SORPTION OF COPPER (II) IONS FROM AQUEOUS SOLUTIONS BY REGENERATED SPENT BLEACHING EARTH

BY

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Sorption of Copper (II) Ions from

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I dedicate this work to my wife Sarah Wamalwa, my daughters Abigail and Deborah Wamalwa, my Parents Dinah and Wilson Wambu Murambakania and to Christ Jesus who enables me do all things.
I owe this work to the unqualified material and moral support of my wife Sara, my daughters Abida Abigail Wamalwa and Deborah Hope Wamalwa, and my parents Dinah and Wilson Wambu Murambakania. But the conclusion of this work would have been inconceivable without the inimitable mentorship of Prof. Gerald K. Muthakia, Dr. Karanja wa Thiong’o both of the Department of Chemistry, Kenyatta University and Prof. Paul M. Shiundu of the Department of Chemistry, The University of Nairobi, Kenya. Much credit is however due to the academic fraternity of the students, the technical staff and the entire teaching staff of the Department of Chemistry, Kenyatta University for their academic, moral and technical support. Mr. Elias Maina and Mr. Asman Panyako were particularly helpful with polr4 computer program. I thank Mr. Christianus Otieno Oloo of the Fine Art Department of Kenyatta University for assisting in calcinations of some of the samples. Suffice to cite Ms Nancy Mwihaki Githaiga for putting her prized computer at my disposal for typing the initial manuscript. But also most sincerely thanked is the Department of Geology and Mines in the Ministry of Environment and Natural Resources of Kenya for allowing us to carry out XRFA on their machines. I thank the Teachers’ Service Commission of Kenya for granting me leave of study from my professional duties to pursue this course. And lastly and by no means least, the teachers, students and the support staffs of Kimugui Secondary School and The Friends’ School Kamusinga Boys for identifying with me independently and in very special ways at different times while I worked on this study.
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### ABBREVIATIONS AND ACRONYMS

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<td>ASDPV</td>
<td>Anodic Stripping Differential Pulse Voltammetry</td>
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<td>BET</td>
<td>Brunauer-Emmet-Teller</td>
</tr>
<tr>
<td>CEC</td>
<td>Cation Exchange Capacity</td>
</tr>
<tr>
<td>CPO</td>
<td>Crude Palm Oil</td>
</tr>
<tr>
<td>DME</td>
<td>Dropping Mercury Electrode</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved Organic Carbon</td>
</tr>
<tr>
<td>I</td>
<td>Ionic Strength</td>
</tr>
<tr>
<td>ISE</td>
<td>Ion Selective Electrode(s)</td>
</tr>
<tr>
<td>OC</td>
<td>Organic Carbon</td>
</tr>
<tr>
<td>OM</td>
<td>Organic Matter</td>
</tr>
<tr>
<td>PDI</td>
<td>Potential Determining Ion</td>
</tr>
<tr>
<td>PZNC</td>
<td>Point of Zero Net Charge</td>
</tr>
<tr>
<td>RSBE</td>
<td>Regenerated Spent Bleaching Earth</td>
</tr>
<tr>
<td>S/W</td>
<td>Sorbent – Water Ratio</td>
</tr>
<tr>
<td>SBE</td>
<td>Spent Bleaching Earth</td>
</tr>
<tr>
<td>SPA</td>
<td>Specific (or Specifically) Adsorbed</td>
</tr>
<tr>
<td>TA</td>
<td>Total Adsorption</td>
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Copper pollution of water systems has increased greatly in the recent years in many parts of the world because of increased industrial demand for copper, its heavy use in agrochemicals and inefficiency of conventional water filtration techniques. The present study was designed to investigate the efficacy of Spent Bleaching Earth (SBE) as a low cost adsorbent for the removal of copper from aqueous solutions. The SBE, a clay waste generated by edible oil refineries, was washed in excess methyl-ethyl ketone and subjected to heat and/or acid treatments at various conditions. The resultant regenerated spent bleaching earth (RSBE) was then used in a series of experiments to assess its ability to sorb Cu (II) ions from aqueous solutions. The time of contact, adsorbate concentration, adsorbent dosage and the effects of change in adsorbate pH were studied among other parameters. The study showed that copper (II) ions could be removed from aqueous solutions by adsorptive method using RSBE. Methyl-ethyl ketone residual oil extraction followed by heat treatment of the material at 350-370 °C was most effective SBE regeneration procedure for copper adsorption. The materials obtained in this way were characterized by high Cation Exchange Capacity (CEC) of up to 6000 mg/g of Na⁺ ions equivalents. They had Point of Zero Net Charge (PZNC) at pH 5.5. The pH, sorbent dosage and initial adsorbate concentrations were key parameters affecting adsorption characteristics of Cu (II) ions onto RSBE. Over 94% Cu (II) removal was recorded at pH 5.5 using 272 mg/l of initial Cu (II) concentration at 0.1 mass (grams) to volume (milliliters) of adsorbent dosage. Based on analysis of changes in solution pH during the adsorption process, it was suggested that that hydrolysis species were more favorably adsorbed onto the RSBE soil particles. The highest distribution coefficient, $K_D$ of 590.76 was recorded for 370 °C regenerated materials and the standard Gibbs free energy ($\Delta G^{\circ}$) (which ranged from -11.9611 kJmol⁻¹ to -5.8042) indicated that the adsorption process was spontaneous and mainly based on physical ion-exchange type interactions between the metal ions and cations at the RSBE surfaces. Analysis of the adsorption kinetics indicated that Cu (II) adsorption on RSBE is a rapid phenomenon reaching its initial equilibrium in less than six hours. The sorption process fitted Lagergren pseudo-second order mechanism in the initial stages although the Moris-Weber intra-particle diffusion mechanism was more favored at prolonged periods of equilibration. The adsorption data was better described by the Langmuir isotherm than the Freundlich Isotherm was. And desorption experiments illustrated that pH adjustments were more effective in recovery of sorbed copper ions from RSBE than competitive cationic desorbing agents. Over 80% removal of sorbed copper was realized showing that the sorbed metal can substantially be recovered from the materials before their final disposal.
CHAPTER ONE
INTRODUCTION

1.1 BACKGROUND

The aesthetic and practical qualities of copper dates back to man’s emergence from the late Stone Age (Lanier, 1965); over 10,000 years ago. Its first metallurgical processing is accredited to Egyptians and the Romans at about 3800 B.C. although it was not until the 19th century that large scale smelting of the metal was reported. World copper consumption since then took extraordinary dimensions towards the end of 20th century reaching 8.5 billion tones per annum in 1976 and more than 22 billions by 1979 (Mikesell, 1976). Copper metal has therefore been considered the most versatile industrial element after Iron (Nriagu, 1979). The metal has found extensive usage in therapy, jewelry, formulation of agro-chemicals owed to its toxicological qualities to the lower biota (Cohen, 1979) and in food supplementation in swine and poultry production (Batey et al., 1972). It is an essential micronutrient associated with prosthetic enzymes. In crustaceans for instance, the metal is the haemocyanin equivalent of iron in the blood hemoglobin. Every adult Human being ingests 2-5 mg in essential copper daily constituting up to 150 mg of the body weight (Massey, 1973).

The vast usage of the metal has therefore created an extensive pollution edge between man and environment. more than 18000 metric tones of excess copper get discharged into the environment pedogenically every year in addition to more than 56000 metric tones of the same from anthropogenic
sources through smelting, mining, fuel combustion, waste incineration, and agricultural activities in addition to domestic and industrial waste effluents (Cohen, 1979; Nriagu, 1979) among other. The escalating levels in copper pollution has put strain on traditional methods of metal removal from sewage waste (see section 2.3) that they can no longer cope with the new scope of pollution without compromise of the efficiency of the process (Ulmuna et al. 2003). These have necessitated innovation of more efficient and more cost effective metal removal mechanisms especially in regard to high bio-toxicity of the metal and the prohibitive costs of traditional methods.

Already, appreciable world revenue is being spent in search of more adaptable aqueous metal removal protocols in form of heavy metal adsorption studies on low cost and waste material adsorbents (Atanassova, 1999; Ulmuna et al., 2003; Silveira and Alleoni, 2003). In the present work, feasibility studies on re-use of Spent Bleaching Earth (an industrial waste from vegetable oil refineries) in the removal of copper (II) ions from aqueous solutions and from copper-containing wastes by adsorption methods are presented.

1.2 PROBLEM STATEMENT AND JUSTIFICATION

The high versatility and extensive usage of copper towards the end of the previous century has made copper one of the most polluting heavy metals today (Abou-Arab et al., 1996). As a result, copper pollution is now rife in regions where heavy metals in general and copper pollution in particular was hitherto unknown. Copper pollution, for instance, has now been documented
in water sources in the coffee growing zones of Kenya's central highlands (Kariuki, 1993), oceanic waters along the Kenya-Mombasa coastlines (Oyugi et al., 2003), municipal water sources in Kisumu (Ochieng, 2000), and Nairobi (Batista, 1996). Elsewhere copper pollution has been reported among horticultural products along the East African coastline at Dar es salaam in Tanzania (Bahemuka and Mubofu 1999), marine products in Egypt (Abou-Arab et al., 1996) and China (Wong et al., 2000) to mention a few. Heavy use of copper based agro-chemicals and inefficient methods of sewage and wastewater treatments have been blamed for this vice (Oyugi et al., 2003).

In view of these new reports on copper pollution and of the high levels of copper bio-toxicity (Cohen, 1979), the urgency to devise more effective and affordable water and sewage copper cleansing protocol to forestall possible copper poisoning of bio-systems cannot be overemphasized. The global production of spent bleaching earth (SBE) by edible oil producing industries is estimated to be over 600,000 tones per annum (Foletto et al., 2002). With almost 40% residual oil content in some cases (Wachira et al., 2005); SBE disposal has become a major environmental concern.

This study was designed to provide a comprehensive investigation into the adsorption characteristics of copper onto regenerated spent bleaching earth. It was anticipated that the proposed method would lead to cost reduction in sewage copper removal by enhancement of efficiency and affordability of sewage treatment by industries and municipalities and enhance waste
elimination by providing alternative SBE utilization to circumvent its disposal problems.

1.3 OBJECTIVES

1.3.1 General Objective

The general objective of this work was to investigate SBE copper adsorption properties and the feasibility of its re-use as a low cost adsorptive material for removal of copper (II) ions from aqueous solution.

1.3.2 Specific Objectives

The specific objectives were therefore to:

(a). Investigate various SBE reactivation procedures in order to identify the most efficient method for SBE regeneration for the purpose of adsorption of aqueous copper (II) ions.

(b). Characterize chemical and surface properties of Regenerated Spent Bleaching Earth (RSBE) so as to elucidate RSBE surface charge and forecast its Cation Retention Capacity.

(c). Investigate the effects of pH, time of contact, initial concentration of Copper and sorbent-water ratio(S/W ratio) on RSBE Cu(II) adsorption efficiency so as to optimize RSBE copper adsorption from aqueous solutions.

(d). Apply Langmuir and Freundlich isotherms to the SBE - Cu sorption data in order to:
i. Objectively quantify the adsorptivity of the metal to the material,

ii. Elucidate the adsorption mechanism, and

iii. Estimate the partition sorption equilibrium constant in order to estimate the stability constants of the Cu-adsorbent complexes in the adsorption.

(e). To investigate desorption of SBE adsorbed copper so as to evaluate the recovery of the adsorbed metal from the materials before their final disposal to the environment.
CHAPTER TWO

LITERATURE REVIEW

2.1 COPPER METAL

Copper is the 29th element of the Periodic Table; chiefly existing as $^{63}\text{Cu}$ and $^{65}\text{Cu}$ at 69.09% and 30.91% respective abundance, with $^{64}\text{Cu}$ isotope in trace amounts (Massey, 1973). It forms Cu (I) and Cu (II) compounds with sparse Cu (III) species. It was the first metal to be used by man for practical purposes (Massey, 1973). It was initially mined from Cyprus by the Romans who called it *aes cyprum* (*i.e.* from Cyprus) the name from which the Latin version *cuprum* and the symbol Cu were coined (Thornton, 1979). Copper is the 25th most abundant element in the earth’s crust at 68-ppm abundance; and is a constituent in biological systems, soil solutions, organic fossils, and natural waters (Boyles, 1979;). The chief ores are chalcopyrites; CuFeS$_2$ and the chacocites; CuS$_2$ (Massey, 1973).

Bioavailability and toxicity of metals in the environment are dependent on the pH, concentration, ligands present, soil mineralogy, and soil organic matter (OM) as well as anthropogenic activities (van der Marel and Beutelscher, 1976). Copper is only second to zinc in environmental pollution, but is twice as toxic (Leeper, 1978). Although the amount required by plants seldom exceeds 30 ppm (Harter, 1983), 500 ppm copper content has been reported in some farmlands especially in Western Europe (Leeper, 1978). The 2.2 million tonnes of world’s copper pollution have been attributed to extensive use of copper-based agrochemicals, wood and fossil fuel combustion, and inefficient
industrial wastewater-sewage treatment procedures (Leeper, 1978) among others. Cu pollution has been reported in the central highlands of Kenya owing to extensive use of copper-based fungicides in the coffee plantations in the region (Kariuki, 1993) and in horticultural products in Tanzania (Buhemuka and Mubofu, 1999).

Toxicity of copper has been blamed for soil ammonification; demineralization of nitrogen; deceleration of soil enzyme activities, depopulation of soil microorganisms and insects and copper-induced plant nutrient deficiencies (Leeper, 1978), among other hazards. High level copper poisoning has been reported in plants and animals (Ulmuna et al., 2003). In people, copper toxicity has been associated with inflammation of the pulmonary organs; respiratory, gastrointestinal, cardiovascular, neurological and skin dysfunctions (Cohen, 1979).

2.2 CLAYS

Clays are sedimentary rock particles with diameters 3.9 µm or less. They are also defined as disperse system of colloidal products of weathering in which the secondary mineral particles of dimensions 2 µm and less predominate.
2.2.1 Clay Minerals

Clay minerals are classified as montemorillonites or koalins based on the mineralogical structure present (van Thoor et al., 1965). The koalins consist of close packed regular alternation of Si-O and Al-O sheets. (Figure 2.1)

![Figure 2.1 Kaolinite Structure](image)

Montemorillonites are 2:1 clay minerals with large lattice charge and characteristic swelling on solvation by water and low molecular weight alcohols. Their lattice consists of Al-O sheets sandwiched between Si-O sheets with inter-lamellar spaces punctuating each set of the sheets (van der Marel and Beutelspacher, 1979) (Figure 2.2). The spaces allow water molecules into...
the structure causing the characteristic swelling of these materials on exposure to moisture (van Thoor et al., 1965). Naturally they contain trace impurities of calcite, felspar, zinc blends, apatite, sphenes and lemonites with variable amounts of Mg and Fe replacing part of Al in the silicate structure giving the formulae; \((\text{Al, Mg, Fe})_4\text{Si}_8\text{O}_{20}(\text{OH})_4\) and resulting in a net negative charge on the material. This charge is neutralized by association with exchangeable cations; \(\text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+, \text{K}^+\) and \(\text{H}^+\) (van der Marel and Beutelspacher, 1979).

Certain types of Montemorillonites (Fullers Earths) have natural capacity to sorb color (van der Marel and Beutelspacher, 1979), metal ions, and other impurities from oils (Low et al., 2003). They are used as universal oil bleaches. They are characterized by high Cation Exchange Capacities (C.E.C) of 80-90 mole equivalents (meq) or more per 100 g of dry mass. Bentonites on
the other hand, refer to montemorillonites that are high in colloids and thixotropy; they require heat and/or acid-activation to desorb the exchangeable metal ions from the active sites to improve their adsorptive ability (Folleto et al., 2002); this opens up the structure making the surfaces electrochemically more active.

2.2.2 Bleaching Clays/Earths

These are essentially montemorillonites and to a lesser extent Attapulgites (or palygorskites—an old name given by a Russian scientist) (Grimshaw, 1971). The latter are similar to montemorillonites having inter-lamellar spaces in their structure (Figure 2.3). For purposes of bleaching, the clays are usually dried at 200-300 °C and ground to various sizes. The attapulgites may require further extrusion under high pressure and low moisture content. The activity of montemorillonites on the other hand is greatly enhanced by acid activation.
2.2.3 Bleaching of Edible Oils

Many methods exist in oil bleaching including; Alkali Treatment and Oxidative Bleaching, Hydrogenation and Heat Treatment at about 220 °C. Adsorption Bleaching by Bleaching Earths however is the most important method of bleaching edible oil (Looney, 1975). Two techniques are usually employed in this bleaching process namely, the percolation and contact methods. In the former, the oil is filtered through a granular product of 250-200 μm (or 10-60 mesh) essentially at low temperatures whereby the coloring matter get adsorbed by the soil as the oil passes through.

In the contact processes, the oil is put in contact with finely ground clay of about 74 μm (or less than 200-mesh) for predetermined period of time to
equilibrate. Filter pressing operation then separates the oil at temperatures in the range of 150-300 °C.

An estimated 200-400 thousands tones of activated clay is required globally by oil refining industries to process crude palm oil (CPO) into final products every year (Low et al., 1998).

### 2.2.4 Spent Bleaching Earth (SBE)

SBE refers to Bleaching Clays already used in edible oil refining to sorb color and other undesirable matter from the oils. It is usually characterized by high oil contents, between 30-40% (Wachira et al., 2005). Direct landfills are the most common current mode of disposal; resulting in severe pollution problems (Folleto et al., 2002). Because of the large volumes of SBE involved, such disposal methods have become increasingly unpopular and even unacceptable in most countries. This has promoted the urgency to innovate ways of SBE regeneration for other adsorptive purposes in addition to the oil recovery for other practical purposes (Folleto et al., 2002).

Solvent extraction of oil and thermal activation, and/or Mineral acids treatment is used in SBE regeneration (Netzer and Beszedits, 1979; Boukerroui and Ouali, 2000). Air, steam, carbon dioxide, transition metal nitrates, and some chlorides have been tested as possible SBE activants with promising results (Namasivayam and Kanchana, 1993). Low et al., (2003) and
Mehmet et al., (2003) have indicated that regenerated SBE is comparable to virgin bleaching clays in the adsorption metal ions and certain organic groups.

2.3 SEWAGE TREATMENT METHODS
Precipitation is the most commonly employed method of heavy metal removal from sewages because it is cheap and requires minimum operation skills. The other techniques include Complexation, Biological uptake, Reverse Osmosis, Ion Exchange, and Adsorption (Nezter and Beszedits, 1979) among others. These are especially useful in removal of metal ions from aqueous solutions at trace levels where precipitation is particularly wanting in efficiency (Ulmuna et al., 2003). They are however, cost-prohibitive to small industries especially in developing countries. This is the major cause of inefficient sewage treatments and the resulting Heavy Metal pollutions in the Developing World (Naidu et al., 1997). To meet legislative standards many industries have been forced either to look for more effective sewage treatment methods or to develop on the existing ones to improve their performance and cut down the costs by employing commonly available natural or wastes material as in adsorption processes.

2.4 DETERMINATION OF SOIL EXTRACTABLE CARBON
Soil organic matter (OM) plays an important role in the sorption of metal ions on soil samples. Their effects stream from their influence on the Point of Zero Net Charge (PZNC) (Appel and Ma, 2001) hence the surface charge and cation retention capacities of the soil (Atanassova and Okasaki, 1997). Naidu
et al. (1997) have indicated that high levels of OM may provide sorptive ligands that may increase metal ion sorption by their adsorptions and formation of secondary adsorption sites. Too much OM however, may retard metal adsorptions by increasing dissolved organic carbon, DOC and formation of soluble complexes with metal ions.

Knowledge of organic carbon content of an adsorbent may provide an invaluable insight into the adsorptive characteristics of the adsorbent. Two methods are normally used in determination of soil carbon content namely Total Combustion Method and the Walkey-Black Method. The former method is used to estimate the total carbon content of a soil sample by calcinations of the sample to constant mass at above 350 °C. At about these temperatures virtually all carbon in the soil sample gets oxidized to carbon dioxide. The mass of carbon is then found as the difference in the mass after calcinations.

For purposes of this work the Walkley-Black method was employed. In this method acidified $K_2Cr_2O_7$ is used to oxidize soil Organic Carbon (OC). The resulting solution is then titrated against a standard $FeSO_4.7H_2O$ solution to determine oxidizable OC equivalents.
2.5 SORPTION STUDIES

2.5.1 Definition

Adsorption is the process of accumulation of materials at chemical interfaces (van Thoor et al., 1965). A number of theories have been advanced to explain the sorption phenomena involving solutes from solutions. In this work we have adopted two of which are reviewed in sections 2.5.2.1 and 2.5.2.2.

2.5.2 Sorption Theories

2.5.2.1. Langmuir theory of monolayer chemisorptions

The basic assumption of the Langmuir theory proposed by Irving Langmuir (Plate 1) is that adsorption takes place at specific homogeneous sites within the adsorbent (Langmuir, 1918). It is then assumed that once a metal ion occupies a site, no further adsorption can take place at that site. The rate of adsorption to the surface should be proportional to a driving force and the available area of free sorptive sites. The driving force is the concentration in the solution, and the area is the amount of bare surface. If the fraction of covered surface is $f$, the rate of adsorption $r_a$ per unit surface area is:

$$r_a = k_a C (1 - f)$$

where, $C$ is the adsorbate concentration and $k_a$ the rate constant.
The simultaneous metal desorption from the surface is proportional to the amount of adsorptive surface already covered by metal ions thus the corresponding rate of desorption $r_d$ is given by,

$$r_d = k_d f$$  \hspace{1cm} 2.2

where $k_d$ is the respective desorption rate coefficient and $f$ is fraction of the surface covered.

At equilibrium, the two rates are equal, and:

$$f = \frac{k_a C_e}{k_d + k_a C_e}$$  \hspace{1cm} 2.3

and the overall equilibrium constant,

$$b = \frac{k_a}{k_d}$$  \hspace{1cm} 2.4

Since adsorbed solute, $q_{eq}$ is proportional to $f$,

$$f = \frac{q_{eq}}{q_{max}}$$  \hspace{1cm} 2.5

The saturated monolayer adsorption capacity, $q_{max}$, can be obtained when $f$ approaches unity, since $q_{eq} \rightarrow q_{max}$. Thus the saturated monolayer isotherm can be represented as:

$$q_{eq} = \frac{q_{max} b C_{eq}}{1 + b C_{eq}}$$  \hspace{1cm} 2.6

The above equation (Eq. 2.6) can be rearranged to the following linear form by taking reciprocals on both sides:

$$\frac{1}{q_{eq}} = \frac{1}{b q_{max} C_{eq}} + \frac{1}{q_{max}}$$  \hspace{1cm} 2.7
where $C_{eq}$ is the equilibrium concentration (mg/L), $q_{eq}$ the amount of metal ion sorbed (mg/g), $q_{max}$ is $q_{eq}$ for a complete monolayer coverage of the material by the adsorbate (mg/g), and $b$ sorption equilibrium constant (L/mg). A plot of $1/q_{eq}$ versus $1/C_{eq}$ should indicate a straight line of slope $1/bq_{max}$ and an intercept of $1/q_{max}$ from which both the adsorption capacity $q_{max}$ and the equilibrium constant $b$ representing the thermodynamic stability of the adsorption constant between the surface and the solute can be determined. In essence therefore, this theory postulates an irreversible adsorption process with high enthalpies in the order of those in the actual stoichiometry of the interacting groups and is monolayer.

An extension of the Langmuir isotherm to multilayer adsorption is the Brunauer-Emmet-Teller (BET) isotherm proposed by Brunauer, Emmet, and Teller in 1935 for whose detailed review is referred to adsorption science text books like Os’Cik (1982) and Noll et al. (1992).

2.5.2.2 Freundlich Adsorption Theory

Another theory concerns physical non-ideal adsorption. H.M. Finlay Freundlich (Plate 2) studied the sorption of a material onto animal charcoal. He found that if the concentration of solute in the solution at equilibrium, $C_{eq}$, (mg/L) was raised to a power $n$, the amount of solute adsorbed being $q_{eq}$, then $C_{eq}^n / q_{eq}$ is constant subject to temperature (Freundlich, 1906). This fairly satisfactory empirical isotherm can be used for non-ideal sorption of metal ions onto an adsorbent and is expressed by Equation 2.8:
\[ q_{eq} = K_f C_{eq}^n \]

According to this equation, generally referred to as the Freundlich Adsorption Isotherm, the value of the constant \( n \) is characteristic of the intensity or loading of the adsorbate on the adsorbent surface whereas \( K_f \) is related to the equilibrium constant of the adsorption process and therefore indicative of the affinity of the adsorbent for the adsorbate particles. The equation is conveniently used in the linear form according to Eq.2.9 by taking the logarithm of both sides as:

\[ \log q_{eq} = \log K_f + n \log C_{eq} \]

Thus, a plot of \( \log q_{eq} \) against \( \log C_{eq} \) is a linear graph of gradient \( n \) and vertical intercept equal to \( \log K_f \). Adherence of adsorption data to the Freundlich isotherm therefore postulates multilayer physical and completely reversible adsorption based on weak van der Waals type of interactions between the sorbent and the adsorbate particles.

According to Mohan et al. (2006), Freundlich and Langmuir constants, \( K_f \) and \( q_{max} \), have different meanings, but their values lead to the same conclusion about correlating the experimental data with the sorption model. \( K_f \) and \( q_{max} \) fundamentally differ. The Langmuir isotherm assumes that the adsorption free energy is independent of both surface coverage and monolayer formation. In contrast, while the surface reaches saturation, the Freundlich isotherm does not predict surface saturation by the adsorbate. Therefore, the surface covering is
mathematically unlimited. In conclusion, $q_{\text{max}}$ is the monolayer adsorption capacity while $K_f$ is the relative adsorption capacity.

### 2.5.3 Experimental Methods

Three methods are commonly used in sorption studies: batch equilibrium, continuous flow and stirred-continuous-flow method. Batch equilibration involves immersion of a pre-determined mass of adsorbent in solution of known concentrations of adsorbate. After equilibration the concentration of the supernatant over the adsorbent is measured and the adsorption calculated from the resultant difference in adsorbate concentrations (Vieira and Mesquita, 2002). In Continuous Flow Column, the adsorbate solution is loaded onto an adsorbent column and the concentration of the eluate measured over that of the eluent (Noll et al., 1992). Continuous stirred flow method is a hybrid of the two; soil solids are kept in suspension as they flow through the adsorption column (Noll et al., 1992).

The adsorbate uptake by the adsorbent is calculated by simple concentration difference (King et al, 2006). The initial concentration $C_i$ (mg/L) and final concentration $C_{eq}$ (mg/L) at any time are determined and the metal uptake $q_{eq}$ (mg metal adsorbed/g adsorbent) is calculated from the mass balance equation (Eq.2.10) as follows:

$$q_{eq} = \frac{v(C_i - C_{eq})}{w1000}$$  \hspace{1cm} 2.10
where $v$ is the volume of the solution in milliliters and $w$ is the mass of the adsorbent in grams. Whereas the percentage adsorption relative to initial sorbate concentration is obtained thus,

$$\%\text{adsorption} = (1 - \frac{C_f}{C_i}) \times 100$$  \hspace{1cm} 2.11

Where, $C_i$ and $C_f$ are initial and final sorbate concentrations respectively.

### 2.5.4 Kinetic Analysis

The study of the kinetics of sorption provides valuable information on the time required to reach equilibrium and is key to understanding the influence of different variables on the sorption process. The rate of sorption is particularly important, mainly in applications such as in the industrial wastewater treatment. Three different models were used in this study to determine the sorption kinetics of Cu$^{2+}$ onto RSBE; the Lagergren first-order rate model (Lagergren, 1898; Taty-Costodes et al., 2003), the pseudo-second order model (Ho and McKay, 2003) and the intra-particular diffusion model (Taty-Costodes et al., 2003). The first-order rate expression of Lagergren based on solid capacity is generally expressed as follows in Eq. 2.12:

$$\frac{dq_t}{dt} = k_{1,ad} (q_e - q_t)$$  \hspace{1cm} 2.12

where $q_e$ and $q_t$ is the amount of metal ions adsorbed onto the material (mg g$^{-1}$) at equilibrium and at time $t$, respectively; $k_{1,ad}$ is the first-order (min$^{-1}$) rate constant of the process. After integration between boundary conditions $q_0 = 0$ at $t = 0$ and $q_t = q_e$ at $t = t$, Eq. 2.12 becomes,
\[
\log(q_e - q_t) = \log q_e - \frac{k_{1,ad}}{2.303} t
\]

2.13

A plot of \(\log(q_e - q_t)\) against \(\log q_e\) should give a linear graph from which the first order rate constant \(k_{1,ad}\) may be calculated.

The pseudo-second order equation is based on the sorption capacity of the solid phase and is expressed as:

\[
\frac{dq_t}{dt} = k_{2,ad} (q_e - q_t)^2
\]

2.14

where \(k_{2,ad}\) is the rate constant of second order sorption (min\(^{-1}\)), \(q_e\) the amount of metal ions adsorbed at equilibrium (mg g\(^{-1}\)) and \(q_t\) the amount of solute sorbate on the surface of the adsorbent at any time \(t\) (mg g\(^{-1}\)). For boundary conditions \(q_0 = 0\) at \(t = 0\) and \(q_t = q_e\) at \(t = t\), Eq. 2.14 becomes the integrated rate law for a pseudo-second order reaction thus:

\[
\frac{t}{q_t} = \frac{1}{k_{2,ad}q_e^2} + \frac{1}{q_e} t
\]

2.15

From this equation a plot of \(\frac{t}{q_t}\) against \(t\) should give a linear graph from which the second order rate constant \(k_{2,ad}\) and the equilibrium adsorption \(q_e\) may be calculated.

In this study the Weber and Morris type intra-particular diffusion model was also employed in the form of Equation 2.16:

\[
q_t = \frac{k_w t^{1/2}}{m}
\]

2.16
where $m$ is the mass of adsorbent (g), $q_t$ the amount of metal ions adsorbed at time $t$ (mg g$^{-1}$) and $k_w$ is the initial rate of intra-particular diffusion (mg l$^{-1}$ s$^{-0.5}$).

McKay (1984), has indicated that according to this model the rate at which the solute is adsorbed and the amount of solute that get adsorbed onto the solid particles may depend on any or more of the four stages in the adsorption process. These are rates of: (i) solute transfer from the solution to the boundary film bordering the adsorbent surface, (ii) solute transport from boundary film to the sorbent surface, (iii) solute transfer from the sorbent surface to the intra-particular active sites and (iv) interactions of the solute molecules with the available sites on the internal surface of the adsorbent. Like in the other two cases, adherence of adsorption data to intra-particle diffusion model is implied by a straight line plot between $q_t$ and $t^{1/2}$ from the slope of which the initial rate of adsorption $k_w$ may be obtained.

2.5.5 Thermodynamic parameters of adsorption
The metal adsorption process can be summarized by the following reversible process which represents a heterogeneous equilibrium. The apparent equilibrium constant ($K_D$) of an adsorption process is given by:

$$K_D = \frac{Q_{eq}}{C_{eq}}$$  \hspace{1cm} 2.17

where $Q_{eq}$ is the concentration of metal ion on the adsorbent at equilibrium and $C_{eq}$ is the corresponding concentration in the aqueous phase. In this case
the activity of the solution should be used instead of the concentration in order to obtain the standard thermodynamic equilibrium constant \((K^0)\) of the adsorption system. If infinite dilution value of \(K_D\) can be obtained by calculating the apparent equilibrium constant \((K_D)\) at different initial concentrations of metal ion and extrapolating to zero, this value will give \(K^0\). The \(K^0\) value is used as in the following equation to determine the standard Gibbs free energy \((\Delta G^0)\) of adsorption:

\[
\Delta G^0 = -RT \ln K^0
\]

The enthalpy \((\Delta H^0)\) and entropy \((\Delta S^0)\) may be obtained from the slope and intercept of a van't Hoff equation of \(\Delta G^0\) versus \(T\) thus:

\[
\Delta G^0 = \Delta H^0 + T\Delta S^0
\]

where \(R\) is the universal gas constant, 8.314 J mol\(^{-1}\)K\(^{-1}\), \(T\) is absolute temperature, \(K\), and \(K^0\) is equilibrium constant at a particular temperature \(T\), respectively. The Gibbs free energy indicates the degree of spontaneity of the adsorption process and the higher negative value reflects a more energetically favorable adsorption.

2.5.6 Metal Sorption on Clays and their Fractions

2.5.6.1 General Sorption Behavior of Metals on Clays and Clay Fractions

Interactions between trace metals and soil particles occur at the soil-solution interface. Heavy metal sorption at soil surfaces are therefore remarkably
affected by surface and chemical properties (Atanassova and Okazaki, 1997) of the soil, the type of soil and soil solution parameters (Chang et al., 2002) among others. The potential in the plane of adsorption and the soil surface charge density are the two most important soil surface properties controlling the nature of interactions between metal ions and soil particles. Less weathered soils as from the temperate regions are characterized by permanent surface charge with variable surface potential. Although the surface potential of permanently charged soils must be constant, it is seldom or ever available to the soil solution. Rather reactions at the surface of the soil depend on the zeta potential, which vary with the composition of the soil solution due to differential filling of the Stern layer on the soil surfaces. In contrast tropical soils are characterized by variable (pH dependent) charge with constant potential on the surfaces due to heavy weathering. The reactive groups responsible for variable charge are usually similar in inorganic colloids and different in organic matter. In these soils the surface chemical properties change in response to changes in the ambient solution parameters. For instance, changes in ambient pH, results in marked variations in the surface positive and negative charges of both inorganic and the organic soil colloids.

For inorganic colloids, the pH at which the positive and the negative charges are equal is referred to as the Point of Zero Net Charge (Sposito, 1989). According to Naidu et al. (1994a) the surface charge is determined by the adsorption of the potential determining ions (H⁺ and OH⁻ ions) onto the surface with the net charge being determined by the ion sorbed in excess. In
the case of the inorganic colloids positive charge is developed at pH values below the PZNC and the negative charge at pH values above. On the other hand in the pH range of most soils organic colloids are able to generate only negative charge as the pH increases. The magnitude of the charge generated is a function of the amount of surface and the potential number of reactive sites exposed to the solution. Since the surface area of a mineral is usually constant, charge generation only affects the surface charge density.

Regardless of the source of the surface charge however, electrical neutrality of the system must be maintained. This requires counter ions to accumulate at the surface from the solution. This creates a region of excess counter ions deficit in co-ions referred to as the electrical double layer at the soil surface. The behavior of the electrical double layer on an electrochemical surface is qualitatively described by the Gouy-Chapman equation (Naidu et al., 1997) thus:

\[
\sigma_o = \left(\frac{2n_c \varepsilon k T}{\pi}\right)^{\frac{1}{2}} \sinh \left(\frac{z e}{2k T}\right) \psi_o
\]

where, \(\sigma_o\) = surface charge density; \(n_c\) = counter ion concentration to the surface charge in this case the index ion; \(\varepsilon\) = dielectric constant; \(k\) = Boltzmann constant; \(e\) = electronic charge; \(z\) = charge of the counter ion; \(T\) = the absolute temperature and \(\psi_o\) = the adsorption surface potential. This means that any variations in the concentration \(n_c\) and valence \(z\) of the counter-ion affect the surface charge density. Thus the surface charge density and by
extension metal solubility (McBride, 1981), CEC and trace metal adsorption by soil systems (Atanassova and Okazaki, 1997) is a function of both pH and the ionic strength of the soil solution.

On the other hand, Naidu and Harter (2001) have indicated that the index cation may retard trace metal adsorptions onto soil fractions by its rivalry for sorptive sites away from its influence on the ionic strength of the soil-solution and on the adsorbent diffuse double layer chemistry. Divalent ions (Harter, 1992) are found to exert greater effects (Naidu et al., 1994a) on metal adsorptions than monovalent ions (Naidu et al., 1994b) because of their larger ionic charge (Raij and Peech, 1972).

The effects of soil mineralogy (Silveira and Alleoni, 2003), organic matter OM, and dissolved inorganic ligands (Naidu et al., 1997) on soil surface metal ions sorptions also stream from their influence on the surface charge and the Point of Zero Net Charge (PZNC) of the adsorbent (Appel and Ma, 2001). Too much OM may retard metal sorptions by increasing dissolved organic carbon (DOC) and complexation. According to Naidu et al. (1997) certain ligands such as the phosphate, silicates, fluorides and organic anions are specifically adsorbed on sesquioxides surfaces irrespective of the initial net surface charge density resulting in increased net negative charge by lowering the soil pH. They also indicated that high levels of OM lower PZNC below the ambient soil pH making the soil to attain an overall negative charge conducive for cation up take.
2.5.6.2 Copper Sorption Properties at the Clays and Clay Fraction

Clays boast four sorptive sites namely: the layer silicates; Al and Fe oxides, Mn oxides; and the OM sites. Cu sorption at the layer silicates occurs at low pH as hexahydrate ions, Cu(H₂O)₆²⁺ (McBride, 1981) but adsorption at these sites may be retarded by high alkali ion concentrations (Naidu and Harter, 2001). At pH ≥ 5, specifically adsorbed (SPA) hydrolysis products, Cu(OH)⁺, Cu₂(OH)₂⁺ are formed (McBride, 1981). The metal sorption at the soil metal oxides is fairly independent of alkali ions (Naidu et al., 1997) forming direct Cu-O-M, [M= Al, Fe, Mn] bonds. Mn oxide sites have the highest affinity for aqueous Cu (Barrow and James, 1981). Sorption at the OM sites is by chelate formation with organic groups (McBride, 1981). OM and Mn oxides sites are most important in keeping Cu from soil solutions (Barrow and James, 1981).

Cu sorption in soils follows the Langmuir isotherm, Freundlich isotherm, or a straight line (Kurdi and Doner, 1983). This means that both specific monolayer (Langmuir type) and diffuse multilayer (Freundlich type) adsorptions may take place. The former is favoured by predomination of high affinity sites provided by soil OM and Mn-Fe oxihydroxides whereas the latter is preferred when less affinity alumino-silicate sites are the more important (Atannosova and Okasaki, 1997). The effects as expected are pH dependent.
2.5.7 Metal Desorption Studies from Clays and their Fractions

Desorption studies are used in assessment of the efficacy of practical industrial application of an adsorbent. Inorganic salts (Amorin et al., 2003), mineral acids and pH adjustments (Gupta, et al., 2000; Onyancha, 2006) and organic reagents like EDTA (ethylene diaamine tetraacetic acid), NTA (nitritotriacetic acid), and DTPA (diethylenetriamine pentaacetic acid) (Zhou et al., 1998) are some of the most commonly used desorbing agents. Certain inorganic anions like $\text{CO}_3^{2-}$, $\text{Cl}^-$, $\text{SO}_4^{2-}$ and $\text{ClO}^-$ are reported to affect certain metal sorptions. These effects are however, pH dependent (Amorin et al., 2003). In all cases, care should be taken to avoid unnecessary excessive and prolonged exposure of the material to the desorbing agent as this may cause alterations and damage to the adsorption surface sites of the sorbent materials (Fry et al., 1992).

2.6 ANALYTICAL TECHNIQUES

2.6.1 Polarography

2.6.1.1 Principles of Polarography

This is an electro-analytical method based on current-voltage variations under conditions of concentration polarization (Crow, 1974). The method employs Dropping Mercury Electrode (DME) as working electrode against a suitable reference electrode like the saturated calomel electrode (SCE) (Figure 2.4).
Figure 2.4  The saturated calomel

Figure 2.5 shows a Basic Circuits for a Three Electrode Polarograph.

Figure 2.5  Basic Circuits for a Three Electrode Polarograph.
The technique is essentially based on the Ilkovic equation which at 25 °C is given by Eq. Eq. 2.21.

\[
E = E_1^\frac{1}{2} + \frac{0.0591}{n} \log \left( \frac{i_d - i}{i} \right)
\]  

Where, \( E = \) potential output,

\( n = \) number of exchangeable electrons

\( i_d = \) cathodic diffusion limited current

\( i = \) current corresponding to a particular potential output \( E \) and

\( E_1^\frac{1}{2} = \) potential when \( i = \frac{i_d}{2} \), (half wave potential).

The value of \( E_1^\frac{1}{2} \) is related to formal reduction potential \( E_0 \) of the element. For example for copper we can write:

\[
E_1^\frac{1}{2} = E_0 = \frac{0.0591}{n} \log \left( \frac{D_{Cu(Hg)}}{D_{Cu^+}} \right)^\frac{1}{2} - E_{ref}
\]  

Where, \( D = \) the diffusion coefficient and \( E_0 = \) the standard electrode potential.

Therefore \( E_1^\frac{1}{2} \) is a useful tool for qualitative determination of electro-active species because it is a measure of how easily such species may undergo an electrochemical transformation.

The total rate of discharge \( \frac{I}{nF} \), of an electro-active species \( M^{n+} \) from its solution is related to its bulk concentration by:
\[
\frac{I}{nF} = \frac{t_+ I}{nF} + \frac{D}{\delta} \left( [M^{n+}] - [M^{n+}]_e \right)
\]

Where, \( I \) = current, \( n \) = number of exchangeable electrons, \( F \) = Faraday's constant, \( t_+ \) = the transference number, \( D \) diffusion coefficient, \( \delta \) the thickness of the diffusion double layer and \([M^{n+}]\) and \([M^{n+}]_e\) the concentrations of \(M^{n+}\) at the bulk and at the electrode, respectively. The migration term in \( t_+ \) is diminished if the ionic strength of the electrolyte is constant as in a large excess of an indifferent electrolyte. Thus, at maximum diffusion gradient, \([M^{n+}]_e \rightarrow 0\) and hence,

\[
\frac{I_{lim}}{nF} = \frac{D}{\delta} [M^{n+}] = \frac{i_{lim}}{SnF}
\]

Where, \( I_{lim} \) = diffusion limited current, \( i_{lim} \) = diffusion limited current density, and \( S \) = electrode surface area.

In the Dropping Mercury Electrode (DME), \( i_{lim} \) varies with the size of the mercury drop and drop life. Thus according to the Ilkovic equation the diffusion limited current \( i_d \) is defined as (Borman, 1982),

\[
i_d = knm^3 D^2 t^6 C
\]

Where,

\( n \) = exchangeable electrons

\( m \) = rate of flow of mercury in the electrode

\( t \) = drop time

\( C \) is the concentration of the analyte and
$k$ is a constant comprising the volume of the mercury drop and it is about 706 at maximum current and about 607 when average current is used instead. Hence equation 2.25 may be re-written as,

$$i_d = 706 nD^2 m^3 r^6 C \quad 2.26$$

where, $i_d$ = diffusion limited current density, $m$ = rate of mass flow, $r$ = drop life and $C = [M^{n+}]$. The plot of $i_d$ versus time $t$, is sporadic and cumbersome to read therefore, average diffusion limited current $\bar{i}$ is used as in Eq. 2.26.

$$\bar{i} = \frac{1}{r} \int i_d dt = 607 nD^2 m^3 r^6 C \quad 2.27$$

Polarograms are obtainable by measuring the current at various potentials. The value of $i_d$ is obtained from the difference between current at the saturation point (highest value), and residual current due to charging of the electrical double layer and impurities. This current is proportional to the concentration of $M^{n+}$ in the solution and is the analytical tool in this method.

### 2.6.1.2 Polarographic Modes

The major limitations of *classical* polarographic methods have been low selectivity and sensitivity in analysis involving mixtures. Sensitivity of this technique is greatly improved by measuring current under conditions of non steady-state diffusion and by increasing the ratio of faradaic current to the double layer charging current. In *pulse polarography* representing an improvement over the *classical polarography*, this is achieved by constructing
the current-voltage curve point by point. This way, each point represents current measured over a short period of time typically 40 milliseconds after application of a voltage pulse towards the final stages of the DME drop.

Selectivity is achieved by differentiating the current-voltage, \((I-E)\) function. The resulting curve gives a peak corresponding to the half wave potential of the species under investigation. Since \(E_1\) is a character of individual electrochemical species this leads to separation of peaks when change in half potential is greater than 50-80 mV. The resulting technique which is an improvement over the classical and pulse polarography is called \textit{Differential Pulse Polarography (DPP)}.

Additional sensitivity is achieved in a technique called \textit{Anodic Stripping Differential Pulse Voltammetry (ASDPV)} by pre-concentrating the analyte into the mercury electrode anode as an amalgam before determination. By measuring the current of re-oxidation of the amalgam called the peak current, detection limits of up to \(10^{-7}\) have been possible. The peak current is dependent on the efficiency of the deposition of the analyte in the electrode according to Eq. 2.28.

\[
I_p = 2.762 \times 10^3 n^\frac{3}{2} A D^{\frac{1}{2}} C_e \nu
\]

where,

\(C_e\) = concentration of the analyte in the electrode and,

\(\nu\) = the rate of stripping.
According to Borman (1982), the factors affecting the efficiency of the deposition process may be summarized by Levich equation thus,

\[ i_{(t)dep} = 0.62nFAD^3\omega^2 \mu^{-6}C(t) \]

where,

- \( i_{(t)dep} \) = deposition current
- \( n \) = cationic charge
- \( F \) = Faraday's constant
- \( A \) = surface area of electrode
- \( D \) = diffusion coefficient
- \( \omega \) = rate of electrode rotation or solution agitation
- \( \mu \) = the kinetic viscosity and
- \( C(t) \) = the ionic concentration during deposition time.

Alterations in any of these parameters affect the amount of the solute deposited and therefore the results of the analysis. Dissolved oxygen must be removed by bubbling with nitrogen because it is electro-active, and the solution must contain about 0.1M KCl or a similar electrolyte to provide adequate conductance. The solution must be neither stirred nor shaken during electrolysis (Tyson, 1988). The longer the deposition period used the greater the deposition efficiency and sensitivity of this technique.

### 2.6.2.2 Quantitative Methods in Polarography

Quantitative analysis for the purpose of evaluation of the amount of the analyte in the test sample may be achieved by calibration curves or the
standard addition method. The latter is the more accurate and popular of the two. An equation of the type shown in Eq. 2.30 is used.

\[ C_\mu = \frac{(i_1 V C_s)}{(i_2 V + (i_2 - i_1) V)} \]  \hspace{1cm} 2.30

Where,

- \( C_\mu \) = analyte concentration
- \( I_{I_1 - I_{\text{max}}} \) of analyte alone
- \( V \) = volume of the standard added
- \( C_s \) = concentration of the standard
- \( i_{2 - I_{\text{max}}} \) after addition of the standard
- \( V \) = volume of the analyte sample

The concentration of the standard \( C_s \) used should be approximately over a hundred-fold compared to the concentration of the analyte \( C_\mu \) under investigation.

2.6.2 X-ray Fluorescence Analysis (XRFA)

When certain atoms are bombarded by high energy particles reminiscent of 20 to 50 keV electrons or nuclei from a radioactive nuclide like the Am-241 they may produce a wide range of energy transmissions causing an X-ray continuum. The continuum contain emission peaks characteristic of the K and L shells of the atom according to Moseley equation

\[ \frac{1}{\lambda^2} = a(Z - b) \]  \hspace{1cm} 2.31

Where,
Z = the atomic number

λ = the wavelength of emission

a = constant

b = constant for all lines in a series for instance, \( b(Ka \text{ lines}) = 1.0 \), and \( b(La \text{ lines} = 7.4) \)

This relation forms the basis for a technique called the *Electron Probe Microanalysis*.

In X-ray fluorescence primary X-rays so produced from the source element are redirected to a secondary target atom (Fig. 2.6). The absorption of the rays involves ejection of inner K or L electrons from the sample atoms causing their excitation. On relaxation these excited atoms may lose excess energy as characteristic fluorescence when the higher electrons fall in the inner ‘holes’ of the ejected electrons increasing the background fluorescence (Tyson, 1988). This increase in the X-ray output is the analytical tool in this technique. The quantity of primary radiation absorbed by the analyte \( I_a \) and the intensity of fluorescence \( I_f \) emitted are related by,

\[
I_f = \Phi I_a \tag{2.32}
\]

where, \( \Phi = \) yield factor referring to the proportion of the excited atom of the analyte that relax through X-ray re-emission.
2.6.3 Flame Photometry

When solutions of certain salts are sprayed into a flame the solvent evaporates to leave fine powder of salt crystals. The salt gets vaporized in the flame, atomized and the valence electrons in the K and L orbitals get excited to higher energy states.
On relaxation they emit radiant energy of characteristic wavelength according to the Plank-Einstein equation (Eq. 2.33).

\[ \Delta E = h \nu = \frac{hc}{\lambda} \]  

Where, \( h \) = planks constant

\( c \) = velocity of light

\( \lambda \) = wavelength of radiation, and

\( \nu \) = frequency of radiation

The intensity of the radiation, read by a suitable detection unit is proportional to the concentration of analyte atoms in the sample which can be obtained from a calibration curve or by sample standards addition method. This is the basis of the technique of flame photometry whose basic instrumentation is illustrated in Fig. 2.7.
2.6.4 Atomic Absorption Spectroscopy (AAS)

AAS is a spectro-analytic method based on the measurement of the attenuation of electromagnetic radiations in the visible and the ultraviolet regions of spectrum by atomic absorptions resulting from changes in the electronic structures. The extent to which radiation is attenuated by atomic vapors is a function of the length of traverse path of the light through the vapors and the concentration of the absorbing atoms analogous to Beer-Lambert law relating samples in solution. Thus for a collimated monochromatic beam of radiation of incident intensity \( I_0 \) passing through an atomic vapors of thickness \( l \),

\[
I_\nu = I_0 e^{-k_\nu l}
\]

where, \( I_\nu \) = intensity of transmitted radiation at frequency \( \nu \) and \( k_\nu \) is the corresponding absorption coefficient.

The value of the coefficient \( k_\nu \) is dependent on the concentration of the absorbing atoms and it is given by,

\[
\int k_\nu d\nu = \frac{\pi e^2}{mc} N_\nu f
\]

where,

\( m \) and \( e \) represent the mass and electronic charge, \( N_\nu \) is the number of atoms per cm\(^2\) capable of absorbing radiation at frequency of \( \nu \) and \( f \) is the oscillator strength defined as the number of electrons per atom capable of being excited by the incident radiation. Thus, transitions from ground state, the Integrated Absorption is proportional to \( N_\nu \) which approximates the concentration of the
analyte in the sample. The typical AAS instrumentation comprises the source of electromagnetic radiation, flame atomizer, a monochromator, detector and the read-out system as summarized in Figure 2.8 (Tyson, 1988).

![Figure 2.8](image)

**Figure 2.8**  *Practical systems for flame atomic absorption spectrometry including a deuterium background corrector*

### 2.6.5 Use of Ion-Selective Membrane Electrodes

Electroanalytical techniques, which measure electrode potential, utilizing the *galvanic cell* concept, fall under the general heading of potentiometry. Such potentiometric methods rely on the measurement of voltage to ascertain chemical information about a system. Ion-selective electrodes (ISE) are a subset of potentiometric methods, which respond *selectively* to a single species. Using a membrane, which allows the ion of interest to pass through but blocks other ions, can generate the selective response. In general, activity differences across the membrane of the electrode generate a potential difference across that membrane which can in turn be used to quantify the ion
under investigation. The mathematical expression, which relates the potential difference across the membrane to the difference in activity, is the Nernst Equation. At 25°C, the Nernst Equation can be written as:

\[ E = E_0 - \frac{0.05916V}{n} \log \frac{a_i^k}{a_2^q} \]

Where \( E_0 \) is the standard reduction potential in volts, \( n \) is the number of electrons in the half reaction, and \( a_i \) is the activity of species \( i \) (and \( i = 1, 2, \ldots \)). Since ion selective electrodes, deal with a single type of ion on each side of the membrane making \( k = q = 1 \). This expression reduces to:

\[ E = E_0 - \frac{0.05916V}{n} \log[C_i] \]

where \( C_i \) is concentration of the analyte as it is conventional to replace activity of an analyte with concentration especially at very low levels. Obviously, the only parameter on which the potential depends is the concentration of \( i \) this is a very useful expression which implies that for every 10-fold change in concentration, a potential difference of 59.16 mV will occur. If the species under investigation is a cation, the slope of the calibration curve will be positive, if an anion, it will be negative. For direct measurement of the species of interest, the slope of the calibration curve should be 59.16 mV. In this work the ISE was used to determine the concentration of chloride ions. In practice, the membrane of an ISE does in fact allow passage of other ions. In which case, the cyanide anion, several other halide anions and the sulfide
anion would also cause a response in the electrode. However, the electrode sensitivity to these other ions is less than it is to chloride. Moreover, none of these ions was expected to be present at a level which will cause a significant interference (Kenkel, 1994; Skoog et al., 1992).
CHAPTER THREE

METHODOLOGY

3.1 SBE PRE-TREATMENT

Spent Bleaching Earth (SBE) was collected at the point of disposal from edible oil processing industries in Industrial Area—near Nairobi, Kenya. The samples were air-dried and the residual oil extracted by batch washing with excess methyl ethyl ketone to a constant mass and until the extract liquor was clear. The material was then dried at room temperature before preserving for experimental tests.

3.2 REAGENTS

Analar grade reagents were used in all analytical procedures in this work. One gram of copper (II) nitrates was dissolved in enough de-ionized water and the solution made up to one liter to obtain 1000 mg/l copper (II) nitrates which was used as the experimental stock solution from which all serial dilutions of the metal concentrations were made. The other reagents were all prepared according to standard procedures.

3.3 PREPARATION OF SBE FOR COPPER ADSORPTION

3.3.1 Heat Reactivation

Two-hundred-gram portions of pre-treated SBE samples were heated in a muffle furnace for 16 hours at pre-set temperatures of 50, 110, 200, 300, 400, 450, 500, 600, 650, 700, 800, and 1000 °C respectively. Each portion was then tested for aqueous copper (II) uptake in adsorption experiments as in section 3.4.2. The sample with the highest copper uptake was designated Heat
Regenerated Spent Bleaching Earth (HRSBE) and preserved for subsequent tests.

3.3.2 Acid-Reactivation of SBE

Fifty-gram portions of fresh pretreated SBE samples were stirred in 200 ml of 0.25, 0.5, 1.0, and 2.0 M HCl respectively for 2 hours. One such portion of the material was stirred in a similar way in 200 ml of distilled water designated as 0.0 M HCl. They were filtered and washed thoroughly with excess distilled water and dried at 110 °C over-night. This was repeated using HRSBE and the samples tested for copper uptake from aqueous solutions according to the procedure described in section 3.4.2.

3.3.3 Comparison of Reactivation Efficiencies of Heat, Dilute Acid and Solvent Treatments

For comparison purposes percentage copper removal efficiency of fresh solvent pretreated samples were evaluated and compared to those of heat and dilute acid treated samples. The samples with highest overall copper removal were designated regenerated spent bleaching earth (RSBE) and preserved for subsequent adsorption experiments.
3.4 EXPERIMENTAL PROCEDURES

3.4.1 SBE CHEMICAL AND SURFACE CHARACTERIZATION

3.4.1.1 Elemental Analysis of the Materials by XRF
A portion of 10.0 g of RSBE samples was ground to fine powder and mixed with 1.0 g of starch as binder flux in a plastic container. The mixture was bound into a pellet and analyzed for K, Ca, Al, Mg, Fe, Mn, and Si by X-Ray Fluorescence Analysis (XRFA) using a Sequential X-ray Spectrophotometer (SRS) Model 3000. The chemical constituents of the sample were recorded in terms of % oxides of the constituent elements.

3.4.1.2 Determination of Potentially Available Copper
Three replicate 2 g portions of Regenerated Spent Bleaching Earth (RSBE) were digested in 10 ml of a 10:1 mixture of 60% perchloric acid and 98% Sulphuric acid in Pyrex tubes at about 200 °C until all the perchloric acid had evolved and the residue had turned white according to Ketterick’s modification of Lundbad’s method (Hesse, 1971). The residue was diluted with 50 ml of water and made up to s100 ml by concentrated ammonia to precipitate iron impurities. 5 ml of extract filtrates were transferred to 50 ml volumetric flasks and diluted further to the 50 ml mark. Copper concentration in the extracts was then determined by Atomic Absorption Spectrophotometer (AAS) using Buck Scientific 210VGP Atomic Absorption Spectrophotometer at a wavelength of 324.75 nm using a calibration curve of copper standards of between 0-25 mg l\(^{-1}\) of Cu (II) ions.
3.4.1.3 Determination Oxidizable Carbon Content

The Organic matter content was estimated according to a modified Wakley-Black method (Hesse, 1971). 1.00 g of reactivated SBE was reacted with 25 ml of 1M K$_2$Cr$_2$O$_7$ in a 500 ml conical flask. 20 ml of concentrated H$_2$SO$_4$ was rapidly added from a measuring cylinder and the solution diluted with 100 ml of distilled water on cooling. 10 ml concentrated ortho-phosphoric acid was added to the mixture followed by 0.5 ml of aqueous Barium Biphenyl sulphonate indicator. It was allowed to cool for 30 minutes before 25 ml of the mixture was pipetted and titrated against 0.5 M Ferrous Ammonium Sulphate and the organic carbon equivalence in the SBE samples determined according to the method described by Wilson (1994).

3.4.1.4 Evaluation of Point of Zero Net Charge, (PZNC)

PZNC was determined according to a method similar to that used by Appel and Ma (2001). Three 1.00 g portions of RSBE were placed in separate 15 ml polythene centrifuge tubes and agitated in 10 ml of 1M NaCl at pre-adjusted pH values between 2 and 8 on a reciprocating shaker for 1 hour. The samples were centrifuged and the supernatant solutions discarded. The procedure was repeated with fresh 10 ml samples of 0.5 M NaCl for 12 hours agitation periods before they were washed five times each by 10 ml portions of 0.01 M NaCl solutions each time adjusting the pH appropriately. The NaCl saturated samples were then extracted five times with 0.5 M Ammonium acetate. The aliquots were combined in a volumetric flask and diluted to standard volume.
They were then analyzed for Na\(^+\) and Cl\(^-\) ions by Flame Photometry and ion selective electrodes, respectively.

### 3.4.1.5 SBE pH Determination
The pH of reactivated SBE (RSBE) samples was measured in triplicate in 1M KCl by soaking 10 g portions of sample in 25 ml aliquots of the solution for 1 hour to allow for equilibration and pH measurements done using a Hanna Instruments pH-211-microprocessor pH meter. The pH meter was calibrated using pH 4 and pH 10 standard solutions.

### 3.4.1.6 Evaluation of Cation Exchange Capacity
A sample of 1.25 g of SBE was placed in 15 ml centrifuge tubes in triplicate, 7.5 ml of 1M sodium acetate were added and the mixture centrifuged at 200 rev/s for 5 minutes until the supernatant solution was clear. It was decanted and the liquor discarded. The procedure was repeated four times with fresh samples of the acetate solution. The soil samples were then centrifuged three times with 7.5 ml portions of 95% ethanol to remove excess acetate solution. The soil was then extracted four times with 7.5 ml portion of 1M Ammonium acetate solution and the extracts collected in 50 ml volumetric flasks. These were diluted to 50 ml mark and the amount of sodium in the extracts determined by Flame Photometry (Hesse, 1971).
3.4.2 ADSORPTION EXPERIMENTS

All adsorption experiments to evaluate aqueous copper uptake by SBE samples unless otherwise specified were done in triplicate at room temperature (22±5 °C) by twelve hours agitation of 1.0g SBE samples in 10.0 ml aliquots of adsorbate solution containing 1000 mg/l copper (II) nitrates in stoppered 25 ml round-bottomed flasks on a reciprocating shaker. The supernatant solution was separated by centrifugation and the copper concentrations in the supernatant solution determined by Anodic Stripping Differential Pulse Voltammetry (ASDPV) using an EG & G Princeton Applied Research Model 264 Polarographic Analyzer/Stripping Voltammeter in 0.1M KCl (aq) as a supporting electrolyte. The voltammetric instrumental settings were adopted from Bard and Faulker, (1980) and Hoyle et al., (1978) as reproduced in Table 3.1.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode</td>
<td>ASDPV</td>
</tr>
<tr>
<td>Initial potential</td>
<td>-0.1V</td>
</tr>
<tr>
<td>Final potential</td>
<td>+0.6V</td>
</tr>
<tr>
<td>Current Range</td>
<td>2mA</td>
</tr>
<tr>
<td>Pulse height</td>
<td>25mV</td>
</tr>
<tr>
<td>Scan rate</td>
<td>2mVs⁻¹</td>
</tr>
<tr>
<td>Purge Time</td>
<td>4 mins</td>
</tr>
<tr>
<td>Equilibration Time</td>
<td>30 mins</td>
</tr>
</tbody>
</table>

Table 3.1 Voltammetric Instrumental Settings

The percentage removal of copper was then calculated according to the relationship: \[
\%\text{removal} = \left(1 - \frac{C_f}{C_i}\right) \times 100
\]

3.1
where, $C_f$ is the final supernatant concentration and $C_i$ the initial copper concentrations.

### 3.4.2.1 Effects of Time of Contact

Triplicate samples of 1.0 g of RSBE were mixed with 10.0 ml aliquots of sorbate solutions containing 1000 mg/l of copper (II) nitrates. The mixture was then agitated on a reciprocating shaker for $\frac{1}{12}$, $\frac{1}{4}$, $\frac{1}{2}$, 1, 2, 4, 6, 12, 24, 36, and 42 hours respectively according to a method similar to one used by Horsefall and Ayebaemi, (2005). The supernatant solution was separated by centrifugation and copper concentration in the supernatant determined.

The equilibration time for which highest copper removal was recorded was designated the optimum time of contact and adopted in all subsequent adsorption experiments unless otherwise specified.

The resultant data from this section was also used to evaluate copper adsorption kinetics on RBSE.

### 3.4.2.2 Effects of Adsorbent Dosage (Sorbent-Water Ratio (S/W))

Similar experiments to those in the preceding section 3.4.2.1 were carried out at optimized time of contact using 0.5, 2, 4, 6, and 8 g of the adsorbent respectively keeping the volume of the adsorbate solution constant and the resulting copper adsorptions determined. The results were used to calculate the
corresponding total and percentage copper adsorption to determine the optimum adsorbent loading.

3.4.2.3  **Effects of Initial Equilibrium pH**

By addition of appropriate amounts of 1M NaOH and/or 1M HNO₃ the pH of adsorbate aliquots was adjusted to pH values of 1, 2, 3, 4, 5, 6, 7, and 8 respectively. These aliquots were then used in batch experiments to investigate the effects of change in the adsorbate initial pH on copper adsorption onto RSBE. Percentage copper adsorption at various initial pH values was then calculated to determine the SBE copper pH adsorption edge.

3.4.2.4  **Effects of Initial Adsorbate Copper Concentrations**

Batch experiments were carried out on Regenerated SBE using aliquots of adsorbate solutions containing 0, 34, 68, 136, 272, and 545 mg/l of initial copper (II) ions. In each case percentage copper uptake was calculated and the experiments repeated with methyl-ethyl ketone de-oiled SBE samples initially heat-treated at 25, 50, 110, 300, 370, 400, 700 and 800 °C for comparison. The resulting data from each sample was fitted to the Langmuir and Freundlich Isotherms and the respective adsorption constants evaluated.

3.4.2.5  **Effects of ionic Strength**

Triplicate batch experiments were carried out by adding 1.0 g of RSBE in 10.0 ml aliquots of 340 mg/l copper (II) ions containing serial dilutions of
potassium chloride between 0-2.0 M concentrations. The mixture was shaken on a reciprocating shaker for six hours. The supernatant solution was then separated and the percentage copper uptake determined.

### 3.4.2.6 Effects of Calcium ions

In this section, batch experiments were carried out by adding 1.0 g of RSBE in 10.0 ml aliquots of 340 mg/l copper (II) ions containing serial dilutions of calcium nitrates between $0-2.5 \times 10^{-1}$ M concentrations. The mixtures were shaken on a reciprocating shaker for six hours. The supernatant solution was then separated and the percentage copper uptake determined. The tests were replicated twice.

### 3.4.3 DESORPTION STUDIES

#### 3.4.3.1 Effects of Initial Concentration on SBE Cu (II) Desorption

Portions of 20 g of Regenerated Spent Bleaching Earth (RSBE) were put in contact with 200 ml of 1600 mg/l Copper (II) nitrates in 250 ml Erlen Meyer flask and the mixture agitated on a reciprocating shaker for six hours. It was centrifuged and the solid weighed to determine the amount of entrenched solution before it was transferred into similar agitation flasks to which 200 ml of 0.5M HCl was added and the mixture stirred by a reciprocating shaker for 8 hours. The procedure was repeated in triplicate using 20 g portions of RSBE initially exposed to copper (II) ions at 0, 50, 100, 200, 400, and 800 mg/l copper nitrates in a similar manner. Each time the mixture was centrifuged and
supernatant solution analyzed for desorbed copper and the percentage desorption determined. The experiments were then repeated using 0.25 M Calcium Chloride, and 0.25 M Sulphuric acid respectively; in place of 0.5 M HCl solution. The results were used to evaluate and compare copper desorption dependence on the initial metal concentration in the solid phase.

3.4.3.2 Effects of Time of Contact on SBE Cu (II) Desorption

Accurately measured twenty gram portions of RSBE were saturated with copper (II) ions using 800 mg/l copper (II) nitrates solution in a method akin to one described in section 3.4.3.1. The copper saturated samplers were then transferred into 250 ml Erlen Meyer flasks to which 200 ml of 0.5M HCl was added and the mixture stirred by a reciprocating shaker for 8 hours. During the shaking 10 ml portions of the suspension were drawn from the mixture at 0, 0.1, 0.25, 0.5, 1, 2, 4, and 8 hours respectively. Each time the mixture was centrifuged and analyzed for desorbed copper and percentage desorption calculated. The experiment was done in triplicate and then repeated using 0.25 M Calcium Chloride, and 0.25 M Sulphuric acid, in place of 0.5 M HCl solution respectively. The results from these tests were used to optimize desorption time as well as to compare desorption efficiencies of the three desorbing agents.
CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 CHEMICAL AND SURFACE PROPERTIES OF RSBE

4.1.1 Chemical Compositions

Metal adsorption capacity and mechanisms onto soils and soil fractions are directly dependent on the chemical (Jeane, 1968) and mineralogical compositions (Naidu et al., 1997) of the soil adsorbents. The results of chemical analysis of RSBE after solvent extraction of residual oil and heat treatment as determined by XRFA are presented in Table 4.1 and in Figure 4.1.

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>% COMPOSITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂O</td>
<td>0.40</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.27</td>
</tr>
<tr>
<td>CaO</td>
<td>0.85</td>
</tr>
<tr>
<td>MgO</td>
<td>1.05</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>11.31</td>
</tr>
<tr>
<td>SiO₂</td>
<td>68.70</td>
</tr>
<tr>
<td>MnO₂</td>
<td>0.09</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.67</td>
</tr>
<tr>
<td>OM</td>
<td>5.3*</td>
</tr>
</tbody>
</table>

Table 4.1 Elemental Composition of SBE
(Note: * Determination not done by XRFA but by Walkey-Black Method described elsewhere in this work)
RSBE was found to be dominated to a large extent (80% by mass) by alumino-silicates minerals and low in high affinity fixed charge components of Fe and Mn oxides and organic matter together constituting less than 12% by mass.

Similar findings have been reported by other workers among them Wachira et al. (2005) and Weng et al., (2006); who also worked on the material and reported comparable percentage compositions.

The findings from this work indicated that the adsorptive activity of RSBE would be mainly based on lower affinity variable charge sites provided by aluminium oxy-hydroxides and the silicates. These kind of adsorptive materials have been associated with diffuse multilayer metal adsorptions and low metal adsorption maxima (Atanassova and Okasaki, 1997). Other specific
cases have however, showed that copper adsorption onto similar materials proceed mainly by Langmuir type adsorptions rather than Freundlich type mechanism (Lee et.al, 2004; Vengris et.al, 2001). Strong Langmuir type Cu(II) ions interactions with RSBE surfaces were therefore anticipated in this work.

4.1.2 Potentially Available Copper in the material

Studies were conducted to evaluate the amount of potentially available copper in RSBE. The material was found to contain 0.0041% of potentially available copper which is equivalent to 41 mg Kg⁻¹ of copper in the material. As expected this value was well below the average soil copper composition of 68 mg Kg⁻¹ (Boyles, 1979). It indicates that RSBE is unlikely to become a source of environmental copper pollution after eventual disposal of the material.

4.1.3 Surface Properties

Metal sorption onto soil systems and/or soil fractions is a complex function of surface properties and a variety of environmental and solution factors. The potential in the plane of sorption and the surface charge density are perhaps the most important surface parameters controlling the nature of metal-soil surface interactions. The point of zero net charge (PZNC) defined as the pH value at which the soil boasts equal positive and negative surface charge equivalents and the cation exchange capacity (CEC), a measure of cation retention ability (hence negative charge density) of the soil surfaces are useful
indicators of these adsorptive properties. In this work PZNC and CEC of RSBE were determined and the results presented in Table 4.2 and Figure 4.2.

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.3 ±0.4</td>
</tr>
<tr>
<td>PZNC</td>
<td>5.5</td>
</tr>
<tr>
<td>CEC (mg/g of Na⁺ ions equivalents)</td>
<td>6000</td>
</tr>
</tbody>
</table>

*Table 4.2 Some Surface Properties of SBE*

![Figure 4.2](image)

*Figure 4.2 The pH dependence of RSBE surface charges showing the point of zero net charge (PZNC)*

The PZNC was above the ambient surface pH indicating that RSBE is an acidic material with a net positive charge on its surface. This is as a result of adsorption of excess H⁺ ions on the surface generating excess positive charge. As can be seen from Figure 4.2 soil samples will develop excess positive charge as shown by higher adsorption capacity of anions (in this case Cl⁻ ions)
and less negative charge (adsorption capacity for the cations in this case Na⁺) when the prevailing surface pH is below PZNC and vice versa (Naidu et al., 1997). The CEC of RSBE at the prevalent surface pH of 3.3 (Table 4.2) was greater than the net negative charge on the surface at the same pH (Figure 4.2). This means that besides electrostatic cation interactions with the surface negative site of the materials, cation sorption onto RSBE must involve addition mechanisms such as inner sphere complexation, diffuse multilayer surface adsorptions and/or possible complexation with neutral groups on the surface of the material to account for the addition cation retention.

4.2 REGENERATION PROPERTIES OF SBE FOR SORPTION OF COPPER

4.2.1 Heat Treatment of SBE

Heat treatment of solid sorbents greatly affects their physical properties and catalytic activities because of either changes in surface area, development of surface-active sites or both (Khoo, 1979). After SBE activation at various temperatures, the material was exposed to 340 mg l⁻¹ copper (II) ions at 0.1 mass (g) to volume (ml) of the adsorbate and percentage copper removal efficiencies calculated. The results of these tests are shown in Table 4.3 and Fig. 4.3.
<table>
<thead>
<tr>
<th>REACTIVATION TEMPERATURE (°C)</th>
<th>% COPPER ADSORPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>46.9 ±0.0</td>
</tr>
<tr>
<td>50</td>
<td>49.5 ±2.4</td>
</tr>
<tr>
<td>110</td>
<td>59.8 ±2.8</td>
</tr>
<tr>
<td>150</td>
<td>60.6 ±2.9</td>
</tr>
<tr>
<td>200</td>
<td>61.0 ±1.1</td>
</tr>
<tr>
<td>300</td>
<td>78.3 ±2.7</td>
</tr>
<tr>
<td>330</td>
<td>83.9 ±2.3</td>
</tr>
<tr>
<td>350</td>
<td>89.4 ±1.9</td>
</tr>
<tr>
<td>370</td>
<td>88.5 ±3.4</td>
</tr>
<tr>
<td>400</td>
<td>82.6 ±2.0</td>
</tr>
<tr>
<td>450</td>
<td>74.9 ±0.5</td>
</tr>
<tr>
<td>500</td>
<td>68.0 ±2.0</td>
</tr>
<tr>
<td>600</td>
<td>65.8 ±1.6</td>
</tr>
<tr>
<td>650</td>
<td>78.8 ±1.0</td>
</tr>
<tr>
<td>700</td>
<td>78.1 ±1.3</td>
</tr>
<tr>
<td>800</td>
<td>60.0 ±2.4</td>
</tr>
<tr>
<td>1000</td>
<td>54.0 ±1.7</td>
</tr>
</tbody>
</table>

Table 4.3  Reactivation efficiencies of different temperatures for SBE uptake of aqueous copper at ambient pH of 3.3.
Figure 4.3  Variation of SBE adsorption of copper with activation temperature

The sorption activity of RSBE initially increased steadily with temperature from room temperature (20 ±5 °C) to about 110 °C. Although no appreciable change in SBE sorption activity was recorded by SBE heat-treatment between 110 and 200 °C, the activity of the materials increased rapidly with rise in heat treatment temperatures from 200 to 300 °C. The highest heat reactivation was recorded within 350-370 °C for which highly sorptive materials with close to 90% aqueous copper removal efficiencies were recorded at 340 mg/l of initial copper concentration. Above 370 °C the activity of the material dropped to a low of 65% between 500-600 °C before rising to another pseudo-maximum of about 80% between 650 and 700 °C.
The initial rise in the activity of the material when heated from room temperatures to 110 °C through 200 °C has previously been reported (Low et al., 1998). This is attributed to the dehydration of physically adsorbed water and volatilization of low boiling point organic matter (OM) from the sorptive sites in the material thereby opening them up for Cu(II) adsorptions. High SBE reactivation between 350 and 370 °C can be ascribed to heat-induced changes on surface functional groups in the materials and combustion of adsorbed organic matter from the adsorptive sites. These result in development of new surface sites and re-opening of existing ones resulting in increased surface activity of the materials as also observed by Khoo et al. (1979), and Low et al. (1998).

According to Lee et al. (1996) heat treatment of clay materials below 400 °C do not necessarily result in increased adsorptive surface area of an adsorbent. Other authors have however indicated that a series of heat-induced structural and surface reactions are triggered by such treatment that may result in increased chemical activity of the materials. Iler (1979) for instance, has indicated that clay minerals of the type of the montemorillonites consist of gibbsite or γ-aluminium trihydroxides (also found in Bauxite and most tropical soils), which on calcination undergoes de-hydroxylation into more chemically active γ-alumina at about 400 °C. The γ-alumina on the other hand converts into relatively inert α-alumina at 1000 °C. The RSBE adsorption peak at 700 °C can therefore be explained on the basis of formation of high surface area p-alumina another predominant product of calcinations of trihydroxides of
aluminium within these temperatures (Downs, 1993). According to Downs (1993), the conversion of aluminium trihydroxides to alumina proceeds via two routes when the clays are heated. The partial dehydroxylation begins at about 225 °C converting gibbsite to Boehmite with loss of water (Eq. 4.1) followed by conversion of Boehmite to alumina from 525 °C (Eq. 4.2).

\[
\text{Al(OH)}_3 \xrightarrow{225 \degree C} \text{AlO(OH)} + \text{H}_2\text{O} \quad \text{4.1}
\]

\[
2\text{Al(OH)}_3 \xrightarrow{525 \degree C} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \quad \text{4.2}
\]

The adsorption increase from 300 °C (Figure 4.1) can therefore be ascribed to direct conversion of the mineral to active alumina that occurs at about 310 °C. Since production of high temperatures is costly and makes the adsorption process expensive, these results indicate that heat treatment of SBE within 350-370 °C can suffice to reactivate SBE for substantial removal of copper (II) ions from aqueous solutions. It was obvious from the lower sorption activity of the material dried below 50 °C that solvent extraction of residual oil alone does not constitute effective reactivation of the materials for copper adsorption.

4.2.2 Effects of Acid Treatment of SBE

The acidic treatment of clay materials has been well known for many years (Komarov, 1970). This process leads to almost full removal of calcium, magnesium, and alkali metal oxides and partially diminishes the iron and aluminium content of clay minerals. The changes in chemical composition and
the mineralogical structure of clay resulting from hydrothermal reactions in acidic solutions are dependent upon the nature of the clay material and on the treatment conditions. In general clays which have low sorption power can have their activity increased by leaching with acids (Kheok and Lim, 1982). In this work, some samples of SBE were exposed to a large excess hydrochloric acid of different concentrations and their percentage copper uptake determined. Other similarly pretreated SBE samples were exposed to the same concentration of the acid for different times of exposure and their percentage adsorptivity of copper determined. Both the concentration of acid and time of exposure of SBE to the acid variously affected copper percentage adsorption onto SBE. These effects are illustrated in Table 4.4 and Figures 4.4 and 4.5 respectively.
<table>
<thead>
<tr>
<th>HCl Concentration (m/l)</th>
<th>% Copper Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>87.8 ±4.39</td>
</tr>
<tr>
<td>0.25</td>
<td>74.5 ±3.28</td>
</tr>
<tr>
<td>0.50</td>
<td>73.1 ±3.87</td>
</tr>
<tr>
<td>1.00</td>
<td>74.0 ±1.24</td>
</tr>
<tr>
<td>2.00</td>
<td>73.8 ±4.16</td>
</tr>
</tbody>
</table>

Table 4.4 Effects of concentration of acid of reactivation on SBE adsorption of copper

![Figure 4.4](image)

Figure 4.4 Effects of change in concentration of hydrochloric acid at 2 hours contact time on % SBE copper adsorption
The results of change in concentration of the acid at constant time of contact using 340 mg/l Cu(II) concentrations showed that the activity of the materials decreased rapidly after acid treatment from about 88% copper removal and stabilized at about 74% when the concentration of the acid was increased from 0 to 0.5 M. This suggests that the sorptive sites in SBE are rapidly saturated with the adsorption of $H^+$ ions when the material is immersed in an acid. This has got the three fold effects of masking the adsorptive sites by $H^+$ ions, increasing the surface positive charge density and lowering the pH of the material all of which discourage the adsorption of $Cu^{2+}$ ions thereby lowering the adsorptive capacity of the materials.
Figure 4.5 on the other hand indicate that when the time of SBE exposure to dilute HCl is further increased to above two hours, the sorption activity of the material rapidly deteriorate even though the acid concentrations is kept constant. This indicated that high acid concentrations (>0.5 M H⁺) and prolonged time of SBE exposure (>2 hours) cause the acid to attack the lattice clay structure of the material destroying its adsorption ability. Similar findings have been reported by several workers among them Low et al., (1998); Kheok and Lim, (1982); Fry et al., (1992); and Pehlivan et al., (2006) on various adsorbents. As a result acid treatment has been associated with decrease in adsorptive ability of bentonites (Pradas et al., 1994). Both Ahenach et al. (1998) and Vengris et al. (2001) have indicated that perhaps Al-pillared montmorillonites (a chief component in Bleaching Clays) are more susceptible to acidic attack incurring heavy loss of the surface area, micropore volume and clay material (25–30%) under acidic modification.

In general therefore, even though some workers have indicated that acid-treatment increase sorption ability of SBE for other adsorbates (Low et al., 1998; and Kheok and Lim, 1982), the results of this work demonstrate that acid treatment of SBE do not comprise an effective protocol of SBE reactivation for aqueous copper (II) uptake. It reduces the ability of the material to sorb the metal ions.
4.2.3 Reactivation Efficiencies for Various SBE Treatment Conditions

Many studies have indicated that the efficiency of clay sorbents in an adsorption process is dependent very much on the mode of pretreatment of the material (Netzer And Beszedits, 1979; Boukerroui and Ouali, 2000; Namasivayam and Kanchana, 1993; Low et al., 2003; and Mehmet et al., 2003). In this study, results from reactivation efficiencies of solvent oil extraction, heat treatment and dilute acid treatment were compared and the results presented in Figure 4.6.

![Figure 4.6 SBE Reactivation Efficiencies of Various Reactivation Conditions](image)

The activity of heat treated material initially decreased with increasing copper concentration before rising to a maximum well above 95% within 136-272
mg/l of Cu(II) ions. These indicate complimentary effects of adsorbent surface and adsorbate concentration in driving SBE copper adsorption equilibrium. It means that high surface area material is generated when SBE is heat treated within the heat-treatment temperatures employed in this work. This is more so because, the result for solvent only de-oiled material shows copper saturation at lower initial metal concentrations. It means that heat treatment of SBE generates additional adsorptive surface area in the material increasing its sorptive activity.

The results from acid treated samples both with and without heat treatment on the other hand, indicate that the adsorption of copper increase with initial copper concentration to a maximum and quickly decline due to saturation at much lower adsorptions percentages. The initial rapid rise in percentage adsorption with increase in Cu(II) concentration means that the adsorbate concentration is the sole driving force in the adsorption process. This indicate that the material do not posses high enough adsorptive area to influence the adsorption equilibrium remarkably.

The disappearance of the effects of adsorptive surface in influencing the equilibrium and remarkable decrease in percentage copper adsorption by heat treated SBE when it is further treated by the acid indicate that acid treatment of the material diminishes the adsorptive surface of SBE. This is owed to masking the adsorptive sites by acid H⁺ ions and/or loss of the clay matter and structural sites to acidic leaching as also discussed by Ahenach et al. (1998)
and Vengris et al. (2001). In view of the foregoing discussion, solvent oil extraction followed by heat treatment at 350-370 °C was the most effective SBE reactivation protocol for aqueous copper uptake.

4.3 EFFECTS OF CHANGE IN VARIOUS ADSORPTION PARAMETERS ON SBE SORPTION OF COPPER

4.3.1 Time profile of Copper Sorption by SBE

As the adsorption process proceeds, the sorbed solute tends to desorb back into the solution. Eventually the rates of adsorption and desorption will attain an equilibrium state when no further net adsorption occurs. The time at which the adsorption equilibrium will occur was studied. The adsorption rate tests were performed on an equilibrium batch basis. 1.0 g of the RSBE was shaken with a 10 ml of copper (II) nitrate solution bearing 340 mg/l of copper (II) ions. The adsorbent was kept in contact with the adsorbate solution for different time intervals up to 42 hours. Time zero samples were also taken in these samples for which the adsorbent was directly separated from the metal-bearing solution within less than one minute contact time. The results of these tests are presented in Table 4.5 and Figure 4.7.

<table>
<thead>
<tr>
<th>AGITATION TIME (HRS)</th>
<th>%COPPER ADSORPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>7.7 ±4.0</td>
</tr>
<tr>
<td>0.08</td>
<td>7.7±3.1</td>
</tr>
<tr>
<td>0.25</td>
<td>30.2±5.4</td>
</tr>
<tr>
<td>0.50</td>
<td>44.7±2.6</td>
</tr>
</tbody>
</table>
Table 4.5  Effects of Time of contact on the SBE Adsorption of Copper

<table>
<thead>
<tr>
<th>Time (Hrs)</th>
<th>%Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>56.2±0.7</td>
</tr>
<tr>
<td>2.00</td>
<td>68.2±5.9</td>
</tr>
<tr>
<td>4.00</td>
<td>74.0±1.7</td>
</tr>
<tr>
<td>6.00</td>
<td>77.7±2.8</td>
</tr>
<tr>
<td>12.0</td>
<td>85.0±0.9</td>
</tr>
<tr>
<td>24.0</td>
<td>81.1±4.2</td>
</tr>
<tr>
<td>36.0</td>
<td>87.9±2.2</td>
</tr>
<tr>
<td>42.0</td>
<td>87.7 ±0.1</td>
</tr>
</tbody>
</table>

Figure 4.7  SBE Copper Adsorption Dependence on Time of Contact

The percentage adsorption of copper onto SBE rapidly increased with increase in time of contact with over 70% of copper removal being realized within the
first six hours. This was followed by a gradual phase extending to over forty-two hours. Slightly over 87% Copper adsorption was recorded.

Similar two phase sorption phenomena have been reported for other soil-heavy metal systems (Vengris et al., 2001; Silveira and Alleoni, 2003; Jardao, 2000). And even more rapid copper uptake rates by soil systems have been reported (Ulmanu et al., 2003; Potgieter et al., 2006). Silveira and Alleoni (2003) have also indicated that the latter gradual phase metal sorption onto clay and clayey systems may extend for weeks before equilibrium is attained. This means that copper adsorption on to RSBE involve two phases initially utilizing the exposed surface functional groups followed by gradual diffusion of the metal ions into less exposed inner core sorptive sites in the materials.

These results indicate that substantial copper adsorption on to RSBE can rapidly be achieved in the initial periods of equilibration. More so to avoid diffusion of the metal ions into inner core sites of the materials which will make it more difficult to recover when it becomes necessary before final disposal of the material to the environment.

4.3.2 Effects of Initial Concentration of Copper

The initial metal concentration provides an important driving force in the sorption process. High initial concentrations of metal ions provide higher sorption force and are associated with faster rates of sorption and the higher
adsorption equilibriums (Pehlivan et al., 2006). The effect of changing the initial concentration of copper ions on adsorption, while keeping the dosage of RSBE constant at room temperature for different samples of heat regenerated SBE is illustrated in Table 4.6 and in Figure 4.8.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Initial Conc. Cu²⁺ (mg/L)</th>
<th>Adsorbed Conc. Cu²⁺ (mg/L)</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>60.0</td>
<td>100.0</td>
<td>71.8</td>
<td>28.2</td>
</tr>
<tr>
<td>70.0</td>
<td>90.0</td>
<td>21.4</td>
<td>78.6</td>
</tr>
<tr>
<td>80.0</td>
<td>90.0</td>
<td>21.4</td>
<td>78.6</td>
</tr>
<tr>
<td>90.0</td>
<td>100.0</td>
<td>21.4</td>
<td>78.6</td>
</tr>
</tbody>
</table>

Copper retention with RSBE further decreased with increasing initial copper concentration. The % removal increased progressively with increasing initial copper concentration by 10% between 60.0 and 80.0 °C. RSBE adsorbed 78.6% and 78.6% at 60.0 and 70.0 °C respectively, after which it started to decline due to saturation of the adsorption site by copper ions.
Copper sorption onto RSBE initially decreased with increasing copper concentration below 68 mg/l of initial copper (II) ions concentrations. It then increased progressively with increasing initial metal concentration up to 272 mg/l for 300, 370 and 400 °C RSBE and 68 and 136 mg/l for 25 and 700 °C RSBE respectively upon which it started to decline due to saturation of the adsorptive sites by copper ions.

<table>
<thead>
<tr>
<th>SBE Reactivation Temperature</th>
<th>% Adsorption at Various Initial Copper Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>17.0 mg/l</td>
</tr>
<tr>
<td>25.0 °C</td>
<td>±2.4</td>
</tr>
<tr>
<td>300.0 °C</td>
<td>100.0</td>
</tr>
<tr>
<td>370.0 °C</td>
<td>±1.8</td>
</tr>
<tr>
<td>400.0 °C</td>
<td>99.0</td>
</tr>
<tr>
<td>700.0 °C</td>
<td>±1.4</td>
</tr>
</tbody>
</table>

Table 4.6 Effects of initial Copper Concentration on its Adsorption by RSBE
The adsorption of solute particles from solution to a solid adsorbent may be illustrated as in Equation 4.3.

\[ A_{\text{solution}} + S_{\text{surface}} \rightarrow AS_{\text{surface}} \]  

where, \( A_{\text{solution}} \) is adsorbate particles in solution, \( S_{\text{surface}} \) the free adsorbent sites in the adsorptive surface and \( AS_{\text{surface}} \) the adsorbat-adsorbent 'complex' in the solid surface. At very low concentrations (as below 68 mg/l in this case for most samples), the adsorption process is mainly driven by a large excess of the free adsorbent surface. This explains the very high equilibrium uptake of copper at 17 mg/l concentration for all the RSBE samples (Fig. 4.7). As the concentration of the solute particles increases the free surface is diminished by rapid adsorption of solute particles reducing its kinetic effects, hence the initial decline in copper adsorption by RSBE samples. At this point the adsorbate
concentration starts to play a more important role in setting the adsorption equilibrium than the free adsorbent surface. That is why for most samples the adsorption equilibrium at this point increased steadily or at least decline at a reduced rate with increasing adsorbate concentration to saturation (in this case at 272 mg/l as can be seen from the diagram).

This indicate that whereas the adsorption capacity is solely dependent on the chemical and surface make-up of the adsorbent the initial concentration of the adsorbate is a key factor in determining the rate and the position of attainment of the adsorption equilibrium by the adsorbent. For optimal adsorption process, it is therefore very important to establish the optimum adsorbate concentrations. In this work copper (II) ions were most effectively removed in solution at low adsorbate concentrations below 34 mg/l whereby almost 100% removal efficiencies were recorded for all heat treated samples. However about 95% copper removal efficiencies were also recorded at 272 mg/l initial copper concentration for 370 °C heat treated RSBE samples.

4.3.3 Effects of Ionic Strength of the Background solution

Ionic strength of the adsorbate solution affects both the development of net adsorbent surface charge as well as the potential in plane of adsorption (Naidu et al. 1994a) and therefore, the subsequent adsorption of metal ions. Experiments with background ionic strength between 0 and 2 M in potassium chloride were conducted using 272 mg/l copper (II) ions solution at 0.1 gml⁻¹ RSBE dosage and the results presented in Table 4.7 and Figure 4.9.
The percentage sorption of copper by RSBE decreased rapidly with increasing ionic strength of the background solution from 85.9% to 55.2% between zero and 0.5 M KCl concentration. Thereafter it followed a more gradual decline to about 46% at 2 M KCl background concentration. As the concentration of
KCl applied in these experiments was relatively high, it can be assumed that the excess K$^+$ ions quickly saturated the sorptive sites of the material thereby reducing its copper uptake activity. These also suggest that the initial interactions between cations and RSBE surfaces may involve high energy electron exchange/sharing mechanisms making them not easily dislodged from the surface.

The highest copper removal was recorded in experiments with zero KCl background concentration. This means that presence of alkali metal ions in the adsorbate solution affect SBE copper uptake activity. Similar findings have extensively been reported on other adsorbates (Raij and Pech, 1972; Naidu et al., 1994a &b; Naidu and Harter (2001).

### 4.3.4 Effects of Calcium Ions on SBE sorption of Copper

Cations in soil solutions play a major role in bioavailability of heavy metals to vegetation. In this work the effects of calcium ions on copper adsorption to RSBE was investigated. This was because first of all, perhaps calcium is the most abundant alkali ions in tropical soils due to its relatively higher resistance to leaching. It is also the most important soil solution cation in as far as the trace metal interactions with soil surfaces are concerned (Appel and Ma, 2001; Naidu et al, 1994b; Naidu et al., 1997). The results of these investigations are presented in Table 4.8 and in Figure 4.10

<table>
<thead>
<tr>
<th>Concentration of Ca(NO$_3$)$_2$ (mol/l)</th>
<th>% Copper Adsorption</th>
</tr>
</thead>
</table>

Table 4.8  Effects of Calcium ions on the SBE Adsorption of Copper

<table>
<thead>
<tr>
<th>Calcium ions (M)</th>
<th>Adsorption (%a) ± Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>81.1 ±2.41</td>
</tr>
<tr>
<td>2.5×10^{-5}</td>
<td>77.6 ±1.80</td>
</tr>
<tr>
<td>2.5×10^{-4}</td>
<td>81.7 ±6.36</td>
</tr>
<tr>
<td>2.5×10^{-2}</td>
<td>66.0 ±2.76</td>
</tr>
<tr>
<td>1.0×10^{-1}</td>
<td>57.9 ±2.8</td>
</tr>
<tr>
<td>2.5×10^{-1}</td>
<td>56.0 ±5.50</td>
</tr>
</tbody>
</table>

Figure 4.10  Effects of Concentration of Background Calcium Nitrates Solution on SBE Sorption of Copper

The adsorptivity of copper onto RSBE decreased progressively in increasing concentration of calcium ions from about 90% at zero calcium ions concentration to only 56% in 0.25 M calcium ions.
This decline in adsorbent uptake of metal ions in presence of calcium ions have been reported in literature (Harter, 1992; Naidu and Harter, 2001). It is attributable to the ability of calcium ions to compete more effectively for the sorptive sites with the adsorbate. Presence of calcium ions also has greater influence on the ionic strength of the soil solution, the diffuse double layer of the adsorbent and hence affecting adsorbent surface charge and the potential in the plane of adsorption.

4.3.5 Effects of Change in Sorbent Dosage

Many studies have demonstrated that in fact the adsorption partition constant $K_D$ for an adsorption system is not a constant. It increases as the ratio of solid sorbent to the adsorbent solution ($S/W$ ratio) decreases (You et al., 1999; Chang et al. 2002). In this work, the effects of varying the amount of RSBE while keeping the amount and concentration of copper adsorbate in contact with the adsorbent constant were studied. 10 ml aliquots of copper (II) ions solution was added to different amounts of the RSBE and the results of SBE copper uptake presented in Table 4.9 and Figures 4.11 and 4.12.

<table>
<thead>
<tr>
<th>S/W RATIO</th>
<th>%COPPER ADSORPTION</th>
<th>SPECIFIC ADSORPTION (mg/g)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>59.7 ±2.3</td>
<td>4059.6 ±157.2</td>
</tr>
<tr>
<td>0.1</td>
<td>71.0 ±3.2</td>
<td>2413.6 ±109.0</td>
</tr>
<tr>
<td>0.2</td>
<td>79.1 ±2.7</td>
<td>1344.8 ±45.0</td>
</tr>
</tbody>
</table>
Table 4.9  Effects of Sorbent-Water Ratio on SBE Adsorption of Copper

<table>
<thead>
<tr>
<th>Sorbent Water Ratio</th>
<th>% Adsorption</th>
<th>Copper Adsorption (mg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>88.4 ±1.0</td>
<td>751.6 ±8.4</td>
</tr>
<tr>
<td>0.8</td>
<td>95.8 ±0.5</td>
<td>407.0 ±2.0</td>
</tr>
</tbody>
</table>

Figure 4.11  Variation of SBE Copper Sorption with Sorbent-Ratio
Although the overall percentage adsorption increased with increase in RSBE dosage as can be seen from Fig. 4.11, the corresponding specific mass-to-mass adsorption of the metal ions was remarkably diminished by increasing the dosage of the adsorbent (Figure 4.12). The highest mass-to-mass adsorption was recorded at the lowest sorbent to sorbate ratio of 0.05 g of sorbent in 10 ml adsorbate solution.

These results are consistent with the findings of Potgieter et al. (2006), Lee et al. (2004) and You et al. (1999) who independently found that increasing the mass of an adsorbent does not result in corresponding rise in adsorptivity of the adsorbate. Furthermore, Chang et al., (2002) have reported that both the intensity and the capacity of soils to sorb copper are affected variously by the soil loading capacities.
These effects are attributed to the ‘solids-effects’ explained as the dilution effects of the solid colloids in an adsorption system. The adsorbent loading capacity is therefore an important parameter to be considered for optimal functioning of an adsorption system. The highest removal efficiency is achieved with the lowest possible amount of sorbent. However at very low adsorbent loading overall percentage removal efficiencies are very low. For instance, at 0.5 g of RSBE in 10 ml adsorbate solution about 4060 mg/g adsorption was envisaged. Nonetheless, the corresponding percentage removal was only 60% since the material get saturated with metal ions. So relatively higher loading capacities from 2.0g RSBE to 10 ml of adsorbate solution at 340 mg/l copper are desirable to achieve higher removal efficiencies of >90%. However, S/W ratio above 0.8 mass (g) to volume (ml) are not practically possible.

4.3.6 Effects of pH

The pH is considered a master variable in heavy metal adsorption on soils (Harter, 1983) and soil fractions (Attanassova and Okazaki, 1996). In this work the effects of pH on copper (II) adsorption onto SBE were studied using 340 mg/l aqueous copper (II) aliquots at 0.1gml⁻¹ of RSBE batch dosage and the results presented in Table 4.10 and in Figures 4.13.
Figure 4.13  Copper Adsorption Dependence on pH

<table>
<thead>
<tr>
<th>INITIAL ADSORBATE pH</th>
<th>%COPPER ADSORPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>3.91 ±0.56</td>
</tr>
<tr>
<td>2.00</td>
<td>48.3 ±1.70</td>
</tr>
<tr>
<td>3.00</td>
<td>63.0 ±1.18</td>
</tr>
<tr>
<td>3.35</td>
<td>87.8 ±1.49</td>
</tr>
<tr>
<td>4.00</td>
<td>78.8 ±0.44</td>
</tr>
<tr>
<td>5.00</td>
<td>83.5 ±1.59</td>
</tr>
<tr>
<td>6.00</td>
<td>91.1 ±0.36</td>
</tr>
<tr>
<td>7.00</td>
<td>88.9 ±1.87</td>
</tr>
<tr>
<td>8.00</td>
<td>87.6 ±1.18</td>
</tr>
</tbody>
</table>

Table 4.10  Effects of pH on SBE Adsorption of Copper

Percentage copper adsorption on RSBE increased rapidly with pH up to pH 6, with highest sorption of 91.1% being recorded at pH 6 before it reached a
limiting value at pH>7. This is because at low pH values below the PZNC soil surfaces develop positive surface charge because of excess H\(^+\) ions sorbed to the surfaces which is unfavorable to cation exchange. As the pH increases two things happen: first excess OH\(^-\) ions in solution forces H\(^+\) ions to desorb from the surface creating sorption room for the cations and secondly the OH\(^-\) ions start to sorb on to the surface increasing the negative surface charge of the material. The two processes provide the necessary driving force that account to the rapid increase in copper adsorption onto RSBE with adsorbate pH. This trend is however, quickly checked towards neutral pH values by the on set of complexation reactions hence the decline in the increase in copper adsorptions at pH 5 to 8.

Plot of final pH against initial pH of adsorption had positive gradient of less than one (Figure 4.14) showing that copper sorption on SBE involved overall drop in pH. This means that the sorption process involved release of H\(^+\) ions into the solution. It indicates that copper adsorption on RSBE is predominated by ion-exchange type mechanism between hydrated monomeric Cu(H\(_2\)O)\(_6\)\(^{2+}\) species and the soil surface hydrogen ions H\(^+\) especially at pH < 3 according to Eq.4.4 as also postulated by Hyun et al. (2000).

\[
2\text{SO-H}_\text{(s)} + [\text{Cu(H}_2\text{O)}\text{)}_\text{6}]^{2+}_\text{(aq)} \rightleftharpoons (\text{SO})_\text{2-Cu(H}_2\text{O)}\text{)}_\text{4(aq)} + 2\text{H}_3\text{O}^+_\text{(aq)}
\]

4.4

where, SO- are soil surface sites.
This was also affirmed by the fact that the plot of individual values of change in pH, \( \Delta pH \) during adsorption obtained according to Equation 4.3 against initial pH of adsorbate solution and presented in Figure 4.15 is positive to the horizontal axis.

\[
\Delta pH = pH_{\text{initial}} - pH_{\text{equilibrium}}
\]
As can been seen from Figure 4.15 the changes in pH decrease rapidly to a low at about pH 3 before increasing to peak at pH 6 when they start to decline once more. The lower values of ΔpH about pH 3 suggest depletion of H⁺ ions from the soil surface due ion-exchange reactions according to Eq.4.4 possibly as the pH values tend to the point of zero net charge (PZNC). The rapid rise in adsorption pH drifts beyond this pH up to the point of inflection of the curve at about pH 4.5 may represents the onset of hydrolysis mechanisms according to Equations 4.5 and 4.6.

$$\text{[Cu(H}_2\text{O)}_6\text{]}^2^+_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{[Cu(OH)(H}_2\text{O)}_5\text{]}^+_{(aq)} + \text{H}_3\text{O}^+_{(aq)}$$  4.5

Then,
Marosits et al., (2000) have indicated that in this pH region simultaneous ion-exchange and hydrolysis mechanism are involved after which only adsorption of hydrolysis and complexation products dominate the process. This means that the rapid increase in the metal adsorption towards neutral pH values may therefore be ascribed to the adsorption of hydrolysis and complexation products as also indicated by Alverez et al., (2005).

![Figure 4.16](image)

**Figure 4.16**  *Change in Copper(II) Speciation with pH in Aqueous phase of solution*  
(adapted from Marosits et al., 2000).

The eventual fall in the changes in pH after pH 6 may signify the onset of precipitation of basic Cu(OH)$_2$ according to Eq. 4.6 as can be seen from speciation diagram adopted from Marosits et al. (2000) and reproduced in Fig. 4.18.
Thus the drop in aqueous copper content in an adsorption system above pH 6 can partly be ascribed to adsorption and partly to the precipitation of insoluble products.

4.4 DATA FIT TO EQUILIBRIUM ADSORPTION ISOTHERMS

In order to optimize a design for an adsorption system to remove metal ions from aqueous solutions, it is imperative to establish the most appropriate correlation for the equilibrium curves. The Linear, Langmuir and Freundlich models are often used to describe equilibrium sorption isotherms. The equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into both the sorption mechanisms and the surface properties and affinities of the adsorbent.

4.4.1 Langmuir Isotherm

The copper adsorption results on SBE samples reactivated at various temperatures were fitted to the double reciprocal linearized Langmuir isotherm (Eq. 4.7.),

\[
\frac{1}{Q_{eq}} = \frac{1}{K_L Q_{max} C_{eq}} + \frac{1}{Q_{max}}
\]

where,

- \( Q_{eq} \) = equilibrium concentration of adsorbate in adsorbent
- \( C_{eq} \) = equilibrium concentration of adsorbate in solution
- \( K_L \) = Langmuir constant and,
$Q_{\text{max}}$ = Langmuir monolayer capacity of the adsorbent.

The Langmuir constants were then obtained by linear regression of $1/Q_{\text{eq}}$ versus $1/C_{\text{eq}}$ and presented in Table 4.11. Figure 4.17 is a representative Langmuir plot for particular conditions but more graphs for the different heat-treated SBE samples are in Appendix I.

![Langmuir plot](image)

**Figure 4.17**  Langmuir adsorption isotherm for 370 °C heat treated SBE

<table>
<thead>
<tr>
<th>Sample Activation Temperature (°)</th>
<th>Langmuir Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_{\text{max}}$ (mgKg$^{-1}$)</td>
</tr>
<tr>
<td>25</td>
<td>1781</td>
</tr>
<tr>
<td>110</td>
<td>3915</td>
</tr>
<tr>
<td>300</td>
<td>6529</td>
</tr>
<tr>
<td>370</td>
<td>7900</td>
</tr>
<tr>
<td>400</td>
<td>3775</td>
</tr>
<tr>
<td>700</td>
<td>6136</td>
</tr>
</tbody>
</table>
The Langmuir Isotherm gave an excellent fit to the adsorption data for most SBE heat reactivated samples with linear correlation, $R^2 \geq 0.96$. The sole outstanding exception was the 700 °C heat-treated material for which it was not possible to carry out the said fitting because the adsorption of the metal did not produce a favorable isotherm.

A comparison of the adsorption affinity $K_L$ and the maximum Cu(II) adsorption capacity, $Q_{\text{max}}$, of RSBE with those of other low cost adsorbents reported in the literature is given in Table 4.12.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$Q_{\text{max}}$ (mgKg$^{-1}$)</th>
<th>$K_L$ (Lmg$^{-1}$)</th>
<th>$K_F$</th>
<th>$n$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>21410</td>
<td>0.229</td>
<td>-</td>
<td>-</td>
<td>Wassana et al. (2004)</td>
</tr>
<tr>
<td>370 °C RSBE</td>
<td>7900</td>
<td>0.0194</td>
<td></td>
<td></td>
<td><strong>This study</strong></td>
</tr>
<tr>
<td>MnO$_2$ coated sand</td>
<td>102.5</td>
<td>538</td>
<td>0.3774</td>
<td>0.3641</td>
<td>Lee et al. (2004)</td>
</tr>
<tr>
<td>Kaolinites</td>
<td>4470</td>
<td>0.15</td>
<td>1.46</td>
<td>4.1667</td>
<td>Ulmanu et al. (2003)</td>
</tr>
<tr>
<td>Bentonites</td>
<td>7590</td>
<td>3.78</td>
<td>18.16</td>
<td>1.3636</td>
<td>Ulmanu et al. (2003)</td>
</tr>
<tr>
<td>Palygorskites</td>
<td>3067</td>
<td>0.11</td>
<td>6.14</td>
<td>2.5800</td>
<td>Potgieter et al. (2006)</td>
</tr>
<tr>
<td>Dowex 50W synthetic Resin</td>
<td>2222.5</td>
<td>14.998</td>
<td>2.6903</td>
<td>2.3641</td>
<td>Pehlivan and Turkan (2006)</td>
</tr>
<tr>
<td><em>Tectona grandis</em> l.f.</td>
<td>9540</td>
<td>0.1346</td>
<td>286.3</td>
<td>0.2766</td>
<td>King et al. (2006)</td>
</tr>
<tr>
<td>Kraft lignin</td>
<td>8768</td>
<td>10.18</td>
<td>1868.8</td>
<td>0.41</td>
<td>Mohan et al. (2006)</td>
</tr>
</tbody>
</table>

Table 4.12  Sampled Literature values of Langmuir and Freundlich constant
The adsorption capacity of RSBE is relatively low when compared with that of the activated carbon (AC). However it is higher than those of most of other clay minerals such as Palygorskites, Kaolinites and MnO$_2$ coated sand. It can be seen that the bio-sorbents, including *Tectona grandis* l.f. (teak leaves powder) and Kraft lignin exhibit slightly higher $Q_{\text{max}}$ than RSBE. Differences in Cu adsorption capacities are due in part to variation in properties of the adsorbents such as specific surface area (SSA), structure, functional groups, etc. Other than the adsorbent properties affecting the adsorption, the mode of the sorbent preparation and the solution parameters such as pH, temperature, organic ligands, and the presence of competing cations would also influence the adsorption to various degrees. Although, the adsorption capacity of SBE is not the highest one, it compares favorably with that of the other adsorbents. Moreover, it can be obtained cheaply and in large quantities.

**4.4.2 Freundlich Equilibrium Isotherm**

The linearized log-log Freundlich isotherm (Eq. 4.8),

$$\log Q_{eq} = \log K_F + \frac{1}{n}\log C_{eq}$$  \hspace{1cm} 4.8

where, $K_F$ and $n$ are constants was employed in this section. The respective Freundlich constants for various samples were determined from the linear plots and given in Table 4.13. The representative plot for the 370 °C heat-treated SBE is shown in Fig. 4.18 but more graphs for the different conditions are in Appendix.
$y = 3.1326x + 0.7726$

$R^2 = 0.9883$

Figure 4.18  *Freundlich isotherm for 370 °C heat treated SBE*

<table>
<thead>
<tr>
<th>Sample Reactivation Temperature (°C)</th>
<th>Freundlich Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_F$ (mgKg$^{-1}$)</td>
</tr>
<tr>
<td>25</td>
<td>100.70</td>
</tr>
<tr>
<td>110</td>
<td>411.56</td>
</tr>
<tr>
<td>300</td>
<td>29.89</td>
</tr>
<tr>
<td>370</td>
<td>5.92</td>
</tr>
<tr>
<td>400</td>
<td>132.35</td>
</tr>
<tr>
<td>700</td>
<td>320.38</td>
</tr>
<tr>
<td>800</td>
<td>218.25</td>
</tr>
</tbody>
</table>

Table 4.13  *SBE-Copper Adsorption Freundlich Equilibrium Constants*

Both the affinity coefficient, $K_F$ and the intensity parameter $n$ recorded indicated effective binding of Cu(II) species by the materials despite the low regression constants $R^2$. For Tryball (1980) and Namasivayam and Yamuna
(1992) have shown that values of $n$ between 1 and 10 are indicative of effective adsorption of the adsorbate by the sorbent. The range of $K_F$ values obtained in this work (5 to 410 mg kg$^{-1}$) indicated that substantial adsorption of metal ions can still take place even when $n \to \infty$ in the adsorption system under investigation. This is because according to the Freundlich isotherm (Eq. 4.8) $K_F$ is the amount of metal ions adsorbed when $C_{eq} \to 1$.

In general, both Langmuir and Freundlich isothermal constants for SBE samples indicated effective adsorption of Cu(II) ions on to RSBE. The data for most SBE heat reactivated samples fitted the Langmuir isotherm better than the Freundlich isotherm as is also reported in most cases in literature (Silveira and Alleoni, 2003; Mesquita and Silva, 2002; Ulmanu et al., 2003). The exception was for 25 and 370 °C heat-treated SBE data where high correlation, $R^2 > 0.97$ was recorded for both isotherms although that of the Freundlich regression was somehow better. Moreover, noteworthy is the fact that although, the total adsorption capacity of RSBE is not the highest one, its relative Cu(II) adsorption capacity ($K_F$) is quite high as compared with other adsorbents (Table 4.12).

### 4.4.3 Linear Partition Equilibrium Isotherm

The distribution coefficient $K_D$ of an adsorptive system, defined as;

$$K_D = \frac{Q_{eq}}{C_{eq}}$$  \hspace{1cm} (4.9)

where, $Q_{eq}$ and $C_{eq}$ are respective equilibrium concentrations in solid and liquid phases has been used by different authors (Atanassova, 1995; Atanassova and Okazaki, 1997; Tiller et al., 1984) alongside Langmuir and
Freundlich isotherms to assess the affinity of adsorbents for the reacting species. But since this linear regressions of adsorbed metal $Q_{eq}$ (mgKg$^{-1}$) against aqueous concentration $C_{eq}$ (mgL$^{-1}$) are often not feasible for the whole range of adsorbate concentrations particularly if high initial concentrations of the adsorbate are used the tests in this study were limited to initial adsorbate concentrations of 272 mgL$^{-1}$ Cu (II) ions or less.

Average values of the distribution coefficient ($K_D$) with respect to total copper adsorption by SBE samples were calculated from the slopes of adsorption curves of best fit (see relevant appendices) and presented in Table 4.14.

<table>
<thead>
<tr>
<th>SBE Heat-Treatment</th>
<th>$K_D$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>60.311</td>
<td>0.9221</td>
</tr>
<tr>
<td>110</td>
<td>35.191</td>
<td>0.9282</td>
</tr>
<tr>
<td>300</td>
<td>42.845</td>
<td>0.9333</td>
</tr>
<tr>
<td>370</td>
<td>590.760</td>
<td>0.8765</td>
</tr>
<tr>
<td>400</td>
<td>34.431</td>
<td>0.8340</td>
</tr>
<tr>
<td>700</td>
<td>93.613</td>
<td>0.9728</td>
</tr>
<tr>
<td>800</td>
<td>19.700</td>
<td>0.8244</td>
</tr>
</tbody>
</table>

Table 4.14 SBE-Copper Adsorption Linear Partition and Regression Constants

As can been seen from the table, most data did not conform to the Linear partition isotherm giving low $R^2 \leq 0.93$. This is because the linear isotherm typically occurs only at very low sorbate concentration in the solution and at low loading on the adsorbent surfaces in proportion to the total available adsorptive surface. It therefore applies under the hypothesis of a large excess of the adsorptive surface. The relatively high correlation coefficients for the
adsorption data from SBE samples regenerated below 110 °C can therefore be ascribed to presence of chemically adsorbed oils and other organic materials which provided additional adsorptive surfaces. In the case of 700 °C heat-treated SBE, Cu adsorption (which did not conform to both Langmuir and Freundlich isotherms) was surprisingly consistent with this isotherm. For, the proportion of adsorbed metal did not vary appreciably with adsorbed amounts. According to Ulmanu et al. (2003), this behavior is typical of high affinity alumino-silicate-dominated clays possessing sites of similar bonding energy. But Iler (1979) and Cook (1981) have indicated that calcination of SBE within 700 °C corresponds to the point of total collapse in the montmorillonite clay structure of the soil. These structural destruction are usually accompanied by the formation of highly reactive quasi-amorphous silica and high surface area alumina. This probably generated a mixture of independent adsorbents with different adsorptive properties which may explain the high adsorptive capacity and non-conformity of the adsorption data from this material to both the Langmuir and Freundlich isotherms.

In general however, the order of decreasing distribution coefficient (K_D) for all samples reflected the adsorption capacities and the reactivation efficiency of the respective temperatures of pretreatment. The highest distribution coefficient, K_D (590.76) was found for 370 °C materials.
4.5 ADSORPTION THERMODYNAMICS

The Gibbs free energy (\(\Delta G\)) indicates the degree of spontaneity of the chemical process and the higher negative value reflects a more energetically favorable adsorption. The standard thermodynamic equilibrium constant (\(K^0\)) for heat treated SBE samples was estimated by extrapolating plots of \(K_D\) versus initial metal concentration \(C_0\) at \(C_0 \to 0\). The resultant \(K^0\) data was used to evaluate the standard Gibbs free energy (\(\Delta G^0\)) according to equation 2.18. The values of standard Gibbs free energy (\(\Delta G^0\)) obtained are shown in Table 4.15.

<table>
<thead>
<tr>
<th>SBE Heat-Treatment Temperature (°C)</th>
<th>(K^0)</th>
<th>(\Delta G^0) (kJmol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>49.1836</td>
<td>-9.6515</td>
</tr>
<tr>
<td>110</td>
<td>100.2376</td>
<td>-11.4155</td>
</tr>
<tr>
<td>300</td>
<td>44.6662</td>
<td>-9.4128</td>
</tr>
<tr>
<td>370</td>
<td>124.9278</td>
<td>-11.9611</td>
</tr>
<tr>
<td>400</td>
<td>49.9088</td>
<td>-9.6878</td>
</tr>
<tr>
<td>700</td>
<td>37.3687</td>
<td>-8.9709</td>
</tr>
<tr>
<td>800</td>
<td>10.4092</td>
<td>-5.8042</td>
</tr>
</tbody>
</table>

Table 4.15 Some Thermodynamic Parameters for Cu (II) Adsorption on RSBE

The negative values of \(\Delta G\) indicate the feasibility of the process and spontaneity of the adsorption. According to Weng et al. (2006), the typical range of bonding energy for ion-exchange mechanism is 8-20 kJmol\(^{-1}\) (1.91-3.82 kcal/mol). In essence standard Gibbs free energies (\(\Delta G^0\)) up to 20 kJmol\(^{-1}\) are consistent with electrostatic (physical) interactions between adsorbent and the adsorbate particles whereas more negative \(\Delta G^0\) values than 40 kJmol\(^{-1}\) are
in the range of charge sharing or charge transfer from the adsorbent surface to
the metal ion to form coordinate bonds. The $\Delta G^0$ values obtained in this work
were well below 20 kJmol$^{-1}$ indicating that physical interactions between the
sorbent and sorbate particles were the more important mechanism in the
adsorption process as also postulated in the kinetic and desorption analysis
reported elsewhere in this work.

4.6 ADSORPTION KINETICS

Sorption kinetics is important in describing the rate of solute uptake by an
adsorbent. They are useful in characterization of the residence time of the
adsorbent in the reactor and hence the efficiency of an adsorbent in the
sorption process. In this study the Lagergren first-order (Lagergren, 1898;
Taty-Costodes et al., 2003) and pseudo-second order rate models (Ho and
McKay, 2003) along with Weber and Morris type intra-particular diffusion
model were employed in the form of Equations 4.8, 4.9 and 4.10 respectively.

\[
\log(q_e - q_t) = \log q_e - \frac{k_{1,ad} t}{2.303}
\]

\[
\frac{t}{q_t} = \frac{1}{k_{2,ad} q_e^2} + \frac{1}{q_e} t
\]

where $q_e$ and $q_t$ are the amounts of metal ions adsorbed onto the material (mg
g$^{-1}$) at equilibrium and at time $t$, respectively; $k_{1,ad}$ is the first-order (min$^{-1}$)
rate constant of the process.
where $k_{2,ad}$ is the rate constant of second order sorption (min$^{-1}$), $q_e$ the amount of metal ions adsorbed at equilibrium (mg g$^{-1}$) and $q_t$ the amount of solute sorbate on the surface of the adsorbent at any time $t$ (mg g$^{-1}$).

and,

$$q_t = \frac{k_w t^{1/2}}{m}$$  \hspace{1cm} 4.10

where $m$ is the mass of adsorbent (g), $q_t$ the amount of metal ions adsorbed at time $t$ (mg g$^{-1}$) and $k_w$ is the initial rate of intra-particular diffusion (mg l$^{-1}$ s$^{-0.5}$).

Data from the batch studies on sorption of Cu$^{2+}$ on the RSBE was analyzed using the three kinetic models to determine the time required to reach equilibrium. In all cases, the models were applied first to the adsorption data for the initial six hour equilibration period then to the latter 30 hour equilibration time separately. The resulting representative linear plots are shown in Figures 4.19 to 4.21 together with regressions for: Lagergren first-order, pseudo-second order and intra-particular diffusion, kinetic models. But more graphs for the different conditions are in the Appendix. The correlation coefficients for the three kinetic models obtained from the linear plots are listed in Table 4.16.
Figure 4.19  First order kinetics for the first six hour of sorption process

Figure 4.20  Pseudo-second order kinetics for the initial 6 hours of the sorption process six hours of the sorption process
Figure 4.21  Intra-particle diffusion models for the first six hours of the sorption process

![Graph showing the relationship between sorption time and sorption capacity for Copper-SBE adsorption kinetics.](image)

\[ y = 73.075x - 1332.2 \]
\[ R^2 = 0.9997 \]

Table 4.16  Copper-SBE Adsorption Kinetics Constants

<table>
<thead>
<tr>
<th>MODEL</th>
<th>R² VALUES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st Portion</td>
</tr>
<tr>
<td>Pseudo 1st Order</td>
<td>0.8092</td>
</tr>
<tr>
<td>Pseudo 2nd Order</td>
<td>0.9991</td>
</tr>
<tr>
<td>Intra-Particle Diffusion</td>
<td>0.996</td>
</tr>
</tbody>
</table>

In all cases, Lagergren pseudo-first order model did not apply well to the whole range of contact times. The sorption system for these materials does not therefore follow a first-order reaction. The insufficiency of the first-order model to fit metal sorption kinetic data is also consistent with many cases in the literature (McKay et al., 1999). The correlation coefficient is considerably lower for intra-particular diffusion for the first-six-hour data compared to that of the pseudo-second order model which is well in excess of 0.99. And the
converse is true for the latter adsorption period after the initial six hours where the intra-particle diffusion data has a more favorable correlation.

According to Ho and McKay (2003), the nature of the rate-limiting step in a batch system can be assessed from the properties of the solute and sorbent. The pseudo-second order model is based on the assumption that the rate limiting step may be a chemical sorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate (Taty-Costodes et al., 1984). According to the equation for intra-particular diffusion by Webber and Morris (Eq. 2.16), the plot for $q$ versus $t^{1/2}$ should be linear indicating that intra-particle diffusion of solute particles into the mesoporous structure of the adsorbent should be the sole rate determining step in such reactions. From this results it is clear that intra-particular diffusion is the sole rate-determining step in the latter phases of copper sorption onto RSBE and that the sorption process involves complementary initial pseudo-second order mechanisms which rapidly give way to intra-particle diffusion mechanism as more exposed reaction sites in the surface of the adsorbent get depleted. This simultaneous surface and inner-core reactions between metal ions and soil surfaces appear to be the case in most systems involving copper adsorption to soil minerals (McBride et al., 1984, Cheah et al, 2002, Jardão et al., 2000, Silveira and Alleoni, 2003; Hyun et al., 2003, Hyun et al., 2005).

These results indicate that most of copper adsorption on to RSBE is a rapid chemical sorption involving valence type forces between adsorbate particles
and the adsorbent; based on exposed surface functional sites on the edges of the clay structure in RSBE. These interactions take place within six hours of sorption and account for about 80% of the metal adsorptions (Table 4.8). Insignificant additional metal adsorption (less than 10%) was achieved by prolonging the contact time 42 hours. This indicates that negligible amount of copper is immobilized inside the mesoporous structure of RSBE. Thus, substantial amounts of the metal could be recovered from the material before its eventual disposal.

4.7 COPPER DESORPTION FROM SBE

Desorption studies of an adsorbate from an adsorbent are important in testing the effectiveness of the adsorbent to bind the sorbate particles and for regeneration of the adsorbent. These usually take the form of column or batch washing of the material in a large excess of a desorbing agent. Most commonly used desorbing agents fall in one or the other of the three categories namely; pH adjustments, use of a competing adsorbate ion to displace the adsorbate from the solid phase and/or complexing ligands that can strongly bind the adsorbate from the adsorbent surface into the aqueous phase and keep it from re-adsorbing. Changes in pH can alter the surface charge of a solid adsorbent thereby changing the potential across the adsorbent-solution interface. This may force the adsorbate to desorb from the adsorbent surface into the aqueous phase (Tiller, 1984). In this work, effects of initial copper concentration and time of exposure of the adsorbent to the desorbing agent
were investigated using 0.25 M H₂SO₄, 0.25 M CaCl₂ and 0.5 M HCl respectively as desorbing agents.

4.7.1 Effects of Initial Copper Concentration on its Desorption from SBE

The concentration of adsorbate particles in the adsorbent plays an important role in influencing the type and position of adsorbent-sorbate equilibrium along the plane of adsorption. In this work, the effects of concentration of adsorbed copper on its desorption from RSBE were studied by exposing 20g of RSBE to 200 ml of copper (II) ions at different concentrations then desorbing the copper (II) ions from the same samples by equilibration in 200 ml of HCl, CaCl₂ and H₂SO₄ solutions respectively. The results of these investigations are presented in Fig. 4.22 and Table 4.17.
### Table 4.17  Effects of Concentration on Copper Desorption from RSBE

<table>
<thead>
<tr>
<th>INITIAL COPPER CONCENTRATION (mg/l)</th>
<th>% DESORPTION IN 0.5 M HCl</th>
<th>% COPPER DESORPTION IN 0.25 M H₂SO₄</th>
<th>% COPPER DESORPTION IN 0.25 M CaCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.0</td>
<td>48.5±6.92</td>
<td>31.9 ±6.93</td>
<td>48.1±4.65</td>
</tr>
<tr>
<td>34.0</td>
<td>48.9±7.57</td>
<td>48.4±5.32</td>
<td>53.3±7.53</td>
</tr>
<tr>
<td>68.0</td>
<td>76.6±5.79</td>
<td>73.5±1.31</td>
<td>47.7±6.92</td>
</tr>
<tr>
<td>136.0</td>
<td>72.6±6.91</td>
<td>74.1±1.59</td>
<td>46.4±5.96</td>
</tr>
<tr>
<td>272.0</td>
<td>83.2±3.09</td>
<td>81.5±5.27</td>
<td>49.1±5.92</td>
</tr>
<tr>
<td>545.0</td>
<td>45.0±6.50</td>
<td>35.4±1.55</td>
<td>31.7±4.57</td>
</tr>
</tbody>
</table>

**Figure 4.22  Desorption efficacies of various copper desorbing agents from copper saturated SBE**
Copper desorption initially increased with copper concentration in the adsorbent. The best desorption efficiency was recorded for 272 mg l\(^{-1}\) initial copper SBE saturation concentration. However there was an initial peak in copper desorption at 68 mg l\(^{-1}\) in all cases. The presence of two desorption pseudo-maxima could be as a result of desorption of the metal initially adsorbed on different adsorption sites and/or in different speciation of the metal ions.

The acid desorbants, 0.25 M H\(_2\)SO\(_4\) acid and 0.5 M HCl gave comparable efficiencies of copper desorption from SBE. The fact that desorption efficiency of 0.25M calcium chloride was relatively lower implies that the H\(^+\) ions and/or lowering the pH of the materials was the more effective mode of desorbing copper from RSBE than the competitive effects of Ca\(^{2+}\) ions. This can be owed to the fact that adsorbed copper speciation is predominantly pH dependent hydrolysis products favored by mid-acidic to neutral pH values as can been seen from other results in this work (section 4.3.5). At low pH, sorbed hydrolysis products quickly desorb from soil surfaces (SO-) according to Equations 4.9 and 4.10.

\[
\text{SO-Cu(OH)(H}_2\text{O})_4(s) + \text{H}_3\text{O}^+_{(aq)} \rightleftharpoons \text{SO-H}_2(S) + [\text{Cu(OH)(H}_2\text{O})_5]^+_{(aq)} \quad 4.9
\]

Then,

\[
[Cu(OH)(H}_2\text{O})_5]^+_{(aq)} + \text{H}_3\text{O}^+_{(aq)} \rightleftharpoons [\text{Cu(H}_2\text{O})_6]^2+_{(aq)} + \text{H}_2\text{O}(l) \quad 4.10
\]

The excess H\(^+\) ions then sit on the adsorptive sites so generated occupying and reducing the net negative surface charge that favor cation exchange (Eq. 4.11).
This prevents re-adsorption of hexa-aquo copper (II) ions, $[\text{Cu(H}_2\text{O)}_6]^{2+}$ onto the RSBE surface.

Furthermore, when the ambient pH of the soil solution falls below the PZNC of the soil, soil surfaces often tend to develop positive charge making the adsorption of metal ions highly unfavorable as a result of development of opposing adsorption potential across the plane of sorption. It can therefore be assumed that the acid solutions used in this work lowered the pH of RSBE solution below its PZNC. This made the soil surfaces to develop positive net charge thereby desorbing the metal ions from the surface. This may explain why pH adjustments were more effective in desorbing copper ions from RSBE than competitive effects of Ca$^{2+}$ ions despite the higher charge density in Ca$^{2+}$ than in H$^+$ ions.

In general however, the results from this section indicated that the concentration of adsorbed copper (II) ions in RSBE provides an important driving force in copper desorption from the material. They show that copper desorption increase with copper concentration up to 272 mg/l RSBE.
saturation concentration then declines. This suggests that above this concentration, copper (II) ions begin to get immobilized inside the mesoporous structure of the adsorbent and/or the aqueous phase of the desorption equilibrium become saturated with the metal ions resulting in an opposite driving force to the desorption process. This is consistent with the results from adsorption analysis (section 4.3.2) which indicated that optimum adsorption equilibrium is established in the region of similar initial metal concentrations.

4.7.2 Effects of Time of Exposure to the Desorbing Agents on Copper Desorption

Establishment of a state of adsorbate equilibrium at the solid-solution interface in adsorption-desorption system is a time dependent process. The time dependence of copper desorption from RSBE was studied by saturating RSBE samples with copper (II) ions by immersing predetermined mass of the material in 272 mg/l copper (II) ions. The resulting copper laden RSBE was agitated in a large excess 0.25M sulphuric (VI) acid, 0.25M calcium chloride and 0.5M hydrochloric acid respectively for periods ranging from a few seconds to 8 hours and percentage recovery of the adsorbed metal determined. The results of this analysis are presented in Table 4.18 and Figure 4.23.
<table>
<thead>
<tr>
<th>TIME (HRS)</th>
<th>% DE Sorption IN 0.5 M HCl</th>
<th>% DE Sorption IN 0.25 M H₂SO₄</th>
<th>% DE Sorption IN 0.25 M CaCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>53.9 ±2.5</td>
<td>46.3 ±3.6</td>
<td>49.4 ±3.1</td>
</tr>
<tr>
<td>0.3</td>
<td>66.6 ±2.7</td>
<td>60.4 ±3.4</td>
<td>50.9 ±1.6</td>
</tr>
<tr>
<td>0.5</td>
<td>75.8 ±3.5</td>
<td>73.2 ±2.5</td>
<td>49.6 ±2.7</td>
</tr>
<tr>
<td>1.0</td>
<td>78.3 ±3.4</td>
<td>80.8 ±2.2</td>
<td>51.3 ±2.0</td>
</tr>
<tr>
<td>2.0</td>
<td>59.8 ±1.0</td>
<td>77.0 ±1.8</td>
<td>48.4 ±3.6</td>
</tr>
<tr>
<td>4.0</td>
<td>49.2 ±2.5</td>
<td>72.7 ±3.2</td>
<td>50.9 ±2.2</td>
</tr>
<tr>
<td>8.0</td>
<td>37.7 ±3.1</td>
<td>67.9 ±1.8</td>
<td>47.9 ±1.6</td>
</tr>
</tbody>
</table>

Table 4.18  Copper Desorption efficiencies of Assorted Desorbing Agents

Percentage desorption of copper initially increased rapidly with agitation time to a maximum before coming down. The highest desorption efficiency (Table
4.14) was recorded for one hour equilibration time in all the three desorbing agents with the overall highest desorption of 80.8% being recorded in 0.25M H$_2$SO$_4$. The latter drop in desorption efficiency may be explained on the migration or re-adsorption of the desorption products into inner-sphere adsorption sites of the material causing a drop in the percentage desorption of the metal. These findings confirm that adsorbed copper is mainly based within surface functional groups of the material as also postulated in kinetic analysis (section 4.5).

There was a marked difference in the desorption efficiency of hydrochloric acid and sulphuric acid; showing that the type of acid counter ion affect copper desorption from RSBE of the acid. This is consistent with the work of Homann and Zasoski (1987) and McNaughton and James (1974) both of whom demonstrated that the presence of some ligand ions in the sorption equilibrium reduces metal ions adsorption on to clay adsorbents through metal-ligand complexation in the aqueous phase. The higher influence of the sulphate ions over the chloride ion on copper desorption reported in this work is attributable to formation of stronger soluble copper-sulphato complexes than the Cu-chloro complexes because of former ion’s higher charge density. This is also consistent with the hard acid-base theory. As can be seen from Table 4.19 the oxygen centers in the sulphate ion are considered hard relative to the chloride ions. They are therefore expected to interact more strongly with Cu$^{2+}$ ions than the latter.
Table 4.19  Ionic and Atomic Radii of Selected Chemical Species in this Work

(adapted from Raymond et al. (1999))

On the other hand, soil surfaces tend to develop net positive charge at low pH values as pointed out in the preceding sections (section 4.6.1). This allows negative ligands in the solution to adsorb and complex with positive centers in the adsorbent. This induces competition with the metal ion for the soil oxide surfaces (according to Equation 4.12 for the sulphate ion) as also postulated by Naidu et al. (1994a).

Again because of its larger ionic charge the $\text{SO}_4^{2-}$ ion would be attracted more strongly to the positively charged soil surface than the chloride thereby exert stronger influence in copper (II) desorption from RSBE than the latter.
The results in this section confirmed earlier postulates that adsorbed copper in RSBE was based on surface functional groups of the adsorbent. The metal ions could therefore quickly be recovered from the material after adsorption process before the material is eventually disposed off to the environment. 0.25M sulphuric acid was found to be the most effective desorbing agent. It exhibited contributory effects between $H^+$ and $SO_4^{2-}$ ions in the copper removal from the material. These findings however, suggest that more investigations about the acid counter ion effects might be required for advantage to be taken of these contributory effects of acid ions in final cleansing of the material from adsorbed copper before its final disposal.
CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

This study showed that the copper (II) ions can be removed from aqueous solutions by adsorption on to Regenerated Spent Bleaching Earth (RSBE). Reactivation tests demonstrated that solvent excess oil extraction followed by heat treatment at 370 °C was most effective in regenerating SBE for copper adsorption. The materials so obtained were found to have large cation exchange capacities of 6000 mgg⁻¹ of Na⁺ ions equivalents. Adsorption experiments demonstrated that pH, adsorbent dosage and initial adsorbate concentrations were the critical factors affecting Cu (II) adsorption on Regenerated Spent Bleaching Clays. Significant adsorption took place within pH 5.5, using 272 mgl⁻¹ initial copper concentrations at 1.0 g of adsorbent in 10 ml of adsorbate solution dosage. Up to 94.8% copper removal was recorded. Based on changes in pH during adsorption at different initial pH values, it was suggested that hydrolysis products were more favorably adsorbed onto RSBE soil particles than the monomeric hexaaquo [Cu(H₂O)₆]²⁺ ion. The kinetic analysis indicated that Cu(II) adsorption on RSBE is principally a rapid phenomenon reaching its initial equilibrium in less than six hours. The process was found to proceed mainly via pseudo-second order mechanism based on the available adsorbent surface in the initial stages supplemented by intra-particle diffusion mechanism in the latter stages.
In majority of the cases the adsorption data was better described by the Langmuir isotherm than the Freundlich isotherm. The highest distribution coefficient, \( K_D \) of 590.76 was recorded for 370 °C regenerated materials. And the standard Gibbs free energy ranged from -5.8042 to -11.9611 kJmol\(^{-1}\) indicating that the adsorption process is spontaneous and mainly based on physical ion-exchange type interactions between the metal ions and the RSBE surfaces.

In the desorption experiments, pH adjustments were more effective in desorbing sorbed copper ions from RSBE than competitive cationic desorbing agents. Under acidic solutions in 0.5M \( H^+ \) ions, copper ions quickly desorbed from SBE in less than one hour indicating that most copper ions in RSBE were loosely bonded on surface sites in the materials and therefore can easily be recovered from the materials before the final disposal.

### 5.2 RECOMMENDATIONS

From the foregoing conclusions we wish to recommend:

i. SBE regeneration procedures described herein and the materials so obtained for the final industrial scale up for adsorptive removal of copper ions from both waste water and water sources.

ii. More investigative work into the role of acid counter-ions in copper adsorption /desorption behavior on RSBE to determine if appropriate advantage can be taken of such to enhance copper RSBE adsorption/desorption properties.
iii. Further studies on the RSBE adsorptive characteristics involving single and interactive systems of other metal ions: Zn$^{2+}$, Pb$^{2+}$, Cd$^{2+}$ etc to assess the performance of the method in removal of other heavy metal ions from aqueous solutions.
REFERENCES


APPENDICES

APPENDIX I: LANGMUIR ISOTHERMS FOR Cu (II) ADSORPTION ONTO RSBE

LANGMUIR ISOTHERM FOR 800 °C REACTIVATED SBE

THE LANGMUIR ISOTHERM FOR 700 °C REACTIVATED SBE
THE LANGMUIR ISOTHERM FOR 400 °C REACTIVATED SBE

The Langmuir Isotherm for 350 °C Reactivated SBE
LANGMUIR ISOTHERM FOR 300 °C ACTIVATED SBE

LANGMUIR ISOTHERM FOR 110 °C HEATED SBE
LANGMUIR ISOTHERM FOR 25 oC DRIED SBE

\[
\frac{1}{Q_{eq}} (Kgmg^{-1})
\]

\[
\frac{1}{C_{eq}} (Lmg^{-1})
\]
APPENDIX II: Freundlich Isotherms for Cu (II) Adsorption onto RSBE

The Freundlich Isotherm for 800 °C Reactivated SSE

The Freundlich Isotherm for 700 °C Reactivated SSE
The Freundlich Isotherm for 350 Reactivated SBE

The Freundlich Isotherm for 400 oC Reactivated SBE
FREUNDLICH ISOTHERM FOR 300 °C ACTIVATED SBE

THE FREUNDLICH ISOTHERM FOR 110 °C HEATED SBE
FREUNDLICH ISOTHERM FOR 25 °C DRIED SBE

LOG Qeq

LOG Ceq

LINEAR ADSORPTION ISOTHERM FOR 700 °C HEAT-TREATED SBE
APPENDIX III: LINEAR PARTITION ISOTHERMS FOR CU (II) ADSORPTION ONTO RSBE

LINEAR ISOTHERM FOR 800 °C HEAT-TREATED SBE

\[ y = 19.794x + 475.99 \]
\[ R^2 = 0.8244 \]

LINEAR ADSORPTION ISOTHERM FOR 700 °C HEAT-TREATED SBE
LINEAR ISOThERM FOR 400 °C HEAT-TREATED SBE

LINEAR ISOThERM FOR 350 °C REACTVATES SBE
LINEAR ADSORPTION ISOTHERM FOR 300 °C TREATED SBE

LINEAR ADSORPTION ISOTHERM FOR 110 °C TREATED SBE
LINEAR ADSORPTION ISOTHERM
FOR 25 °C DRIED SBE

\[ y = -0.0021x + 2.9 \]
\[ R^2 = 0.99 \]

\[ Q_e \quad \text{vs} \quad C_{eq} \]

\[ Q_e \quad \begin{array}{c}
0 \\ 200 \\ 400 \\ 600 \\ 800 \\ 1000 \\ 1200 \\ 1400 \\
\end{array} \]

\[ C_{eq} \quad \begin{array}{c}
0 \\ 5 \\ 10 \\ 15 \\ 20 \\
\end{array} \]
APPENDIX IV: ADSORPTION KINETICS MODELS

1ST PORTION PSEUDO-FIRST ORDER KINETICS MODEL

\[ y = -0.0021x + 2.9409 \]

\[ R^2 = 0.8092 \]

2ND PORTION PSEUDO-FIRST ORDER KINETICS MODEL

\[ y = -0.001x + 2.6099 \]

\[ R^2 = 0.7518 \]
1ST PORTION PSEUDO-SECOND ORDER
KINETICS MODEL

\[
y = 0.0185x + 0.0007 \\
R^2 = 0.9991
\]

1ST PORTION INTRA-PARTICLE DIFFUSION
KINETICS MODEL

\[
y = 0.0306x + 0.0007 \\
R^2 = 0.6281
\]
1ST PORTION INTRAPARTICLE DIFFUSION KINETICS MODEL

\[ y = 56.883x - 793.47 \]
\[ R^2 = 0.996 \]

SQUARE ROOT OF TIME (t_{1/2}) (MIN-1/2)

1200
1000
800
600
400
22 24 26 28 30 32 34 36
qt (mg/kg)

2ND PORTION INTRAPARTICLE DIFFUSION KINETICS MODEL

\[ y = 73.075x - 1332.2 \]
\[ R^2 = 0.9997 \]

t_{1/2} (MIN-1/2)

1600
1500
1400
1300
1200
1100
34 35 36 37 38 39
qt (mg/kg)