ADSORPTIVE POTENTIAL OF MAIZE TASSEL-ETHYL ACRYLATE BIOPOLYMER EMBEDDED MAGNETIC NANOHYBRID TOWARDS THE REMOVAL OF Cd(II) FROM AQUEOUS SOLUTION: AN EXPERIMENTAL DESIGN METHODOLOGY

By

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DEDICATION

I dedicate this project to me, myself and I;Ihave been through a lot to achieve this dissertation.

ACKNOWLEDGEMENT

He is a faithful God and His never ending love and blessing have been pouring in my life. Thank you for showing me that everything is possible.

To DrManaseKudzaiChiweshe,thank you so much for believing in me and encouraging me to go the extra mile when I could not pull through anymore.

To my mum and sister,thank you very much for your never-ending moral support. I would not have done it without you.

I extend my deep felt gratitude to my supervisor DrGuyofor your continual support throughout this project, the Department of Chemical Technology staff and Ministry of Mining and metallurgy laboratory staff. I am forever grateful.

ABSTRACT

A novel maize tassel-ethyl acrylate biopolymer embedded magneticnanohybrid(MTEA-MN)was designed for the adsorption of Cd (II) in batch experiments.Copolymerization parameters such as solvent amount, initiator concentration, monomer concentration, temperature and reaction time on grafting percentage were optimized.Characterization of the adsorbent was byFourier transform infrared spectroscopy (FTIR). The effect of pH, contact time, initial concentration and adsorbent dosage and their interaction influence on Cd(II) adsorptiononwasinvestigated using response surface methodology following a central composite design (CCD). The optimum removal (95.26%) was obtained at pH 3.5, contact time 240 min, adsorbent dosage 0.53 g and initial concentration 44.6 mg/Lusing the GRG non-linear solving method on Excel solver. The data best fitted the non-linearLangmuir adsorption model with greaterR^2(0.998)smallersum of square deviation (SSD) value (1.6956) relative to Freundlich model with R^2= 0.974 and SSD = 2.8786. The maximum sorption capacity of the MTEA-MN for Cd (II) was 459.37 mg/g. Kinetics studies revealed that the adsorption process followed the pseudo-second order model (lowest sum of square error (SSE) values and correlation coefficients (R^2) >0.9). The calculated thermodynamic parameters showed that the adsorption process was feasible, spontaneous and endothermic in nature. Consequently, the present study demonstrated that MTEA-MNcould be used as an adsorbent for the removal of Cd (II) ions from aqueous solutions.

DECLARATION

I, TafadzwaMakawa, hereby declare that I am the sole author of this dissertation. I authorize Midlands State University to lend this dissertation to other institutions or individuals for the purpose of scholarly research.

Signature ……………………………

Date …………………………………

APPROVAL

This dissertation entitled '*Adsorptive Potential Of Maize Tassel-Ethyl Acrylate Biopolymer Embedded Magnetic Nanohybrid Towards The Removal Of Cd(II) From Aqueous Solution: An Experimental Design Methodology*: by TafadzwaMakawa meets the regulations governing the award of the degree of Chemical Technology of the Midlands State University, and is approved for its contribution to knowledge and literal presentation.

Supervisor …………………………………

Date ………………………………………

LIST OF ABBREVIATIONS

FTIR	Fourier Transform Infra-Red
SEM	Scanning Electron Microscope
XRD	X Ray Diffraction
CCD	Central Composite Design
mL	Milliliters
mg/L	Milligrams per litre
$T^{o}C$	Temperature in degrees celsius
Min	Minutes
g	Grams
µm	Micrometre
cm^{-1}	per centimetre
2^{θ}	Degree Two theta degree
3D	Three Dimensional
M	Molar
%	Percent
h	Hour

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CHAPTER ONE: INTRODUCTION

1.1 Background

Water pollution has increased vastly in the last decade proven by recent statistics ref. This alone has brought forward enough justification for the need of efficient and environmentally friendly methods which can be used to treat the polluted water bodies. Thereisa wide range of pollutants which are polluting the water bodies. Due to the industrial boom in the world at large, the amount of heavy metals in water bodies for human consumption has increased. By definition heavy metals are metallic compounds in the periodic table, which have high density, and a toxic in very low concentration. Mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium(Ti) and lead (Pb) are classified as the toxic heavy metals. Water pollution has greatly become a cause of great concern due to the health risks which are posed by consumption of heavy metals. The chemical nature of heavy metals allows themto be non-biodegradable, which means that they tend to persist and accumulate in the environment.

Heavy metals even in very low concentrations have been associated with a wide range of diseases, which affects plants, animals and humans at large [1]. Consumption of these heavy metals by the plant and animals bodies results in different problems because they cannot be processed and utilized by the body. Therefore, heavy metals tend to circulate in the plant or animal system causing diseases [2].Cadmium is one of the most toxic heavy metals which when present in the environment causes a danger to the people and plants. Cadmium is a naturallyoccurringheavy metal which is found in highconcentration in areas such as shales, oceanic and lacustrine sediments, and phosphorites[1]. Industries and agriculture sectors are the major cadmium pollutersthe environment[3]. There are different processes in industries which pollute the air these includingmineral oil processing, smelting, mining, alloy processing and industries that use Cd as a dye (CdS: yellow; $CdSeO_3$: red)[4] include references. All these contribute to cadmium which will be in the air and converted in water bodies as soluble cadmium[5].

Cadmium is one of the heavy metals that are very toxic even in low concentrations. This has led to the world health organization (WHO) to recommend the standard limit of cadmium which can be allowed in the drinking water to be 5 parts per billion (ppb) or 0.005 parts per million (ppm)[6] whilst Food and Drug Administration (FDA) states that the concentration of cadmium in bottled drinking water should not exceed 0.005 ppm (5 ppb).Cadmium is a bio-accumulative heavy metal that is absorbed by the animal lipids[7]. In areas that depend on rice as a staple food they suffer from cadmium poisoning since rice is a plant with high affinity of cadmium in acidic soil[8].

Environment chemical researchers have been undertaking different studies in the effort of addressing the effects of caused by heavy metals[9],[10],[11]. All these studies aim to eliminate theseheavy metals from aqueous solution and the environment at large. Conventional methods have been used before in the effort of removing heavy metals. These technologies include chemical precipitation, ion exchange, adsorption, osmosis, biosorption, membrane filtration, coagulation–flocculation, flotation and electrochemical methods[12][13]. These conventional methods are expensive to implement and carry out at large scale hence most countries are failing to religiously use these systems. One of the most environmentally friendly methodsis bio sorption that is also exceptionally very cheap. This method utilizes natural plants to remove heavy metals.

These plants or organic matter are treated or modified to generate a medium, which is effective in environmental remediation. Various reagents or activators are used in efforts to increase the physical and chemical properties of the bio sorbent in heavy metal sorption[14]. This enhances the ability of the sorbents to remove the heavy metals in the polluted water.

Maize is the stable food plant in Southern Africa hence it is found in abundance[15]. Usually the maizecob is the mostly utilized part of the plant. The rest is left for producing organic manure and a little is used for stock feeding. Maize tassel is one of the maize plant partswhich have been used vastly by environmental chemist[16]. This plant has been used for biosoprtion of heavy metals for many years[17]. In all the research which has been carried out it has proved to be effective in removing heavy metals such as barium, cadmium, chromium, lead, mercury, selenium, and silver[18]. The main chemical compound, which constitutes maize tassel, is cellulose and starch[19].

One of the majorsetbacks of using raw plant material in water treatment is that they are prone to bacterial attack. They tend to react with the water impurities, which will cause formation of algae and formation of bacteria, which rots the biomass[20]. Therefore, there is a need to modify these maize tassels by carbonizing them. This process enables the biomass to be reused andthe chemical structure will not be affected. Carbonizing biomass increases the surface area, which was exposed for supporting on heavy metals, and also gives room for further chemical modifications[21].[2223]. Generally carbon has high affinity for attracting for substrates hence making it making it a very good absorbent[24].

Nanotechnology has proved to be very useful in water treatment and has led to the vast improvement in the sector refs. Due to these advantages scientist have been currently researching on water nanomaterial bases bio sorbents. Nanoparticles add chemical and physical properties to materials[25]. This has lead the nanomaterial to be exploited as different bio sorbent materials have been modified with nanoparticles, to improve its properties. Nanoparticles are very minute and have a size range of (1 nm-100 nm) molecular and atomic particles and their application[26]. They have distinctive characteristics such as morphology, size and distribution[27]. Metal nanoparticles such as MgO, Fe_3O_4, Cu, Ag, Fe, Au, ZnO, ZrV_20_7 and TiO_2 have been recently used in different fields and have generated impressive results[28].

The combination of graftedmaize tasselandmagnetic nanoparticles enhances the adsorbent properties as magnetic properties are introduced and surface area increased, which allows (II) ions to be easy removed. This study seeks to investigate the effect of modifying carbonized maize tassel grafted with ethyl acrylate and coated with magnetite nanoparticles on the removal of Cd (II) ions from simulated wastewaters.

1.2 Problem statement

Water pollution due to heavy metals is increasing significantly and hence causing environmental problems. Due to the properties of these heavy metals they tend to be very soluble in water hence difficult to detect to detect with the naked eye hence there is need for analytical instruments to be used[29]. Most of the people, animals mostly in developing countries tend to drink untreated water which is polluted. Plants was watered using the polluted water and the non-degradability of these metals they cannot be detoxified biologically and tend to accumulate in the food chain[30]. Recent researches [31]][32]have shown much evidence that cadmium as one of the heavy metals pose a health risk to humans and the environment even in low concentration on the metal ions due its toxicity. Cadmium in aqueous solution produces heavy metal ions, which interact with the protein structures hence denaturing the enzymes and hormones in the human. The denaturing of these biological chemicals cause inhibition of various vital processes, which sustain plant and animal life resulting in death. Cadmium is toxic to unborn babies as it is ingested by pregnant mothers without their knowledge and thisin turn affects the fetus and child growth of the baby[33]. There are many techniques, which are currently being used to remove heavy metals in water. The major problem is that these methods are very expensive and need large capital investment to install and service. Biomaterials also tend to decompose and affected by microorganisms like algae and tend to decompose.

1.3 Researchhypothesis

Maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybridenhances the removal of Cd (II) ions from simulated wastewaters.

1.4 Aim

- To remove Cd (II) ions from simulated wastewaters usingmaize tassel-ethyl acrylate biopolymer embedded magnetic nanohybrid.

1.5 Objectives

- To prepare maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybrid
- To characterize the maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybrid using FTIR.
- To investigate the effect of monomer concentration, initiator concentration, reaction time, solvent concentration and reaction temperature on percentage grafting.
- To optimize the batch adsorption experimental conditions (pH, contact time, adsorbent dosage and initial concentration) using a central composite design.
- To characterize the adsorbent before and after sorption using Fourier transform infrared spectroscopy (FTIR.
- To generate the equilibrium, kinetic and thermodynamic data for the cadmium pollutant.

1.6 Justification

Maize tassel are considered as waste in most farming activities hence the utilization of the maize tassels in generation of a bio sorbentfor cadmium removal in waste water will be waste beneficiation[34]. Raw maize tassel tend to be prone to bacterial attack when left in waster for along. Carbonization of the material significantly improvesthe properties of maize tassel. Recent studies involved iron oxide magnetic nanoparticles have been carried out and these posed the need for further modifications on carbonized maize tassel[35]. The grafting of carbonized maize tassel with ethyl acrylate increases the adsorption capacity of the sorbent. The durability of the maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybridalso improves as polymers tend to more be chemically stable.

Recently studies on magnetic nanoparticles have raised attention due to their properties and functions, which they exhibit from recent scientific studies[36]. These magnetite nanoparticles tend to exhibit distinctive properties including super paramagnetic, nano-range size and high surface area to volume ratios and this therefore has provided the reason why wide studies need to be carried out on how natural plants can be modified to synthesize these magnetic nanoparticles[37]. Modified nano materials have vast advantages such non-toxicity; relatively high sorption capacities and selectivity to the low concentration of pollutants and nanoparticle sorbents could be infinitely recycled.

Nano materials of plant origin have unique properties and have led to intensive research in the area of magnetic nanocellulosic materials. Maize tassel have cellulose and starch in abundance hence is very cheap as compared to polymeric and zeolite materials, which is currently used in water treatment. Moreover, they are renewable and biodegradable polymers. Surface coating mediums play a key role in determining the size distribution, morphology, magnetic properties and surface chemistry of magnetic nanomaterial[38]. At present, the more popular adsorbents for removal of heavy metals include zeolites, organic resins, and bio sorption, however these sorbents are expensive and their availability is limited. Due to the high increase in economic activities such as mining, agriculture and industrial development, there is vast increase in the contamination of the water bodies with heavy metals hence cheaper and renewable methods of heavy metals removal need to be introduced and applied.

Surface coating mediums play a key role in determining the size distribution, morphology, magnetic properties and surface chemistry of magnetic nanomaterial's. At present, the more popular techniques for removal of heavy metals such as the use of zeolites, organic resins, biosoprtion, however these methods are expensive, their availability is limited. Due to the high increase in economic activities such as mining and agriculture there is high increase in the contamination of the water bodies with heavy metals hence cheaper and renewable method of heavy metals need to be known and applied. The fusion of nanochemistry and polymer chemistry gives the material properties, which are desirable. These properties include increase capacity for cadmium removal, increased surface area, and chemical stability of the sorbent as it makes it difficult to be decomposed.

CHAPTER TWO: LITERATURE REVIEW

2.1 Introduction

Industrial boom in the whole world has greatly increased the rate of pollution especially the air and water. This has led to deposition of heavy metal in the water. World Health Organization classified the following metals as heavy metals cadmium, mercury, lead, arsenic, manganese, chromium, cobalt, nickel, zinc, selenium, silver, antimony and thallium. Heavy metals are defined as metals which has a relatively molecular weight causing it to be dense[39]. These metals are regarded as toxic due to the fact that plants, animals and humans cannotprocess the metals in their bodies hence they tend to bio accumulate[40,41].

There are acceptable ranges which are allowed to be in the water which is used by humans[42], industrial activities, mining, textile industry and agricultural activities have contributed the contaminated water then causes health risks to animals, humans and plants. Plants such as rice have high intake of heavy metals. There are a vast of methods which are used for water treatment such as precipitation, evaporation, solvent extraction, ion exchange, reverse osmosis, membrane separation but these have major drawbacks such they are expensive in operation cost[43]. These major drawbacks have led to the need for the development of water treatment processes, which are effective and cheap for environmental remediation.

2.2 Cadmium and environment

Cadmium is one of the heavy metals, which is found in wastewaters. Cadmium has a relative molecular weight of 112.4 g, which classify it to be a heavy metal. Cadmium is one of the metals, which is found naturally in the earth's crust. It is exposed to the environment due to activities such as volcanoes, rock weathering and mining activities. Cadmium is usually found in zinc, copper and lead ores in the form of oxides and carbonates not pure metal

Cadmium is widely used especially in industries due to highly favorable physical properties such as low melting temperatures, corrosion resistance, good ductility and good thermal conductivity and also electrical conductivity. Cadmium is used widely in the form of cadmium hydroxide to manufacture Ni- Cd batteries. The battery industry also disposes this cadmium as nickel cadmium batteries are disposed without being recycled. In mining industry release cadmium through dust which is generated from the electric arc furnace

The textile industry, paint manufacturing also uses cadmium in the form of cadmium sulfoselenide and cadmium lithopone as these are pigments which ranges from yellow to deep maroon. These cadmium compounds have favorable properties which makes them widely used these include high covering power, excellent resistant to weathering. In engineering, cadmium is used to manufacture alloys which can be used for electroplating on iron, aluminum ant non – ferrous metals. Cadmium is uses because it is corrosion resistant and can withstand. In Plastic engineering cadmium stearate and cadmiumlaurate are used as high and light stabilizers and also improve on electrical conductivity of the plastics

2.3 Cadmium human exposure

There are various methods which enables cadmium to be exposed to humans, who will latter on be consumed. Tobacco smokers are the ones who pollute the air with cadmium to a greater extend. This is mainly because cadmium is absorbed in large amounts in tobacco leaves. Hence every smoker depositscadmium into the air. Averagely 1.7g of cadmium is exposed to every smoker every time they smoke one cigarette.

Some developed countries they haveplants, which focus on recovering cadmium from batteries. This alone leads to deposition of cadmium in effluent water systems. The use of cadmium in pigments also exposes cadmium to humans. Air pollution with cadmium cause the natural rainfall to be cadmium polluted as it enables the cadmium to dissolve and sink into the water table. The water will then take by the plant and the cadmiumbio accumulates into the plant. High cadmium concentrations are significantly high in vegetables such as lettuce, spinach, cereals and legumes, which are starchy.

2.4 Current cadmium removal methods

Conventional methods have been widely used to remove cadmium from wastewaters. There are several processes which have been used and these include precipitation, ion exchange, reverse osmosis, solvent extraction, electrochemical treatments, membrane filtration, evaporation, flotation, oxidation and bio sorption processes[44,45,46,47]. Major throwbacks suchas cost and renewability are experienced when using these techniques hence there is need to look for better ways to remove heavy metals

This has led to deposition of heavy metal in the water[48].

2.4.1 Reverse osmosis

The technique utilizes the effect of differential osmotic pressure to remove heavy metals in waste wasters. The machinery, which is required to, is so expensive and also difficult and fragile to service. Themembranes selectively eliminate charged particles. This allows heavy metals to be removed from contaminated water. The charge of the dissolved particles is also important as charged particles are bound to be rejected by the membrane than those that are not charged[49]. Reverse osmosis permits pure water because it is not charged and all the pollutants are rejected. One of the most cost effective process it the procurement of sediment and carbon pre-filtration process which prevent membrane fouling hence adding additional operational cost hence being expensive[50]. Other down fall of the process is that it is slow and time consuming hence treatment of large water quantizes getsdifficult. Reverse osmosis is advantageous in that there is high regeneration rate for a wide range of contaminants and very cost effective in the long term.

2.4.2 Ultra-filtration

The modification of the simple filtration process by the use of porousmembranes, which are pressure driven the process, is expensive as there should be a constant supply of pressure and the process depends wholly on the pressure. There is the use of ultra-finefilteringmembranes and they tend to be clogged by the differentpollutants, whichwas in the waste water[26].

2.4.3 Electro dialysis

It is an electrically driven process that utilizes semi permeable ion selective membranes with high voltage to promote the movement of charged ions[51]. There is the application of an electric current between membrane electrodes such that ions migrate to respective electrodes depending on their charges[52]. It makes use of alternating semipermeable cation and an anion transfer membranes in a direct voltage potential field. Low energy consumption is required and non-ionized and ionized components can be treated. The formation of metal hydroxides poses a great challenge of this process hence the complete removal of the metal species from the aqueous solution is hindered. Due to the formation of this metal hydroxide the electrode membranes are clogged and the maintenance of the system becomes expensive.

2.4.4 Ion exchange

The uses of zeolites, which are made from inorganic and polymeric materials, are used for ion exchange. The process involves the swappingof specific functional groups, whichwasat the active site for the reaction to take place. The heavy metals ion was removed as they were left on the resin and in exchange an ion, which is not toxic to the environment, is released[53]. Ion exchange resins are expensive to build and they are not renewable. There are high chances of the water not being properly treated due to full utilization of the ion exchange sites. Hence the process requires monitoring and constant replacement of the resin[54].

2.4.5 Chemical precipitation

It precipitation agents are utilizes in this method, these chemicals form a reaction with the heavy metal which will the precipitates and the filtered off[55]The main limitations of this method if environmental pollution as the generated sludge is difficult to dispose. Precipitation agents such as lime are utilized inthis process.

2.5 Biosoprtiontechnology

2.5.1 Biosoprtion

The use of biomass, which is either modified or treated physically or chemically, is referred to as biosoprtion. Biomass involves microbial, live and dead plant matter. This biomass stand as a medium of bio-remediation of the environment using active sites. These active site contain chemical groups such as carboxyl, carbonyl, hydroxyl, amino, sulfhydryl and sulphate[56]. These groups are responsible for reacting with the heavy metal hence treating the water. Naturally these groups are found abundantly on cellulose, protein and starch which all has a capacity to remove metal ions from aqueous solutions.

2.5.2 Biosoprtion mechanisms

There are wide ranges of mechanisms, which are involved in biosoprtion. These mechanisms are explained fully with Atkins. Mechanisms such as physisorption, chemisorption, ion exchange, chelation, coordination, micro-precipitation and entrapment in inter or intra-fibrillary capillaries and spaces of the structural polysaccharides networks of the bio sorbent to mention a few. Heavy metals ions which was present in aqueous will absorb to the surface of the sorbentchemically or physically on the reactive sites of the biomass[57]. These processes are usually determined by the time of active groups which was at the biomass. Bio sorption has many limitations and they are explained below.

2.5.3 Factors affecting biosorption

1. Initial concentration of the metal ion

   Initial concentration of the ion increases as the rate of bio sorption increases. This happens until a point of saturation occurs which will then indicate that all the active sites on the biosorbent are occupied. Any increase in metal concentration does not show any difference on biosorption rate. The metal ions adsorbed per unit mass increases with an increase in initial ion concentration of the metal ion. There is a fluctuation on the electrostatic interaction involving sites of progressively lower affinity for ions could be the main reason why the rate increases[58].

2. pH

   One of the major physical properties of heavy metals in solution which is solubility is affected mainly by pH.pH levels in solution determine whether the metal was soluble or not. It also contributes to destabilization of the active sites which was available for biosorption.[59]

3. Surface area

   Biomass quantitydetermines the surface area which was available for biosorption process. As the surface area increases so is the rate of biosorption of the metal ion on the biomass. Large surface area increases adsorption of the metal ion to the sorbent. The size of the biomass also determines the rate of biosorption the more finely grinded the faster the rate of biosorption[60].

4. Temperature

   Temperature depend mainly on the type of biomass used and whether the chemical modifications of the biomass and stand certain temperatures. So modifications are denatured when high temperatures are employed. Generally there are specific temperatures which favours generally at the 20 to 40°C ranges for optimum conditions[61].

5. Contact time

   Increase in contact time between the biomass and metal ion in solution determines the rate of biosorption. Optimum contact time is that time where removal of metal ions does not increase regardless of the contact time[62].

2.5.4 Advantages of biosorption

- It is very inexpensive due to the fact that the biosorbent, which are generally used, do not have a significant use and are regarded as waste[63].
- Minimization of chemical and biological sludge.
- biosorption can be used over a wide range of temperature, pH and initial metal concentrations in solution and still remains effective[64].
- It is also possible to regenerate the adsorbent and the metals after the sorption process is complete. Hence it can be reused
- No sludge generation and it is very cheap as the adsorbent is readily available.

2.6 Desorption

Chemists define the effectiveness of a biosorbent by tis ability to be regenerated[30]. [30]. This involves the removal of the metal ions, which will have been,absorb on the biosorbenteffortless. The process should be costless and environmentally friendly. Usually desorption if carried out using acids as they promote metal ion precipitation.

Percentage desorption $= \frac{Qdes}{Qads} \times 100\%$................................ (2.1)

Where Q_{des} and $Q_{ads}$is the amount of particles desorbed and adsorbed respectively[65] .

2.7 Nanotechnology Chemistry

Nanotechnologies have applications in various disciplines from medicine through chemical technology to the construction industry [66, 67]. The infinite size of nanoparticles, the surface area is relatively large enable nanoparticles to have high reactivity and sorption to various heavy metals [68]. The use of nanotechnology in the development of nanoparticles in the removal of heavy metals has recently been of major interest in the heavy metal treatment of water and its combination with a biosorbent will lead to a cheaper and more effective method of cadmium removal from polluted aqueous solutions[69].

Synthesis of magnetite (Fe_3O_4) nanoparticles are of great interest because of their characteristic as ferrofluids, and these exists as a colloidal suspension of suitably coated magnetite particles in a liquid medium having magnetic effects[70] . In the recent years, along with the development of nanotechnology, iron compounds nanoparticles (such as hematite, goethite, and magnetite) have been used for biological purification of polluted soil[71]. Synthesis of Fe_3O_4 nanoparticles is highly preferred as the nano tubes have distinctive characteristic such as finite-size effect, high ratio of surface-to-volume [72] . The magnetic properties improve the adsorption capacity for the nanoparticles in the heavy metal removal[73]. The easy separation of metal loaded magnetic adsorbent from solution and an external magnetic field cam is used to recover the nanoparticles.

2.7.1 Uses of magnetic nanoparticles

Magnetic Nanoparticles in combination with an external magnetic field allow the delivery medication to specific positions is released and this eliminates side effects and also reduce the dosage required[74]. Super paramagnetic iron oxide nanoparticles; have been extensively used for separation and purification of cells and biomolecules in biological processes[75]. Feng and other researchers carried out sorption studies so arsenic using iron oxide nanoparticles and their research was useful [76]. These nanoparticles have been widely used in different catalysis processes because they have of high dispersion and reactivity with easy separation. Recycling of these magnetic nanoparticles is easy and very cheap[77]. Iron oxide and titanium dioxide are good sorbents for metal contaminants and this is because of the Spherical aggregates of these nanoparticles[78]. These nanoparticles have a similar size and shape to the resin beads already used in water purification[79]. Magnetic nanostructured particles of Fe_3O_4 can be successfully combined with the technique of bio sorption from the maize tassel activated carbon to create a medium, which removes the heavy metals effectively[80]. As one of the inorganic materials, carbon based nanomaterials are widely used due to its nontoxicity and high sorption capacities.

2.7.2 Magnetic nanoparticles synthesis processes

Magnetic nanostructured particles of Fe_3O_4 can be synthesized using different methods this are co- precipitation, thermolysis of precursors, reverse micelles and micro-emulsion technology[81].

2.7.2.1 Co-precipitation

Co-precipitation is the most efficient chemical method magnetic particles [82]. Stoichiometric mixture of ferrous and ferric salts in aqueous medium at a pH of between 8 and 14 are used to make the magnetite. Controlling pH, ionic strength, temperature and nature of the salts produces nanoparticles which range from 5 to 100 nm in size[83]. Reverse micelles and micro-emulsion technology involves the use amphoteric surfactants to create water-swollen reversed micellar structures in nonpolar solvents[84]. Nano droplets of different ranging from micelles (1-10 nm) and water-in-oil emulsions (10-100 nm) aqueous iron salt solutions are encapsulated aqueous iron salts forms nonreactors, which improve nanoparticle growth[85]. Different size range of nanoparticles is obtained by varying the nature and amount of surfactant, cosurfactant, temperature and the surfactant concentration.

2.7.2.2 Thermal decomposition

Monodisperse magnetite nanoparticles have been synthesizes using thermolysis of precursors Organic solution-phase decomposition of the iron precursor organic solution phase is exposed to temperatures above 200°C. Iron oxide nanoparticle synthesis which are syntheses using this method have high uniformity in the mean size, the size distribution and the crystallinity of magnetic iron nanoparticles [86]. The type of solvent, temperature, and time, are the factors, which affect the monodispersity of the nanoparticles[87]. Magnetic nanocomposites of Fe_3O_4 are coated with inorganic material such as silica, gold or silver. Inner iron oxide core with an outer shell of inorganic materials was the physical structure of the nanoparticles[88]. The stability of the nanoparticles in solution and the covalent binding with specific ligands to the nanoparticle surface are the properties of the nanoparticles, which are enhanced by using this method.

2.7.2.3 Microemulsion

It is a thermodynamically stable isotropic dispersion of two immiscible phases, which are missed with a surfactant. The surfactant form a layer between the two phases, which was having hydrophobic tails of the surfactant molecules, dissolved in the oil phase and the hydrophilic head groups in the aqueous phase [89]. Spherical and cylindrical micelles to lamellar phases are structures of nanoparticles, which are formed[90]. Microemulsion produces which a relatively were smaller in size and were higher in saturation magnetization[91].

2.7.2.4 Hydrothermal synthesis

Hydrothermal synthesis is a wet chemical technique of crystallizing substance in a sealed container from the high temperature ranging from 130 to 250°C and high pressure of 0.3 to 4 MPa[92]. This technique generates highly crystalline iron oxide nanoparticles. Highly crystalline and pure iron oxide nanoparticles can be obtained by this method [93] This method can be also combined with other methods mentioned in order to first synthesis the nanoparticles and use hydrothermal method to coat them with stabilizers. A simple, environmentally friendly hydrothermal stripping route for synthesizing highly size controlled spherical ferric oxide nanoparticles is also reported recently[94]. Purity of the particles and crystals obtained greatly influence the magnetic properties[95].

2.7.2.5 Sonochemicalsynthesis

Bubbles of a liquid is the medium for the formation, growth of the iron oxide nanoparticles The implosive collapse of the bubble generates a localized hotspot through adiabatic compression within the gas phase of the collapsing bubble[96]. The conditions formed in these hotspots have been experimentally determined, with transient temperatures of 5000 K; pressures of 1800 atm, and cooling rates in excess of 1010 K/s produced nanoparticles with the desired structures[97]. Sonication of solutions of Fe (II) or Fe (III) complexes or salts under inert atmosphere or ultrasonic decomposition of iron carbonyl precursors leads to amorphous nanoparticles of narrow particle size distribution. Amount of water and rate of sonication are two important factors that found to affect the final particle size and magnetic properties[98].

2.8 Iron oxide properties

Iron oxide is a metal oxide, which has the following properties, the coordination environment of surface atoms, the redox properties[99], and the oxidation state at surface layers, which makes it suitable as an adsorbent[100]. The metal oxide has electrons in the orbitals that enable it to function as an absorbent[101]. Fe3O4 magnetite is a ferromagnetic and super paramagnetic; α-Fe2O3 is hematite with weakly ferromagnetic or antiferromagnetic magnetic properties and γ-Fe_2O_3maghemite, which is ferromagnetic[102]. The magnetic property of the iron oxide nanoparticles depends upon shape and size of the particle. These magnetic properties of iron oxide nanoparticles can be easily oxidized in air and resulting in the loss of magnetism therefore there is need for surface coating using biosorbents to stabilize the magnetic iron oxide nanoparticles hence the use of maize tassel activated carbon [103].

Spinel crystal structure is the on which Fe_3O_4 exhibits and oxygen form FCC closed orientation, wherein the oxygen atoms form a FCC closed packed orientation[104]. Bulk iron oxide consists of both Fe^{2+} and Fe^{3+} atoms and exhibits ferromagnetic behavior[105]. Magnetism originates from electron orbital motion or intrinsic spin from the presence of unpaired electrons in a complex[106]. Iron has unpaired electrons, which enable its oxide to have magnetic behavior.

The magnetic properties of materials are classified into five basic types of magnetism:

1. **Diamagnetism**: arises from the orbital motion of electrons, which respond to oppose an applied field. It is present in all materials. For this reason diamagnetism is linearly proportional to an applied field, but in the opposite direction. Therefore susceptibility is negative. It is also independent of temperature. All materials have diamagnetism, but materials with filled electronic shells show only diamagnetism[107].

2. **Paramagnetism**: this is due to permanent magnetic moment from unpaired electrons in partially filled orbital. Outer electrons was not coupled hence spin atomic moment is generated[108].

3. **Ferromagnetism:**atomic magnetic moments due to the unpaired electrons in the atoms produce a strong molecular field that aligns magnetic moments parallel to the applied field to surrounding electrons[109].

4. **Antiferromagnetism:** materials with two sublattices have their magnetic Moments coupled by an exchange of electrons over an oxygen atom. This leads to antiparallel magnetic moments on adjacent sublattices[110].

2.9 Properties of maize tassel biomass

Maize Tassel is the male inflorescence of the maize plant, which forms at the top of the stem. Maize tassel are fibrous and rich in carbohydrates; they contain a high proportion of polysaccharides with cellulosic surface hydroxyl groups that can bind metal cations[111]. The availability of lignin in the dried maize tassel contributes to the adsorption of heavy metal ions in water pollutant[112]. Maize tassel require to be modified so as to improve the morphology and the sorption capacity to enable to remove heavy metals effectively[113].

Tassel is an agricultural waste that has shown good potential for the removal of heavy metals[114]. Other natural adsorbents such as, cotton stalks, plum kernels, corncobs, bagasse, peanut hulls and nutshells, and olive stones have been used by different researcher in the effort of eliminating heavy metals in the environment[115]. Maize tassel are able to remove significant amount of metals to a level within the permissible guideline values for arsenic, lead, mercury and manganese in drinking water. Activated carbon is the most widely used adsorbent for removal of some undegradable organic pollutants, but activated carbon is expensive hence the need to find cheaper ways of producing activated carbon hence the use of maize tassel[116]. Maize tassel possesses these functional groups on its surface –H, -O-H, NH^2,-C=O and –COOH due to cellulose, hemicelluloses and lignin as main components[117]. These groups makes the maize tassel to be polar hence enabling the binding to heavy metals on these active sites.

2.10 Effect of pre-treatment of biomass

The pretreatment of the biomass with alkalis, acids, detergents and heat, increase the metal ion absorption capacity of the biomass[118]. The pretreatment of biomass can increase, decrease or not change the metal adsorption capacity of the biomass[119]. In this case ethyl acrylate is being used which used for grafting the maize tassel. Before the grafting process the maize tassel are carbonized using muffle furnace which increases the surface area of the biomass. Carbonization of biomass also reducesmicrobiologicalactivities, which may occur on prolonged exposure of the biomass in water.The maize tassel carbonization introduces functional groups such as

–COOH, and –OH due to partial oxidation of the biomass[120]. This improves the surface of the sorbent hence creating more active sites for the metal ion to bond to.

2.11 Techniques for sorbent analysis

XRD have been known for decades and are capable of analyzing polydispersed samples. The synthesized nanoparticles were characterized using X-ray diffraction, which provides most definitive structural information such as crystallinity of nanoparticle, interatomic distances and bond angles within the nanoparticle[121].

2.11.1 FTIR

Fourier transform infrared spectroscopy technique is used for the determination of the functional groups responsible for the sorption process. Adsorption in the infarred region occurs due to vibrational and rotational motions giving rise to stretching and bending of molecular groups[122] .

2.12 Biosorption equilibrium

The adsorption isotherm is of great importance when describing the interaction of the adsorbent and the sorbent species. The properties such as affinity of the adsorbent and its surface properties can be investigated using the adsorption isotherms[123]. With the aid of the isotherms, an adsorption system can hence be designed. Some of these isotherms include the Langmuir and the Freundlich isotherm equations based on the type mechanism of sorption[124]. For example, the Langmuir equation only applies for monolayer sorption with the surface containing a finite number of identical sites. In this Langmuir model, there is a strong assumption that there is no interaction of any kind that is no chemical reaction between the species that get adsorbed onto neighboring sites on the same surface[125]. The Langmuir equation is expressed as follows:

$$\frac{Ce}{qe}=\left[\frac{1}{qmb}\right]+\left[\frac{1}{qm}\right]C \qquad (2.2)$$

Where C_e is the equilibrium concentration (mg/L), $q_e$being the amount adsorbed at equilibrium (mg/g). The constants established by the Langmuir isotherm; q_m (mg/g) and b (l/mg) are used to describe the monolayer adsorption capacity and the heat of the adsorption process respectively[126]. The Freundlich isotherm is based on the assumption that the sorption if occurring at a heterogeneous surface and hence describes multilayer adsorption. This is possible due to presence of the heterogeneous surface energies. The Freundlich isotherm is expressed as follows:

$$Inqe = InKf + \left(\frac{1}{n}\right)InC (2.3)$$

Where K_f is referring to the adsorption capacity (mg/g) and 1/n is an empirical parameter that is related to the intensity of adsorption[127]. In general, the intensity of the adsorption is found to vary with the heterogeneity of the adsorbent surface. The acceptable values of 1/n for which adsorption is favorable are in the range $0.1< 1/n< 1$. Also as the K_f value is increased, adsorption is favored. Sorption experiments must be carried out for the removal efficiency of a particular metal and can be calculated using the following equation

$$PercentageRemoval = \left(\frac{Co-Ce}{Co}\right) \text{ x } 100 (2.4)$$

Where C_0 and C_e are the initial and final metal concentrations (mg/L) respectively.

Kinetic studies are most popular models that are used to describe the reaction kinetics of many adsorption processes are the pseudo first order and second order models[128]. These models do quantify the respective extend of uptake of the heavy metal ions in the adsorption kinetics and are hence used to investigate and establish the respective mechanisms of adsorption and possible rate influencing steps.

For the first order kinetic model, the rate expression is as follows:

$$\log(qe - qt) = \log Qe - (k_{1/(2.303)})t(2.5)$$

Linear plots of the above equation with respect to log (q_e-q_t) versus t indicate the applicability of the model. The pseudo second order model is expressed as:

$$\frac{t}{qt} = \frac{1}{k_{2qe^2}} + \frac{t}{qe}(2.6)$$

And again the linearity of the plot of t/$q_e$against t determines the applicability of the model.

Information on the kinetics of solute uptake rate is required to select the optimum condition for full-scale sorption process. Several kinetic models have been established to describe the order of sorption based on the solution concentration. However the pseudo first order and pseudo second order kinetic model are most well linked to sorption studies.

2.13 Nanotechnology

Nanotechnology, biosorption andpolymerization major processed which was discussed in this paper. The fusion of these three recent developments in the removal of heavy metals has never been exploited before. There are a vast of advantages and properties, which will be facilitated by the use of these three major processes, whichwas explained in detail in the discussion. The main reason why the fusion of these processes in mainly that the limitations of the other process arecompensated by the benefits of the other resulting in an efficient and cheapest water treatment medium.

Magnetite nanoparticles, which are synthesis using Fe_3O_4 nanoparticles, are highly preferred mainly because they posesdistinctive characteristic such as finite-size effect,high ratio of surface-to-volume[129]. These nanoparticles have the ability to attract the heavy metals in the contaminated waste water it also enable the water treatment sorbent to be separated from the water medium [130]. The magnetite nanoparticles were removed using an external magnetic field, which will attract the magnetite nanoparticles.

Magnetite nanostructured particles of Fe_3O_4 can be successfully combined with the technique of biosorption from the ethyl acrylate grafted maize tassel to generate anon-biodegradable water treatment sorbent. Maize tassel have been used widely in water treatment but they tend to be attached with microorganisms hence the need of carbonizing the raw maize tassel[131]. Carbonization of maize tassel are carried out using different methods such treatment of the biomass with an acid either organic or inorganic acids such as sulphuric acid and hydrochloric acid. This method is veryexpensive and also not environmentally friendly. The second method utilizes the use of high temperatures to burn the carbon. The temperatures should not enable combustion hence it is carried out in a mufflefurnaces there are no other treatments which are requires hence it is cheap and environmentally friendly. Carbon basedmaterials are widely used due to the fact that they are so cheap and are readilyavailable.

Magnetic nanostructured particles of Fe_3O_4 can be synthesized using different methods this are co- precipitation, thermolysis of precursors, reverse micelles and micro-emulsion technology. According to Jolivetet al, 2004, Co-precipitation is the most efficient chemical method tosythesise magnetic particles. Stoichiometric mixture of ferrous and ferric salts in aqueous medium at a pH of between 8 and 14 are used to make the magnetite[132]. Controlling pH, ionic strength, temperature and nature of the salts produces nanoparticles which range from 5 to 100 nm in size. Reverse micelles and micro-emulsion technology involves the use amphoteric surfactants to create water-swollen reversed micelle structures in nonpolar solvents Deng et al. Nano droplets ofdifferent ranging from micelles (1-10 nm) and water-in-oil emulsions (10-100 nm) aqueous iron salt solutions are encapsulated aqueous iron salts forms nonreactors, which improve nanoparticle growth. Different size range of nanoparticles is obtained by varying the nature and amount of surfactant, surfactant, temperature and the surfactant concentration.

Monodisperse magnetite nanoparticles have been synthesizes using thermolysis of precursors Organic solution-phase decomposition of the iron precursor organic solution phase is exposed to temperatures above 200°C. Iron oxide nanoparticle synthesis which are synthesis using this method have high uniformity in the mean size, the size distribution and the crystallinity of magnetic iron nanoparticles[133]. The type of solvent, temperature, and time, are the factors, which affect the monodispersity of the nanoparticles. Magnetic Nano compositeof Fe_3O_4 are coated with inorganic material such as silica, gold or silver. Inner iron oxide core with an outer shell of inorganic materials was the physical structure of the nanoparticles. The stability of the nanoparticles in solution and the covalent binding with specific ligands to the nanoparticle surface are the properties of the nanotubes, which are enhanced by using this method

Iron oxide is a metal oxide, which as the following properties, the coordination environment of surface atoms, the redox and the oxidation state at surface layers which makes it suitable as anadsorbent. The metal oxide has electrons in the dorbitals, which enables it to function as an absorbent. Fe_3O_4 magnetite

Is a ferromagnetic and super paramagnetic, α-Fe_2O_3 is hematite with weakly ferromagnetic or antiferromagnetic magnetic properties and γ-Fe_2O_3maghemite, which is ferromagnetic. The magnetic property of the iron oxide nanoparticles depends upon shape and size of the particle. These magnetic properties of iron oxide nanoparticles can be easily oxidized in air and resulting in the loss of magnetism therefore there is need for surface coating using biosorbentbiosorbentsto stabilize the magnetic iron oxide nanoparticles hence the use of maize tassel activated carbon.

2.14 Polymerization

Polymers have recently gained attention globally in scientific, medical and industrial purposes. There are different types of polymers, which are categorized into natural and synthetic polymers. Polymers offer a wide range of advantages over other materials such as metals and ceramics. These advantages include being able to be tailored into desired polymeric materials by the use of addition on fillers and the most novel technologies such a nanotechnology. The properties of polymers can be doped with different materials so as to give it properties such as magnetic, electrical conductivity.

Biobased polymers has recently being exploited due to these factors, they are cheap, reduced environmental pollution, renewability and the most favorable one is that they are renewable. Grafting polymerization has also being used to modify biomass. There are different types of grafting polymerization such as chemical initiation and radiation initiation. Graft polymerization using radiation is fast but it is very expensive as compared to chemical initiation where the biomass is soaked into the solution and heated or refluxed so as to open up reactive sites.Maizetassel are one best option for polymer grafted due to the fact that they possess hydroxyl and amino groups (NH_2 and OH) these groups are the ones which participate to breakage by the chemical initiator. Grafting occurs in certain stages, whichare chain initiation, propagation and termination.

2.14.1 Controlled radical polymerisation

Controlled Radical Polymerisation (CRP) is mainly used in the generation of polymers which have a specific molecular weight. CRP polymerization determined the molecular weight of the polymer waybefore its synthesis[134]. This technique is achieved using three main methods whichTransfer Radical Polymerisation (ATRP), Nitroxide Mediated radical Polymerisation (NMP) and Reversible Atom-Fragmentation Polymerisation (RAFT). Of the three methods highlighted above (ATRP) is the most preferred by most polymer chemist due to its advantages[135]. Although there are a number of hindrances such as oxidation of the reactants, lack of control over the polymer crystallinity and denaturing of the polymer when high temperatures are used[136].

2.14.2 Atom transfer radical polymerisation

Atomic transfer radical polymerisation (ATRP) involves the transferring of atoms, which are involved in the reaction, and this is the main process, which controls molecular weight of the polymer[137]. Catalysts are a vital aspect of this type of polymerization and these are in the form of either ligands or metal halides.There are stages which are involved in ATRP polymerization, the first stage is homolytictransfer reaction of the free radicals to a transition metal complex initially in a lower oxidation state thereby forming an active organic radical[138]. The reaction which occurs involves thedonation of the transferred atom back to the growing radical reforming the dormant species and the transition metal complex back to its lower oxidation state completing the transfer reaction.Although free radicals are used in the polymerization, the stability of the reaction dependsonstability of the free radical species.

2.15 Catalyst

The main role of a catalyst is to facilitate the rate of reaction but without changing any chemical structure of the reagents[139]. This catalyst should be transition metal and a ligand. The use of copper, nickel, cobalt, and iron are frequently used in ATRP and in many cases they are coupled with complexing ligands such as nitrogen and phosphine based structures molecules to improve their effectiveness[140]. The metal center must have at least two readily accessible oxidation states separated by one electron for the catalyst to be accepted for ATPR polymerization. The factors below should be the characteristic of catalyst.

- Halogen affinity of the metal centre should be high
- There should be expansion of the metal centre upon oxidation to enable accommodation of a (pseudo)-halogen.
- The ligand should complex the metal relatively strongly.

2.16 Ligands

Ligands are classified as transition metals. In polymerization these saves a purpose of being a metal solubilizer and its structural, steric and electronic characteristics have a significant effect or influence on the catalytic activity and the reduction potential of the transition metal and also control of the ability of the polymerization. There are different types of ligands and N-based ligands generally change the properties of the catalyst depending on the solubility of the catalyst. In ATRP polymerization tridentate nitrogen ligands like N,N,N′,N′,N″-pentamethyl-diethylenetriamine (PMDETA) and tetra-dentate nitrogen ligands such as tris [2-(dimethylamino)ethyl]amine (Me6TREN) and 1,4,8,11-tetramethyl-1,4,8,11 tetraaza-cyclotetradecane have been used in ATRP reactions successfully to synthesize well-controlled polymers, such as poly(methyl acrylate).

2.17 Initiators

The initiation of polymerization depends on the initiator. This depends greatly on the chemical structure of the initiator. It also mimic the propagating radical structure hence facilitating polymer growth. The initiator can be either a low or high molar mass compound or even a part of an insoluble material, such as when initiators are tethered to the surface of modified particles, flat wafers, or even fibers. In ATRP only alkenes that form stabilized radicals can be used such that the inner sphere electron transfer process is reversible and the activation or deactivation reactions are repeated until all the unsaturated substrate is consumed.

In most ATRP reactions the initiator used is an alkyl pseudo halide. The nature of the alkyl halide should correlate with the ATRP equilibrium constants and its activity decreases as the alkyl group is varied from 3° > 2° > 1° with the activity of the alkyl bromide being larger than that of the corresponding chloride. The transition metal catalyst (Mt^n/Ligand) reacts with the alkyl halide initiator to generate the initiating system comprising of the alkyl halide, the transition metal and the ligand ($R-X/Mt^n/L$). This initiating system is then used to create a radical and a transition metal complex by transfer of the halogen to the catalyst. As the radical propagates by reacting with the monomer, it is rapidly deactivated by reaction with the oxidised transition metal halide ($X-Mt^{n+1}/L$) to reform the original catalyst and an oligomeric alkyl halide.

2.17.1 Typical initiators used and their structures

Choosing the correct conditions for initiation of an ATRP reaction is the first step that has to be taken in order to be able to carry out a well-controlled ATRP. Control over the initiation procedure is critical for the preparation of materials where exploitation of other aspects of controlled material synthesis is desire. Typically, the initiator, such as a peroxide (e.g. benzoyl peroxide, BPO) or a dialkyldiazene (e.g. 2,2'-azobisisobutyronitrile, AIBN), which is used to generate radicals, decomposes slowly compared to the rate of polymerization such that chains are continuously being generated and terminated. In order to exploit the benefits of a CRP, initiation should be fast and complete at low monomer conversion since this provides control over molecular weight, PDI, structure, functionality. When applied to preparation of materials that may result in large-scale production initiation procedures should be robust, inexpensive, and provide a clean ATRP.

2.18 Solvent

ATRP can be carried out in a variety of different solvents and conditions, including water at room temperature, and is tolerant of most functional groups. The solvent effects on ATRP are small except when water is used as it accelerates the rate of polymerization due to change in equilibrium affected by its polarity. Solvent effects on catalytic activity are a function of the reducing power of the complex and the affinity of the halide ion in a particular solvent. The polymerization environment and parameters can be altered, providing control over reaction kinetics.

2.19 Temperature

ATRP reaction temperatures range from room temperature to 150^0C, but can be altered depending on the desired conditions. The reaction can be done under vacuum or pressure and can be conducted in the presence of moisture but even in the presence of water under homogeneous or heterogeneous conditions. However for the process to continue in a controlled way, the reagents have to be in a homogeneous system as a heterogeneous system may result in low catalyst solubility, which may retard the polymerization process and might result in contamination of product.

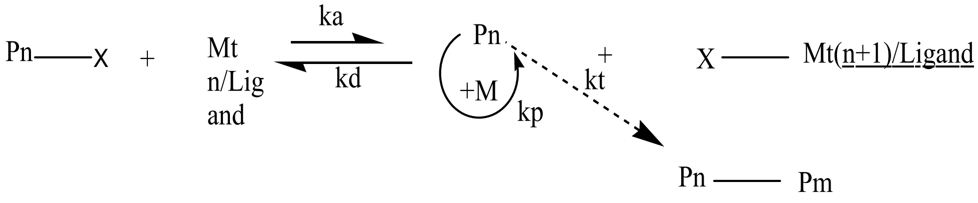
2.20 Oxygen

ATRP reactions are sensitive to oxygen and its presence during polymerization will result in oxidation of the transition metal catalyst to an oxidation state that is not effective. Only a little amount is tolerated hence oxygen should be removed from the reaction medium. Reducing agents can be added to the reaction medium such as ascorbic acid, reducing sugars or amines. Zero valent metals can also be used to enhance the rate of polymerization through reduction of the deactivator Cu (11) and also reduces the oxygen content in the reaction medium. The order of addition of reagents may vary but most often the initiator, or catalyst activator, is the last reagent to be added to a preformed solution of the catalyst in the monomer or solvent. Addition of a small amount of Cu (11) at the beginning of a reaction enables the deactivation process to occur immediately without requiring spontaneous formation by termination reactions thus providing higher initiator efficiency, reduced costs and instantaneous control.

2.21 Mechanism of ATRP

The ATRP technique was proposed as a controlled radical polymerization method depending on a reversible equilibrium between free radicals and dormant species realised by a redox reaction of a particular transition metal complex. It proceeds by a halogen abstraction from an alkyl halide to form a radical, followed by the radical addition to an alkene, then re-abstraction of the halogen to form the desired molecule. The transition metal complex is responsible for the homolytic cleavage of the alkyl halogen bond in dormant chain resulting from the alkyl halide reacting with the transition metal, e.g. Copper, in an inner sphere electron transfer process which generates the corresponding higher oxidation state and a propagating radical.

General mechanism for ATRP process



2.20.1 ATRP mechanism

Radicals are very reactive species that add quickly across double bonds to form long chains. This process continues until the chain end reacts with another radical to terminate the growth process. One way to observe this is to plot the molecular weight of the polymers as a function of conversion of the monomer into polymer. At very low conversion, high molecular weights are obtained and they remain at approximately the same level throughout the reaction. This process leads to a statistical distribution of molecular weights since the conditions change to favour longer or shorter chains. Termination reactions may occur due to radical disproportionation and coupling but as the reaction progresses radical termination is diminished as a result of the persistent radical effect (PRE), increased chain length, as well as conversion and viscosity. Termination is also minimized by low concentrations of activating species i.e. propagating radicals and high concentrations of the dormant species. Consequently, the equilibrium is strongly shifted towards the dormant species. Polymerisation effectiveness is due to the persistent radical effect which diminishes radical termination resulting in increased polymer growth.

2.20.2 Persistent radical effect

In ATRP, the halogen atom is reversibly transferred to a metal complex in a lower oxidation state and thereby propagating radicals are formed, which are the transient species, together with the complex in an oxidised state[141]. The oxidised form of the complex takes the form of the persistent radical species i.e. it does not self-terminate or propagate. In the reversible reaction of the ATRP equilibrium, the transient and persistent species will form simultaneously and disappear with equal rates.

If the equilibrium reactions are the only reactions occurring in the reaction medium, it is assumed that the concentration of the transient and persistent species should increase equally in time and reach a steady state value at equilibrium. With time the transient species are consumed through irreversible termination by coupling or disproportionation whereas the persistent species remain. This results in an increased concentration of the persistent species compared to the transient species as it balances the loss of the transient species from the system thus a steady state cannot exist apart for infinitive time when all the radicals have self-terminated.

As time increases, the decreasing concentration of the radicals will diminish the likelihood of their bimolecular termination. Increasing concentration of the persistent species results in the cross coupling of the transient species and the persistent species being the dominant reaction pathway[142]. Self-termination, though it does not cease completely, inhibits itself as the reaction proceeds. Product formation thus becomes evident as there is only one reversible radical formation such that he starting materials was constantly reformed and show very long lifetimes. However some reactions parallel to the reformation process may become important product forming steps which may result in false mechanistic conditions. The transient species may transform to other species such that the reaction products of the persistent species with the transformed transient species becoming dominant.

2.20.3 Reactions of ATRP

The dynamics of ATRP are important for a polymerisation result. Several factors affecting the equilibrium have been investigated and the optimum conditions for the polymerisation set[143]. K_{ATRP} can be defined by the bond strengths of the alkyl halide and the copper halide bond of the deactivator towards homolysis. This is due to the presence of the C – X bond strength of the alkyl halide, the bond strength between the transition metal and the halogen atom, radical stability and steric effect on alkyl halide, radical and metal centre[144]. The C – X bond strength and radical stability affects the alkyl halide reduction potential i.e. a more stable radical and a weaker C – X bond strength tend to shift the equilibrium towards the radical species increasing the alkyl reduction potential (E_{RX}). The metal halide bond strength affect the halidophilicity while the steric effects on the alkyl halide and the radical affect E_{RX} and the steric effects on the metal complex affect E_{Cu} and K_X. The inverse of the Cu (11) – X bond homolysis is termed halogenophilicity and portrays the formation of a Cu^{11} – X bond between the Cu (11) and the halogen atom radical. Side reactions may occur and these include potential deleterious outer sphere electron transfer processes, monomer coordination through pi-bonds, β – H abstraction and disproportionation of the copper (1) species in aqueous media.

CHAPTER THREE: RESEARCH METHODOLOGY

3.1 Introduction

This chapter gives a full detailed procedure of how the objectives of this study were addressed. There is the list of reagent and instruments that were used. Sampling and preparation of the adsorptive potential of maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybrid, the effect of the initiator and the polymer concentration, monomer concentration, reaction time, solvent concentration and reaction temperature , were investigated. The physico-chemical characterization of the maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybridbefore after heavy metal adsorption was investigated. This was achieved using batch experiments using the central composite design and equilibrium studies were fully explained.

3.2 Materials and Methods

3.2.1 List of materials

All the chemicals used were of analytical grade, hydrochloric acid (32%, (Associated chemical Enterprise), methyl red dye (A.C.E), sodium hydroxide (99.9%, (A.C.E), distilled water (M.S.U), potassium bromide (99.9%, skylabs), ammonium hydroxide (95.6%, 120mL) A.C.E), $FeCl_24.H_2O$ (A.C.E, 98.3%), $FeCl_3.6H_2O$ (A.C.E, 99.9%) distilled water midlands state university.

3.2.2 List of instruments

Fourier transform infrared spectroscopy (FTIR) Nicolet 6700, Flame Atomic Absorption Spectroscopy (FAAS) AA-6800, pH meter (Orion star, A211), analytical balance (Electronic scale, JJ22BC,) oven (Thermo scientific, China) rotary shaker (Rajendra, electrical industries),FTIR (Brucker6700)

3.2.3 Collection and preparation of carbonized maize tassel adsorbent

The maize tasselwas collected from Midlands State University field. The collected maize tasselwas washed with distilled water to remove impurities such as water-soluble organic compounds[145]. The washed maize tassel was first air dried to remove moisture and then oven dried at 105°C for 24 h to remove all the residual moisture.[146] The dried maize tasselwasblended using an electrical blender and the pulverized maize tassel burnt for 200°C in a muffle furnace. The carbonized maize tassel in then stored in sealed glass containers.

3.2.4 Preparation of grafted ethyl acrylate carbonised maize tassel

The ethyl acrylate was purified,byrunning the polymer through a column packed with aluminum oxide. Carbonized maize tassel powder (60g) was weighed using an analytical balance in a clean dry beaker. The weighed carbonised maize tassel wasslurriedinto 100 mL of (16 % w/w) acetic acid solution. The acetic acid and carbonized maize tassel was slurried in 15 mL distilled water and 3 mL of ethyl acrylate (0.17 M) was added into the refluxing cylinder and the resulting solution was stirred. (0.0035 M)of $K_2S_2O_8$ was added to the mixture which was stirred and then the reaction contains heated under reflux at 70°C for 2hr[147]. The precipitate was then filtered and washed with methanol then air dried for 24h. The resultantmaize tassel-ethyl acrylate biopolymer was stored,in a dry airtight glass container for further modification.

3.2.5 Preparation of grafted ethyl acrylate carbonised maize tassel embedded magnetite nanohybrid

Grafted ethyl acrylate carbonized maize tasselpowder(30.047g) was suspended in 120mL of distilled water. $FeCl_24H_2O$(15.008g) and $FeCl_36H_2O$(30.021g) were added into the suspension. The mixture was placed on the reciprocal shaker for 24 h and 25mL of ammonium hydroxide was added so as to maintain pH and further agitated for 10 minutes. A dark precipitate was formed which was vacuum filtrated and then washed with distilled water and dried to constant mass in the oven. The resultant maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybridwas then stored into glass containers for further investigation.

3.2.6 Characterization of the adsorbent

FT-IR was used for characterization of the synthesized resultant maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybridbefore and after adsorption. Approximately 15 mg of the maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybrid sample, plus 1 g of KBr were weighed out, milled and ground in a mortar and pestle for 5 min, until a fine smooth powder of even particle size is obtained[148.]Approximately 0.25g of resultant maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybridand KBr mixture were then pressed with a steel die into a pellet which was later analysed in the FTIR.

3.2.7 Maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybrid (MTEA-MN) Exchange Capacity

The removal efficiency and amount of exchanged Cd^{2+}ion by the grafted ethylacrylate carbonised maize tassel coated with magnetite nanoparticles weight was calculated using

Uptake (%) = $\frac{(C_O - C_k)}{C_O}100$(3.1)

Where: C_0 and C_k are the initial and final concentration of the cadmium (mgL^{-1}) respectively

The sorption capacity was calculated from the following equation:

A= $\frac{(C_O - C_k)}{m}V$(3.2)

Where: A: the adsorption capacity ($mg\ g^{-1}$); C_0 and C_k: the initial and final concentration of cadmium ($mg\ L^{-1}$); V: the sample volume (L); m: the magnetite maize tassel activated carbon.

3.2.8 Influence of reaction parameters on grafting percentage

The grafting efficiency was investigated using the effect of initiator concentration, effect of monomer concentration, effect of temperature, solvent concentration and reaction time were the variables which were investigated.

3.2.9 Grafting percentage

The grafting percentage (GP) indicates the increase in weight of original carbonized maize tassel biomass. The effect of grafting on the biomass by a polymeric polymer with a monomer and is calculated generally by the following

Equation:

$$Graftingpercentage = \frac{weightofpolym}{initialweightofbackbone} X100 (3.3)$$

3.2.10 Effect of initiator concentration on the grafting percentage

The ethyl acrylate was purified through a column packed with aluminum oxide. 1g of maize tassel powder was weighed used by the mass balance and placed into a clean dry beaker. The weighed carbonised maize tassel was dissolved into 1L of (2 % w/w) acetic acid solution. A range of (0.5, 1, 1.5, 2, 2.5 g) of $K_2S_2O_8$ wasadded to the different mixtures containing 1g of carbonised maize tasselwhich was then heated at 70°C under reflux for 2h. The precipitate was filtered and washed with methanol then it was air dried for 24h. The contents were heated at 75°C which was the optimum temperaturetemperature and a pH of 6 for the different stated temperaturetemperature ranges above and the resultant grafted product was then sun dried and weighed and grafting percentage was calculated from the mass

3.2.11 Effect of monomer concentration on graftingpercentage

Different volumes of the ethyl acrylate(5, 10, 15, 20, 25 mL)wereadded to separate containers. The fractionated maize tassel powder (1g) was weighed by a mass balance in a clean dry beaker. The weighed carbonised maize tassel was dissolved into 1L of (2 % w/w) acetic acid solution. A range of (0.5, 1.0, 1.5, 2.0, 2.5 g) of $K_2S_2O_8$ was added to the different mixtures containing 1g of carbonised maize tasselwhich was heated at 70°C under reflux for 2h. The precipitate was filtered and washed with methanol then it was air dried for 24h.

3.2.12 Effect of temperature on grafting percentage

The fractionated maize tassel powder (1g) was, weighed and placed into a clean dry beaker. The weighed carbonised maize tassel was dissolved into 1L of (2 % w/w) acetic acid solution. A range of temperatures(25, 50, 75, 85 and 100 ^{o}C) were used to investigate the effect of temperature on grafting . A mass of 0.5g of $K_2S_2O_8$ wasadded to the different mixtures containing 1g of carbonised maize tasselwhich wias then heated at 75^{o}C under reflux for 2h. The precipitate was filtered and washed with methanol then it was air dried for 24h. The contents were heated at 75^{o}C which was the optimum temperature and a pH of 6 for the different stated temperature ranges above and the resultant grafftedbiomass was then sun dried and weighed and grafting percentage was calculated from the mass

3.2.13 Effect of reaction time on the grafting percentage

The carbonized maize tassel powder (1g) was weighed by a mass balance in a clean dry beaker. The weighed ethyl acrylate carbonised maize tassel was dissolved into 1L of (2 % w/w) acetic acid solution. A range of (60, 120, 180, 240 and 390 min) were used to investigate the effect of reaction time on grafting. A mass of 0.5gof $K_2S_2O_8$ was added to the different mixtures containing 1g of carbonised maize tasselwhich wias then heated at 75^{o}C under reflux for different times stated above.The precipitate was filtered and washed with methanol then it was air dried for 24hrs. The contants were heated at 75^{o}C which was the optimum temperature and a pH of 6 for the different stated temperature ranges above and the resultant biopolymer nanohybridwas then sun dried and weighed.Thegrafting percentage was calculted using the equation stated above.

3.3 Sorption studies

3.3.1 Experimental design

A central composite design (CCD)was used to determine the parameters which were used to determine the effects of pH (2-6), contact time (5-425 min), adsorbent dosage (0.1-1 g) and initial Cd (II) concentration (5- 45 mgL^{-1}) on Cd (II) ions removal from aqueous solution. The central composite design generated an experimental domain. Optimum levels were determined using the variables above. The experimental domain was presented. The percentage removal of Cd (II) ions was to be taken as the response variable. The experiments were designed using a software calledDesign expect Version 9.

3.3.2 Thermodynamicstudies

The thermodynamic study of the cadmium adsorption experiments was carried out at four different temperatures (20, 30, 40 and 50°C). Optimum conditions of 25ppm initial concentration, pH of 6.0, 320 min and dosage of 0.6 g of sorbent were used to determine thermodynamics of the reaction. A magnetic stirrer was used to mix the contents and thermometer was used to measure and monitor the temperature of the contents. Residual cadmium concentration was measured and the thermodynamic nature of cadmium studied and calculations done using the equation below. The thermodynamic parameters ΔG^o, ΔS^o and ΔH^o for this adsorption process was determined by using the following equations[149]:

$$\Delta Go = \Delta Ho - T\,\Delta So \qquad (3.4)$$

where:

$$-\Delta G\ o\ ads = RT\ In\ (K)$$

ΔG^o is the free energy change (kJ/mol),

Tis the absolute temperature (K),

R is the universal gas constant (8.314 J mol/K)

K is the Langmuir constant.

The Gibbs free energy of adsorption (ΔG^o) can be related with the equilibrium constant K which correspond to the reciprocal of the Langmuir constant b.

3.3.3 Regeneration of theadsorbent

Desorption of the cadmium ions, the concentration of 25ppm was used with 0.6 g of absorbent per 100 mL. The 100 mLsolutions were transferred to labelled bottles containing 0.6g of sorbent. The sorbent was filtered after the solutions were shaken at 120 rpm for 60min.The solutions will then filtered and analyzed using the FAAS and maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybrid (MTEA-MN) was washed with different concentrations of HCl ranging 0.5,1.1.5,2,2.5. The 100 mLsolutions containing the above concentrations of HCl were transferred to labeled bottles containing 0.6g of sorbent[150]. The sorbent was filtered after the solutions were shaken at 120 rpm for 60 minutes, which was used before progress of the adsorption was checked by analysing for the residual concentration of the metals using the FAAS for cadmium ions.

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 Introduction

This chapter outlines the results obtained in the research and the discussions on the deductions made from the obtained data. This chapter also gives a detailed discussion regarding the results, which were obtained from the investigation of the effect of grafting ethyl acrylate on carbonized maize tassel and the biosorption studies, which were carried out.Kinetic, thermodynamic and isotherm studies were also investigated.

4.2 Fourier transform infrared (FTIR) Analysis

Fourier Transform Infrared Spectrometer (Bruker) was used in the characterization of maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybridbefore and after biosorption of cadmium. Table 4.1 of the results obtained with their respective functional group assignments. FTIR analysis enables the identification of peaks of different functional groups which were present referring to information from the literature. Fig 4.1 presents carbonized maize tassels.

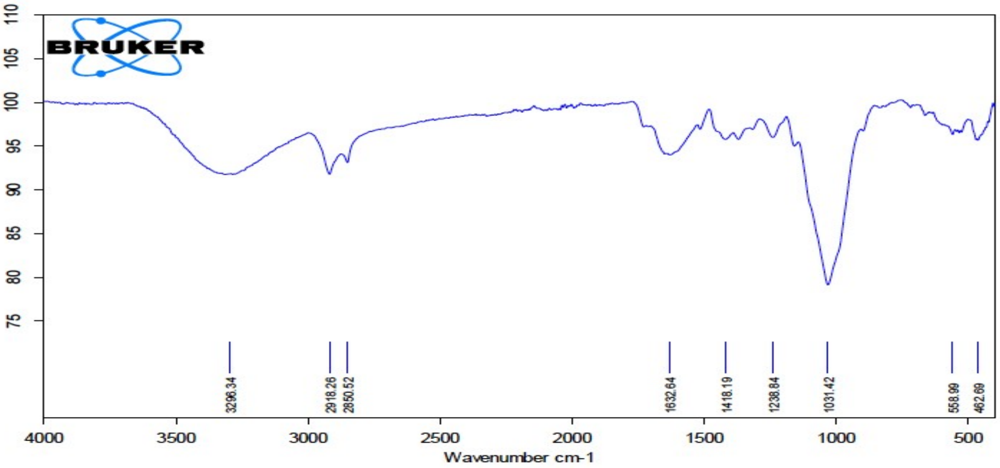


Figure 4.1: Carbonized maizetassel

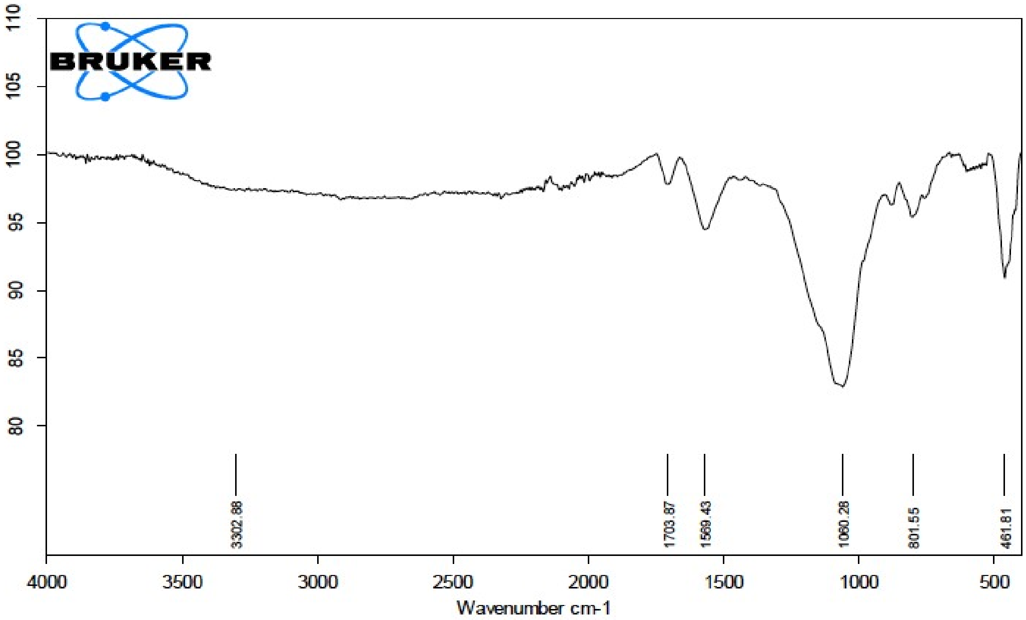


Figure 4.2: FTIR spectrum of MTEA-MN

Table 4.1: Comparison of peak positions of Raw Carbonized Maize Tassel and maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybrid (MTEA-MN)

	Wave number (cm^{-1})	
Peaks	Carbonized maize tassel	Carbonized maize tassel modified with magnetic nanoparticles
O-H stretching	3302.68	3296.34
C-H stretching	1713.44	2918.26
C-O-H bending	1557.50	1632.64
N-H stretching	1401.19	1400.39
C-H stretching	617.83	558.99
Fe-O stretching		462.09

Hydroxyl groups, carboxyl, carbonyl, amino and nitro groups are the peaks which were detected on the raw tassel before modification and these sites are the ones which makes the biosorbent very effective in heavy metals removal. After modification with magneticnanoparticles, the alcoholic group found at 3296.34cm^{-1} on the carbonized maize tassel widens and shifts to 3302.68 cm^{-151}. The C-H bond found at 1713.44 cm^{-1} on raw tassel before modification sharpens to 2918.26. The C-O-H peak found at 1557.50 cm^{-1} also broadens to 1632.64 cm^{-1} on the carbonized maize tassel modified with magnetic nanoparticles[152]. There are many peaks which are present on the carbonized maize tassel modified with magnetic nanoparticles these following peaks confirm that the raw maize tassel were modified to produce a better sorbent with many active sites which can participate in biosorption of cadmium., C-H stretching at 617.83 cm^{-1} and Fe-O cm^{-1} bond at 462.09 cm^{-1} bond.

As for the carbonised maize tassel modified with magnetic nanoparticles, several functional groups can be seen to have been added due to modification. The sharp peak at 3296.34 cm^{-1} and 2918.26 cm^{-1} can be assigned to the stretching of the O-H of alcohols, phenols and carboxylic acids. The peaks observed at 2924.45 cm^{-1} and 2928.54 cm^{-1} are the stretching vibrations of C-H bonds of carboxylic acids and these have very strong intensities. The peaks observed at 1632.64 cm^{-1}, 1418,19 cm^{-1} can be assigned to the C=O of carboxylic acids and the -C-O-H bending and N-H bond is assigned to 1418.19 cm^{-1}bonds . The peak observed at 1031.42 cm^{-1} can be assigned to the stretching vibrations of the phosphate group which has strong intensity.

4.2.1 Comparison of Peak Positions of Carbonized Maize Tassel Raw Coated With Magnetic Nanoparticles and maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybrid (MTEA-MN)

4.2.2

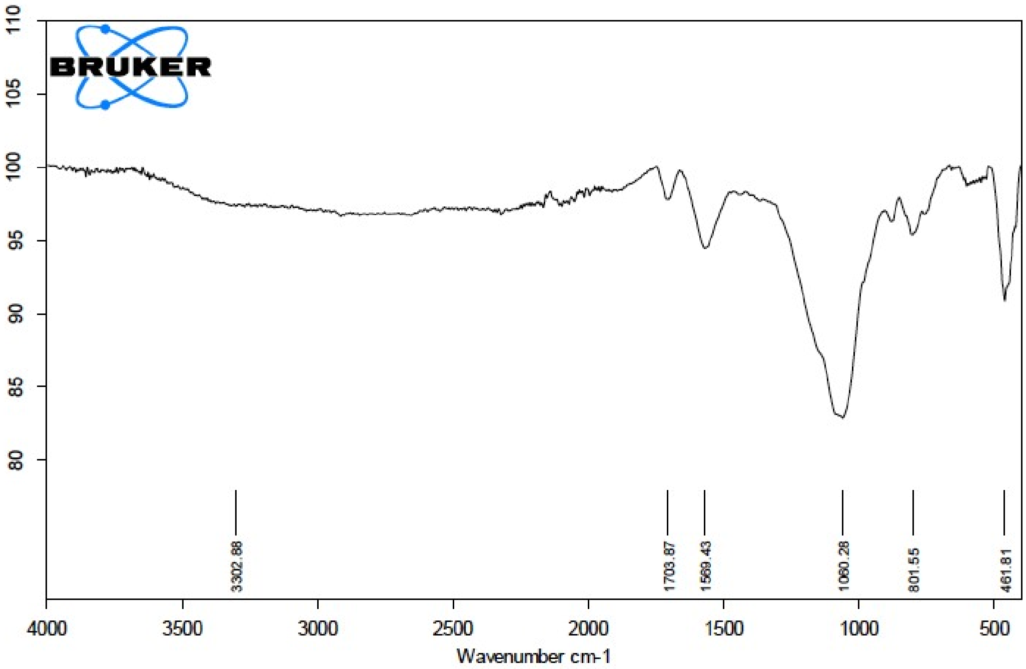


Figure 4.3: Carbonised maize tassel coated with magnetic nanoparticles

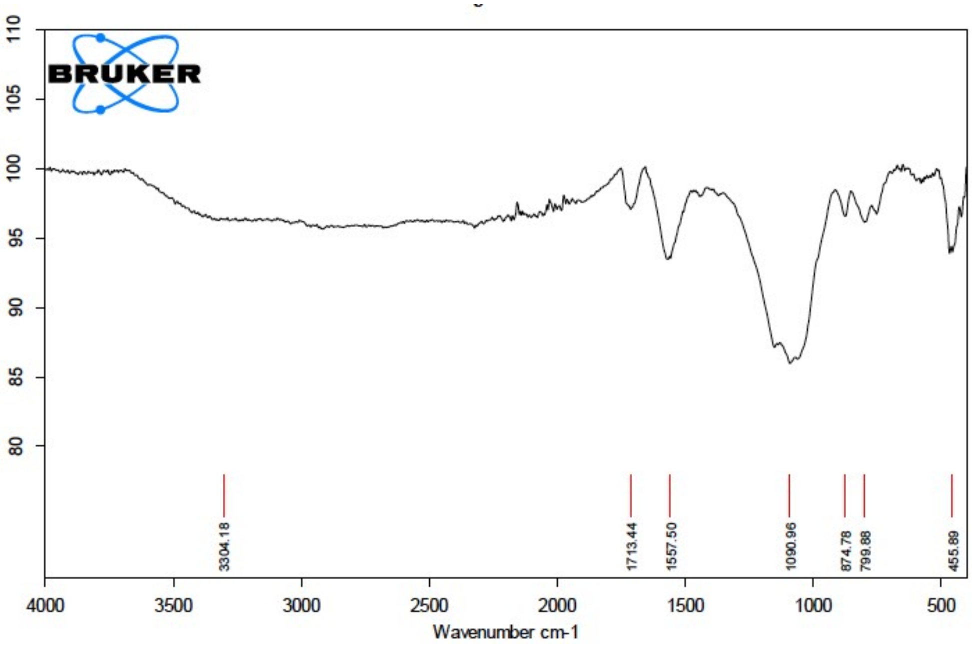


Figure 4.4: maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybrid (MTEA-MN)

The following Figure 4.2 and 4.3 shows carbonized maize tassel modified with magnetic nanoparticles and ethyl acrylate grafted carbonized maize tassel. The table of the results obtained below shows respective functional group assignments of FTIR analysis hence enabling the identification of peaks to different functional groups which were present in the ethylacylate grafted carbonized maize tassel with magnetic nanoparticles referring to information from the literature.

Table 4.2: Comparison of FTIR Bands of CarbonizedMaize Tassel Coated with Magnetic Nanoparticles and Maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybrid (MTEA-MN)

	Wave number (cm^{-1})	
Peaks	Ethylacyrate grafted carbonized maize tassel coated with magnetic nanoparticles	Carbonized maize tassel coated with magnetic nanoparticles
O-H stretching	3304.18	3296.34
Aliphatic acid	1713.44	
C=O Stretching		2918.26
Alkyl C-H Stretch		
C-O-H bending	1557.50	1632.64

N-H stretching	1009.96	
C-H stretching		1400.39
Aromatic C-H Bending	799.88	558.99 462.09
Fe-O stretching	455.89	

Peaks appeared at 455.89 cm^{-1}, 779.88cm^{-1}, 897.87 cm^{-1}, 1009.96 cm^{-1}, 1557.50 cm^{-1}, 1713.44 cm^{-1}, and at 3304.18 cm^{-1}. The peak at 455.89 cm^{-1} is attributed to the magnetitic nanoparticles. The sharp peak at 799.88 cm^{-1} is due to the out of plane CH-bending of the aromatic ring with all the C-H bonds oscillating in a phase which is typical of mono-substituted aromatic ring [153]. The peak at 897.87 cm^{-1} is attributed to the deformation vibrations in the aromatic ring. The peaks at 1009.96 are characteristic of the presence of a C-O-C vibration of the ester group present in acrylate polymers. The sharp peak at 1557.50 cm^{-1} is due to the stretching vibrations of the carbons in the aromatic ring. The C=O bond is confirmed by the peak at 1713.44 cm^{-1} showing the presence of the acrylate ester group while the peak at 1609.96 cm^{-1} may also be used to confirm the C=C stretching vibration in a conjugated system of the phenyl ring on the styrene molecule[154]. 3304.18 cm^{-1} is assigned to the stretching vibrations of the CH_2 groups in acrylate polymer and the C-H groups in the aromatic ring. This confirms the presence ethyl acrylate grafting on carbonized maize tassel coated with magnetic nanoparticles.

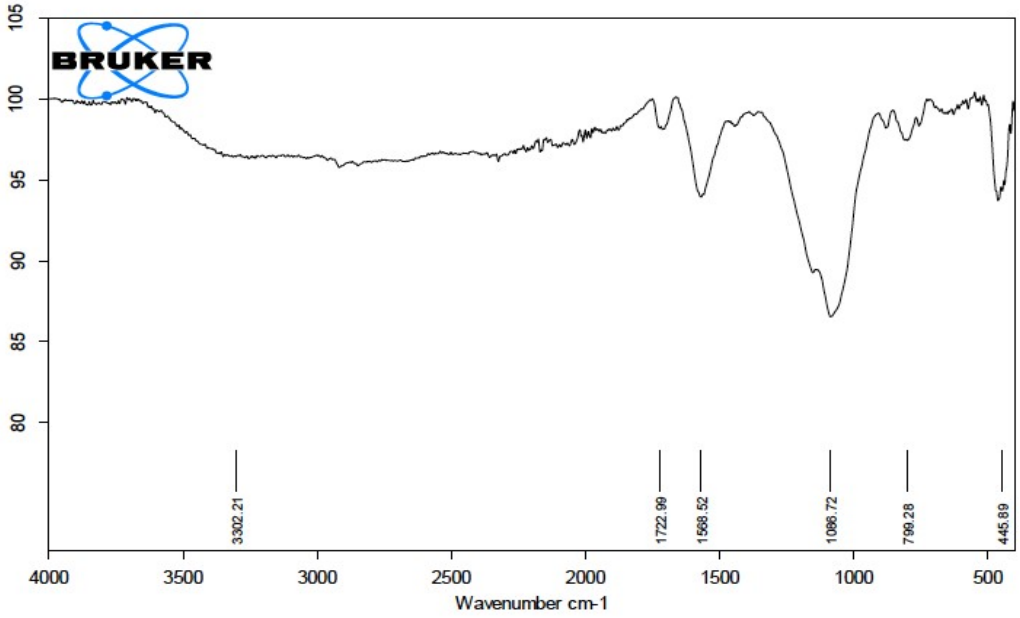


Figure 4.5: Maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybrid (MTEA-MN) loaded with cadmium

Table 4.3: Comparison of FTIR Bands of beforeMaize tassel-ethyl acrylate biopolymer embedded magnetic nanohybrid (MTEA-MN) and after Cadmium Absorption

	Wave number (cm^{-1})	
Peaks	Before cadmium sorption	After cadmium sorption
O-H stretching	3304.18	
C-H stretching	1713.44	1713.44
C-O-H bending	1557.50	1556.76
N-H stretching	1009.96	1075.14
C-H stretching	799.88	
Fe-O stretching	455.89	416.69

After the sorption of cadmium, grafted erhlyacylate carbonized maize tassel coated with magnetic nanoparticles, several functional groups can be seen to have been disappeared. Fe-O bond at 416.96 cm^{-1} intensity decreased cm^{-1} and C-H stretching bond at 617.83 cm^{-1} and O-H stretching bond at 3304.18 cm^{-1} all disappeared indicating that indeed biosorption of cadmium occurs and these groups participated in the removal of this heavy metal.

4.3 Grafting reactions

4.3.1 Effect of monomer concentration

The grafting percentage of maize tassel-ethyl acrylate biopolymer was studied as a function of theamount of monomer concentration. Figure 4.6 below shows that the degree of ethyl acrylate grafting on carbonized maize tassel increased steadily with an increase in the amount of monomer. A further increase in the amount of monomer resulted decrease in the degree of grafting, which was attributed to the excess polymer will be forming in the solution instead of occupying active sites, which was present on the sorbent. Optimum concentration of monomer was reached and the monomer molecules reacted with each other, leading to EA homo-polymerization and ultimately decreasing the degree of grafting.

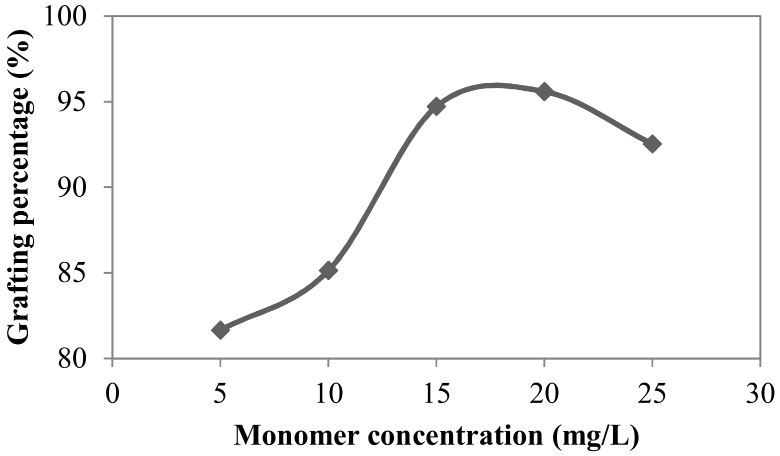


Figure 4.6: Effect of monomer concentration on grafting

Effect of initiator concentration

Figure 4.7 depicts the effect of $K_2S_2O_8$ initiator ratio in the degree of grafting. There is an increased with increasing initiator until it reached a point when it decreased. The initial increase in percentage grafting was attributed to the formation of a large number of free radicals in the reaction system, which facilitated the graft copolymerization synthesis reaction[155]. Optimal ratio was reached, the free radicals that initiate grafting were saturated and extra free radicals initiated homo-polymerization of ethyl acrylate, causing a decrease in the degree of grafting.

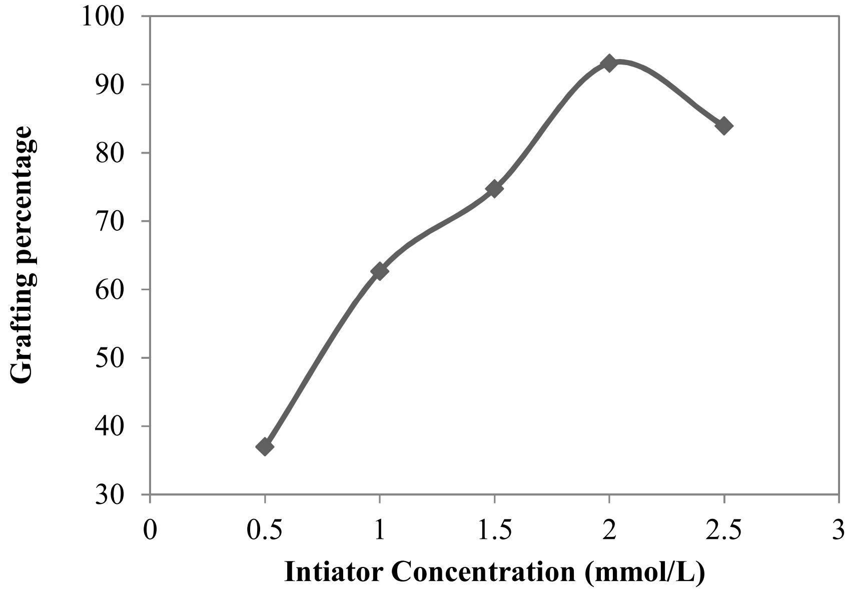


Figure 4.7: Effect of initiator concentration on grafting

4.3.2 Effect of reaction temperature

Graft copolymerization of ethyl acrylate and carbonized maize tassel coated with magnetite nanoparticles was carried out at different temperatures, ranging from 25 to 100 °C and Figure 3 shows the effect of reaction temperature on graft copolymerization. The degree of grafting increased with increasing temperature up to 75 °C while it decreased at higher temperatures. The decrease in the degree of grafting was attributed to homo-polymerization at higher temperatures as the reaction was accelerated with the increasing level of kinetic energy. In addition, disintegration of the graft copolymers may have occurred at higher temperatures.

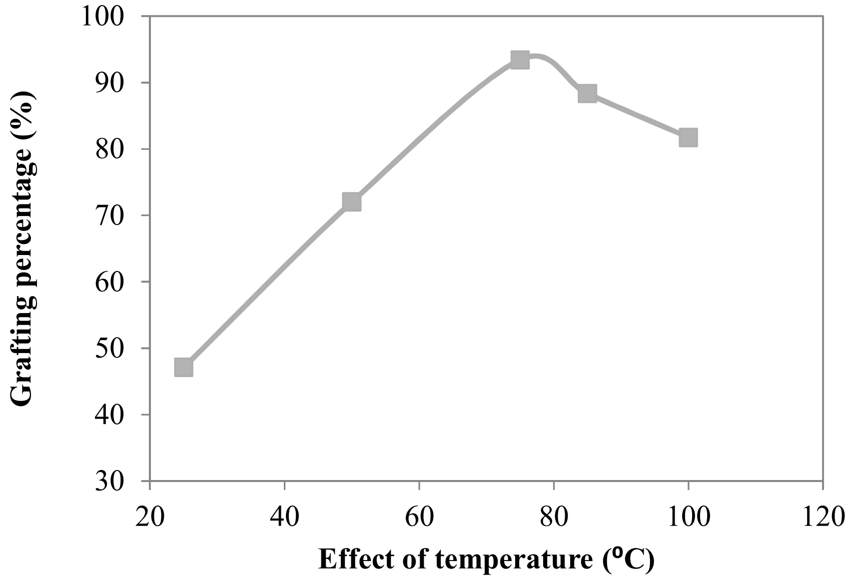


Figure 4.8: Effect of temperature on grafting

4.3.3 Effect of reaction time

The degree of grafting of ethyl acrylate onto carbonized maize tassel coated with magnetite nanoparticles onto was studied as a function of reaction time and the results are presented in Figure 4.9. The degree of grafting initially increased with an increase in reaction time and then decreases. The percentage grafting was found to increase to an optimum value and decreases due to the abridged availability of radical sites on onto maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybridback bone. The abridged availability of the radical sites has been attributed to the abstraction process

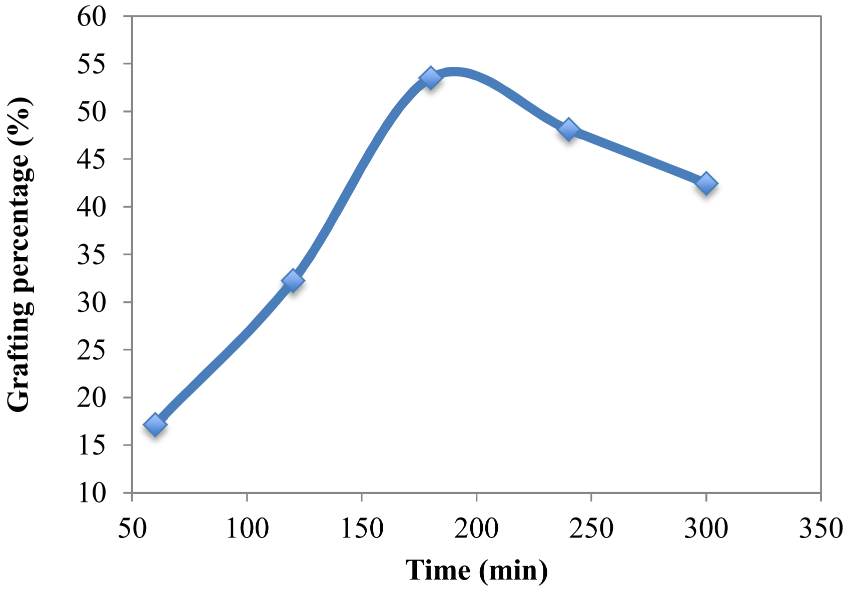


Figure 4.9: Effect on reaction time on grafting

4.3.4 Effect of solvent concentration

The degree of grafting of ethyl acrylate onto carbonized maize tassel coated with magnetic nanoparticles was studied as a function of the amount of solvent acetic acid. Figure 5 shows that the degree of grafting increased steadily with an increase in the amount of acetic acid up to 10mL. A further increase in the amount of solvent resulted in a decrease in the degree of grafting, which was attributed to the fact that higher amounts of acetic acid may have inhibited the interaction between the two reaction components (carbonized maize tassel coated with magnetic nanoparticles and the growing graft chains) leading to a lower degree of grafting.

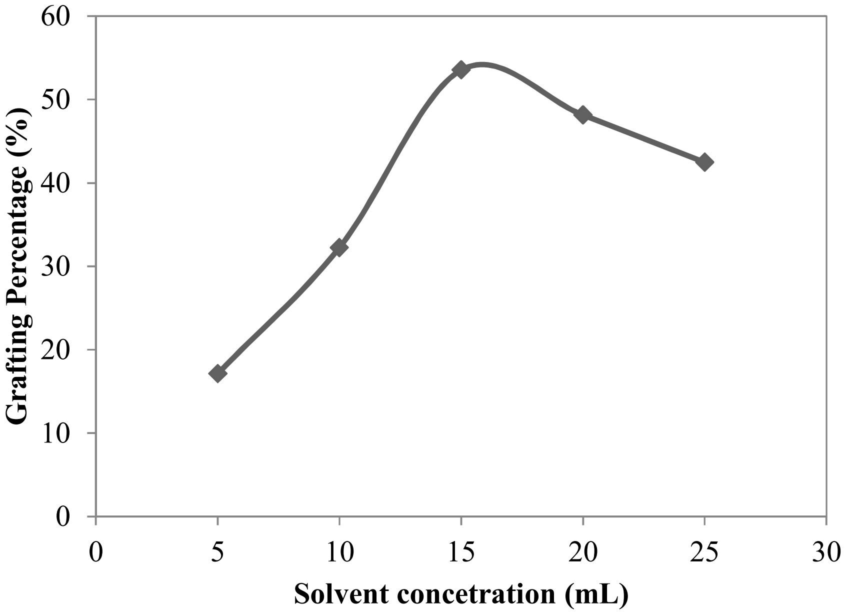


Figure 4.10: Effect of solvent on grafting

4.4 Batch adsorption studies

Batch studies were carried out using maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybrid. These studies were carried out following the experimental domain in Table 4.4. Synthetic cadmium was prepared in the laboratory and results in Table 4.5 were obtained.

Table 4.4: Experimental domain

	pH	Contact time (minutes)	Initial Concentration (mg/L)	Dosage (g)
Min point	2	5	5	0.2
Max point	10	425	45	1
Mid point	6	215	25	0.6

4.4.1 Central composite design

The design enable the generation of crucial formation of regression mathematical model which generates Logit transformations which, enable the data to be restricted from 0% - 100% and to improve on the model based on lack of fit test. Surface model response was described using the regression model generated from a central composite design[156]. The experimental variables and results obtained for this response are shown in Table 4.5 below

Table 4.5: Experimental variables and experimental response

Run	**Factor A:pH**	**Factor B:Contact time**	**Factor C:Dosage**	**Factor D:Initial metal concentration**	**Response Cd removal**
		min	G	mg/L	%
1	6	215	0.2	25	**85.66**
2	10	215	0.6	25	**90.04**
3	6	215	0.6	25	**94.62**
4	4	320	0.4	15	**79.98**
5	4	320	0.4	35	**82.19**
6	6	215	0.6	25	**94.61**
7	6	215	0.6	25	**94.61**
8	6	215	0.6	5	**97.84**
9	8	110	0.4	35	**84.50**
10	4	110	0.4	15	**82.29**
11	6	5	0.6	25	**50.10**
12	4	320	0.8	35	**81.15**
13	6	215	0.6	25	**94.61**
14	2	215	0.6	25	**73.72**
15	6	215	0.6	45	**95.65**
16	6	215	0.6	25	**94.62**
17	8	110	0.8	15	**85.59**
18	4	110	0.8	35	**82.01**
19	8	320	0.8	35	**86.07**
20	8	320	0.4	35	**84.73**
21	6	215	1	25	**99.61**
22	6	425	0.6	25	**95.25**
23	6	215	0.6	25	**94.62**
24	8	110	0.8	35	**85.99**

25	4	110	0.8	15	**81.12**
26	8	320	0.8	15	**83.63**
27	4	320	0.8	15	**82.15**
28	8	110	0.4	15	**82.44**
29	8	320	0.4	15	**83.84**
30	4	110	0.4	35	**79.94**

4.4.2 Response surface modeling

The general non transformation model was used for response surface analysis

The final regression model equation after removal of all insignificant independent variables is as follows:

Logit $R= b_o + p + t + d + c + p^2 + t^2 + d^2 + c^2 + pt + pc + td + tc + dc$

Where A= pH and B = contact time, C= initial concentration and D= dosage
Model parameters (Qe):

Table 4.6: Response surface modelling

Source	Value	Standard error	T	Pr> |t|	Lower bound (95%)	Upper bound (95%)
Intercept	-0.011	1.607	-0.007	0.994	-3.458	3.435
p	0.415	0.237	1.752	0.102	-0.093	0.924
t	0.011	0.004	2.545	**0.023**	0.002	0.019
d	-7.990	2.852	-2.801	**0.014**	-14.107	-1.873
c	0.287	0.045	6.359	**<0.0001**	0.190	0.384
p^2	-0.033	0.014	-2.287	**0.038**	-0.063	-0.002
t^2	0.000	0.000	-3.974	**0.001**	0.000	0.000
d^2	7.033	1.835	3.832	**0.002**	3.097	10.970
c^2	0.000	0.001	0.275	0.787	-0.001	0.001
pt	0.000	0.000	-0.045	0.965	-0.001	0.001
pd	-0.042	0.184	-0.231	0.821	-0.436	0.351
pc	0.002	0.004	0.638	0.534	-0.006	0.010
td	-0.001	0.003	-0.200	0.845	-0.008	0.007
tc	0.000	0.000	0.200	0.845	0.000	0.000
dc	-	0.037	-	**<0.0001**	-0.336	-0.179

0.258	7.017

The data above in table 4.6 indicates that the data fits well to the proposed model as the t values are below 1.

Model fits the data well but there is need for model validation to enable the results which was produced by the model to be accepted and noted as good data description[157]. There are several tests which are used to validate the model these include normal probability plot, checking for outliers, study of standard residuals versus predicted results and the lack of fit test which should be below 0.05[158] . The normal probability plot graphs utilises the quantiles of the data to be tested against the corresponding quantiles of a theoretical normal distribution with the same mean and standard deviation which would have been observed by the model. These plots are produced by a statistical program. Normally distributed data has to be scattered randomly around the line and from the results exhibited by the graph above the residuals are close to the straight line and are scattered randomly around it with no particular pattern which concludes that the data is normally distributed and hence it is suitable for modeling[159].

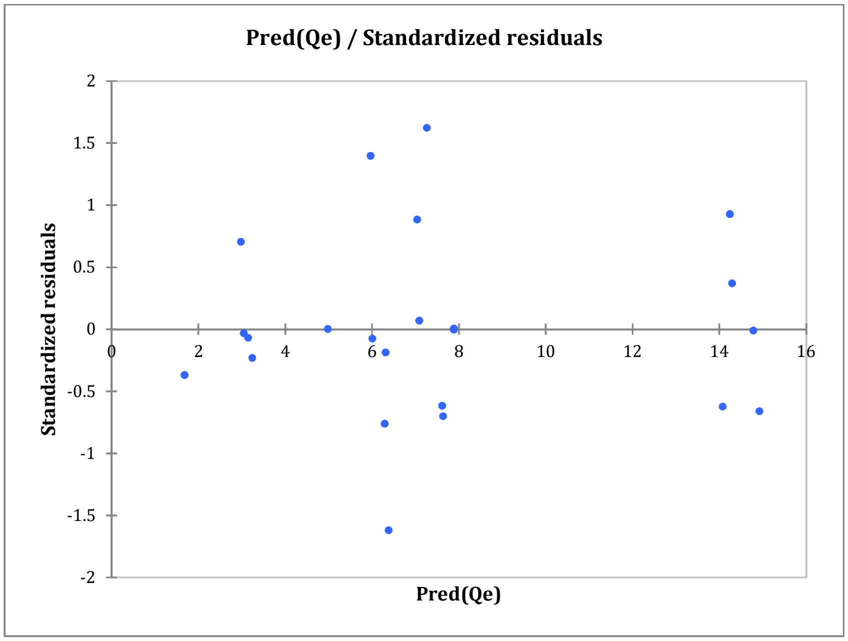


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Figure 4.11: Normal Plot of StandardizedResiduals

The data above in Fig 4.11 shows that the results were spreading a scattered manner across the centre line without a defined pattern. This alone shows how reliable the model is in the analyis of the values obtained.

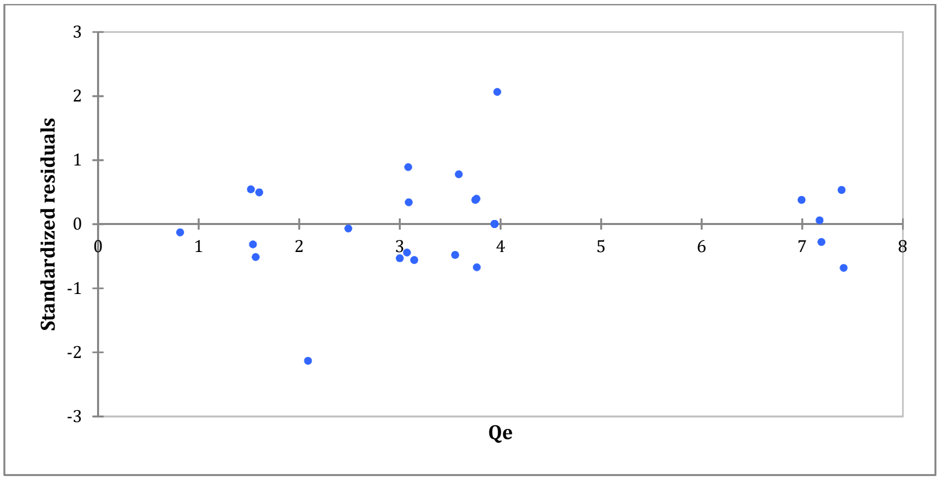

Figure 4.12:PredictedPlot of Standardized Residuals

The residual versus outlier t-value shows no outliers. There is also random distribution of responses residual versus predicted values which also shows that the results do not follow a certain pattern hence the method is validated[160]. After validating the model it may be used to interpret the data.

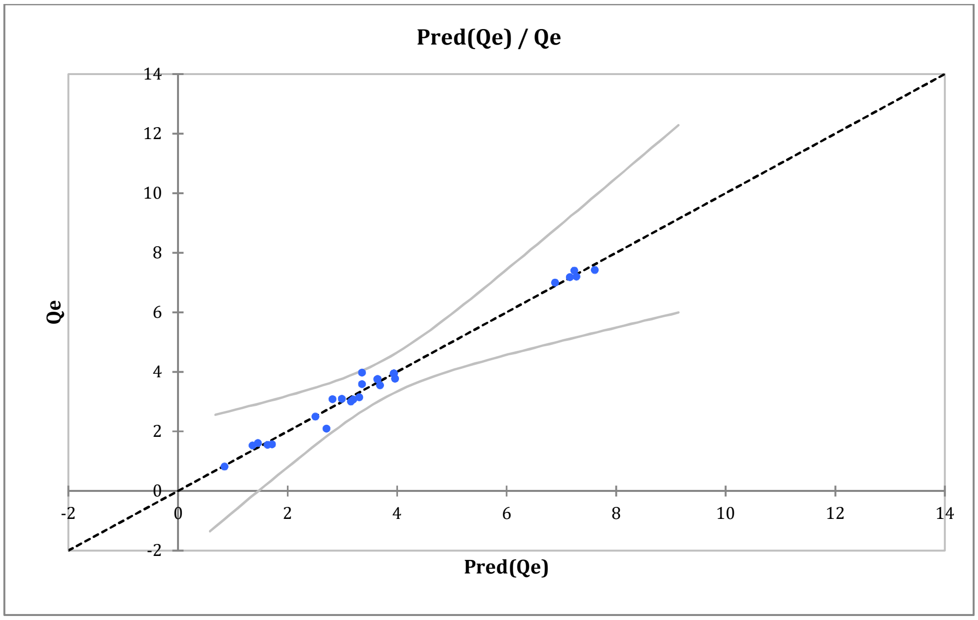

Figure 4.13: Plot of standard residuals vs predicted values

4.5 Equilibrium Studies

Adsorption isotherms are used for analyzing the relationship between adsorbate-adsorbent interactions. These interactions occur during the sorption studies and the isotherms were used to enable the validation of the interactions involved in adsorption studies.In this study, the equilibrium data was expressed using two isotherms Langmuir and Freundlich.

4.5.1 Langmuir Isotherm

The isotherm describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. It shows the equilibrium distribution of metal ions between the solid and liquid phases and it is only valid for monolayer adsorption onto a surface containing a finite number of identical sites[161]. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface.

The non-linear Langmuir isotherm is given by:

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \quad (4.1)$$

. The Langmuir constant b was in the range (0.1 <q_e< 1), showing that adsorption is favourable[162].

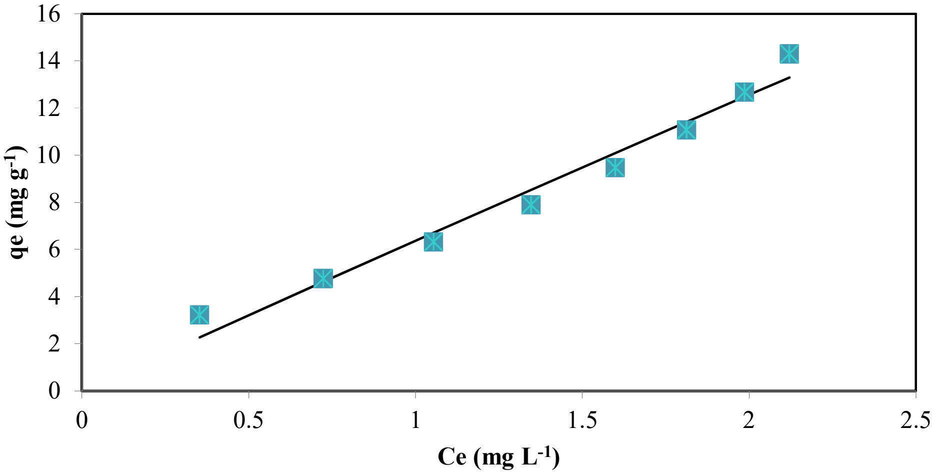

Figure 4.14: Langmuir isotherm

4.5.2 FreundlichIsotherm

Freundlich isotherm describes the adsorption characteristics for the heterogeneous surface on sorption studies.

The non-linear Freundlich isotherm is given by:

$q_e = K_F C_e^{1/\square}$,a straight line was generated by the plot of Inq$_e$vsInC$_e$ and the n and the K_F were be calculated from the slope and intercept respectively. The calculated value of Freundlich constant qe was 0.467which is in the range (0.1 <qe< 1), showing that adsorption is favourable. The sorption studies fitted this isotherm due to its R^2 value of 0.974 which the high when comparing it with the other isotherms.

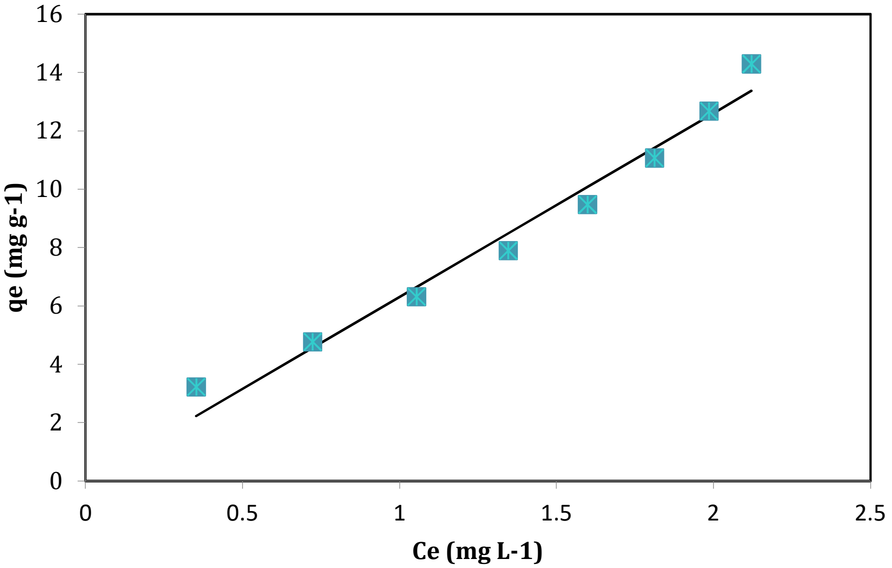

Figure 4.15: FreundlichIsotherm

Table 4.7: Equilibrium parameters obtained adsorption isotherms analysis

Adsorption isotherm	**Parameter**	**Value**
	q_{max} (mg g^{-1})	459.37
Langmuir	K_L(mg L^{-1})	0.014
	R^2	0.987
	SSD	1.695
Freundlich	K_f	0.7436
	n	0.4679
	R^2	0.9740
	SSD	2.878

4.6 Thermodynamics

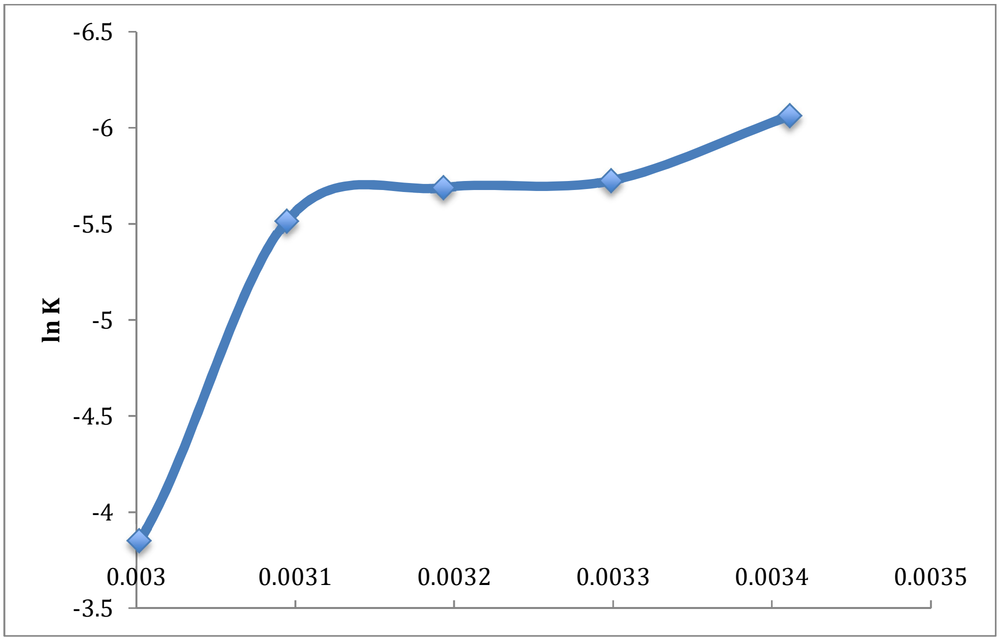

Figure 4.16: The Van't Hoff Plot for Adsorption of Cd (II) onto Ethyl acrylate Grafted Carbonised Maize Tassel Coated with Magnetite Nanoparticles

The adsorption studies were carried out at different temperatures within the range of 20 – 60°C and the data, which was obtained, was used to plot the Van't Hoff graph. The Van'tHoffplot, which is shown in Fig 4.15, was used to calculate and plot from $\ln K_c$ versus 1/T, which yielded a straight line with a slope of $\Delta H^o/T$ (kJ mol^{-1}) and an intercept of $\Delta S^o/T$ (kJ mol^{-1} K^{-1}). Table 9 shows the calculated thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ for the sorption of Cd (II) ions onto magnetite nanoparticles modified carbonised maize tassel.

Table 4.8: Thermodynamic Parameters of Adsorption of Cd (II)

T (K)	ΔG°(KJ/moL)	ΔH°(KJ/moL	ΔS°(KJ/moL)
293	14.776	-569.3	+11.52
303	14.430		
313	14.812		
323	14.817		

The enthalpy ΔH° value of -569.3 $kJmol^{-1}$was calculated this value indicated that which adsorption process is endothermic because it is smaller than $40KJmol^{-1}$. The Gibbs free energy (ΔG°) which was calculated using $\Delta G^o = -RTInK_c$. The values obtained indicated that the reaction does not occur spontaneous since energy is required due to the positive values for all the temperatures. It also note that the value of ΔG°become more negative with the increase of temperature, which indicates that the reaction is more favourable at even at low temperatures. The increase in temperature increased the adsorption capacity.

The enthalpy change (ΔH°) for physorption is not in the range 40-120 kJ/mol[163]. Since the value of ΔH° observed in the system is -569.3, which is higher than, 40 kJ/mol. There are different ranges of the free energy change (ΔG°), which are used to determine the nature of adsorption, which occur in biosorption. A positive value of ΔS° indicated that there is the presence of structural changes on the sorbent which result in the increase in the randomness at the solid-solution system.

4.7 Adsorption Kinetic Studies

Adsorption kinetics studies were investigated using the Lagergren pseudo-first-order and the Ho pseudo-second-order. The results from this study illustrate the adsorption mechanism. The pseudo-first-order model is calculated. The pseudo-second-order modeling calculated using:

$$t/q_t = 1/K_2 q_e^2 + 1/q_e \quad (4.2)$$

where; K_2 is the equilibrium rate constant (g/mg-min). Therate constant K_2 is derived from the slope, and intercept from the plot of t/ qtvs t.

4.7.1 Pseudo First Order Kinetic Model

The data plots of log (q_e-q_t) versus t were used to determine the value K_1 (min^{-1}) from the equation slope from Figure 4.16

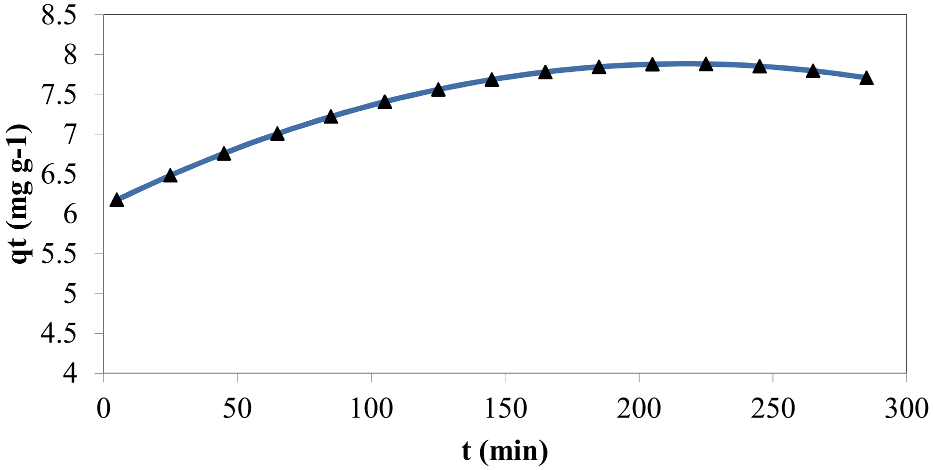

Figure 4.17: Pseudo First Order Kinetic Model Fit for Cd (II) Ions

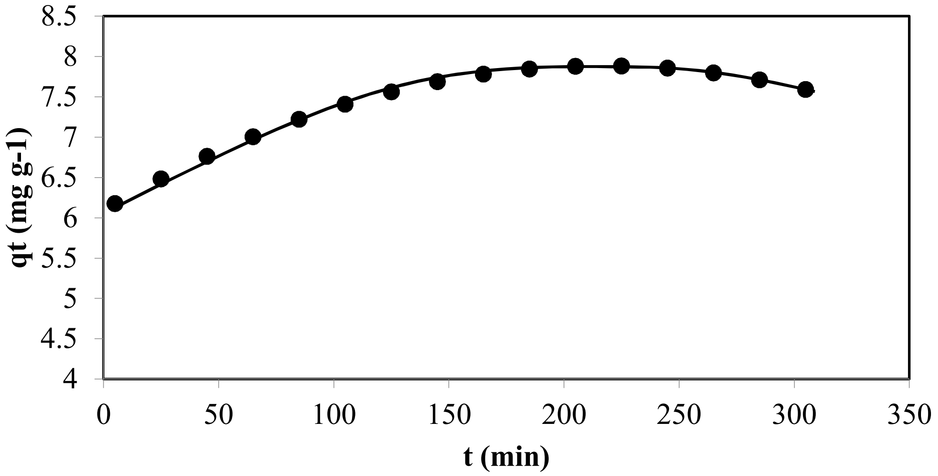

Figure 4.18: Pseudo Second Order Model for Cd (II) Ions

The model which best suit the data of the study was pseudo second order which has correlation coefficient of R^2 value of 0.992 while Pseudo first order has a value of 0.968 which is illustrated in Table 4.17. The reaction mechanism of adsorption for this study is physorption.

Table 4.9: Parameters and Correlation Coefficients Calculated for the Kinetic Models

Model	R^2	K_1 (min^{-1})	Q_e (mg/g)
Pseudo 1st order	0.968	0.3472	7.4919
Pseudo 2nd order	0.992	0.1165	7.3994

CHAPTER FIVE: CONCLUSION

5.1 Introduction

This chapter is based on the finding of the study and how they were met. It also highlights were the study was a success or not. Recommendations, which are based from the finding of the study, are highlighted so as to improve the results of the study.

5.2 Conclusion

The present study shows that maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybridhas much potential as an adsorbent for the removal of Cd (II) from aqueous solution. The influences of pH, adsorbent dosage, contact time, and initial concentration on adsorption of the metal ion and their interactions were investigated by a response surface methodology. The desirability function optimization showed that the optimum removal 95.22%. The Langmuir isotherm model best described the adsorption mechanism with maximum adsorption capacity of 459.37-mg/ g. The kinetic study was performed based on pseudo-first-order and pseudo-second-order. The results show that the adsorption follows pseudo-second-order. The results obtained in the present work showed that the maize tassel-ethyl acrylate biopolymer embedded magnetic nanohybridcould be used as effective adsorbent for removal Cd (II) ions from aqueous solution.

5.3 Recommendations

1. Further studies on application of the adsorbent on real effluent samples
2. Studies should be investigated and carried out to determine if the cadmium trapped in the ethyl acylate grafted carbonized maize taseel coated with

magnetite nanoparticles modified carbonized maize tassel can be liberated and reused.

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