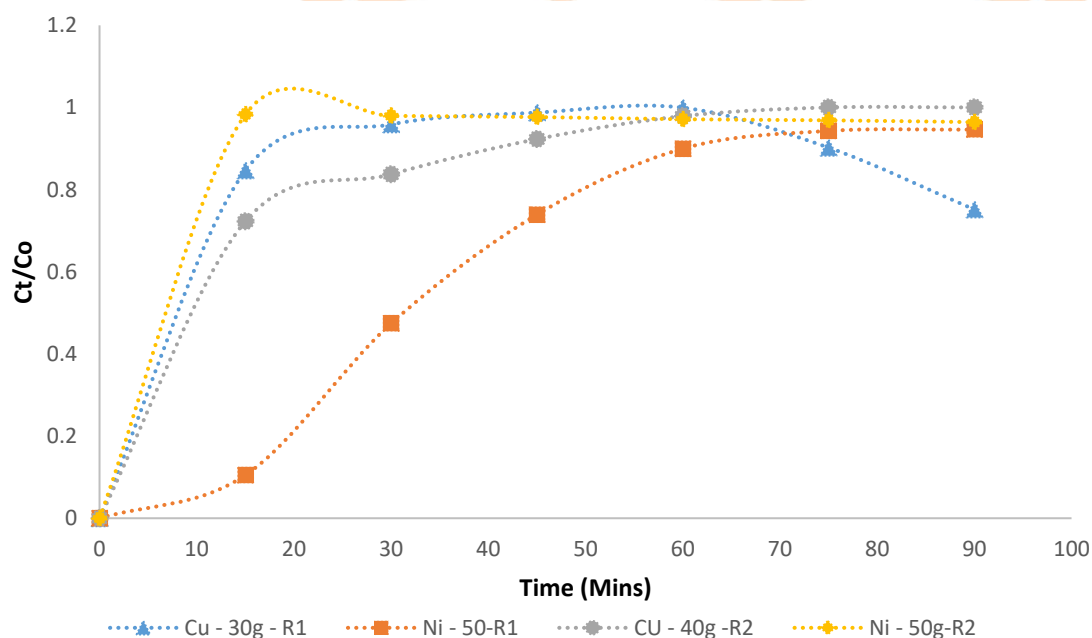


Figure 6.1: Effect of Bed Height on removal of Cu and Ni by Morupule fly ash; Flowrate = 15 ml/min

6.3. Effect of Flowrate

To test the effect of flowrate, the process was run at three different flowrates being 10, 15 and 20 ml/min. According to [Nwabanne and Igbokwe \(2012\)](#), an increase in flowrate shortens the saturation time and creates an unfavourable ion exchange and the results in [Figure 6.2](#) show that a flowrate of 10 ml/min was more favourable for copper removal while for nickel a 15 ml/min was more favourable. For copper, in the first 30 minutes of the process, 97% was removed at 20 ml/min, 85% was removed for 15 ml/min and 83% was removed at 10 ml/min while for nickel, 86% was removed at 15 ml/min after 60 minutes, 60% was removed at 20 ml/min and 49% was removed at 10 ml/min. At a lower flowrate, maximum uptake is achieved because the contact time between the adsorbate and adsorbent is maximised.

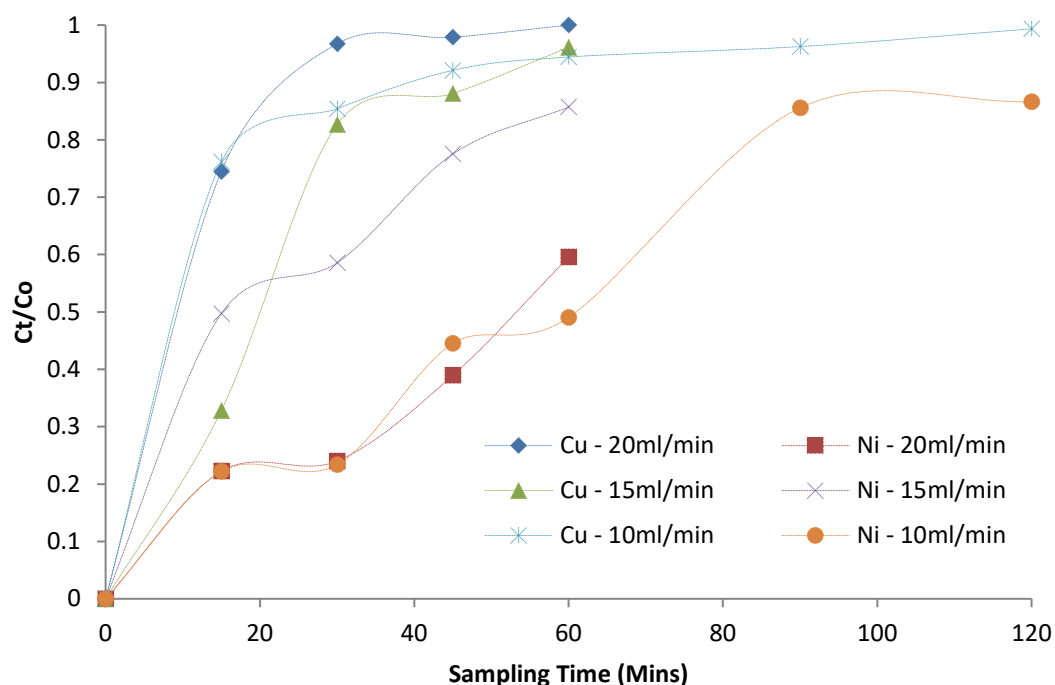


Figure 6.2: Effect of Flowrate on removal of Cu and Ni by Morupule fly ash; Media load = (3% Cu and 5% Ni)

6.4. Breakthrough Table

[Table 6.1](#) shows a summary of the breakthrough time (t_b), exhaustion time (t_e) and the volume of effluent consumed (V_{eff}). The concentration at breakthrough point was chosen arbitrary at some low value [Negrea A et al. \(2011\)](#) and when the effluent concentration reaches 90% of inlet adsorbate concentration the adsorbent is then considered exhausted. The breakthrough time for Cu^{2+} was relatively short for all the tested parameters compared to that of Ni^{2+} and this may be attributed to competitive

strengths of Cu^{2+} for surface sites in fly ash for a breakthrough concentration of 10% of inlet adsorbate concentration. Similarly, copper reaches exhaustion time faster than nickel due to its higher competitive strength. The volume of effluent at exhaustion time was found to be relatively low for copper.

Table 6.1: Summary of the breakthrough time, exhaustion time and volume of effluent

		Flowrate (mL/min)			Bed Height (mm)	
		10	15	20	210	280
Cu^{2+}	t_b (min)	2.0	5.0	2.0	1.5	2.0
	t_e (min)	30.0	32.0	20.0	17	40
	V_{eff} (ml)	300	480	400	255	600
					360-Run1	360-Run2
Ni^{2+}	t_b (min)	6.0	3.0	6.0	15	2.0
	t_e (min)	90.0	60.0	0.0	60	13
	V_{eff} (ml)	900	900	0	900	195

6.5. Kinetic Models

Two models were analysed in this study being the Thomas and Yoon – Nelson models to describe the column performance. The Thomas and Yoon – Nelson models are widely used and are mathematically equivalents in describing the fixed bed column sorption process.

6.5.1. Thomas Model

The model assumes that the process follows the Langmuir kinetics and its greatest limitation is that it is derived based on second order kinetics and the sorption process is controlled by mass transfer. [Figure 6.3](#) and [Figure 6.4](#) show the Thomas models at varied bed heights and flow rates respectively.

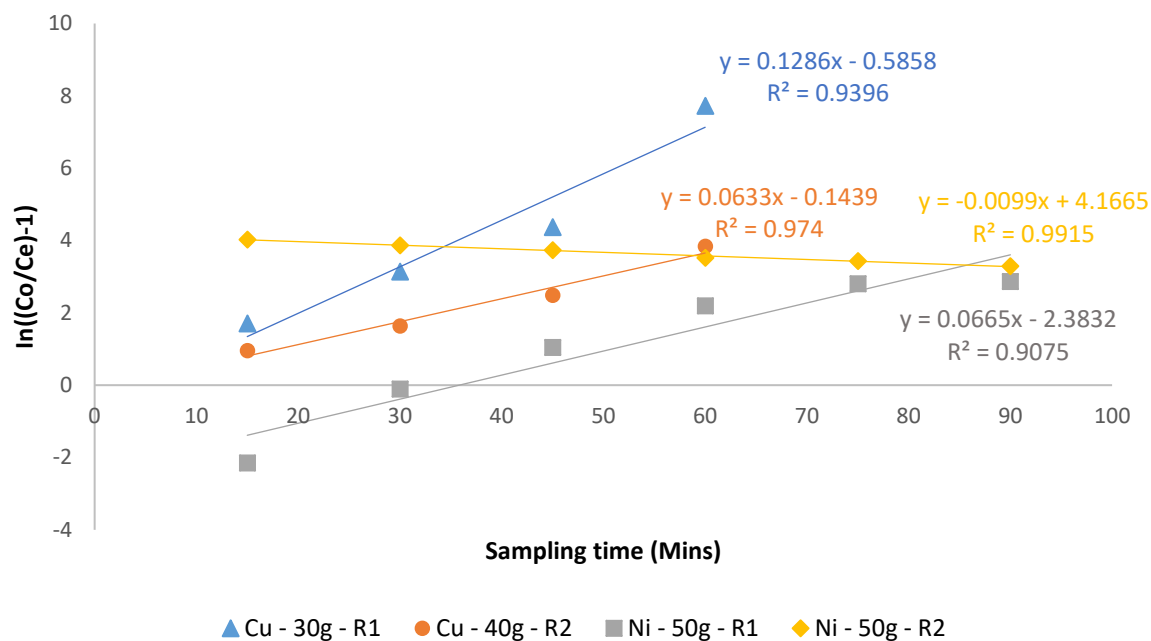


Figure 6.3: Thomas Model at Different Bed Heights

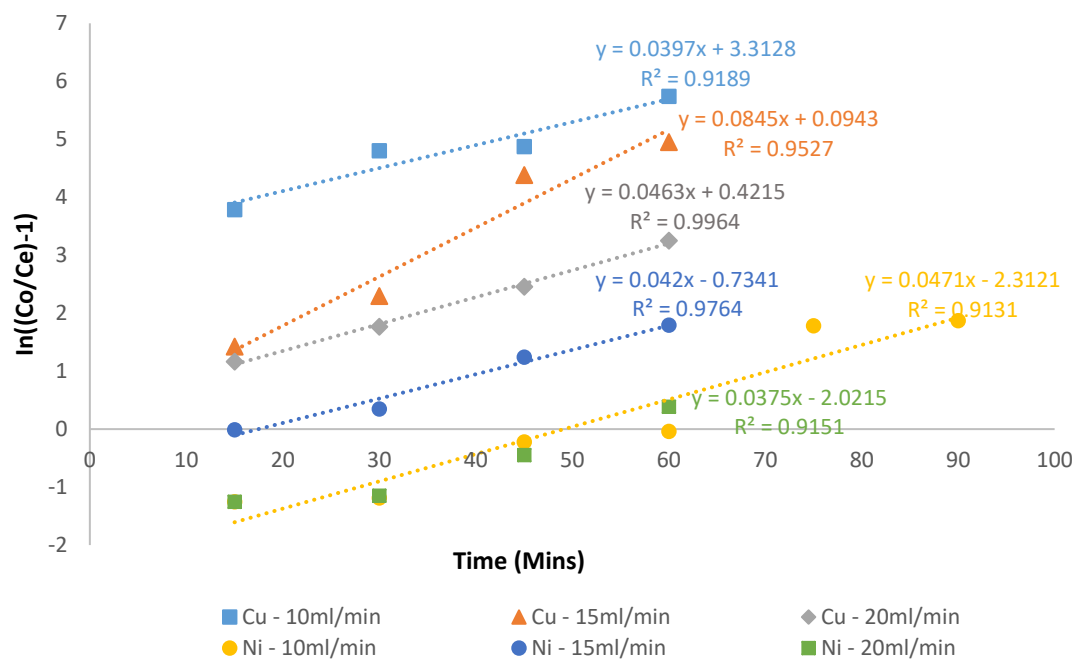


Figure 6.4: Thomas Model at Varied Flowrates

6.5.2. Yoon Nelson Model

Figure 6.5 and Figure 6.6 show the Yoon – Nelson models at different bed heights and flowrates respectively. The models works on a range of concentrations to describe the breakthrough and saturation time of the column.

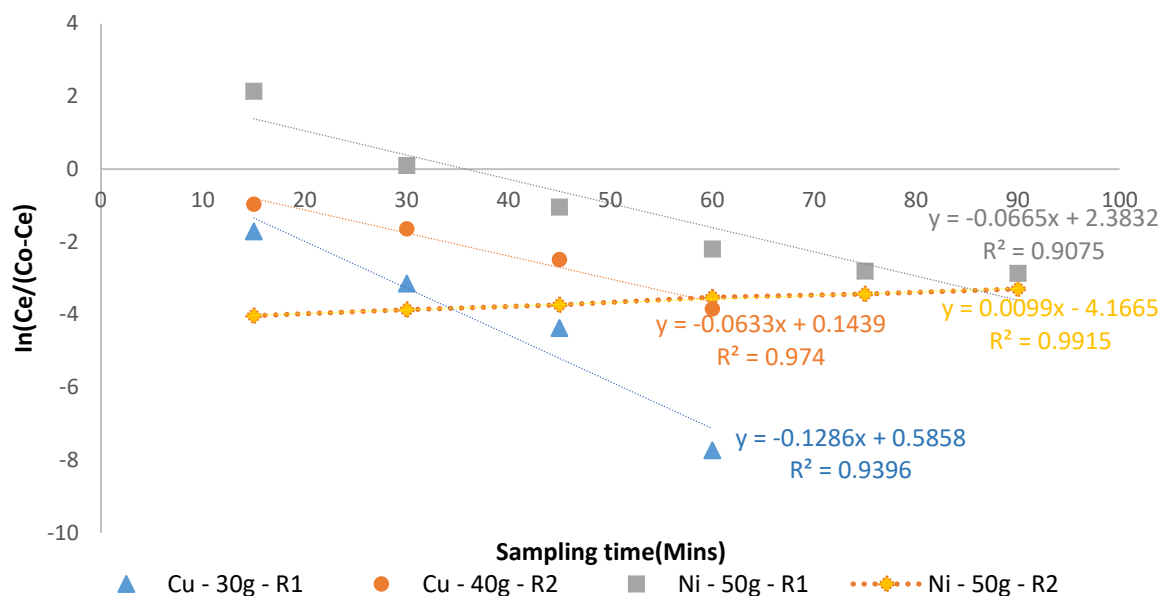


Figure 6.5: Yoon - Nelson Model at Different Bed Heights

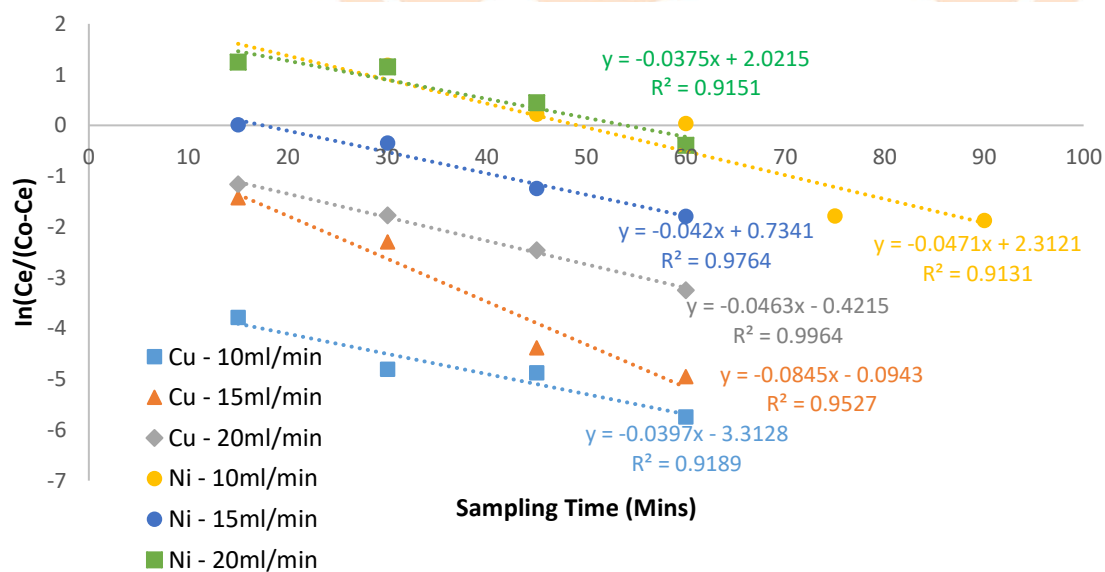


Figure 6.6: Yoon – Nelson Model at Varied Flowrates

6.5.3. Summary Tables for the Thomas and Yoon – Nelson Model

Both models show a greater fit to the experimental data because they all have higher values of the correlation coefficients. The adsorption capacity decreases for copper with 11.388 mg/g at 210 mm and 4.262 mg/g at 280 mm. This shows that the smaller bed has a greater removal capacity than the higher bed. It takes more time to reach 50% sorbate breakthrough in a smaller bed than a higher bed as shown by the τ in the Yoon – Nelson model and this may mean that the more time it takes to reach breakthrough, there is more contact between the adsorbate and adsorbent.

Table 6.2: Parameters for the Thomas and Yoon – Nelson Models based on Bed Height

Species		Cu ²⁺		Ni ²⁺	
Bed Height (mm)		210	280	360-Run 1	360-Run 2
Thomas Model	Kt(L/min.mg)	0.000257	0.000127	0.000119	1.675E-05
	qo(mg/g)	11.388	4.262	59.918	746.132
	R ²	0.9396	0.9740	0.9075	0.9915
Yoon - Nelson Model	Kyn(min ⁻¹)	0.1286	0.0633	0.0665	0.00990
	τ (min)	4.555	2.273	35.838	420.859
	qyn	11.388	4.262	59.918	746.132
	R ²	0.9396	0.9740	0.9075	0.9915

Table 6.3: Parameters for the Thomas and Yoon – Nelson Models based on Flowrate

Species		Cu ²⁺			Ni ²⁺		
Flowrate(ml/min)		10	15	20	10	15	20
Thomas Model	K _{Th} (L/min.mg)	0.000079	0.00017	0.000093	0.000094	0.000149	6.297E-05
	qo(mg/g)	139.076	2.790	30.346	49.089	14.740	128.406
	R ²	0.9189	0.9527	0.9964	0.9131	0.9764	0.9151
Yoon - Nelson Model	Kyn(min ⁻¹)	0.0397	0.0845	0.0463	0.0471	0.042	0.0375
	τ (min)	83.446	1.116	9.104	49.089	17.479	53.907
	qyn	139.076	2.790	30.346	49.089	14.740	128.406
	R ²	0.9189	0.9527	0.9964	0.9131	0.9764	0.9151

6.6. Conclusion

A fixed bed adsorption study was also used to test the efficiency of Morupule fly ash in removing copper and nickel. The key parameters tested were bed height and flow rate of the effluent and smaller bed heights and flowrates have shown a greater removal capacity. Copper was best removed at 210 mm (3 g/100 ml) and a flow rate of 10 ml/min while nickel was best at 360 mm (5 g/100 ml) and a flow rate of 15 ml/min. Copper attains breakthrough in a short space of time and reaches exhaustion faster than nickel does. This is attributed to a higher competitive strength of copper due to its smaller atomic radius. Both metal ions show a higher fitting relationship with the two kinetic models tested because the models are mathematically equivalent.

6.7. References

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Chapter 7 : CONCLUSION AND RECOMMENDATIONS

7.1. Conclusion

Adsorption is among the many processes used for the removal of borderline metal ions from waste water. In this project, simulated waste water was prepared by dissolving sulphate salts of copper and nickel in distilled water. The study shows that fly ash is an effective adsorbent in the removal of Cu^{2+} and Ni^{2+} ions as tested using different parameters such as pH, temperature, contact time and solid loading.

For batch studies, a single component study was conducted and the highest removal of copper was achieved at 3% solid loading, pH of 6.6, temperature of 338 K and a residence time of 105 minutes while for nickel the highest removal occurred at 5% solid loading, pH of 7.8, temperature of 338K and residence time of 105 minutes. Both metals followed the pseudo first order model at 298 K and pseudo second order model at 338K while the Langmuir kinetic isotherm fitted well for both metals at 298 and 338 K. The thermodynamic study showed that the process is spontaneous with higher degrees of freedom at the solid – liquid interface and is endothermic in nature.

The binary mixture study was conducted in two ways being the simultaneous and 2 – stage removal process. It was discovered that when the metal ions are removed simultaneously, copper achieves a 100% removal while nickel shows a lower removal rate of less than 20% because copper has a small atomic radius thus making it easily removed than nickel. A 2 – stage removal approach was therefore conducted with copper being removed in the first stage at 3% solid loading and nickel in the second stage at 5% solid loading. This approach proved effective because both metal ions were removed at higher rates with copper achieving a 100% removal rate at a pH of 5.46 and a temperature of 313 K while nickel achieved a 91.8% removal at a pH of 7.15 at the same temperature as used for copper after 120 minutes. The kinetic studies showed that both metals followed the pseudo second order model and the Langmuir kinetic isotherm showing that the process takes a monolayer approach and a chemisorption mechanism. A positive ($+\Delta H$), positive ($+\Delta S$) and a negative ($-\Delta G$) show that the process requires energy with a lower interaction of the adsorbate and the adsorbent and a spontaneous adsorption process.

A column study was also conducted with the aim of finding the breakthrough time, exhaustion time, volume of effluent and devising the kinetic models that define the mechanisms of the process. A

flowrate of 10 ml/min was more effective for copper removal at 210 mm bed height while nickel removal was more effective at 15 ml/min flowrate at a bed height of 360 mm. The short breakthrough and a faster exhaustion time for copper are attributed to its greater competitive strength. Copper and nickel showed a better fit for both the Thomas and Yoon – Nelson model. The Thomas model assumes that the process follows the Langmuir kinetics and it is derived based on the second order kinetics and that sorption process is controlled by mass transfer.

7.2. Recommendations

The work was conducted using simulated waste water and untreated fly ash. It is recommended that for future work the following be done:

- ❖ Consider a multi-cation removal because due to industrialisation most metal ions are found in waste water hence the need to consider an approach to remove them all.
- ❖ Activation of the lime rich fly ash or the development of geo-polymers from the fly ash to enhance the properties of the fly ash for better removal of the metal ions.
- ❖ The use of industrial waste water for further research because it will contain more of the metal ions and anions whose interactions may affect the adsorption of different ions.
- ❖ BET of the fly ash should also be carried out to help find the area of the fly ash which may also help compare the surface area of the untreated ash and the treated ash in terms of its adsorption capacity.
- ❖ Potential recovery and further use of the metals removed in water as a way of recycling them.