



UNIVERSITY OF THE
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Adsorptive removal of heavy metals from wastewater using chitosan coated bentonite beads

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A research report submitted to the Faculty of Engineering and Built Environment, University of Witwatersrand, Johannesburg, in partial fulfilment of the requirements for the degree of Master of Science in Engineering

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DECLARATION

I declare that this research report is my own unaided work. It is being submitted to the degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any other degree or examination in any other University.

MChiwawa 29 April 2021 _____

Maxwell Chiwawa

ABSTRACT

The contamination of water by heavy metals from anthropogenic and/or natural contamination is a world-wide environmental problem. Advanced wastewater treatments such as adsorption, are economically and environmentally friendly in removing non-biodegradable toxic heavy metals from the wastewater. The focus of recent studies has been specifically finding effective and low-cost adsorbents. Thus, the present study focuses on the use of chitosan coated bentonite beads prepared from low molecular weight chitosan and bentonite to remove heavy metals from wastewater. Chitosan and bentonite adsorbents are preferred due to natural occurrence, abundance, non-toxicity, potentially a lower cost compared to other adsorbents.

Chitosan coated bentonite beads were successfully prepared in this study using low molecular weight chitosan and bentonite. The prepared chitosan coated bentonite beads were characterised using Fourier transform infrared (FT-IR), Scanning electron microscopy (SEM), and swelling tests. The characterisation tests proved that the prepared chitosan coated bentonite beads possess very good physicochemical properties for adsorption. In addition, chitosan coated bentonite beads proved to have a complex chemical structure due to the presence of several functional groups such as O-H, NH₂, C=O, C-O-H, Al-O, Si-O and Si-O-Al. Functional groups such as O-H and NH₂, are cation binding groups which cause the chitosan coated bentonite beads to be suitable for adsorption of heavy metals.

Synthetic wastewater with Fe and Cu was prepared to evaluate the prepared chitosan coated bentonite beads. The Fe and Cu metals were chosen to simulate wastewater in this study based on the abundance in the acid mine drainage. A 2³-factorial design of experiments was used to study various conditions on the adsorption capacity of the prepared chitosan coated bentonite beads. Experimental results proved that the chitosan coated bentonite beads could remove Fe and Cu from wastewater with a maximum adsorption capacity of 12mg/g resulting in a percentage removal up to 99.5% and 95.2% for Cu and Fe, respectively. The adsorption capacity was found to vary with initial pH. For a pH range between 2 and 4, an increase in pH significantly increased the removal of Fe and Cu from synthetic wastewater. The optimal pH for adsorbing Cu and Fe in this study was found to be pH 4, a further increase in pH from pH of 4 to a pH of 6 proved to have a lesser effect on the removal of Fe and Cu from wastewater. Furthermore, the study also proved that both chitosan and bentonite possess different physical and chemical properties. Through evaluation beads of different chitosan bentonite compositions, it was proven that the optimal bead should have a composition of 50% chitosan/bentonite composition.

DEDICATIONS

This research is dedicated to my grandmother *Gogo Marozva* and my late brother *James Mahori Chiwawa* for being more than just family to me since day one.

'Chinokura choga isango munda kukura huona tewe'

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Nomenclature

C_o	Initial metal concentration in solution	mg/L
C_t	Metal concentration at time t	mg/L
C_e	Metal concentration at equilibrium	mg/L
MC	Mass of carbon	g
MS	Mass of solution	kg
K	Rate constant	mg/kg.hr
V	Volume of concentrated gold solution added	L
Q_E	Adsorption capacity	mg/g
T	Time taken for adsorption	hr

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Safe and portable water for human consumption is becoming scarcer due to anthropogenic and/or natural contamination of water bodies. Effluents which contain a significant amount of heavy metals are generated from industries such as electroplating, paint manufacturing, leather tanning, mineral processing and metal fabrication continue to be discharged into water bodies (Saravanana et al., 2012). Heavy metals are elements with a specific gravity that is approximately greater than 5.0 (Becker, 2016). Most of these metals are the most tenacious pollutants in industrial wastewater. They pose a serious risk to the environment and human health. The non-biodegradability of heavy metals makes them toxic to living organisms, because of the accumulation and transformation inside the living organism's tissues. Some of the heavy metals such as Cu (II) and Cr (III) are essential to human nutrition in adequate amounts (Futalan et al., 2010). However, if consumed in excess they can lead to serious health issues (Futalan et al., 2010).

Apart from the anthropogenic causes, heavy metals can also be introduced into the environment through natural phenomena such as weathering or volcanic eruptions. Figure 1.1 shows a river flowing with high concentrations of heavy metals.



Figure 1.1: River with high concentrations of heavy metals (Ntwampe, and Moothi, 2018).

Research has shown that the disposal of chemicals and mineral tailings with heavy metals contribute significantly to environmental degradation (Ntwampe and Moothi, 2018). Despite the fact that heavy metals can pose a risk to the environment and human health, their use in our day to day lives

is unavoidable. In addition to that, heavy metals hold a high economic value. Therefore, the removal of these heavy metals from industrial effluents to the recommended concentrations becomes also unavoidable and/or is paramount (Dalida et al., 2010).

The traditional methods of removing heavy metals from wastewater include ion exchange, membrane technology, adsorption, electrodeposition, and precipitation. Unfortunately, most of the traditional methods cannot remove heavy metals to very low concentrations (Dalida et al., 2010). The other major challenge is the high operating costs of treating the effluents, which can cause the end-to-end process unprofitable (Dalida et al., 2010; Pillai et al., 2009). Through the most common traditional methods used to remove heavy metals from wastewater as stated already include electrodeposition, adsorption, precipitation, and membrane bioreactors, adsorption is one of the most effective and economical method that has been lately commercialised (Dalida et al., 2010). Activated carbon has been widely used as the adsorbent, but it is an expensive material.

Recent studies on possible low-cost materials for adsorption have been conducted on materials such as chitin, chitosan, maize leaf, pumpkin waste and saw dust (Dalida et al., 2010; Pillai et al., 2009). These studies targeted natural materials that can be found in abundance. In addition, in the past years, there has been an increased interest in the synthesis and characterisation of natural polymers such as chitosan and cellulose for the removal of heavy metals from wastewater (Pillai et al., 2009).

Chitosan is a derivative of chitin and has lately been identified as a good adsorbent option (Gao, 2014; Gerente et al., 2007; Ngah and Hanafiah, 2005; Pollard et al., 1992). Chitosan is the second most abundant naturally occurring polymer after cellulose which, in addition to its naturally occurring abundance, has attracted more interest due to its non-toxicity, hydrophilicity and biodegradability (Pillai et al., 2009). Chitosan is a product of N-deacetylation of chitin. It has amine (-NH₂) and hydroxyl (-OH) functional groups that serve as active sites for heavy metal adsorption (Paul and Sharma, 2009). However, chitosan has limitations because it is very soluble in dilute organic acids and it agglomerates to form a gel in aqueous solutions (Ngah and Hanafiah, 2005). To transcend that, the physical and chemical properties of chitosan are modified by blending it with other materials such as bentonite so as to make a composite with desired physical and chemical properties (Ngah and Hanafiah, 2005).

This study is aimed at preparing, characterizing and evaluating chitosan coated bentonite beads for the removal of heavy metals from wastewater. This set of objectives were achieved firstly, through the preparation of chitosan-bentonite beads. The adsorption experiments were then carried out using synthetic wastewater and chitosan coated bentonite beads at specific set conditions. Analytical methods which were used for the evaluation and characterisation of the chitosan coated bentonite beads include the Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and atomic absorption spectrometry (AAS).

1.2 Problem statement:

Potable water for human consumption and use is becoming scarcer due to the increase in anthropogenic contamination of water bodies. Amongst the many contaminants in the water bodies are heavy metals which pose a serious threat to human health and other living organisms due to their high toxicity. The heavy metal pollution from industrial activities into water bodies have become a worldwide problem and society has become more concerned (Celenza 2000; Davis et al., 2003). This concern has triggered the need to find ways to curb this problem.

At the moment, traditional methods of removing heavy metals from wastewater have proven to be quite costly. However, recent studies have been conducted on low-cost materials such as chitin, chitosan, maize leaf, pumpkin waste and saw dust (Dalida et al., 2010; Pillai et al., 2009). This study looks at the potential use of chitosan and bentonite to adsorb heavy metals from wastewaters.

1.3 Research objectives

The specific objectives of this study are as follows:

- Prepare chitosan coated bentonite beads to be used for the removal of heavy metals from wastewater.
- Characterize the chitosan coated bentonite beads with the focus on:
 - Physical properties: focusing on surface morphology.
 - Chemical properties: looking mainly at the functional groups present in the beads.
- Evaluate the chitosan coated bentonite beads on the removal of two heavy metals from synthetic wastewater.

1.4 Dissertation layout

This document consists of seven main chapters which focuses on an end-to-end analysis from identifying the problem to recommending solutions through experimental studies and literature. The layout is summarised in the schematic view in Figure 1.2 below:

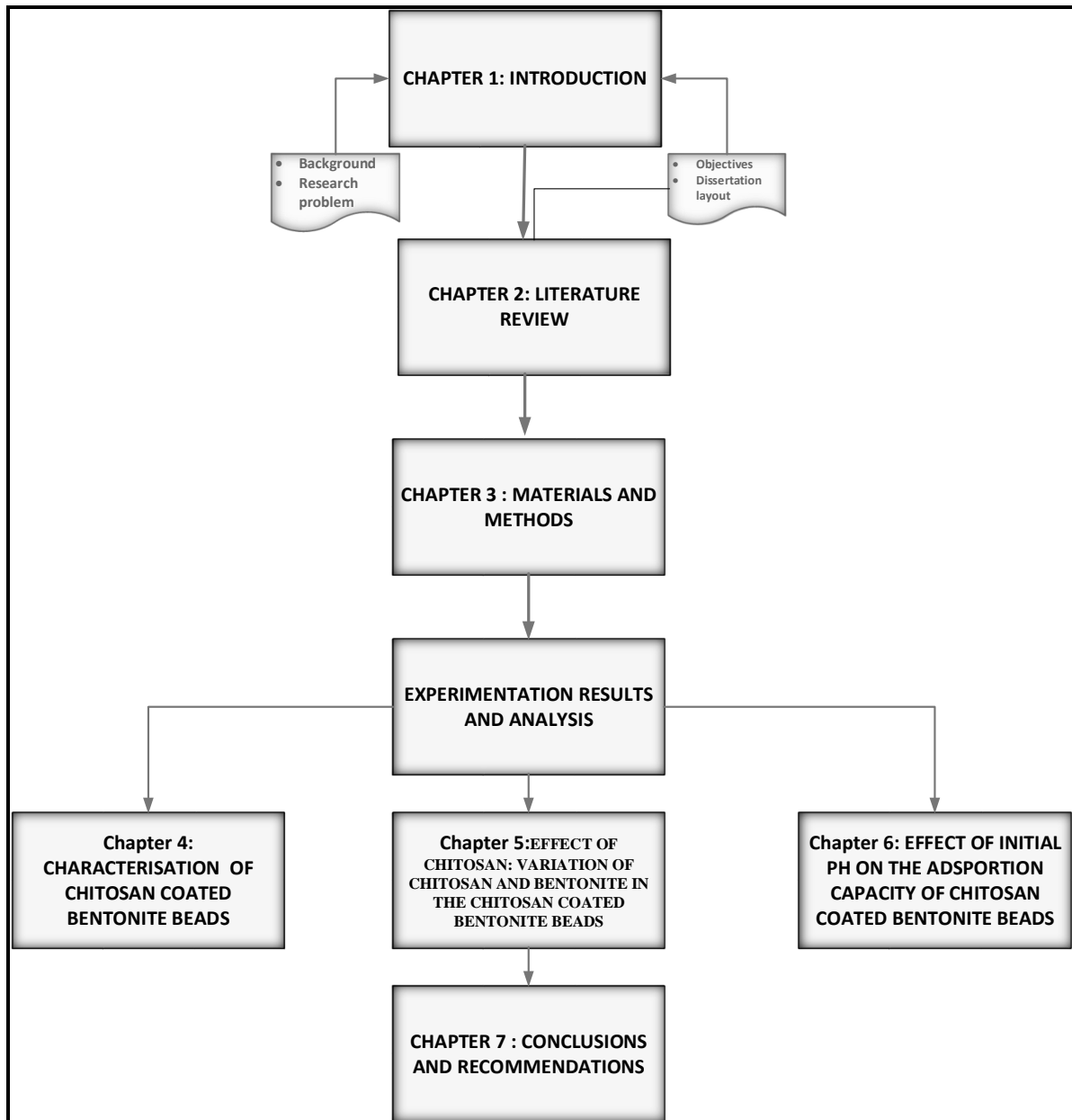


Figure 1.2: Dissertation layout

CHAPTER TWO
LITERATURE REVIEW

Chapter Two is literature review, which includes general knowledge on the removal of heavy metals from wastewater. Current methods used in removal of heavy metals were explored with a specific focus of the use of chitosan and bentonite in the removal of heavy metals from wastewater.

2.1 Wastewater characteristics

A good understanding of the characteristics of wastewater is fundamental before attempting to design a water treatment model. Wastewater is comprised of solid and/or liquid waste discharged from commercial properties, residences, agricultural land and industrial facilities (Peters et al., 1985). Wastewater can consist of a wide range of contaminants. Figure 2.1 shows a summary of how wastewater can be characterised.

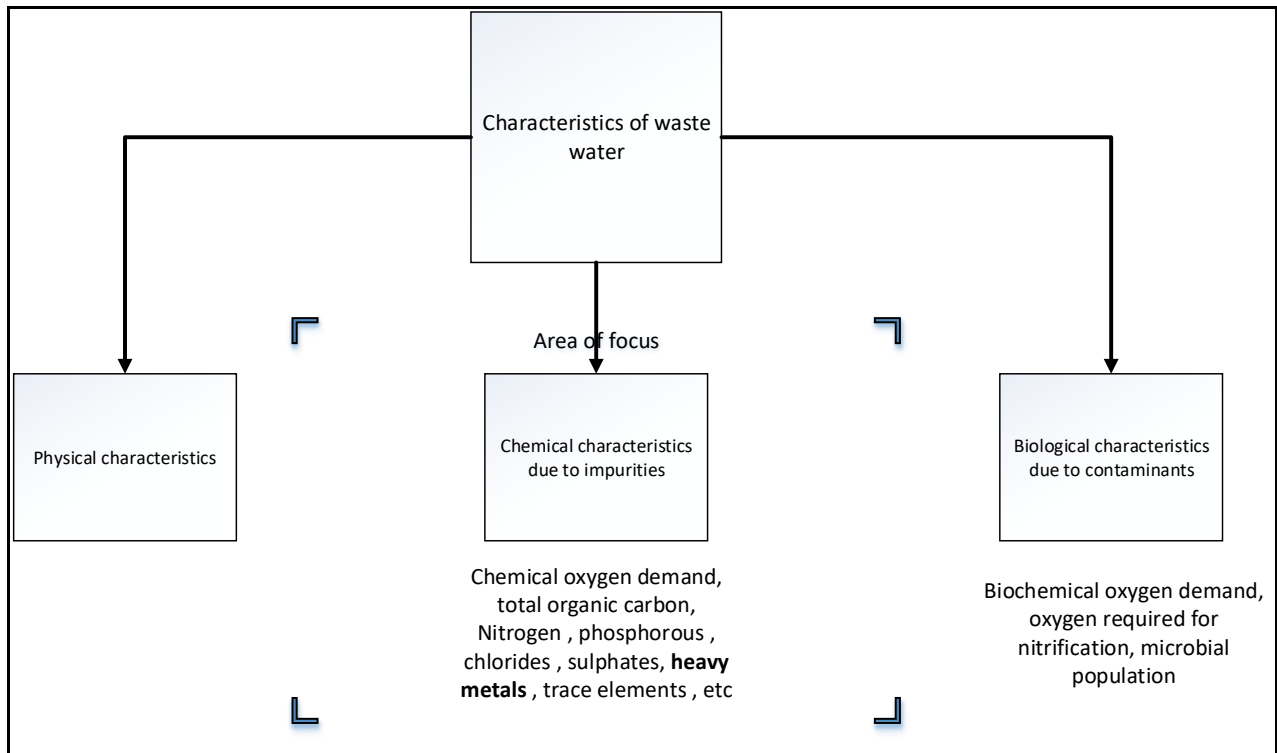


Figure 2.1: Characteristics of wastewater (Ngah et al., 2008).

The study will focus more on the chemical properties, specifically on heavy metals from wastewater. The wastewater with heavy metals is predominantly found in acid mine drainages.

2.1.1 Acid mine drainage

The acid mine drainage (AMD) is typically characterised with low pH, high sulphates, and high concentrations of dissolved heavy metals in form of ions such as Fe, Cu, Co, Cr, Mn, Zn and Cd (Ntwampe and Moothi, 2018). The concentration of heavy metals in AMD highly depends on the geochemical properties and degree of mineralisation in the mine tailings. According to past studies, Fe was found to be the most found metal with high concentrations up to 100 mg/L (Ntwampe and Moothi, 2018). Fe is also quite easy to recognise through the orange precipitates (Fe^{3+}) as shown in Figure 2.2.



Figure 2.2: AMD characteristic with high concentrations of Fe (Musapatika et al., 2010)

The discharge of heavy metals to the environment is mainly through ore processing and discharge of mine tailings. Heavy metals sources can be iron sulphide minerals such as pyrite (FeS_2), pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$), chalcopyrite (CuFeS_2), arsenopyrite (FeAsS), sphalerite (ZnS) and galena (PbS) (Musapatika et al., 2010).

2.1.2 Impacts of wastewater

The use of heavy metals has increased in the past decade. Thus, resulting inevitably in the increase of heavy metals discharge to the environment (Nghah et al., 2005; Nghah and Koay, 2004). Heavy metals can easily rank high among in toxicity compared to other contaminants due to their non-biodegradability (Hatar et al., 2013). This means that a continuous discharge of heavy metals to the environment will cause bioaccumulation in the living cells. When heavy metals exceed recommended concentrations in the human body, they can cause a serious and severe and neurological damage in the human body (Hatar et al., 2013).

2.2 Current techniques used for the removal of heavy metals from wastewater

2.2.1 Membrane bioreactor techniques

Membrane bioreactors (MBR) are an activated sludge system with a sludge/water separation step that takes place via micro/ultra-filtration membranes. The use of membrane technology for the removal of heavy metals can be quite expensive. The application of the membrane technology for bio-treatment of wastewaters was first reported in 1996 (Brindle et al., 1996). There were various studies that came after to incrementally improve the use of membrane technology in bio-treatments.

Brindle (1996) further stated the main limitations found in Membrane bioreactor systems which are:

- Operational problems associated with the cleaning and reusability of membranes.
- Very high capital and operational costs.
- Elevated energy consumption due to an increase of endogen respiration in the reactor, and the aeration and recirculation required for membranes.

2.2.2 Chemical precipitation techniques

Chemical precipitation is the addition of chemicals to water bind with metal compounds in a form of precipitate, which is subsequently removed by solid/liquid separation (Geets et al., 2004).

Forming a solid in precipitation involves two steps:

- Nucleation- the process by which dissolved species in supersaturated solution change from solution to a solid phase.
- Crystal growth- the subsequent growth of nuclei that succeed in achieving the critical cluster size.

Equilibrium position is very important as the technique requires engineering the process to shift its equilibrium position to insoluble forms. Precipitation is very dependent on solubility which is also a function of temperature and pH (Geets et al., 2004).

The disadvantages of chemical precipitation are the chemical consumption and subsequent formation of the sludge.

2.2.3 Oxidative techniques

Oxidative techniques are used to crack heavy metals with the aid of a strong oxidising agent such as hydrogen peroxide. Chemical oxidation can remove heavy metals, reducing them to a very low concentration (Karavaiko and Moshniakova, 1971).

The major downfall for the oxidative techniques is the formation of the by-products and their possible toxicity. In addition to that, the oxidative techniques prove to be very costly.

2.2.4 Adsorption Techniques

Introduction

Adsorption is the attachment of substances in solution to a fixed surface. Activated carbon is widely used for the removal of the heavy metals (Khulbe and Matsuura, 2018).

Adsorption media is chosen based on:

- Selectivity for the desired heavy metal removed.
- Large surface area for adsorption.
- Easy stripping for adsorbed metal(s) under controlled conditions.

Currently, adsorption is regarded as the most favourable technique to remove heavy metals from water, but the commonly used adsorbents such as activated carbon have low adsorption capacities, poor elective sorption and poor regeneration ability (Khulbe and Matsuura, 2018).

Mass transfer in adsorption

Mass transfer gives an extensive application of chemical engineering separation process, where mass balance on components is performed. The mass transfer gives us an idea of the rate limiting step which will ultimately determine the overall rate of the process (Girish and Murty, 2015). Adsorption is a time-dependent process in the removal of heavy metals from wastewater. The rate at which adsorption happens is pivotal in design, control and the evaluation of the adsorbent (Cooney,1998).

The adsorption of heavy metals from wastewater process is summarised in three steps below:

- The transportation of metal ions in solution from bulk solution to the film.
- Internal diffusion from the film to the adsorbent pores.
- Adsorption of the metal ions on the surface of the adsorbent through binding the ions to the active sites.

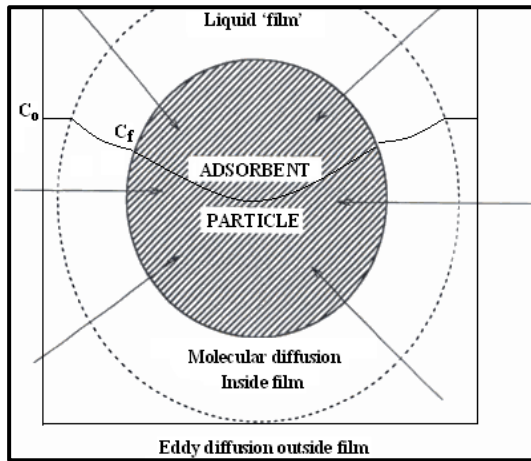


Figure 2.3: Schematic view of the adsorbent particle in solution (Cooney, 1998)

Figure 2.3 shows that there are mainly two mass transfer resistance types, which are internal and external diffusion. The rate determining step depends on a couple of factors, but not limited to the following:

- Particle size of the adsorbent.
- Degree of mixing.
- Concentration gradient.

Literature shows that external transport is usually the rate limiting step for a system with poor degree of mixing and low concentration gradient (Girish and Murty, 2015).

2.3 The use of chitosan and bentonite in the removal of heavy metals from waste waters.

Due to the higher adsorption capacities of synthesised polymers or biopolymers with special functional groups (e.g. amine groups) there has been an interest to look at polymer membranes for removal of heavy metals.

Chitosan coated bentonite beads act as an adsorbent to remove heavy metals from wastewater. The adsorbent is made from connecting functional groups attached to the surface and the pore wall of the polymer membrane. The functional groups selectively bind and target the heavy metals in wastewater when the water passes through the permeable membrane (Zhang et al., 2014)

Chitin and chitosan are valuable natural biopolymers derived from number of different marine and terrestrial sources (Muzzarelli, 1997; Shahidi et al., 1999). For example, crab shells consist of chitin (15-20%), protein, and calcium carbonate. The product was first discovered in the 1800s, but its

importance was materialised in the 1970s when fishing companies were prevented from dumping shells of crabs and lobsters in the sea (Muzzarelli, 1997; Shahidi et al., 1999).

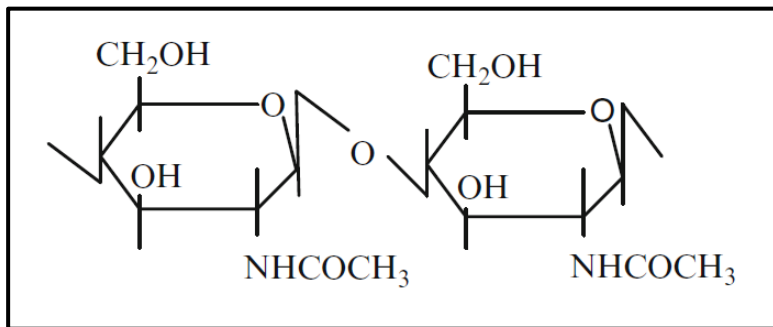


Figure 2.4 : Chitin chemical structure (Muzzarelli, 1977; Shahidi et al., 1999).

Chitin (β -1, 4-poly- N -acetyl- D -glucosamine) is the second most plentiful natural polymer after cellulose on earth (Muzzarelli, 1977; Shahidi et al., 1999). Figure 2.4 illustrates that chitin is composed of three functional groups, an amino group and C-2 position, primary hydroxyl group at C-3 position and secondary hydroxyl group at the C-6 position (Furusaki et al., 1996; Roberts, 2008).

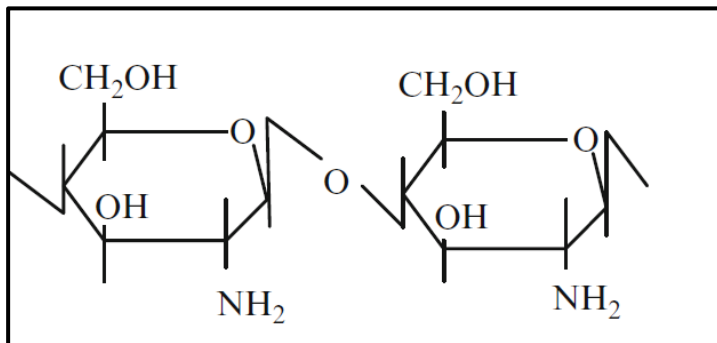


Figure 2.5: Chitosan chemical structure (Muzzarelli, 1977; Shahidi et al., 1999).

Chitosan is a low acetyl-substituted form of chitin and is composed primarily of glucosamine known as (1–4)-2-amino-2-deoxy- β - D -glucose as illustrated in Figure 2.5 (Furusaki et al., 1996; Roberts, 2008).

2.3.1 Interaction of chitosan with metal ions in wastewaters

The application of chitosan has been extensively investigated as adsorbents for the removal of metal ions from water and wastewater. According to Muzzarelli, (1997) chitosan has a high adsorption potential which can be attributed to:

- Various functional groups in the polymer.
- High chemical reactivity of the functional groups.
- High hydrophilicity due to large number of hydroxyl groups of glucose units.
- Flexible polymer chain structure.

Chitosan can be used as an adsorbent, either by using the reactive functional sites which adsorb metal ions by forming a surface complex or via ion exchange mechanism. Reusability is a very important factor that determines the process economy where process cost can be massively reduced by using an adsorption membrane with a favourable regeneration capacity (Muzzarelli, 1997; Shahidi et al., 1999).

The use of Chitosan in the removal of heavy metals has drawn much attention due to a few attributes amongst many such as:

- The low cost it has compared to other adsorbents (e.g. activated carbon) because it is a naturally occurring biopolymer in abundance.
- The high adsorption potential.
- Biocompatibility and admirable biodegradability with ecological safety.
- The low toxicity with versatile biological activities such as low immunogenicity.

Work previously done has proved chitosan's potential in removing heavy metals, by mostly focusing on the adsorption potential of chitosan flakes. The Cu-chitosan interaction is by far the most studied metal ion -chitosan system. Chitosan has showed excellent ability to adsorb Cu (II) with a capacity of 1.8-2.2-mmol/g dry mass (Bhatnagar and Sillanpaa, 2009).

Figure 2.6 shows that Cu (II) coordination with amine groups and anions. Rhazi et al (2002) proposed that there are two different stable complexes ($[\text{Cu}(-\text{NH}_2)]^{2+}, 2\text{OH}^-, \text{H}_2\text{O}$) in the pH range from 5 to 5.8, and ($[\text{Cu}(-\text{NH}_2)_2]^{2+}, 2\text{OH}^-$) is more stable for pH values above 5.8.

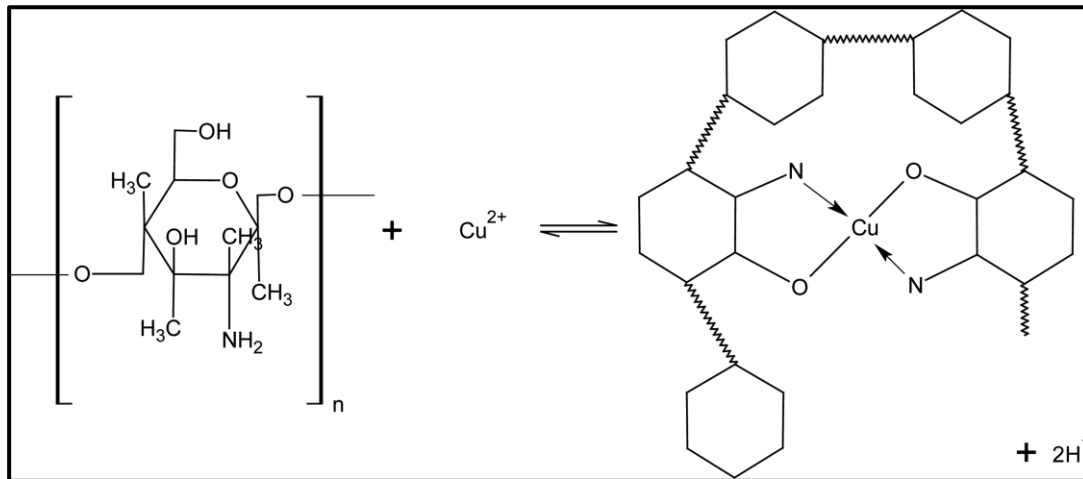


Figure 2.6: Formation of chelates with Cu ions (Muzzarelli, 1977; Shahidi et al., 1999).

This proves that there are factors that affect the chelation mechanisms of chitosan-metal ion systems (Gerente et al., 2007).

The range of factors that affect the mechanisms of chitosan metal-ion systems includes:

- The pH of the solution.
- Speciation.
- Physical form of chitosan.
- Metal ion selectivity.
- Degree of deacetylation.

Some of the factors are going to be observed in the review through characterising and evaluating synthesised chitosan-bentonite membranes, to check how the chelation of metal ion-chitosan system can be maximised.

2.3.2 Chitosan bentonite complex

Bentonites are mostly composed of montmorillonite and other clay minerals. Bentonite clay (hydrated aluminium silicate) has proved to be a very efficient at removing metals such as copper, zinc, lead and cadmium in solutions (Khalek et al., 2012). The challenge is that it is not easy to separate the suspended fine solids of bentonite from aqueous solution (Choi, 2008). The solution to that would be binding bentonite with a polymer in this case which would be chitosan.

Polymer/clay blends have attracted extensive interest due to some attributes such as:

- Improved storage modulus.
- Decreased thermal expansion coefficients.
- Reduced gas permeability.
- Enhanced ionic conductivity because of increased interfacial surface area (Khalek et al., 2012).

There are limited known studies that have looked at the use of bentonite clay blending with polymers (chitosan in this case). This review also looks at the effect of bentonite composition in the chitosan coated bentonite beads for removal of heavy metals from wastewaters.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Introduction

Chapter Three is material and methods, which includes the gathering of materials, experimental design and analytical methods that were used to achieve the research objectives. The output of the section is experimental data that can be used to draw conclusions and recommendations for the study.

3.2 Materials and reagents

Low molecular weight chitosan with 75% to 85 % degree of deacetylation and bentonite were procured from Merck. Heavy metals were obtained in the form of metal salts, i.e., $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The two elements were chosen amongst other heavy metals because of their abundance in industrial effluents particularly acid mine drainages (Ngah et al., 2005; Ngah and Koay, 2004). All the solutions were diluted with deionized water.

3.3 Synthesis of wastewater

Synthetic wastewater was made to represent acid mine drainage. Acid mine drainage is characterized by high concentrations of sulphates and low pH. This comes from the oxidation of mineral ores, particularly iron pyrite, which is the main source of acid mine drainage (Hatar et al., 2013). The metals investigated were selected based on the abundance in the acid mine drainage, since the metal concentration build up results in toxicity (Ngah et al., 2005; Ngah and Koay, 2004). Synthetic wastewater was chosen for this study to simplify the analysis of the effectiveness of chitosan coated bentonite beads in removing heavy metals from wastewater. Real waste water samples were going to include other complexities such as competitive adsorption if there are many metals. The wastewater was simulated within ranges of real AMD metal concentrations and solution. Appropriate guidance was taken from AMD characterisation studies done by Smith et al., (2021) with samples from Mpumalanga South Africa.

All the solutions were prepared using deionized water. A measured amount of metal salt was dissolved in deionized water to make 1000 mg/L, Therefore, all the aqueous stock solutions made

contained 1000 mg/L of metal ions. Sample calculations on how to calculate the metal salts amounts are shown in Appendix A.

3.4 Experimental methods

3.4.1 Design of experiments

Three aims of this study can be summarised as:

- Synthesis of the chitosan coated bentonite beads to be used for the removal of heavy metals from wastewater.
- Characterization the chitosan coated bentonite beads with the focus on:
 - Morphology.
 - Mechanical and thermal properties.
- Evaluation of chitosan coated bentonite beads using adsorption tests.

The experiments were designed in such a way that the three aims were sufficiently met. The experimental methods were divided into three parts, the synthesis of chitosan coated bentonite beads, characterization of chitosan coated bentonite beads and evaluation of chitosan coated bentonite beads.

3.4.2 Synthesis of chitosan coated bentonite beads

Introduction

The chitosan coated bentonite beads were synthesized, to use them to remove heavy metals from the synthetic wastewater. The chitosan coated bentonite beads were made by varying the chitosan to bentonite ratio to determine the optimum ratio which gives a better adsorption capacity.

Experimental procedure

Figure 3.1 conceptually shows the process used to synthesize the chitosan coated bentonite beads.

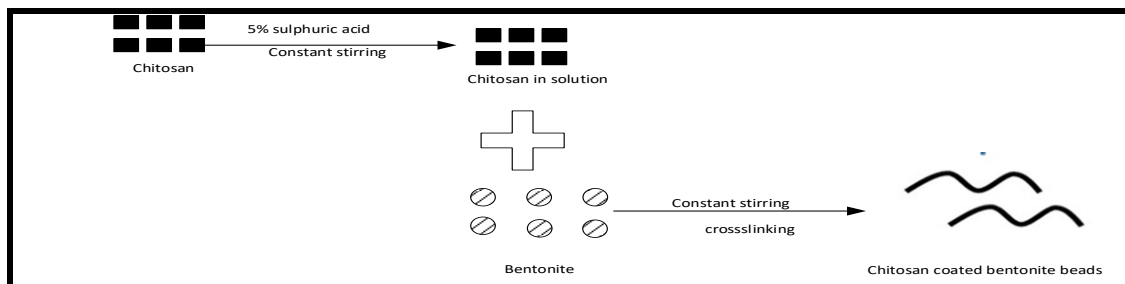


Figure 3.1: Synthesis of chitosan coated bentonite beads

A measured amount of low molecular weight chitosan was dissolved in a 250 mL Erlenmeyer flask containing 150 mL 5 % (v/v) H₂SO₄ solution. The solution was stirred at a constant rate of 300 rpm using a laboratory shaker for 2 hours at room temperature, which was enough time for the chitosan to dissolve (Kumar et al., 2020). A measured amount of bentonite was then added and then mixed for 3 hours under constant stirring of 300rpm using a laboratory shaker at room temperature (Kumar et al., 2020).

Figure 3.2 shows the prepared chitosan-bentonite solutions under constant stirring to ensure enough crosslinking.



Figure 3.2: Crosslinking of chitosan and bentonite under constant stirring in a shaker

The chitosan to bentonite composition was varied as specified in Table 3.1. The table shows a design to vary chitosan and bentonite amounts in the chitosan coated bentonite beads.

Table 3.1: Chitosan and Bentonite weight variation in chitosan coated bentonite beads (CCB).

<i>Chitosan coated bentonite beads (CCB_n)</i>	<i>Chitosan(g)</i>	<i>Bentonite (g)</i>	<i>Chitosan % in chitosan coated bentonite beads</i>
<i>CCB₁</i>	2	3	40
<i>CCB₂</i>	3	3	50
<i>CCB₃</i>	5	3	62.5
<i>CCB₄</i>	2	2	50
<i>CCB₅</i>	2	1	66.7
<i>CCB₆</i>	2	0	100

The resulting chitosan-bentonite solution was neutralised with 1 M NaOH, which was added drop by drop as shown in Figure 3.3, until precipitation of bentonite bead was achieved. It is known that chitosan is soluble in weak acidic conditions and insoluble in alkaline conditions (Dalida et al., 2010). The chitosan coated bentonite beads were allowed to settle and then they were filtered out from the solution. The chitosan to bentonite amounts and ratios were selected based on previous studies as well as trial and error (Dalida et al., 2010; Kumar et al., 2020; Ngah et al., 2005). Feasibility studies on the formation of beads were also conducted to verify the amounts and ratios of chitosan to bentonite. It was also determined that the extreme end of bentonite alone was impossible as it was impossible to form beads with bentonite alone. Bentonite simply goes into the water forming a murky mixture.



Figure 3.3: The precipitation of chitosan bentonite beads by dropping NaOH into the chitosan bentonite mixture

The resulting chitosan coated bentonite beads were thoroughly washed with deionized water to remove any impurities and excess NaOH. Figure 3.3 also shows the chitosan coated bentonite beads in a tray ready to be dried in an oven at 65 °C for 24 hours to remove all the water in the beads (Kumar et al., 2020).

After drying, the chitosan coated bentonite beads were pulverised to a range of 0.35 to 0.70 mm (Kumar et al., 2020).

3.4.3 Characterisation tests

Introduction

Characterisation tests were conducted to determine the surface morphology, chemical and mechanical properties of the chitosan coated bentonite beads. The prepared chitosan coated bentonite beads were characterised using the Fourier transform spectroscopy (FT-IR) for its functional group identification and scanning electron microscope for its surface morphology. Swelling tests were done to determine the mechanical strength of the beads. The degree of swelling

assists, in this case, to predict which samples of beads will have a better adsorption capacity. Swelling provides an increase in pore size, allowing adsorbate ion to penetrate through the pores more ease, thus better adsorption efficiency (Paul and Sharma, 2009).

Experimental procedure

Fourier-transform infrared: Samples of chitosan coated bentonite were pulverised to ensure homogenization. The optically clear beads were mounted on the FT-IR spectrometer system and analysed using the FT-IR spectrometer system. The FT-IR spectra were produced at room temperature and the functional groups present in the chitosan coated bentonite beads were determined.

Scanning electron microscope analysis: The surface morphology of the chitosan coated bentonite beads was determined using the SEM analysis. The surface appearance, shape and size of scanning electron micrograms are useful to perform textural characterisation of full and cross sectioned adsorption beads. The SEM analysis uses a focussed high energy electron beam to produce a variety of signals on the surface of solid samples. The SEM analysis provided information on the internal structure of the different samples of beads. The interior spaces confirm the spaces available for adsorption.

The chitosan coated bentonite beads surface and the internal morphology with their shape were analysed using a SEM system within a voltage range from 4kV to 30kV. Pulverised samples in a sample size ranging from 400 to 500 microns were mounted with a double coating of carbon to eliminate charging which compromises the image quality. The double coating was later done after the single carbon coating gave a lot of charging due the negative charge from the chitosan coated beads. Magnifications ranging from 500 X and 2000 X were used for estimating the exterior and interior of the chitosan coated bentonite beads.

Swelling: The chitosan coated bentonite beads of the same sizes were dried to a constant weight (X_0) and then soaked in deionized water for 24 hours to ensure maximum swelling results (Vaishali and Sharma 2018). The beads were taken out and wiped with a filter paper to remove surface

moisture. The chitosan coated bentonite beads were then weighed, and the weight was recorded as X_t . The degree of swelling was calculated using the Equation 1 (Vaishali and Sharma, 2018).

$$\text{degree of swelling} = (X_t - X_o)/X_o \quad (1)$$

3.4.4 Adsorption tests

Introduction

The adsorption experiments were used to evaluate the prepared chitosan coated bentonite beads. The chitosan to bentonite ratio and initial pH were chosen as independent variables and the adsorption capacity as the dependent output response variable. The 2^3 -factorial design was utilised with a minimum of 8 experimental points and replicated to eliminate error in the estimation procedure. Table 3.2 shows a full experimental design indicating all the test parameters.

Table 3.2: Experimental design for evaluating the chitosan coated bentonite beads

Test type	Test parameters	Replicates	Sample tested
Repeatability	<ul style="list-style-type: none"> • CCB₃ • pH 4 • C₀ = 100 mg/L 	2	Metal concentration (C _t)
Effects of chitosan/bentonite composition.	<ul style="list-style-type: none"> • CCB₁, CCB₂, CCB₃, CCB₄, CCB₅, CCB₆ • pH 4 • C₀ = 100 mg/L 	1	Metal concentration (C _t)
Effect of pH	<ul style="list-style-type: none"> • CCB₁ • pH 3, pH 4, pH6 • C₀ = 100 mg/L 	1	Metal concentration (C _t)

Experimental procedure

Adsorption experiments were carried out in batch set ups. Adsorbent (chitosan coated bentonite beads) weighing 1g per sample was put into a 250 mL Erlenmeyer flask containing 150 mL of synthetic wastewater. Initial pH was set when the adsorbent was already in the 250 Erlenmeyer flask for accuracy. In as much as the beads were washed for excess NaOH, some NaOH were left within

the beads, which raises the solution pH when the beads start releasing the OH⁻ ions. The initial solution pH was adjusted accordingly for the experimental run according to the experimental design.

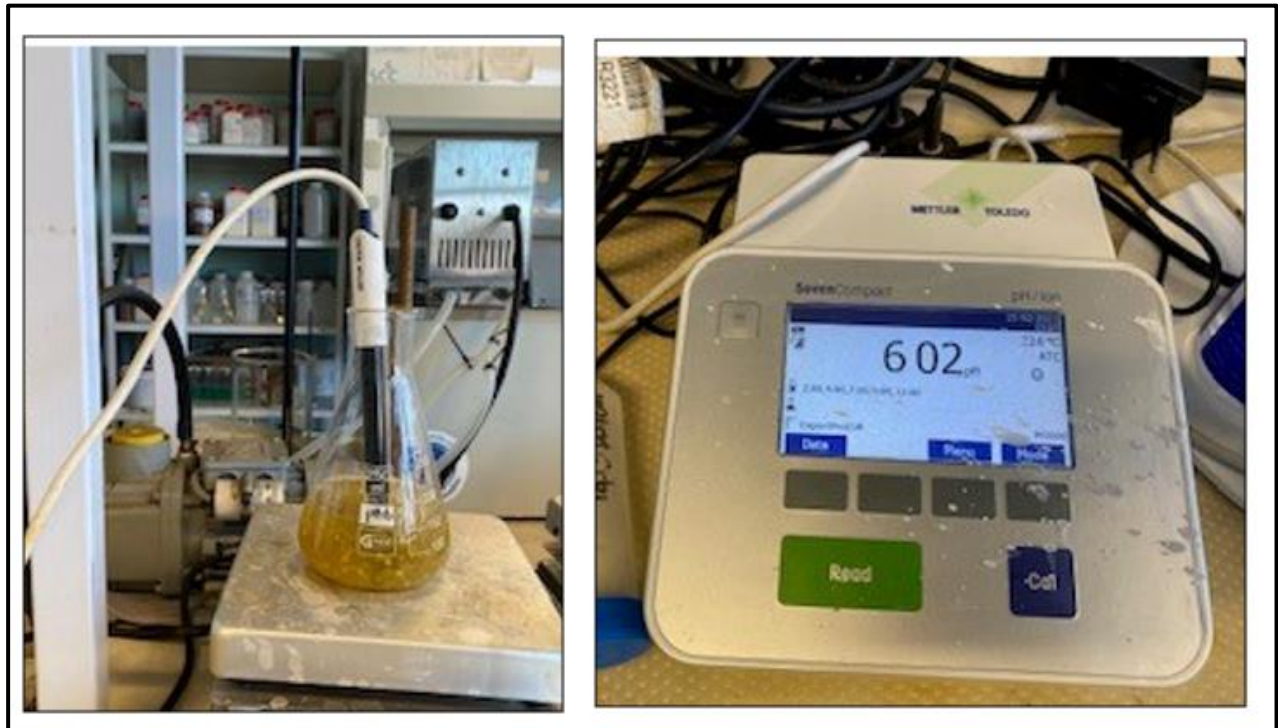


Figure 3.4: Setting of the initial pH and monitoring of pH

The Erlenmeyer flasks were covered with a parafilm and agitated at 150 rpm using a laboratory shaker so as to ensure sufficient mixing (Paul, and Sharma, 2009). Samples were taken at hourly intervals for a total adsorption time of 6 hours, since equilibrium is reached at approximately 6 hours (Paul, and Sharma, 2009).

The samples were collected for analysis using the atomic absorption spectrometer which gives the metal concentrations. Equation 2 shows the calculation of the chitosan coated bentonite beads adsorption capacity (q_e) in mg/g.

$$q = (C_0 - C_t)V/1000 \times W \quad (2)$$

Where the C_0 (mg/L) is the initial metal concentration, C_t (mg/L) is the final metal concentration. V (mL) is the volume of the synthetic solution and W (g) is the measured weight of the chitosan coated bentonite beads.

CHAPTER FOUR

CHARACTERISATION OF CHITOSAN COATED BENTONITE BEADS

4.1 Scanning electron microscopy analysis

4.1.1 *Introduction*

Scanning electron microscopy analysis was used to examine the surface morphology of the chitosan coated beads. Prior to the analysis, the chitosan coated bentonite beads samples were double coated with carbon to reduce charging.

4.1.2 Results and discussion

The images shown in Figure 4.1 exhibits the SEM images from the chitosan coated bentonite beads.

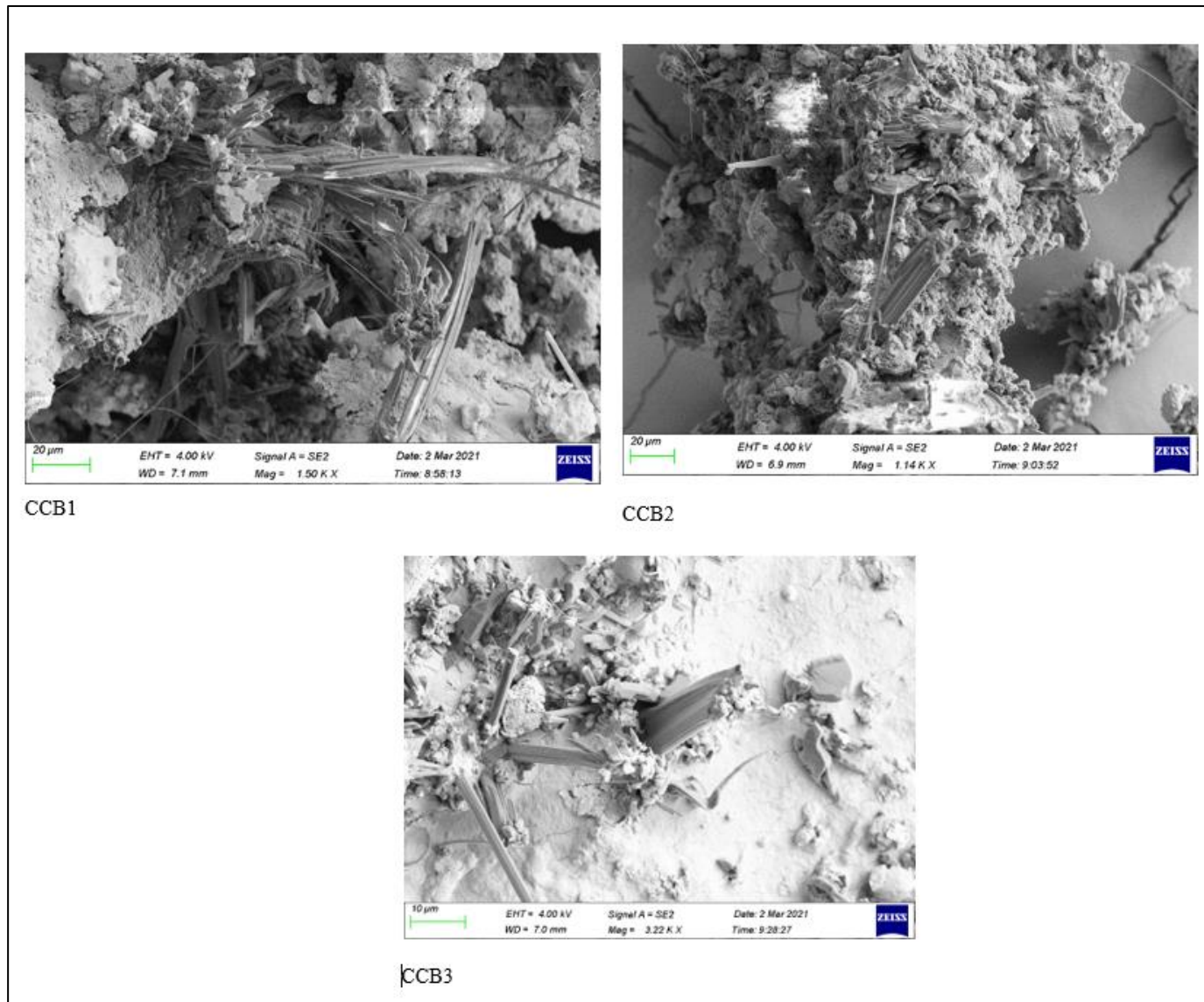


Figure 4.1: SEM micrographs of chitosan coated bentonite beads CCB₁, CCB₂, and CCB₃.

The images clearly show the internal structure of the beads with their magnification. The interior of the beads appears to have micropores and tube like micro interior space. The images also exhibit a rough, rubbery fibrous and protrusions surface. The surface properties shown by the images confirm high porosity of the polymeric beads as similarly discussed by Chen et al. (2013).

The chitosan composition differs in CCB₁, CCB₂ and CCB₃, and increases from CCB₁ to CCB₃. CCB₃ appears to be more fibrous than CCB₁ and CCB₂ indicating the high presence of tube like

micropores. Increase of chitosan would increase the polymetric nature of the beads and potentially increasing the porosity and provision of more active sited for adsorption. It can also clearly be seen that as the chitosan is added the beads roughness becomes to decrease, which shows the importance of enough bentonite in the beads for optimal adsorption surface area. In a study done by Vaishali and Sharma (2018) , SEM images for chitosan crosslinked with bentonite showed a rough, rubbery fibrous and folded surfaces with wrinkle which is in agreement with the findings of this study.

The figure 4.2 shows the CCB₅ bead which has chitosan and bentonite and CCB₆ which has pure chitosan.

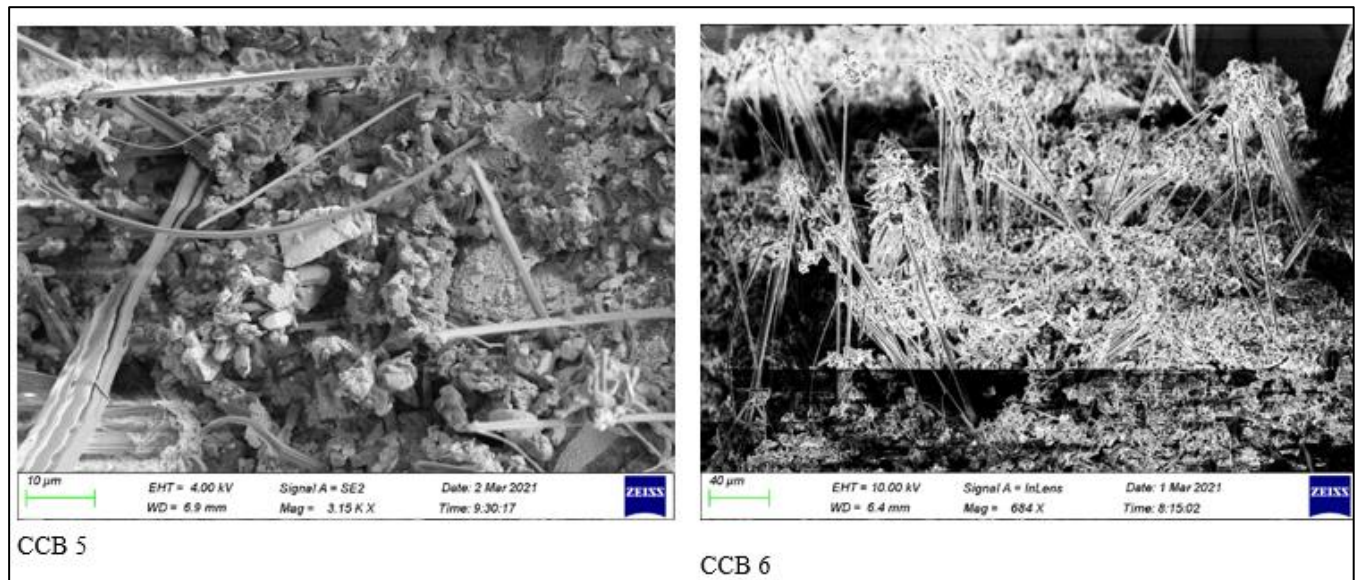


Figure 4.2: SEM micrographs of chitosan coated bentonite beads CCB₅ and CCB₆.

Figure 4.2 shows CCB₅ which is a coated chitosan coated bentonite beads sample where CCB₆ is pure chitosan. From the SEM images, the CCB₅ appears to exhibit more interior surface roughness as compared to CCB₆. The CCB₆ shows more of the tube-like micro interior space.

Both images show that the two samples are equipped for adsorption, but the combination of chitosan and bentonite will give the adsorbent both good chemical and physical properties. This observation concurs with previous studies that the presence of bentonite in the chitosan coated bentonite beads gives the adsorbent good physical properties which ultimately gives a good adsorption capacity as well (Chen et al., 2013; Khalek et al., 2012; Nesic et al., 2012).

4.2 Fourier-Transform Infrared

4.2.1 Introduction

The FT-IR spectra data was plotted to determine the vibration frequency differences in the functional groups of the adsorbent. The understanding of functional groups present in the adsorbent is key as it determines the mechanism of heavy metals that are binding to the adsorbent. Raw data for all the FI-TR spectra in this section is found in Appendix B.

4.2.2 Results

The FT-IR spectra is shown in Figure 4.3. Several peaks in the plot shows the complex nature of chitosan coated bentonite beads.

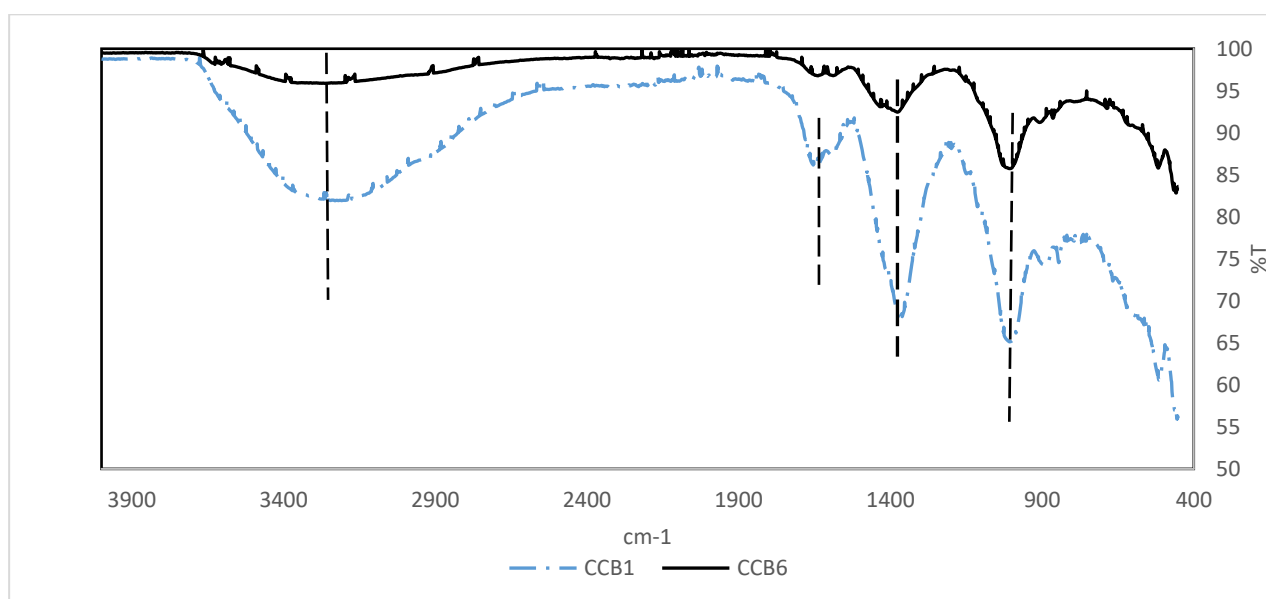


Figure 4.3: FT-IR spectra of pure chitosan and chitosan coated bentonite beads, CCB₁ and CCB₂

Figure 4.3 shows a comparison between the pure chitosan (CCB₆) and chitosan coated bentonite beads (CCB₁). The peaks that appear at range between 3000 and 3600 cm⁻¹ on both curves due to the overlap stretching shows the presence of O-H and NH₂ functional groups. It is also quite evident that both samples possess C=O group which is seen at the peak of 1600 cm⁻¹. The FT-IR spectra shows other linkages including C=O, C-O-H and C-O-C are attained at ranges between 1000 and 1100 cm⁻¹. The presence of bentonite in CCB₁ will show that bentonite has other functional groups that include a significant presence of Si-O linkages at range between 700 and 900 cm⁻¹. Other groups that show the presence of bentonite are Al-O and Si-O-Al which was attained at a vibration

band of 983 cm⁻¹ and 476 cm⁻¹. When looking at the functional groups present, the chitosan coated bentonite beads show a good formation. In a study done by Roberts (2008) shows similar functional groups as found in this study. The presence of bentonite adds more complexity and more vibration in the curve.

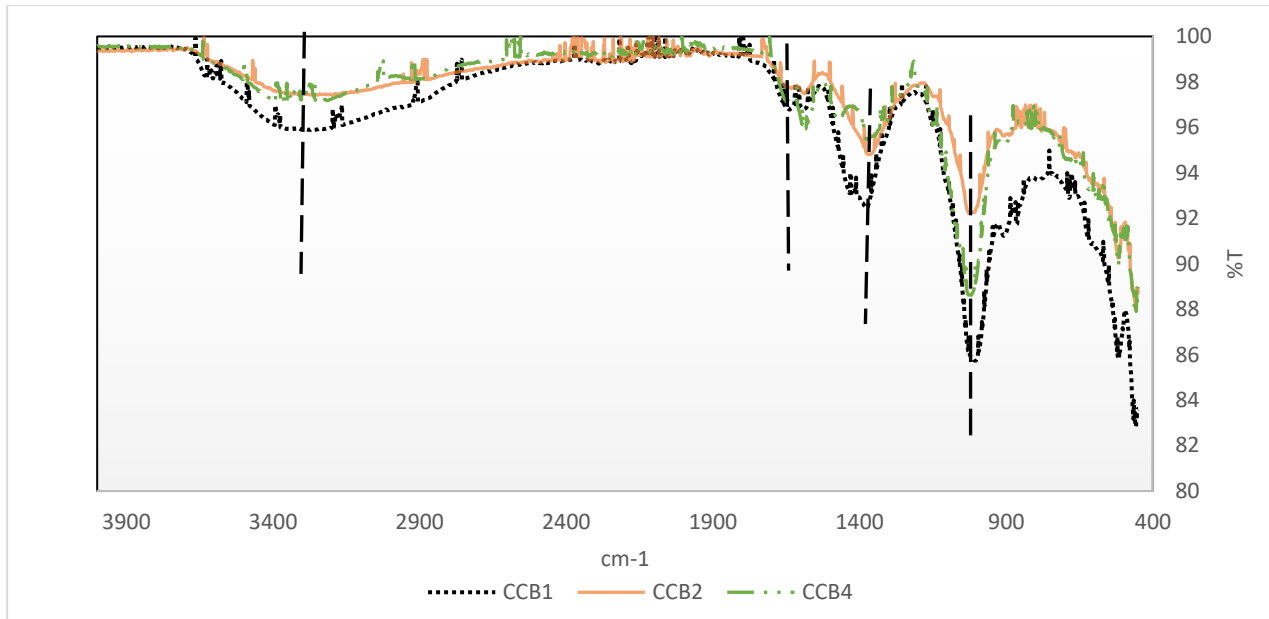


Figure 4.4: FT-IR of chitosan coated bentonite beads, CCB₁, CCB₂, CCB₄

Figure 4.4 shows changes in functional groups by changing chitosan composition in chitosan coated bentonite beads (from CCB₁ to CCB₂), and changes in the bentonite composition (from CCB₄ to CCB₁). The curves indicate to us that the same functional groups shown in Figure 4.4 are the same which prove repeatability and uniformity in the samples. The curve introduces more vibration when moving from CCB₁ to CCB₂ which potentially depicts the intensity of presence of the major three functional groups (NH₂, O-H and C-O groups). The increase in bentonite from CCB₄ to CCB₂ shows an addition of complexity in the curve, potentially depicting increase in other functional groups e.g., Si-O, Al-O and Si-O-Al.

4.3 Swelling

4.3.1 Introduction

The water adsorption behaviour of chitosan coated bentonite beads (CCB₁, CCB₂, CCB₃, CCB₄, CCB₅, CCB₆) was carried out using the swelling tests. The swelling tests were all carried out at constant set conditions of pH 7, ambient conditions, and a total immersion time of 24 hours (Vaishali and Sharma 2018). Pre-feasibility experiments were conducted to determine the optimal swelling time, and it was obtained that no significant further swelling happens after 24 hours. The pH was kept at 7 to eliminate the effect of pH on the behaviour of the beads as the effect of pH was studied separately. Temperature was chosen to be at ambient condition and kept constant across all experiments of this studies.

4.3.2 Results and discussion

Figure 4.5 shows the different swelling rates for all the chitosan coated bentonite beads samples.

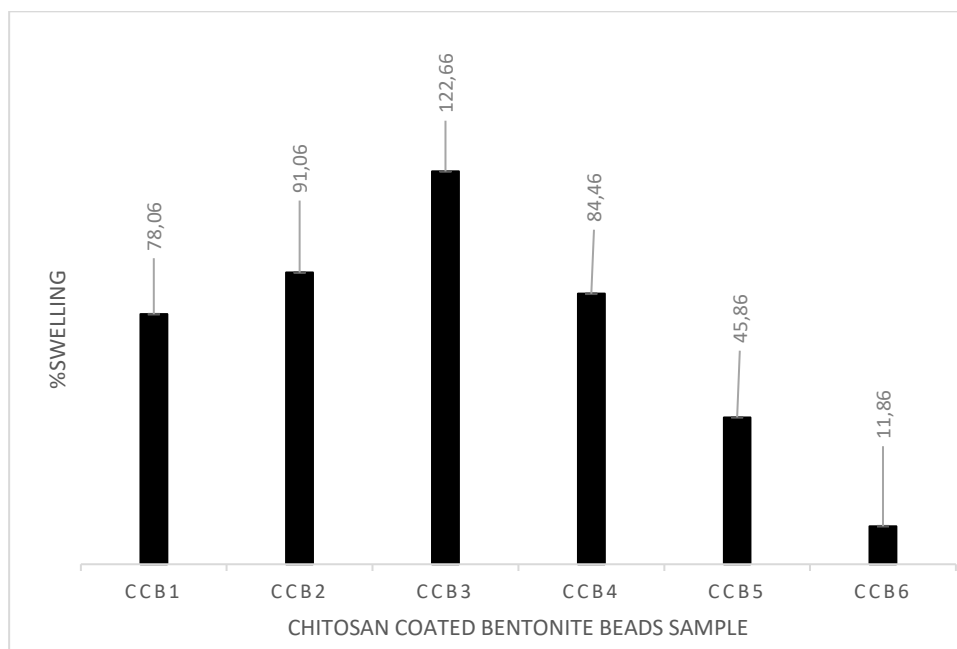


Figure 4.5: Swelling rates of chitosan coated bentonite beads [Temperature: 25 °C, 1 atm pressure, pH 7]

CCB₆ (100% chitosan) sample, which is pure chitosan showed the lowest swelling percentage, whereas CCB₃ (62.5% chitosan) sample showed the highest swelling percentage. In addition to that, observations on the dissolution of samples showed that the CCB₆ seemed to be slightly soluble as compared to the other samples which were completely insoluble.

The presence of bentonite in the chitosan coated bentonite beads evidently appeared to enhance the diffusion of water to the chitosan coated bentonite beads. Increase in chitosan from CCB₁ (40% chitosan) to CCB₃ (62.5% chitosan) proved to enhance the swelling behaviour of the beads. This could be explained by the fact that as more chitosan is added more NH₂ and OH groups become available to be protonated (Vaishali and Sharma 2018; Nesic et al., 2012). This effect will also mean that better swelling rates means better adsorption capacity. Further increase of chitosan % to 66.7% in CCB₅ proved to decrease the swelling behaviour. In conclusion, chitosan and bentonite complements each other to give a better adsorption capacity and, in this case, the optimal beads composition is 62.5% chitosan (CCB₃). In a characterisation of crosslinked chitosan and bentonite study by Vaishali and Sharma (2018) showed that the degree of swelling of crosslinked beads increased when the weight of chitosan was increased. The increase of chitosan weight decreased the crosslinker density and the diffusion of water into the beads becomes easier which resulted in higher degree of swelling. This agrees with this study which prove an increase in chitosan proved to enhance swelling behaviour of chitosan coated bentonite beads.

CHAPTER FIVE

EFFECT OF CHITOSAN: VARIATION OF CHITOSAN AND BENTONITE IN THE CHITOSAN COATED BENTONITE BEADS

5.1 Introduction

Chitosan and bentonite add different desirable physicochemical properties to the chitosan coated bentonite beads. The optimal blending of the two becomes quite pertinent to achieve the best adsorption capacity for the beads. The results presented in this section evaluate the prepared chitosan bentonite beads. The chitosan coated bentonite beads were prepared using different chitosan and bentonite amounts as shown in table 5.1. This was done to determine the optimal amounts of bentonite and chitosan in the chitosan coated bentonite beads.

Table 5.1: Variation of chitosan and bentonite composition in chitosan coated bentonite beads (pH =4, temperature = 25 °C, adsorbent dosage = 1g, Waste water volume = 150 ml with 80 mg/L Fe and 80 mg/L Cu).

<i>Chitosan coated bentonite beads (CCB_n)</i>	<i>Chitosan(g)</i>	<i>Bentonite (g)</i>	<i>Chitosan percentage (%)</i>
<i>CCB₁</i>	2	3	40
<i>CCB₂</i>	3	3	50
<i>CCB₃</i>	5	3	62.5
<i>CCB₄</i>	2	2	50
<i>CCB₅</i>	2	1	66.7
<i>CCB₆</i>	2	0	100

For the effect of chitosan and bentonite variation, pH was kept constant at pH 4 which is a common optimal pH in previous studies (Chen et al., 2013; Khalek et al., 2012; Nestic et al., 2012). Adsorption tests for all the chitosan coated bentonite beads samples were carried out to determine the adsorption capacity for each chitosan coated bentonite bead variation. The adsorption results for CCB₁, CCB₂, CCB₃ were used to determine the effect of varying the composition of chitosan in the chitosan coated bentonite beads. The adsorption results for CCB₅, CCB₄ and CCB₁ were used to

determine the effect of varying bentonite composition in the chitosan coated bentonite beads. Raw data used to determine results is found in Appendix B, and C and sample calculations for results calculations are in Appendix A.

5.2 Results and discussion

Adsorption capacity was plotted against adsorption time to determine the optimal amounts of chitosan and bentonite in the beads. Figures 5.1 and 5.2 show variation of chitosan composition in the chitosan coated bentonite beads.

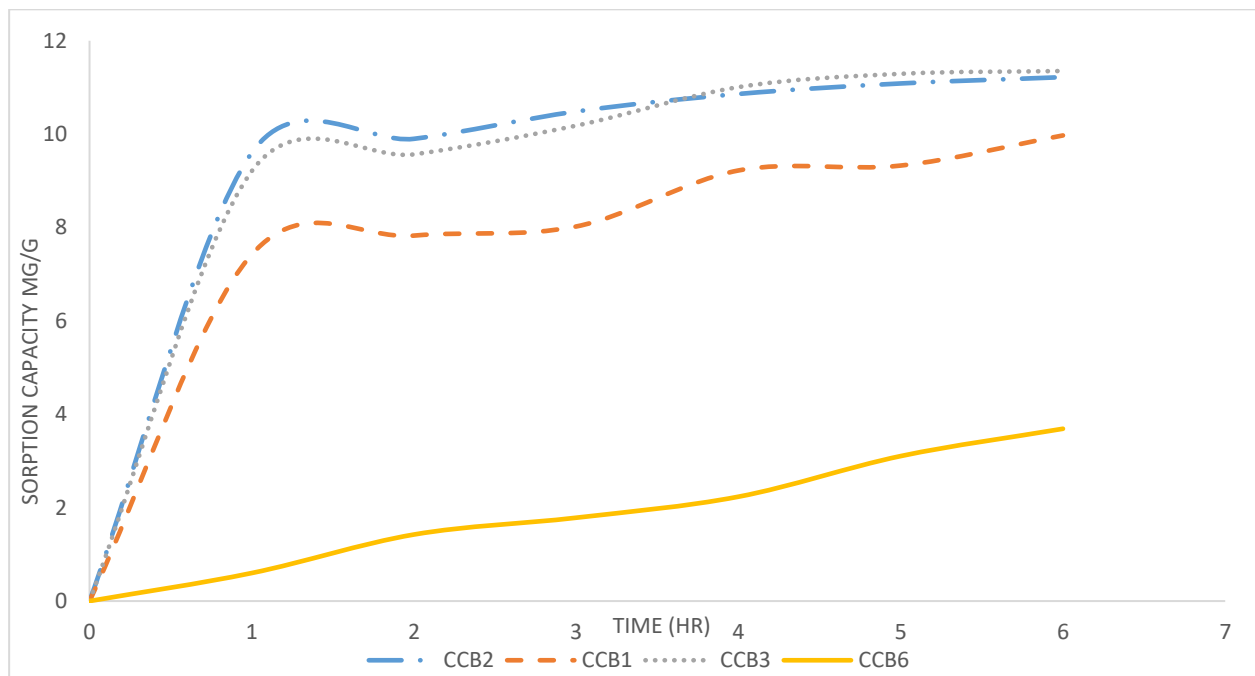


Figure 5.1: Effect of chitosan composition in the chitosan coated bentonite beads for the adsorption of Fe. pH =4, temperature = 25 °C, adsorbent dosage = 1g, Waste water volume = 150 ml with 80 mg/L Fe

For the iron adsorption, it shows an increase of adsorption capacity from the second hour when chitosan percentage was increased from 40% in CCB₁ to 50% in CCB₂. When the chitosan amount was further increased from 50% CCB to 62.5% in CCB₃, a slight increase in the adsorption capacity was observed. However, an increase in chitosan composition to 100% proved to decrease adsorption significantly. The use of pure chitosan for the adsorption of heavy metals has limitations due to its weak mechanical properties as well as instability in acidic media (Roberts, 2008).

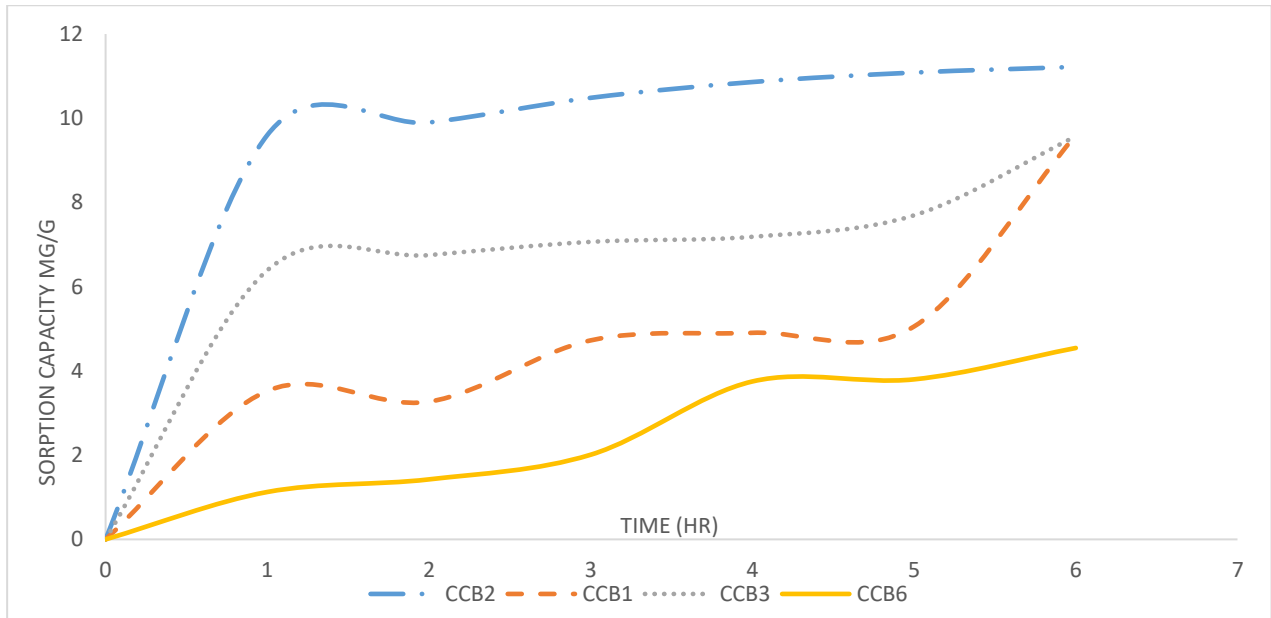
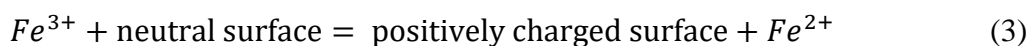


Figure 5.2 Effect of chitosan composition in the chitosan coated bentonite beads for the adsorption of Cu. pH =4, temperature = 25 °C, adsorbent dosage = 1g, Waste water volume = 150 ml with 80 mg/L Cu

Similarly, with Fe adsorption CCB₁ shows less adsorption capacity as compared to CCB₂. For the adsorption of Cu, a slightly different trend is observed, Further increase in chitosan composition in CCB₃ gave more adsorption capacity initially compared to CCB₁ but later ended up intersecting at the end. Further increase of chitosan composition from 50% to 62.5 % proved to decrease the adsorption capacity.

The chitosan coated adsorption beads can remove Cu and Fe at a maximum adsorption capacity of 12mg/g. Cu and Fe exhibit important interactions and possible competitive inhibition of transport and binding of the metal ions on the active sites (Reinstein et al., 1984; Brewer et al., 1985). The effect of chitosan shown to be more evident in Cu adsorption more than that in Fe adsorption. The effect of Cu/Fe's competitive inhibition could be the reason behind the suppression of chitosan's effect in the adsorption of Fe. Fe can also exist in Fe²⁺ and Fe³⁺, as shown in equation 3 below (Nourmohamadi et al., 2019).



The Fe²⁺/Fe³⁺ system can add complexities, making the adsorption surface positively charged, which means that the adsorption of the metal onto the adsorbent surface could be reduced. Figure

5.3 shows that an increase in the bentonite composition from CCB₅ (33% bentonite) to CCB₄ (50% bentonite) shows a very small impact on the adsorption capacity of Fe.

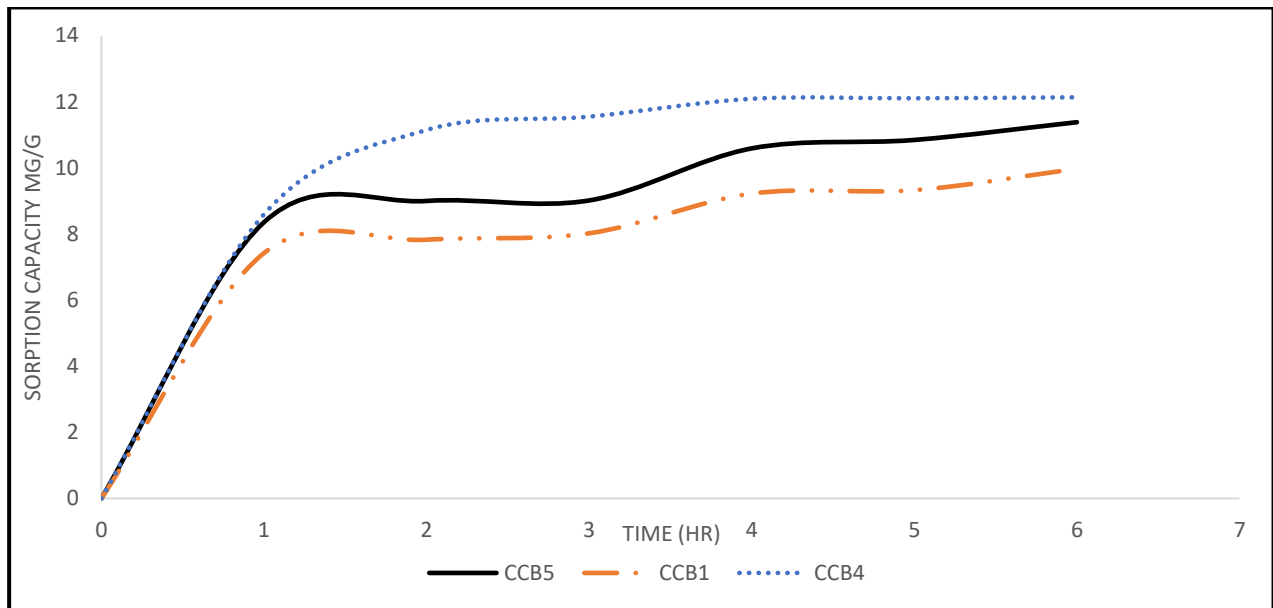


Figure 5.3: Effect bentonite in the chitosan coated bentonite beads on the adsorption of Fe. pH =4, temperature = 25 °C, adsorbent dosage = 1g, Waste water volume = 150 ml with 80 mg/L Fe

The limitations of chitosan are that it is very soluble in dilute organic acids and it agglomerates, forming a gel in aqueous solutions (Nghah et al., 2005). Bentonite adds to the physicochemical properties of the beads to transcend the limitations of chitosan. However, it is noted that a further increase in bentonite from CCB₄ (50% bentonite) to CCB₁ (60% bentonite) exhibits a decrease in the adsorption capacity. Too much of the bentonite has proven the possibility of adversely affecting the adsorption capacity of chitosan coated bentonite beads.

The trends found in this study proves that chitosan-bentonite compositions are a major factor in determining the optimal chitosan coated bentonite beads for the adsorption of heavy metals from wastewater. The two components (chitosan and bentonite) possess different physical and chemical properties which complement each other and can only be utilised if right the compositions are obtained. The study shows that iron and copper can be optimally adsorbed by a bead composition of 50% chitosan/bentonite. Khalek et al. (2012) argued that increasing bentonite content in a chitosan-bentonite composite on removal of Hg²⁺, Pb²⁺, and Cd²⁺ ions increased the removal of metal ions up to 10% after that a decrease occurred. The findings of Khalek et al. (2012) agrees

with this study that the composition of the two components plays a major role on the adsorption capacity of metal ions. Appropriate addition of the bentonite improves the polymeric networks which enhance adsorption, and the bentonite would reduce the production cost as it is significantly cheaper than chitosan (Cooney, 1998).

CHAPTER SIX

EFFECT OF INITIAL PH ON THE ADSORPTION CAPACITY OF CHITOSAN COATED BENTONITE BEADS

6.1 Introduction

The acidity of the solution is one of the most important factors affecting the adsorption process (Singha and Das, 2011). The initial pH of the chitosan coated adsorption beads – wastewater system was set at 2, 4 and 8. Other variables such as adsorbate dosage, temperature, and solution volume were kept constant. The pH was varied from a pH of 2 to pH 6, which gives a good range from acidic to slightly acidic since the acid mine drainage is abundantly found in acidic conditions. Appropriate guidance from previous researchers was also used in choosing the pH range (Singha and Das, 2011).

6.2 Results and discussion

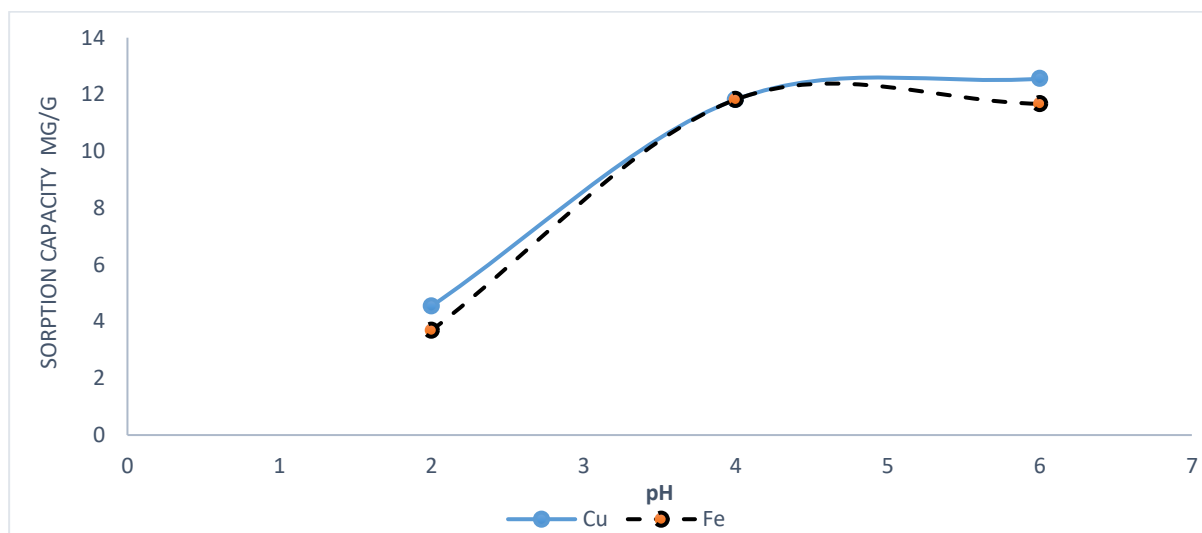
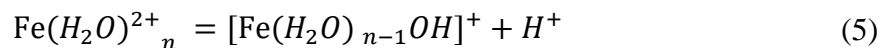
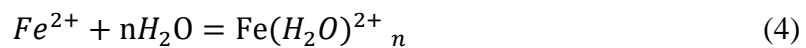


Figure 6.1: Effect pH on the adsorption capacity of chitosan coated bentonite beads CCB₂. Temperature = 273K, time of adsorption = 6 hours, adsorbent dosage = 1g, Waste water volume = 150 ml with 80 mg/L Fe and 80 mg/L Cu.

According to the Figure 6.1 that is showing the different trends for both Fe and Cu adsorption, at pH 2, the highest adsorption capacity recorded is 3.7 mg/g and 4.5 mg/g for Fe and Cu respectively.

When the pH was increased to 4, the highest adsorption capacity recorded was 11.8 mg/g for both Cu and Fe which shows a significant increase as pH increases. The increase in pH exhibited a greater affinity for metal ions towards the chitosan coated bentonite beads. The pH of the system determines the surface charge of the adsorbate, which effectively influences the degree of ionization and speciation (Nghah et al., 2005). At low pH the surface of adsorbate becomes protonated/ positively charged which triggers repulsion with the metal ions ($\text{Cu}^{2+}/\text{Fe}^{2+}/\text{Fe}^{3+}$). When the binding sites are protonated, this results in competition for adsorption between the H^+ ions and the $\text{Cu}^{2+}/\text{Fe}^{2+}/\text{Fe}^{3+}$ ions.

The functional groups present in the chitosan coated bentonite beads as observed through characterisation tests are mainly NH_2 , O-H, C-O-H and Si-O linkages. When the pH increases, these functional groups are activated hence causing an increase in the adsorption capacity. Naiya et al. (2009) points out that metal ions may undergo hydrolysis and solution in aqueous solution as shown by an equation 4:



The equations below show that the metal ions interaction with the aqueous solution can itself introduce H^+ ions to the system. The experimentation has shown that low pH values are undesirable for metal adoption. Setting the initial pH to higher values will be the best thing to do to counteract the proton effect.

The further increase of pH from 4 to 6 exhibited a slight dip in adsorption capacity from 11.8 mg/g to 11.7 mg/g for Fe. The same increase in pH exhibited a very slight increase in adsorption capacity from 11.8 mg/g to 12.6 mg/g for Cu. The result shows a lower of pH increase effect compared to the effect exhibited from increasing pH from 2 to 4. This could be a result of an

introduction of other factors that come with high pH values. According to Figure 6.2 when pH becomes greater than 4, Fe²⁺ and Fe³⁺ ions start precipitating.

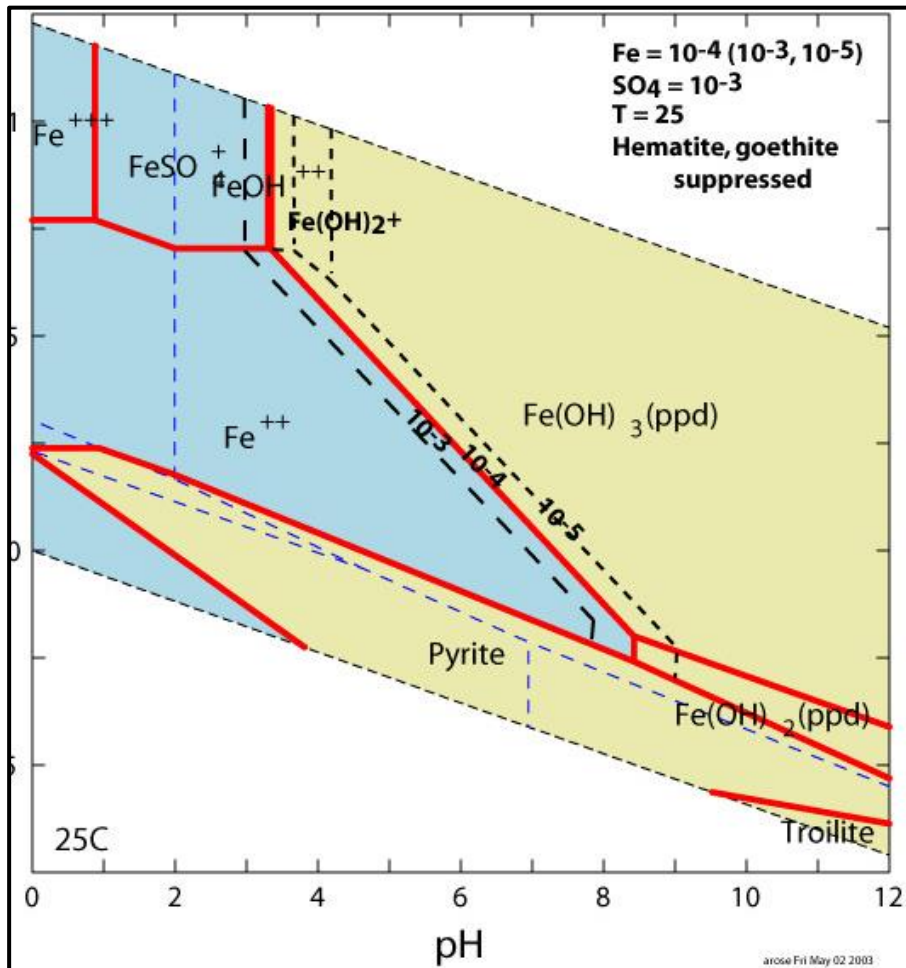


Figure 6.2: Eh-pH diagram for Fe, showing fields of solubility of dissolved species (blue) and solid species tan (Brookins, 1987).

In these tests it means that the metal recovery will be a result of both adsorption and precipitation. The adsorption tests done only measures the amount of metal recovered through adsorption and not precipitation, which explains a slight dip in the adsorption capacity for Fe when the pH was further increased from 4 to 6.

Figure 6.3 shows that when pH becomes greater than 6 the Cu ions starts precipitating at a solubility of approximately 80 mg/L which is equivalent to the experimental conditions of this study.

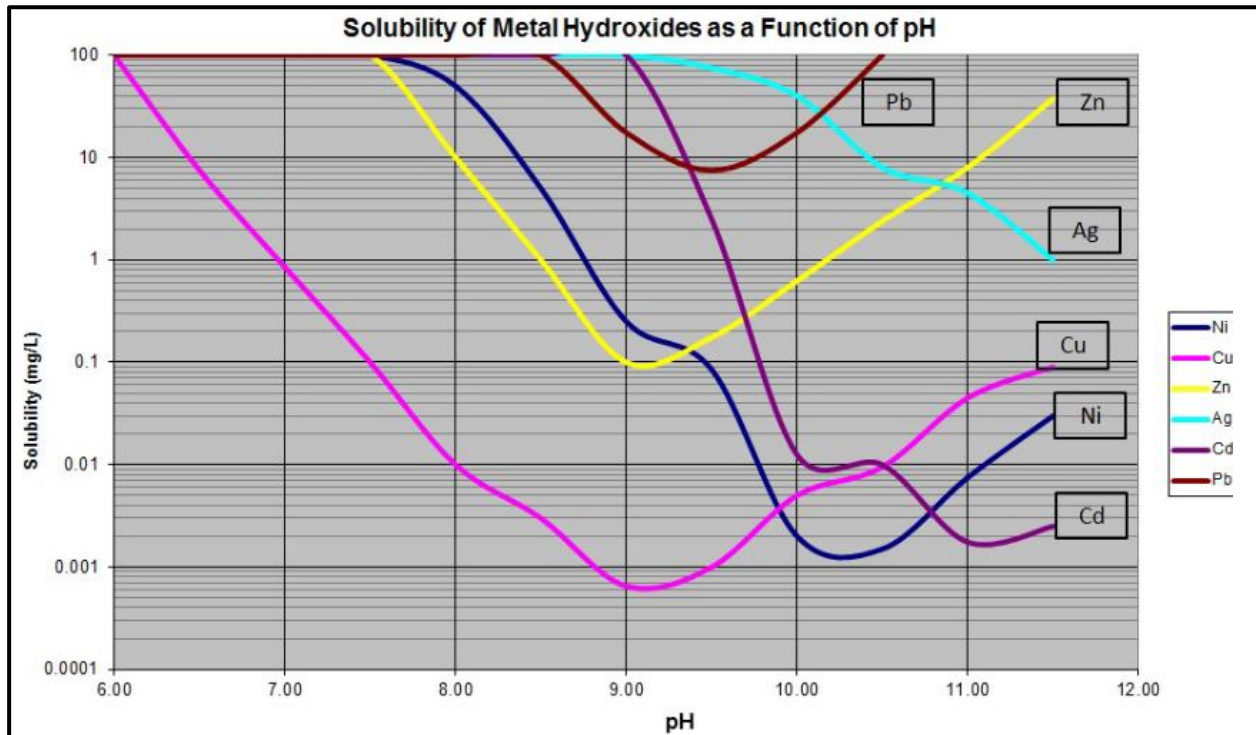


Figure 6.3: Solubility vs pH plot (Brookins, 1987).

The experiments were conducted at 80 mg/L initial metal concentration; hence the solution would start precipitating at pH slightly above 6. This, however, is just a reflection of hydroxide precipitation. There could also be sulphide precipitation which could start at a lower pH. This explains the effect of pH increase from 4 to 6 being lesser than that of the increase from 2 to 4. The introduction of precipitation reduces the adsorption capacity of the chitosan coated bentonite beads. This is due to less metal ions available to be adsorbed as they will be going into a precipitate. The optimal pH value was found to be pH 4. Several other researchers have corroborated these findings (Saravanana et al., 2012; Naiya et al., 2009; Ngah et al., 2005).

CHAPTER SEVEN

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The three main objectives of this study were to prepare, characterise and evaluate chitosan coated bentonite beads. The prepared chitosan coated bentonite beads were successfully characterised using the FT-IR, SEM and swelling techniques. Furthermore, the prepared chitosan coated bentonite beads were evaluated using batch adsorption tests.

In this study wastewater was synthesised to mimic the industrial effluents, and a multi-metal effluent was used since in industry it is rare to find a single metal effluent. Fe and Cu were chosen ions based on the abundance in industrial effluents. The chitosan coated bentonite beads were successfully prepared in this study using low molecular chitosan and bentonite procured from Merck. Additionally, the characterisation methods such as swelling tests, FT-IR, and SEM analysis were used to characterise the prepared chitosan coated bentonite beads. Adsorption experiments were designed to study the adsorption of Fe and Cu using prepared chitosan coated bentonite beads. The interactive effects of operating parameters such as pH and amount of chitosan and bentonite in the chitosan coated bentonite beads were investigated.

Experimental results proved that the chitosan coated bentonite beads could remove Fe and Cu from wastewater with a maximum adsorption capacity of 12mg/g resulting in a percentage removal up to 99.5% and 95.2% for Cu and Fe respectively. The following conclusions were made based on the investigations done in this study:

- a) Chitosan coated bentonite beads could be a promising solution for the removal of heavy metals from wastewater based on the high percentage removals for Cu and Fe in this study.
- b) The crosslinking of chitosan and bentonite proved to improve the adsorption properties of the individual components. According to Paul and Sharma (2009), the use of chitosan alone has limitations because it is very soluble in dilute organic acids, and it agglomerates to form a gel in aqueous solutions. To transcend that, physical and chemical properties are modified

by blending it with another material such as bentonite, to make an adsorbent with desired physical and chemical properties. This agreement with the investigation results in this study that a blend of chitosan and bentonite have better adsorption capacities. The amounts of chitosan and bentonite in chitosan coated bentonite beads showed an influence on the adsorption capacities of the chitosan coated bentonite beads. The optimal chitosan bentonite composition in the chitosan coated bentonite beads was found to be 50% chitosan/bentonite.

- c) The adsorption capacity was found to vary with initial pH. For a pH range from pH value of 2 to 4, an increase in pH resulted in a significant increase in the adsorption capacity which led to high removal of heavy metals. The results suggest the importance of the involvement of the ion exchange mechanism which is affected by the pH. The optimal pH was found to be 4, and a further increase in pH from pH value of 4 to 6 proved to have a lesser effect on the removal of Fe and Cu from wastewater. This was suggested that it could be due to the introduction of precipitation as the Fe and Cu starts precipitating at high pH values.

In general, commercial activated carbon is still the best adsorbent to remove heavy metals from wastewaters. Studies by Rahim et al. (2020) showed a maximum adsorption capacity of 185 mg/g for Cu adsorption onto activated carbon. More experiments are recommended to improve the performance of chitosan coated bentonite beads in future work. The physicochemical properties of the adsorbent prove to have a significant impact on the performance of the adsorbent. The findings of the study '*as-is*' can assist in the design of heavy metal removal from wastewater.

7.2 Recommendations for future work

The findings in this study gave promising results. However, several recommendations can be made for future work. Since the physicochemical properties of the adsorbent proved to have a significant impact on the adsorption capacities, further pre-treatment studies can be done to improve properties such as surface area and pore volume. A good example will be a study of the effect of pulverisation of the chitosan coated bentonite beads in order to get an optimal particle diameter of the particles. A study could be done on the adsorption properties of chitosan coated bentonite beads in dust form rather than beads.

This study also showed that operating conditions can also significantly impact the recovery of heavy metals from wastewater. Further experimental studies can be done on the operating conditions such as initial metal concentration in the wastewaters. This will also help to ascertain if pre-treatment of

the wastewater is needed to either concentrate the wastewater or to dilute the wastewater for optimal initial concentrations. The degree of mixing can also be investigated to get an optimal degree of mixing for the adsorption of heavy metals from wastewater.

In order to cover a variety of metals in the industry, further studies can be done using real wastewater samples. This will give a wide range of metals that can be removed by chitosan coated bentonite beads. A study on the effect of co-adsorption/competitive adsorption can also be done. This could also mean that a blend of methods can also be used. For example, pre-treating the wastewater using the precipitation methods and then using the chitosan coated bentonite beads to treat the resulting effluent. Toxic metals such as cadmium and lead should also be included in future studies due to their toxicity to the environment and humans.

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APPENDIX A: SAMPLE CALCULATIONS

Preparations of stock solution and dilutions:

Fe: 1000mg/L, Cu: 1000 mg/L

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

$M_r \text{ CuSO}_4 \cdot 5\text{H}_2\text{O} = 1 \cdot 63.5 + 32.1 + 4 \cdot 16 + 5 \cdot 18 = 249.69 \text{ g/mol}$

For us to get 1000 mg/L of Cu in solution we need $\frac{249.69 \text{ g/mol}}{63.5 \text{ g/mol}} = 3.931 \text{ g CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 1 L deionised water.

3.931 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ weighed and added to a 1 L volumetric flask. Same calculations are used to calculate the amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ needed. 4.97 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added to the same 1 L volumetric flask, and then water was added to make up 1L. The result was 1000 mg/L of stock solution.

Further dilutions were made for the desired ion concentration using the formula below.

$$C_1 V_1 = C_2 V_2$$

Diluting 1000 mg/L (C_1) to 100 mg/L (C_2), $V_2 = 1\text{L}$ calculate what V_1 is?

$$V_1 = \frac{C_2 V_2}{C_1} = \frac{\frac{100 \text{ mg}}{\text{L}} * 1 \text{ L}}{1000 \text{ mg/L}} = 0.1 \text{ L} = 100 \text{ mL}$$

Hence, we add 100mL of C_1 to a 1L volumetric flask, then top up to fill with water.

Calculation of heavy metal recovery

Table 0.1 Data to calculate metal recovery

Time(hr)	[Fe]/mg/L	[Cu]/mg/L
0	83,88	81,3
1	34,4	57,8
2	31,7	59,5
3	30,4	49,8
4	22,4	48,6
5	21,7	47,6
6	17,4	17,3

Calculating Fe recovery from Table 9.1

$$\text{Fe recovery} = ([\text{Fe}]_{t=0\text{hrs}} - [\text{Fe}]_{t=6\text{hrs}}) / [\text{Fe}]_{t=0\text{hrs}} = (83.88 - 17.4) / 83.88$$
$$= 79.2 \% \text{ Fe recovery}$$

Calculation of adsorption capacity

Table 0.2: Data used to calculate adsorption capacity

Time(hr)	[Fe]/mg/L	[Cu]/mg/L
0	83,88	81,3
1	34,4	57,8
2	31,7	59,5
3	30,4	49,8
4	22,4	48,6
5	21,7	47,6
6	17,4	17,3

Calculating adsorption capacity (q) of Cu at $t=6$ hours. $W = 1\text{g}$ (weight of the adsorbent) and $V = 150\text{ mL}$ which is the volume of the solution.

$$q = (C_{t=0\text{hrs}} - C_{t=6\text{hrs}})V / 1000 * W$$

$$q = 81.3 \frac{\text{mg}}{\text{L}} - 17.3 \frac{\text{mg}}{\text{L}}) 150/1000 * 1g)$$

$$= 9.6 \text{ mg/g}$$

Calculation of Swelling percentages

Table 0.3: Data used to calculate the % degree of swelling

Sample	W2(g)	W1(g)	%Swelling
CCB1	8,9031	5	78,06
CCB2	9,5531	5	91,06
CCB3	11,1331	5	122,66
CCB4	9,2231	5	84,46
CCB5	7,2931	5	45,86
CCB6	5,5931	5	11,86

Calculate the % degree of swelling for CCB1. Swelling tests were done for 24 hours.

$$\% \text{ degree of swelling} = (W_{t=24hrs} - W_{t=0hrs}) / W_{t=0hrs}$$

$$\% \text{ degree of swelling} = (8.9031g - 5g) / 5g$$

$$= 78.06\%$$

APPENDIX B: CHARACTERISATION DATA

Raw data of the FTIR plots to be included in the CD.

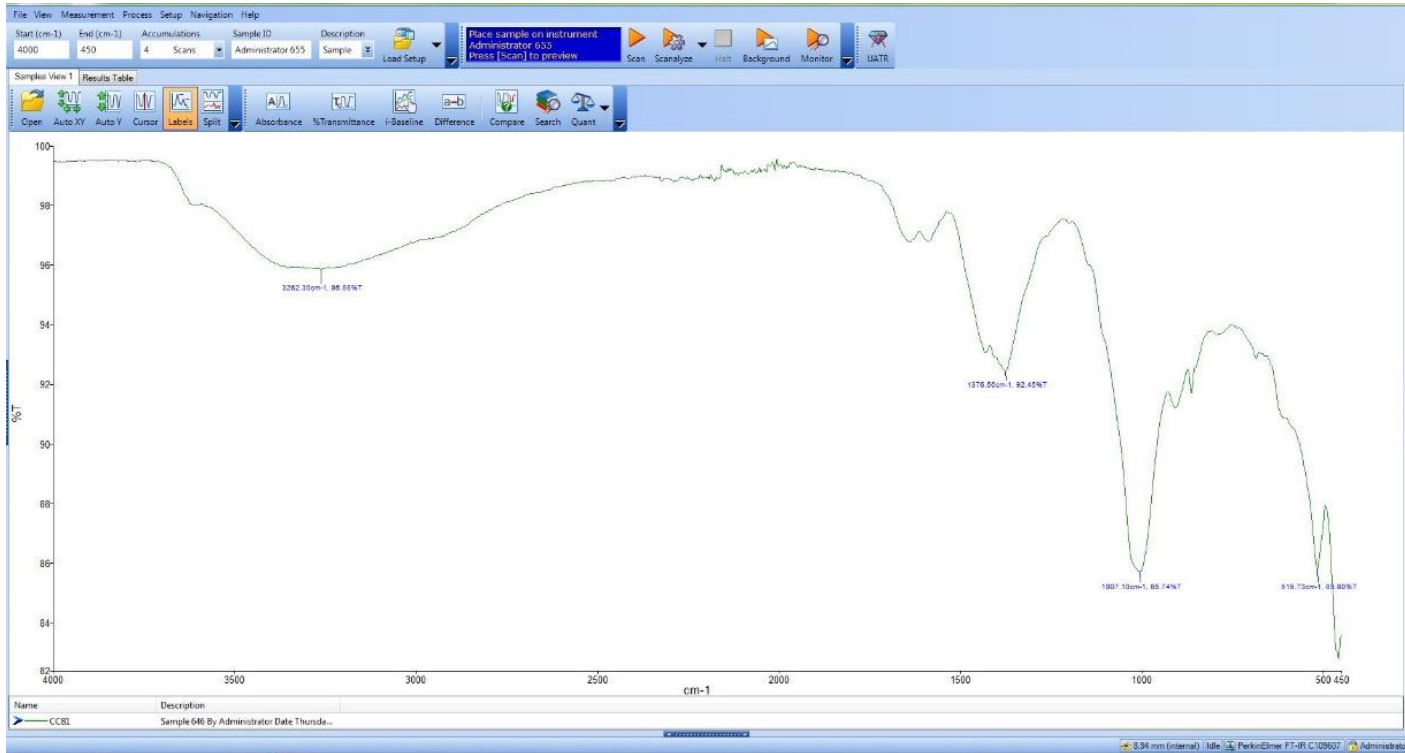


Figure 0.1: FT-IR spectra CCB1 before use

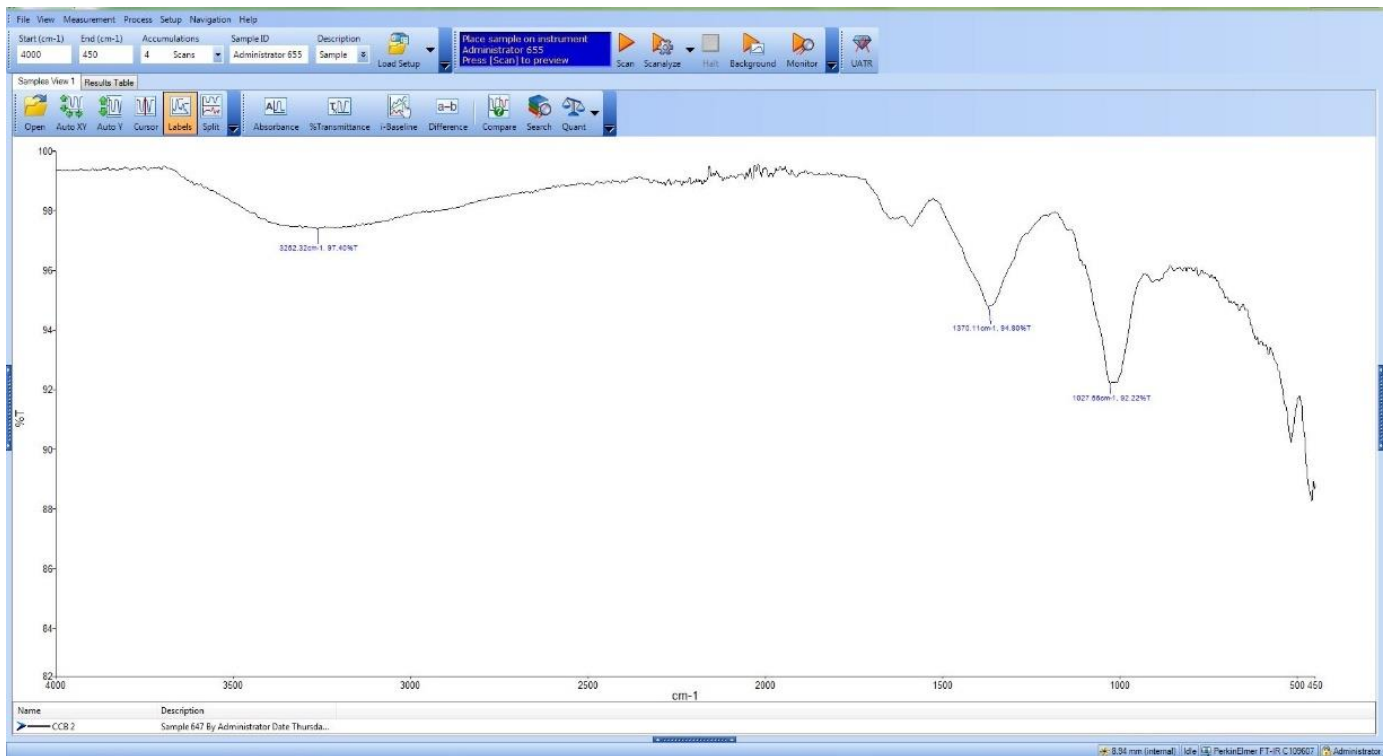


Figure 0.2: FT-IR spectra CCB2 before use

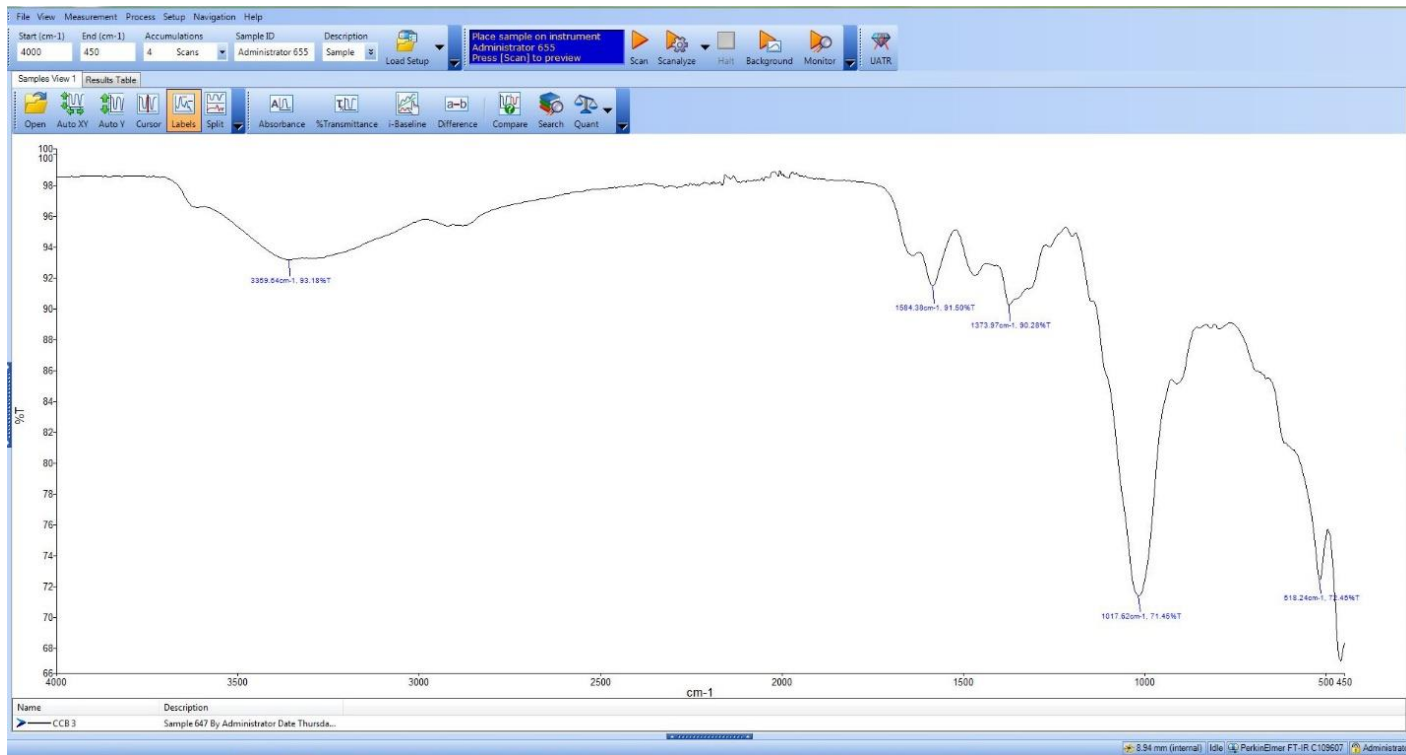


Figure 0.3: FT-IR spectra CCB3 before use

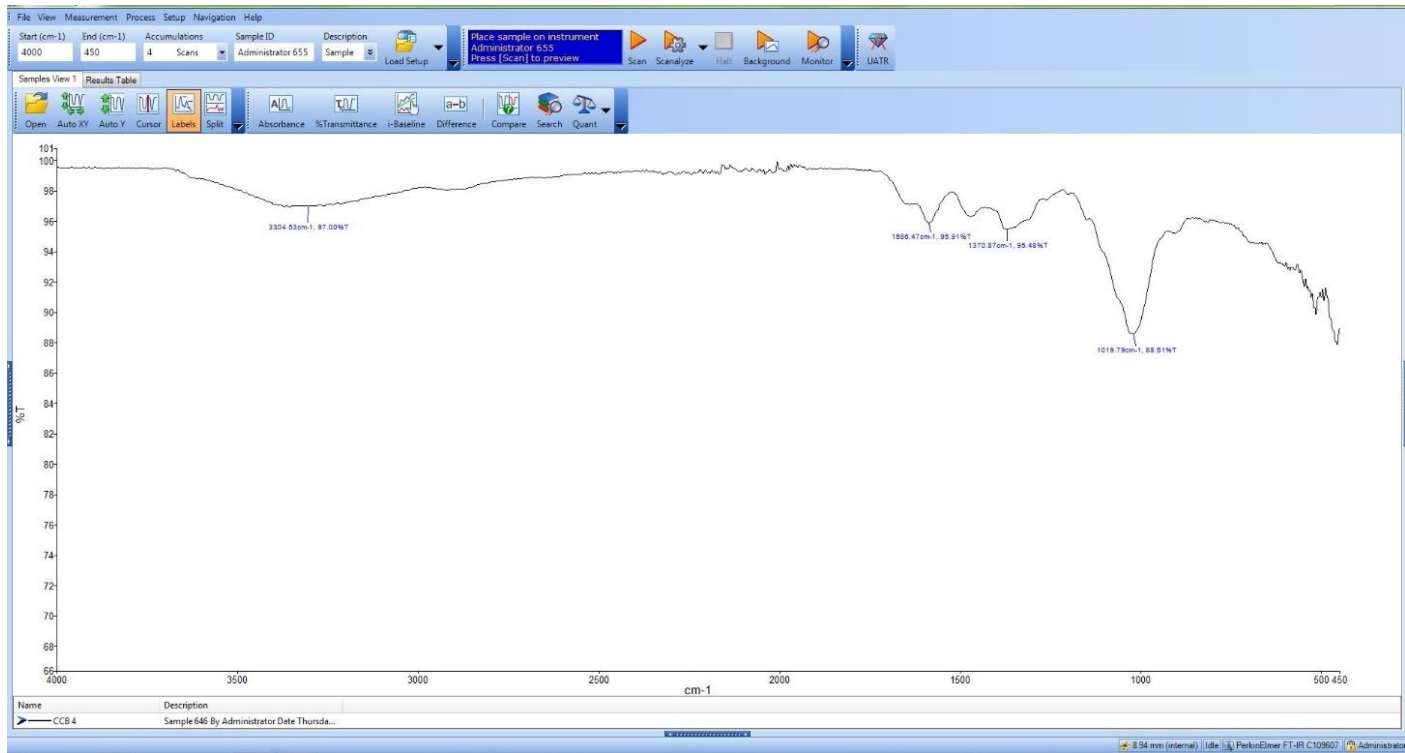


Figure 0.4: FT-IR spectra CCB 4 before use

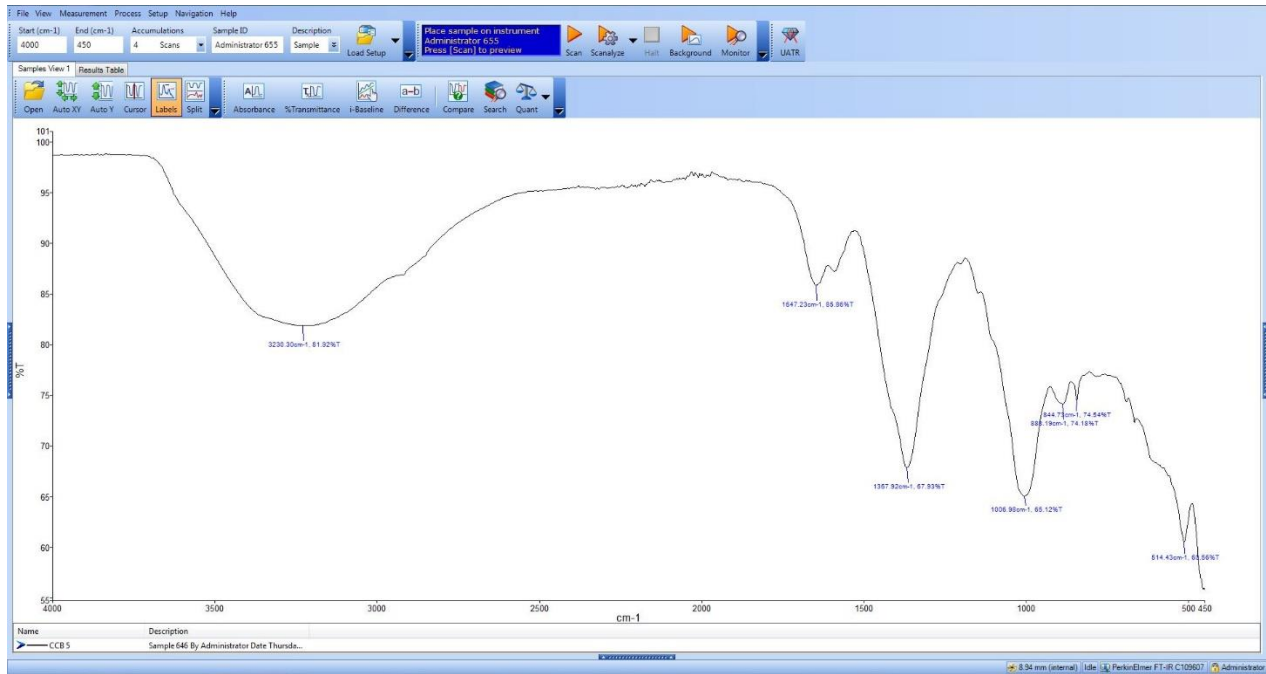


Figure 0.5: FT-IR spectra CCB 5 before use

Table 0.1: Data used to determine swelling percentages for chitosan coated bentonite beads

Sample	W2(g)	W1(g)	%Swelling
CCB1	8,9031	5	78,06
CCB2	9,5531	5	91,06
CCB3	11,1331	5	122,66
CCB4	9,2231	5	84,46
CCB5	7,2931	5	45,86
CCB6	5,5931	5	11,86

APPENDIX C: DATA USED TO DETERMINE ADSORPTION CAPACITY

Table 0.1: Data used to determine adsorption capacity for CCB1 at pH 4

Time(hr)	[Fe]/mg/L	[Cu]/mg/L
0	83,88	81,3
1	34,4	57,8
2	31,7	59,5
3	30,4	49,8
4	22,4	48,6
5	21,7	47,6
6	17,4	17,3

Table 0.2: Data used to determine adsorption capacity for CCB2 at pH 4

Time(hr)	[Fe]/mg/L	[Cu]/mg/L
0	83,88	81,3
1	25,6	17,3
2	18	15,3
3	6,7	11,4
4	5,9	8,9
5	3,4	7,4
6	3	6,5

Table 0.3: Data used to determine adsorption capacity for CCB3 at pH 4

Time(hr)	[Fe]/mg/L	[Cu]/mg/L
0	83,88	81,3
1	22,5	38,7
2	20,1	36,3
3	16	34,2
4	10,5	33,4
5	8,6	30
6	8,2	17,5

Table 0.4: Data used to determine adsorption capacity for CCB4 at pH 4

Time(hr)	[Fe]/mg/L	[Cu]/mg/L
0	83.88	81,3
1	22.8	24
2	12,41	7
3	9,2	4,3
4	7,3	0,7
5	5,4	0,6
6	5,3	0,4

Table 0.5: Data used to determine adsorption capacity for CCB5 at pH 4

Time(hr)	[Fe]/mg/L	[Cu]/mg/L
0	83,88	81,3
1	20,4	25,6
2	12,41	21,3
3	9,4	21,2
4	6,9	10,7

5	6,4	9
6	5,5	8

Table 0.6: Data used to determine adsorption capacity for CCB2 at pH 2

Time(hr)	[Fe]/mg/L	[Cu]/mg/L
0	82,7	85,3
1	78,7	77,8
2	73,2	75,8
3	70,8	71,9
4	67,8	
5	62	
6	58,1	55

Table 0.7: Data used to determine adsorption capacity for CCB2 at pH 4

Time(hr)	[Fe]/mg/L	[Cu]/mg/L
0	83,88	81,3
1	25,6	17,3
2	18	15,3
3	6,7	11,4
4	5,9	8,9
5	3,4	7,4
6	3	6,5

Table 0.8: Data used to determine adsorption capacity for CCB2 at pH 6

Time(hr)	[Fe]/mg/L	[Cu]/mg/L
0	82,7	85,3
6	4,9	1,593