



**Sudan University of Science and Technology**

**College of Graduate Studies**



**Synthesis, Characterization and Application of  
Cellulose Grafted Acrylamide Polymers**

**تحضير وتوصيف وتطبيق بولييمرات السليلوز المطعمة بالاكريلاميد**

**A Dissertation Submitted in Partial Fulfillment of the Requirements for  
the Master Degree in Chemistry**

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## **Dedication**

I dedicate this work to the soul of my parent and to my beloved husband for his endless encouragement and support.

## **Acknowledgement**

First and foremost I would like to praise Almighty Allah who blessed me to complete this research. I would like to thank my respected supervisor Dr. Essa Esmail Mohammed, Department of Chemistry, College of Science, Sudan University of Science and Technology, for his patience and useful advice during work.

Also I would like to extend my gratitude to all whom help me to complete this research sisters, brothers, and friends.

## Abstract

The aim of this study is to synthesize, characterize and utilize cellulose grafted acrylamide copolymers. Cellulose was prepared from corn cob husk fibers by treatments with sodium hydroxide, followed by bleaching with sodium hypochlorite. Copolymerization was performed using a free radical generation method using acrylamide as a monomer and ammonium persulphate as initiator at 90°C and 6hour reaction time. The highest percentage of grafting was 28% under the following reaction conditions: 0.66g of acrylamide and 1.4g of ammonium persulphate and 0.5g of cellulose.

Grafted cellulose was characterized by Fourier-transform infrared spectroscopy (FTIR). Grafted cellulose have displayed the presence of a new characteristic peak of  $-\text{CONH}_2$  group at  $2357\text{ cm}^{-1}$ .

Grafted cellulose was applied to remove ferric ions from aqueous solution under different pH, contact time and initial concentrations. The highest removal efficiency was found to be 94% at pH3 and 30 minutes of stirring at room temperature.

## المستخلص

هدفت هذه الدراسة لتحضير وتوصيف واستخدام بوليمرات السيللوز المطعم بالاكريلاميد. تمت تنقية السيللوز من الياف قشر الذرة الرفيعة بمعاملتها بهيدروكسيد الصوديوم والتبييض بهيبوكلوريت الصوديوم. تم اجراء البلمرة المشتركة المطعمة باستخدام طريقة توليد الجذور الحرة وذلك باستخدام مادة الاكريلاميد كمنومر وفوق كبريتات الامونيوم كمادة بادئة وذلك فى درجة حرارة 90 درجة مئوية ومدة تفاعل 6 ساعات. بينت النتائج ان اعلى نسبة تطعيم بلغت 28 بالمئة تحت ظروف التفاعل التالية: 0.66 جرام من الاكريلاميد و 1.4 جرام من فوق كبريتات الامونيوم و 0.5 جرام من السيللوز. تم تشخيص السيللوز المطعم بواسطة مطيافية الاشعة تحت الحمراء واطهرت النتائج وجود زمرة مميزة جديدة لمجموعة الاميد عند 2357 سم<sup>-1</sup>. تم تطبيق السيللوز المطعم لازالة ايونات الحديدك من محلولها المائى وذلك عند قيم اس هيدروجينى مختلفة ووقت تلامس مختلف التراكيز الابتدائية. تم العثور على اعلى كفاءة للازالة بنسبة 94 بالمئة عند قيمة اس هيدروجينى 3 وزمن تحريك 30 دقيقة عند درجة حرارة الغرفة.

## List of Abbreviations

<b>Abbreviation</b>	<b>Meaning of the abbreviation</b>	<b>Page</b>
DMSO-PF	Dimethyl sulfoxide-paraformaldehyde	1
PAN	Poly acrylonitrile	1
EC-g-PDEAEMA	Ethyl cellulose grafted poly(2-diethylamino) ethyl methacrylate	2
RIF	Rifampicin	2
TSA	Temperature Swing Adsorption	2
ATRP	Atom-Transfer Radical Polymerization	2
LiCl-DMAc	Lithium chloride-dimethylacetamide	7
NMP-LiCl	N-methylpyrrolidone-lithium chloride	7
cuam	cuprammonium	8
cuen	cupriethylenediamine	8
AAM	Acrylamide	17
CTS	Chitosan	17
MBA	Methylene Bis-Acrylamide	17
APS	Ammonium persulfate	17
GP	Grafting percentage	17
GE	Grafting efficiency	17
TGA	Thermal gravimetric analysis	17
FT-IR	Fourier transform infrared spectroscopy	17
SEM	Scanning electron microscope	17
EDX	Energy dispersive X-ray	18
CNFs	Cellulose nanofibers	20
Phen-DEZ	Diethyl(1,10-phenanthroline N1,N10)zinc complex	20
DSC	Differential Scanning Colorimetry	20
PMMA	Polymethyl methacrylate	21

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## Chapter One

### Introduction and literature Review

#### 1.1 Introduction

Graft copolymers have attracted much attention in many fields over the past few decades. Different methods of the graft polymerization of monomers onto cellulose were carried out by radical, ionic and ring opening or living radical polymerizations (Elkony *et al.*, 2020). The applications of cellulose graft copolymers change with the structure of polymer grafted on cellulose. For example, cellulose graft copolymers with poly (acrylic acid), N-vinyl-2-pyrrolidone or polyacrylamide grafts which are hydrophilic in structure, have high water absorption capacity for that reason, they could be used as body fluid absorbent in medical applications. The grafting of water-soluble vinyl monomers onto amine-treated cotton fiber gave a graft copolymer with enhanced moisture sorption ability that can be used in fabrics, such as underwear and athletic wear. Cellulose graft copolymers synthesized in DMSO–PF solvent system has been used as permselective membranes. Cellulose-thiocarbamate-g-PAN had high antimicrobial activity (Gürdağ and Sarmad, 2013). Choudhary *et al.*, (2020) reported that N-isopropyl acrylamide and methyl acrylate-grafted cellulose as template in the crystallization of  $CaCO_3$  has better nucleating property than cellulose. In addition, cellulose graft copolymers obtained by grafting of vinyl monomers acrylamide, acrylic acid,

acrylonitrile and 2-acrylamidomethylpropan sulphonic acid with functional groups have been used in the adsorption of hazardous contaminants such as heavy metal ions or dyes from aqueous solutions. The product of poly(4-vinyl pyridine)-grafted cellulose with sodium borohydride has been used as reducing agents for various carbonyl compound such as benzaldehyde, cyclohexanone, crotonaldehyde, acetone, and furfural. Bashir *et al.*, (2020) reported that pH responsive poly(2-diethylamino) ethyl methacrylate grafted-ethyl cellulose (EC-g-PDEAEMA) synthesized by ATRP can be used in the pH-responsive release of rifampicin (RIF). In addition, another graft product obtained by ATRP, which is graft copolymer of ethyl cellulose with azobenzene-containing polymethacrylates was reported to be used in the some applications such as sensors and optical materials. In recent years, cellulose graft copolymers with thermosensitive graft chains such as poly(N-isopropylacrylamide or poly(N,N-diethylacrylamide) have been used in the removal of heavy metal ions from aqueous solutions by temperature swing adsorption (TSA) which is different from the removal of metal ions by complexation or ion exchange (Gürdağ and Sarmad, 2013).

## **1.2 Natural fibers**

Fiber is a type of material that is intact, long, thin, and simple to bend to form an elongated tissue. According to the sources of the materials, fibers are categorized into three groups, namely natural, semisynthetic, and synthetic

sources. Natural fiber is abundant and more affordable in comparison with synthetic fiber specifically lower density and energy requirements, renewability, no skin irritation, higher strength to-weight ratio, higher aspect ratio length to diameter (L/D) of around 100, and higher strength and elasticity modulus, showing great potential as glass, carbon, or other synthetic fiber replacements. Natural fiber consists of plant, mineral fibers, and animal. Protein and cellulose, respectively, are the principal components of animal and plant fibers. Generally, all plants contain cellulose, hemicellulose and lignin, which constitute the three major organic constituents of plant cell walls and these natural structural polymers are known as lignocellulose. In addition, natural fibers also contain pectin, waxes and water-soluble substances and oil (Kalia *et al.*, 2011; Karimah *et al.*, 2021).

The plants, which produce natural fibers, are classified as primary and secondary depending on their utilization. Primary plants are those grown for their fiber content while secondary plants are plants in which fibers are produced as a by-product. Jute, hemp, kenaf, and sisal are examples of primary plants. Pineapple, oil palm and coir are examples of secondary plants. There are six basic types of natural fibers. They are classified as: 1- bast fibers (jute, flax, hemp, ramie and kenaf). 2- leaf fibers (abaca, sisal and pineapple). 3- seed fibers (coir, cotton and kapok). 4- core fibers (kenaf, hemp and jute). 5- grass and reed fibers (wheat, corn and rice) and all other types (wood and roots). The properties of cellulosic fibers are strongly influenced by many factors e.g.,

chemical composition, internal fiber structure, microfibril angle, cell dimensions and defects, which differ from different parts of a plant as well as from different plants ( Kalia *et al.*, 2011; Sequeira *et al.*, 2012).

The use of natural fiber from both resources, renewable and nonrenewable such as oil palm, sisal, flax, and jute to produce composite materials, gained considerable attention in the last decades, so far. On the other hand, natural fibers are not free from problems and they have notable deficits in properties. The natural fibers structure consists of (cellulose, hemicelluloses, lignin, pectin, and waxy substances) and permits moisture absorption from the surroundings which causes weak bindings between the fiber and polymer. Furthermore, the couplings between natural fiber and polymer are considered a challenge because the chemical structures of both fibers and matrix are various. Accordingly, natural fiber modifications using specific treatments are certainly necessary. These modifications are generally centered on the utilization of reagent functional groups which have ability for responding of the fiber structures and changing their composition. As a result, fiber modifications cause reduction of moisture absorption of the natural fibers which lead to an excellent enhancement incompatibility between the fiber and polymer matrix (Mohammed *et al.*, 2015).

It was proved that the tensile properties of natural fibers increase as the amount of cellulose content in the fiber increases. Therefore; the higher amount of cellulose content in the fibers indicates advanced mechanical properties of

fibers. Accordingly to a reasonable amount of cellulose substances in the fiber increases, there was higher strength and there was a lesser amount of density in composite materials produced; this shows that low weight composite material formed for applications.

### **1.2.1 Chemical composition of natural fibers**

Any natural fiber contains different chemical compositions. It varies from plant to plant and the types of sources of fiber extracted such as stem, leaf, and root. The significance of chemical composition investigation was to identify the amount of cellulose, hemicellulose, lignin, moisture, wax and ash contents in the existing fibers that help to select the strength and bonding ability of the fiber materials (Geremew *et al.*, 2021). In modern technology, applications of cellulose based natural fibers are associated with some essential advantages such as easy availability, renewability, nontoxic nature, lightweight, and low cost. The resulting properties of a particular natural fiber are correlated with the proportion of different structural constituents. The mechanical properties of natural fiber depend on total amount of cellulose in the fiber and degree of polymerization of cellulose. Also, natural fibers are strongly hydrophilic in nature due to the presence of cellulose. In addition, natural fibers were found to be cheaper as compared to usual synthetic fibers such as carbon, aramid, and glass fibers (Roy *et al.*, 2021).

## 1.2.2 Cellulose

Cellulose is one of the most abundant biopolymers on earth, occurring in wood, cotton, hemp and other plant-based materials and serving as the dominant reinforcing phase in plant structures (Siró and Plackett, 2010). Cellulose, a linear homopolysaccharide composed of  $\beta$ -D-anhydroglucopyranose units, is the promising renewable resource for the future production of biobased materials and fuels. Cellulose is found in a wide variety of species, such as higher plants, tunicates, algae, fungi, bacteria, invertebrates, and amoeba. In nature, cellulose is found in hierarchically structured multicomponent materials, which at the lowest hierarchical level feature assemblies that contain individual cellulose in a uniaxially ordered (semi)crystalline organization (Wohlhauser *et al.*, 2018).

### (i) Structure of cellulose

Cellulose is a linear chain of ringed glucose molecules and has a flat ribbon-like conformation. The repeat unit is comprised of two anhydroglucose rings ( $(C_6H_{10}O_5)_n$ ;  $n = 10\ 000$  to  $15\ 000$ , where  $n$  depends on the cellulose source material) linked together through an oxygen covalently bonded to C1 of one glucose ring and C4 of the adjoining ring (1 - 4 linkage) and so called the  $\beta$  1–4 glucosidic bond. The intrachain hydrogen bonding between hydroxyl groups and oxygens of the adjoining ring molecules stabilizes the linkage and results in the linear configuration of the cellulose chain. During biosynthesis, van der Waals and intermolecular hydrogen bonds between hydroxyl groups and



oxygen atoms of adjacent molecules promote parallel stacking of multiple cellulose chains forming elementary fibrils that further aggregate into larger microfibrils (5–50 nm in diameter and several microns in length). The intra- and inter-chain hydrogen bonding network makes cellulose a relatively stable polymer, and gives the cellulose fibrils high axial stiffness (Moon *et al.*, 2011).

These cellulose fibrils are the main reinforcement phase for trees, plants, some marine creatures (tunicates), algae, and bacteria (some bacteria secrete cellulose fibrils creating an external network structure) (Eichhorn *et al.*, 2010; Moon *et al.*, 2011).

Cellulose is probably one of the most ubiquitous and abundant polymers on the planet, given its widespread industrial use in the present age, but also in the past for ropes, sails, paper, timber for housing and many other applications. By far the most commercially exploited natural resource containing cellulose is wood. Since cellulose is classed as a carbohydrate (a substance containing carbon, hydrogen and oxygen), it is necessary to point out that although this term applies to a large number of organic compounds, cellulose is unique in that it can be either synthesised from, or hydrolysed to, monosaccharides (Eichhorn *et al.*, 2010).

Cellulose can be dissolved in DMSO–PF (dimethyl sulfoxide–paraformaldehyde), LiCl–DMAc (lithium chloride–dimethylacetamide), N-methylpyrrolidone–lithium chloride (NMP–LiCl), etc. Cellulose also dissolves in strong concentrated acids such as  $H_2SO_4$  and  $H_3PO_4$  and certain metal

complexes such as cuprammonium (cuam) or cupriethylenediamine (cuen) that they break the hydrogen bonds between the cellulose chains. Cellulose has two crystal forms: cellulose I and cellulose II. In the former, cellulose chains are oriented in parallel conformation, and in the latter, antiparallel one. Cellulose has other polymorphic forms of cellulose III and cellulose IV (Gürdağ and Sarmad, 2013).

Cellulose is an environmentally benign material that is a constituent of dietary fiber and is used to produce a wide variety of products such as regenerated fiber, composites and bioethanol. The physical and chemical properties of a cellulose substrate can be changed by grafting several functional monomers onto cellulose (Okada *et al.*, 2021). Cellulose fibers are being used as potential reinforcing materials because of so many advantages such as abundantly available, low weight, biodegradable, cheaper, renewable, low abrasive nature, interesting specific properties, since these are waste biomass, and exhibit good mechanical properties. Cellulose fibers also have some disadvantages such as moisture absorption, quality variations, low thermal stability, and poor compatibility with hydrophobic polymer matrixes.

## **(ii) Modification of cellulose**

Properties of cellulose can be improved by the modification of cellulose which can be achieved by various techniques like grafting, crosslinking, blending and composite formation. Cellulose is frequently modified in the preparation of a wide range of new materials that have proved to be very useful in several and

diverse fields of application. The presence of three reactive hydroxyl groups on each glucan unit of cellulose makes it relatively easy to modify. One method of modifying cellulose that has been extensively studied is graft copolymerization. Great numbers of grafting methods have been developed, but the free radical methods of generating radicals on the cellulose backbone before grafting have received the greatest attention. Cellulose graft copolymers are very attractive because their products can readily be made to possess any number of the required properties (Jideonwo and Adimula, 2006).

### **1.3 Graft polymerization**

Grafting is a process where a parent polymer is employed as a backbone onto which branches of second polymer are connected at different points. In other words, polymer grafting is a method in which monomers are covalently bonded onto the polymer chain (Gowda *et al.*, 2016). Grafting is an attractive approach to impart a variety of functional groups onto a polymer. Thus, many amendment practices have been shown to increase the inherent properties of the conventional polymer backbone under required conditions. By introducing new reactive sites, the surface morphology of polymers can be tailored to improve certain properties for developing essential products. The incorporation of such reaction sites makes them hydrophilic or hydrophobic and provide chemical and thermal stability to the acid-base attack (Kalia *et al.*, 2011). Surface modification by graft polymerization proved to be a robust approach, in which some of the physical and chemical properties can be

tailored at will. Graft polymerization of surfaces can be performed using “grafting to”, “grafting from”, or “grafting through” methods. The grafting through method involves the functionalization of solid substrates with polymerizable functional groups, e.g., acrylic moieties, followed by in situ polymerization. While the grafting to method involves the connection of preformed polymeric chains with the surface through reactive end groups, the grafting from strategy concerns the growth of polymer chains via surface-initiated polymerization either from a substrate containing functional groups capable of initiating the polymerization reaction, or by immobilization of an active initiator species to the substrate surface. Due to the steric hindrance often encountered while utilizing the grafting to approach, the grafting from approach has the advantage of well-controlled polymer graft lengths and high polymer tether grafting density (Wohlhauser *et al.*, 2018; Elkony *et al.*, 2020). Different types of the graft polymerization of monomers onto cellulose were carried out by radical, ionic and ring opening or living radical polymerizations (Elkony *et al.*, 2020).

#### **1.4 Graft Copolymers**

Graft copolymerization is a significant technique to add the advanced properties of backbone polymers. It is a chemical technique which modifies the desired features in natural fiber without affecting their inherent behavior. It has already referred to giant molecules of long molecular chains of carbon atoms, often literally “branched ” like a tree or linked together crossways in

various directions. These chains can be provided by nature, as in the case of cellulose, or are built up from single short molecules known as “ monomers ” by uniting them into a chain to give “ polymers, ” which is known as polymerization. When monomers of different kinds are united, the product is known as a “copolymer” and the process of uniting different monomers is copolymerization (Bhattacharya, Rawlins and Ray, 2009; Choudhary *et al.*, 2020). Depending on the alignment sequence of different monomers in a polymer chain, copolymers are diversified in their property profiles. Copolymers with an alternate sequence of monomers are alternating copolymers, whereas random copolymers do not follow any definite sequence in alignment patterns of the constituent monomers. Any property gain it is rarely expect any property gain from such compositions. Block copolymers are composed of long sequences (blocks) of one monomer unit, covalently bound to sequences of unlike type. Depending upon the chemical nature of the monomers block copolymers may be di - , tri - , tetra - , or even multi - block. “Physiosorption,” “grafting,” and “crosslinking” are the techniques by which the association of monomers and polymers is described. The term physiosorption signifies that it is related to physical attractive forces. The process is a reversible one and is achieved by the end functionalized polymers on to the solid surface or self - assembly of polymeric surfactants, where “ grafting ” can be described as the covalent attachment process and irreversible (Bhattacharya, Rawlins and Ray, 2009; Choudhary *et al.*, 2020). Graft

copolymers are prepared by polymerizing a monomer in the presence of a polymer of different backbone chain. Grafting results into retention of desirable properties of base polymer and incorporation of favorable properties in grafted. Graft copolymer synthesis is important for the development of polymer science with potential uses in areas such as composites, medical applications, fiber modifications *etc.*(Kumar *et al.*, 2017; Choudhary *et al.*, 2020)

#### **1.4.1 Grafting Techniques**

There are a high amount of conventional methods for the preparation of graft copolymer such as biochemical (enzymatic), chemical, photochemical and physical (plasma-induced) techniques, which are reliable (Choudhary *et al.*, 2020). Chemical grafting is, widely, used method of grafting by free radical generation, ionic generation method and through living polymerization. In chemical method, grafting by free radical technique is initiated by an initiator, which react with the polymer to form grafted polymer whereas in ionic generation method, grafting occur through an ionic mode. Grafting can also be carried out by atom transfer radical polymerization.

##### **(i) Free radical generation method**

Initiator chemicals are used to initiate free radicals in chemical grafting process. The reaction involves transfer of high energy radical to substrate polymer, which reacts with monomers to cause modification of the polymer. Radicals are formed by either direct or indirect method (Gowda *et al.*, 2016).

Radical polymerizations is a useful method for the polymerization of a wide variety of vinyl monomers and can be plagued by a lack of control over the mechanism, radical polymerizations have many different simultaneously occurring reactions namely initiation, propagation, termination by coupling, disproportionate or chain transfer. Extending the versatility of radical polymerizations and radical graft copolymerization have been successful in terms of obtaining a grafted derivative, however grafted product characterizations are being inherently difficult as it is further complicated by homopolymer which is amply generated during the reaction. Graft copolymers have biodegradation products are used in agriculture, textile, paper industry, medicine and petroleum industry as flocculants and thickening agents. Graft copolymerization can be done with or without the presence of different initiator systems by conventional and non-conventional methods. Generally, ammonium persulphate, potassium persulphate or ferrous persulphate are used as initiators for graft polymerization. When an aqueous solution of persulphate is heated it decomposes to yield sulfate radical along with free radical species (Kumar *et al.*, 2017).

It is well noted from the literature that with an increase in the concentration of persulphate initiator, percentage grafting initially increased, but with further increase in [persulphate initiator] beyond certain limit, these grafting parameters showed decreasing tendency. This behavior was explained by the fact that with the increase in [persulphate initiator] there is concurrent increase

in free radical formation which is able to attack polysaccharide chain of GG derivatives. This results in the formation of more macro radicals capable of grafting vinyl monomers on them. On further increasing the [persulfate initiator] above the threshold value equivalent to maximum grafting, large number of free radicals are formed which may initiate homopolymerization of vinyl monomers at the expense of grafting (Kumar *et al.*, 2017).

### **1.5 Applications of graft copolymers**

Graft copolymers are biodegradable with advanced property and are used in agriculture, textile, paper industry, medical treatment and in the petroleum industry as flocculants and thickening agents (Kumar *et al.*, 2017).

Graft copolymers have so many applications in food packaging, nanomaterial, wastewater treatment, tissue engineering and pharmaceutical field as well as in mucoadhesive excipient, diluents in tablets and capsules manufacturing, wound healing property.

#### **1.5.1 Wastewater treatment**

Continuously increasing water pollution is a very serious concern for the entire animal kingdom. All animal and plant beings are directly or indirectly affected by the discharge of industrial, domestic and medical wastes along with agricultural effluents into the rivers and groundwater, thus disturbing the biological balance of the aquatic system. A huge population is not able to get safe, clean and pure drinking water. Water pollution became a serious issue in industrialized regions. Textile, paper, pharmaceuticals, tannery and bleaching



industries and other metal processing industries have a major role to pollute the water resources. These poisonous metals ions and dyes are not only probable human health hazards but also hazardous for plants as well as for aquatic life; this is especially true for dyes as these remain unaltered in the environment for long period. Many graft copolymers have been prepared for adsorbing metal ions and dyes.

### **1.5.2 Food industries**

Food packaging is commonly, used to maintain the quality and increase the shelf life of food products and to keep them safe and edible for a long time. Various types of plastic, glass, cardboard, metal, and paper are used for food packaging. These materials provide physical protection to food products, as well as create appropriate physicochemical conditions for food products that are essential for the safety and quality of foods. Although the use of packaging materials increases the life of food products, packaging materials pose a serious environmental problem as they are not easily biodegraded. Biopolymers specifically polysaccharides are used to solve this environmental problem. Applications of polysaccharide based films in food product packaging may provide new prospects to develop new food packaging systems. In addition, biodegradable films can reduce environmental problems associated with food packaging.

### **1.5.3 As antimicrobial agents**

Microbial infections are one of serious concerns because it is one of the leading cause of death worldwide, especially in medical institutions, where the public are mostly more vulnerable this due to the persistence of the presence of pathogenic microbes (bacteria, viruses and fungi) in various places, such as healthcare products, textiles, medical equipment, sanitary facilities and water purification equipment. So, the prevention of microbial infections is very difficult. Some graft copolymers with antibacterial activity are applicable for the direct removal of bacteria and can serve antibiotics. Regarding these issues, the scientific community prepared the antimicrobial macromolecules for combating the multi-drug resistant microorganisms. The use of polysaccharide as antimicrobial candidates generally shows various benefits since it has low long-term activity and low residual toxicity, chemically stable, non-volatile and does not penetrate via skin.

### **1.5.4 Drug delivery systems**

Some graft copolymers comfortable and safe with drugs as a carrier in drug delivery systems due to their pulsated release of drug at the desired temperature and pH for targeting site. Considering these impressive polymeric properties for polysaccharides, which is a biologically active natural polymer and possess very interesting biological properties, namely nontoxicity, biodegradability, biocompatibility, cytocompatibility, antimicrobial, antioxidant, anticholesterolemic, anti-inflammatory, analgesic, hemostatic and

mucoadhesion. These polysaccharides have been used in a variety of applications, most relevant in the medical as well as in pharmaceutical fields. On the other hand, polysaccharides have not shown considerable applications in drug delivery, due to its poor solubility in water. To resolve this problem, grafting is the greatest option to modify the native characteristics of this polysaccharides for drug delivery applications (Kumar *et al.*, 2020).

Galal Ibrahim, ( 2019) prepared hydrogel polymers via graft polymerization of acrylamide (AAM) onto chitosan (CTS) backbone in the presence of methylene bisacrylamide (MBA) as cross-linker and ammonium persulfate (APS) as an initiator. Optimizing the crosslinking graft reaction of AAM onto CTS was studied by varying the concentration of CTS and MBA cross-linker and discussing the effect of these conditions on the gel fraction and the grafting parameters. The grafting parameters; grafting percentage (%GP), grafting efficiency (%GE), Add-on (%A) and homopolymer (%H) were studied as a function of the chitosan and the cross-linker concentrations. Also the swelling properties of the prepared hydrogel were examined. In this research, the simple second order kinetic model proposed by Schott has been carried out to describe the swelling mechanism. The effect of the grafting reaction on the thermal properties of the chitosan was also investigated by the thermal gravimetric analysis (TGA). The structure of the prepared hydrogel polymer was confirmed by FT-IR spectra. The porous structure of the hydrogel was observed by the Scanning Electron Microscope (SEM) and also the

elemental composition of the prepared hydrogel was identified by using the energy dispersive X-ray (EDX).

Enoh and Ogwuche, (2014) grafted acrylamide and methylmethacrylate monomers onto bleached cellulosic fibres using  $K_2S_2O_8$  and a redox system of  $K_2S_2O_8$ - $Na_2S_2O_5$  as initiators at room temperature while varying time, monomer concentration and concentration of initiator. The study have shown that percentage grafting increases as the concentration of monomers, concentration of initiators and graft time were increased. The study also confirms the selectivity of initiators for monomers. For example, using  $K_2S_2O_8$  as initiator, acrylamide attained a maximum percentage graft of 42.4% at  $7.4 \times 10^{-2}$  mol/dm<sup>3</sup> initiator concentration; further increase in initiator concentration lead to the formation of a gel. On the other hand, the maximum percent graft for methylmethacrylate using the same initiator was 29.8% at initiator concentration of  $14.8 \times 10^{-2}$  mol/dm<sup>3</sup>. Similarly, using a redox system of  $K_2S_2O_8$ - $Na_2S_2O_5$ , acrylamide attained a maximum percentage graft of 23.7% at the maximum concentration of initiator tested while methylmethacrylate attained a maximum percentage graft of 70.2% at the same initiator concentration.

Lele and Kumari, (2021) grafted acrylamide onto Sago Starch by free radical polymerization using Potassium persulphate as initiator. The optimum conditions for grafting have been evaluated by studying reaction variables, viz. polymerization time, material- to- liquor ratio and solvent. The formation of

graft copolymers was confirmed by three methods namely, gravimetric estimation, FTIR spectroscopy and X-ray diffraction.

Czarnecka and Nowaczyk, (2021) synthesized three polymers with excellent absorption properties by graft polymerization: soluble starch-g-poly (acrylic acid-co-2-hydroxyethyl methacrylate), poly(vinyl alcohol)/potato starch-g-poly(acrylic acid-co-acrylamide), poly(vinyl alcohol)/potato starch-g-poly(acrylic acid-coacrylamide-co-2-acrylamido-2-methylpropane sulfonic acid). Ammonium persulfate and potassium persulfate were used as initiators, while N, N-methylenebisacrylamide was used as the crosslinking agent. The molecular structure of potato and soluble starch grafted by synthetic polymers was characterized by means of Fourier Transform Infrared Spectroscopy (FTIR). The morphology of the resulting materials was studied using a scanning electron microscope (SEM). Thermal stability was tested by thermogravimetric measurements. The absorption properties of the obtained biopolymers were tested in deionized water, sodium chromate solutions of various concentrations and in buffer solutions of various pH.

Jideonwo and Adimula, (2006) grafted acrylamide onto holocellulose derived from cocoa (*Theobroma cacao*) wood meal have been produced using hydroquinone enhanced  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  redox system. The addition of hydroquinone to the redox system affected the effectiveness of the redox system to initiate graft copolymer formation. The effects of time, monomer

concentration, initiator concentration, and temperature were studied to determine the optimum condition for graft copolymer formation.

Chami *et al.*, (2021) synthesized graft copolymer by using microwave-assisted graft copolymerization reaction of acrylamide on xanthan. The synthesized copolymer with optimized grafting parameters has been characterized by Infrared Spectroscopy and Thermal Analysis (DSC). Rheological analysis by steady shear and oscillatory flow experiments have been subsequently performed for xanthan and grafted xanthan under reservoir conditions. In steady shear, as expected the grafted polymer solutions flow as shear-thinning materials and apparent viscosity showed good fits with Cross's model. The viscosity losses due to salinity or temperature are more controlled for the grafted xanthan compared to pristine xanthan. When the grafted polymer concentration is increased to 2000 ppm the losses were halved. In oscillatory shear, the copolymer solutions followed a global behavior of semi-dilute entangled systems; furthermore, all dynamic properties were influenced by the brine salinity. Compared to xanthan, the elastic properties of xanthan-g polyacrylamide solutions have been significantly improved in saline media and the losses in elasticity of grafted polymer solutions are lower.

Okada *et al.*, (2021) successfully grafted methyl methacrylate onto cellulose nanofibers (CNFs) at room temperature in an emulsion system using a diethyl(1,10-phenanthroline N1,N10)zinc(II) complex (Phen-DEZ) with oxygen as the radical initiator. The effects of reaction temperature, initiator

concentration, and monomer content on the grafting reaction were investigated. The molecular weight of the non-grafted PMMA, which was produced during graft polymerization, was more than 1 million, as determined by size exclusion chromatography. The PMMA-grafted CNFs were analyzed by Fourier Transform Infra Red (FTIR) Spectroscopy, Thermo Gravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM), which confirmed the grafting of PMMA on the nanofiber surface. The study presents a strategy for the grafting of high-molecular weight PMMA onto CNFs in an emulsion system using Phen-DEZ and O<sub>2</sub>.

## **1.6 Objectives of the study**

The main objective of this study is to modify cellulose purified from corn cob husk fibers by grafting of acrylamide.

### **1.6.1 The specific objectives are:**

- 1.** To purify cellulose from corn cob husk fibers using chemical method.
- 2.** To modify purified cellulose by grafting of acrylamide under various experimental conditions.
- 3.** To characterize purified and grafted cellulose.
- 4.** To evaluate efficiency of the grafted cellulose towards ferric ions.



## **Chapter Two**

### **Materials and Methods**

#### **2.1 Sample collection and pretreatments**

Corn-cob husk fibers were obtained from the local market in Khartoum state, Sudan. The corn-cob husk fibers were washed thoroughly with tap water, air-dried in ambient conditions then ground using laboratory grinder.

#### **2.2 Chemicals**

Sodium hydroxide pellets (Min assay 98%, LOBA Chemie, India). Hydrochloric acid (Min assay 35-38%, LOBA chemie, India). Acrylamide SD fine chem limited (SDFCL), India. Ammonium persulphate, SD fine chem limited (SDFCL), India. Acetic acid (Min assay 99%, Alpha Chemika, India). Clorox (Aqueous solution of 5.25% Sodium hypochlorite). Acetone (Alpha Chemika).

#### **2.3 Extraction of cellulose**

(120g) of corn-cob husk fibers were soaked in 500 mL of 1M (4% NaOH) at 80C for 4 hours at constant stirring and washed with distilled water. The washed product bleached with a white Clorox solution (contains 1.7% NaOCl), sodium hydroxide 2.5% and acetic acid (75mL) for 4 hours at 80C. The bleaching steps were repeated four times and washed with distilled water several times until the odor of hypochlorite disappeared then dried at room temperature.

#### **2.4 Graft polymerization of acrylamide onto cellulose**

(0.5g) of cellulose were immersed into 30mL of distilled water then stirred under nitrogen gas for 10minutes to remove oxygen during the grafting process. (0.7g) of ammonium persulphate dissolved in 10mL distilled water were added as an initiator. Before the acrylamide monomer aqueous solution addition, the cellulose slurry was kept for 5minutes for pretreatment by the initiator to suppress the formation of the polyacrylamide homo-polymer. The mass ratio between cellulose and acrylamide was 1:1, then (0.22g) of

acrylamide were dissolved in 5mL distilled water and added. The reaction continued for 6hours at 90C in hot plate magnetic stirring. At the end of the reaction, the mixture was cooled and filtered. The resulting product washed by 200mL distilled water and 10mL acetone and dried and weighted.

This procedure was repeated using various concentrations of acrylamide monomer (0.44g, 0.66g) and ammonium persulphate initiator (1.4g) and mass ratio of (1:2, 1:3) between cellulose and acrylamide, (1:2) between cellulose and ammonium persulphate.

The percentage of grafting (GP) was determined using equation:

$$\text{Grafting percentage (GP)} = (W_2/W_1) \times 100 \dots\dots\dots 2.1$$

Where:

$W_1$  is the weight of parent polymer (cellulose)

$W_2$  is the weight of grafted polymer as polyacrylamide

## **2.5 Fourier transform infrared spectroscopy (FT-IR) analysis of cellulose and grafted cellulose**

The infrared spectroscopic analysis was carried out for the isolated cellulose and grafted cellulose using Thermo Nicolet IR300 spectrophotometer in the range (400-4000)  $\text{cm}^{-1}$ . Few milligrams of each of the samples were mixed thoroughly with few milligrams of a spectroscopic grade KBR powder, pressed into a transparent disk and the FTIR spectrum was recorded.

## **2.6 Metal binding capacity for ferric ion**

### **2.6.1 Preparation of stock solution of ferric ion**

(2.9g) of ferric chloride were accurately weighted, dissolved in distilled water, transferred into 1000mL volumetric flask and completed to volume with distilled water to prepare concentration (1000ppm).

### **2.6.2 Preparation of stock solution of ammonium thiocyanate**

(7.612g) of ammonium thiocyanate were accurately weighted, dissolved in distilled water, transferred into 100mL volumetric flask and completed to volume with distilled water to prepare concentration (1M).

### **2.6.3 Preparation of standard solution of ferric ion**

Standard solutions of 50mL of ferric chloride were prepared (10, 20, 30, 40, 50 ppm) from the stock solution and added to each one 5mL of ammonium thiocyanate solution (1M) and absorbance was measured using UV/Visible spectrophotometer.

### **2.6.4 Determination of optimum pH for removal of ferric ion**

Exactly (0.05g) of the grafted cellulose were immersed into ferric ion solution of 50mL of 50ppm in pH (1, 1.5, 2, 2.5 and 3) and stirred for 30 minute at room temperature, then the grafted cellulose was separated by filtration and ferric ion concentration was determined by UV/Visible spectrophotometer after addition of ammonium thiocyanate to the filtrate.

### **2.6.5 Removal of ferric ion from aqueous solution by grafted cellulose**

Exactly (0.05g) of the grafted cellulose were immersed into ferric ion solution of 50mL of (10, 20, 30, 40 and 50 ppm) in pH(3) and stirring for 30 minutes at room temperature, then the grafted cellulose separated by filtration and ferric ion concentration was determined by UV/Visible spectrophotometer after addition of ammonium thiocyanate to the filtrate.

The initial and final readings (after adsorption) of ferric ion concentration were calculated according to the equation:

$$\text{Adsorption (\%)} = ((C_0 - C_t) / C_0) \times 100 \dots \dots \dots 2.2$$

Where:

$C_0$  is the initial concentration of the metal solutions

$C_t$  is the concentration of metal after adsorption

## Chapter Three

### Results and Discussion

#### 3.1 Extraction of cellulose

The cellulose was purified from corn-cob fibers. The amount of the purified cellulose is presented in Table 3.1

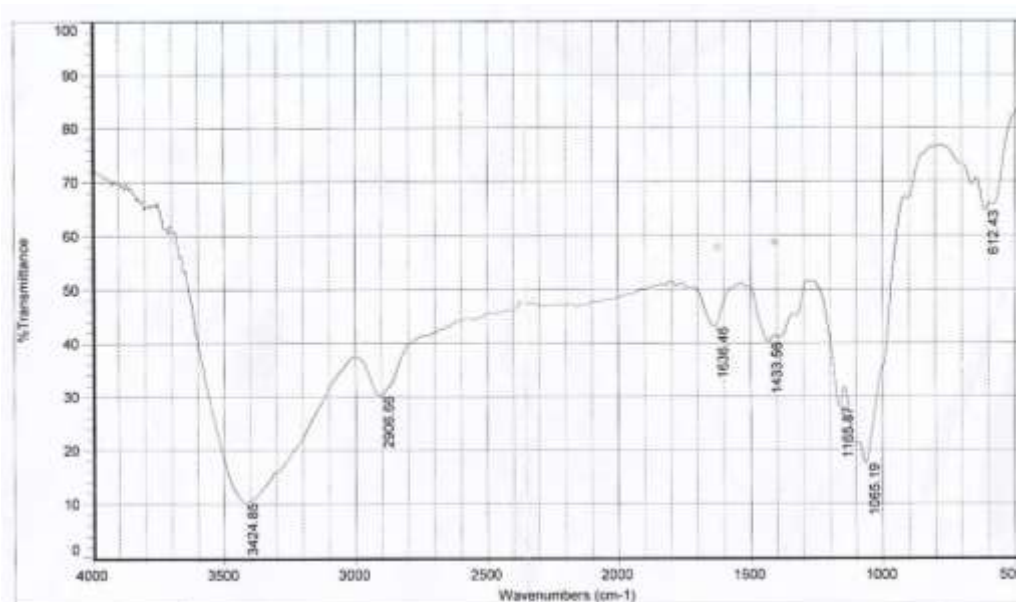
**Table 3.1 corn-cob fibers and the purified cellulose**

Component	Weight (g)
Raw corn cob fibers	120
Extracted cellulose	30.26

Percentage yield =  $30.26/120 \times 100 = 25.2\%$

#### 3.2 Fourier Transform Infrared (FT-IR) analysis of cellulose

The successful extraction of pure cellulose from raw corn-cob fibers was investigated by FT-IR spectrum. The FT-IR of purified cellulose is given in figure 3.1



**Figure 3.1: FT-IR spectrum of cellulose**

The spectrum of the original cellulose evidently display the presence of C-H and -OH functional group moieties, indicated by the broad absorption at 3424  $\text{cm}^{-1}$  which due to the stretching vibration of intra and intermolecular hydrogen bonding of -OH group and 2906  $\text{cm}^{-1}$  which due to C-H asymmetric

stretching vibration. The absorption band at  $1636\text{ cm}^{-1}$  is attributed to the bending vibration of the  $-\text{OH}$  group. The absorption bands appeared between  $1433$  and  $1065\text{ cm}^{-1}$  could be attributed to bending vibrations of  $-\text{CH}$ , stretching vibrations of  $\text{C-O}$  and stretching vibrations of  $\text{C-C}$ . In Figure 3.1 it could be noticed the absence of the stretching vibration of the carbonyl group ( $\text{C=O}$ ) of hemicellulose at  $1700\text{-}1800\text{ cm}^{-1}$  and also the stretching vibration of the aromatic double bond ( $-\text{C}=\text{C}-$ ) of lignin at  $1500\text{-}1600\text{ cm}^{-1}$  indicating the successful purification of cellulose from corn-cob fibers.

### 3.3 Grafted copolymer of polyacrylamide onto cellulose

The cellulose grafted polyacrylamide was obtained by a free radical initiating process using ammonium persulphate as an initiator. The reaction temperature and period were  $90\text{C}$  and  $6\text{hours}$ , respectively. The results of the produced cellulose grafted polyacrylamide is presented in Table 3.2.

**Table 3.2: Weights and grafting percentage of cellulose grafted polyacrylamide under different reaction conditions**

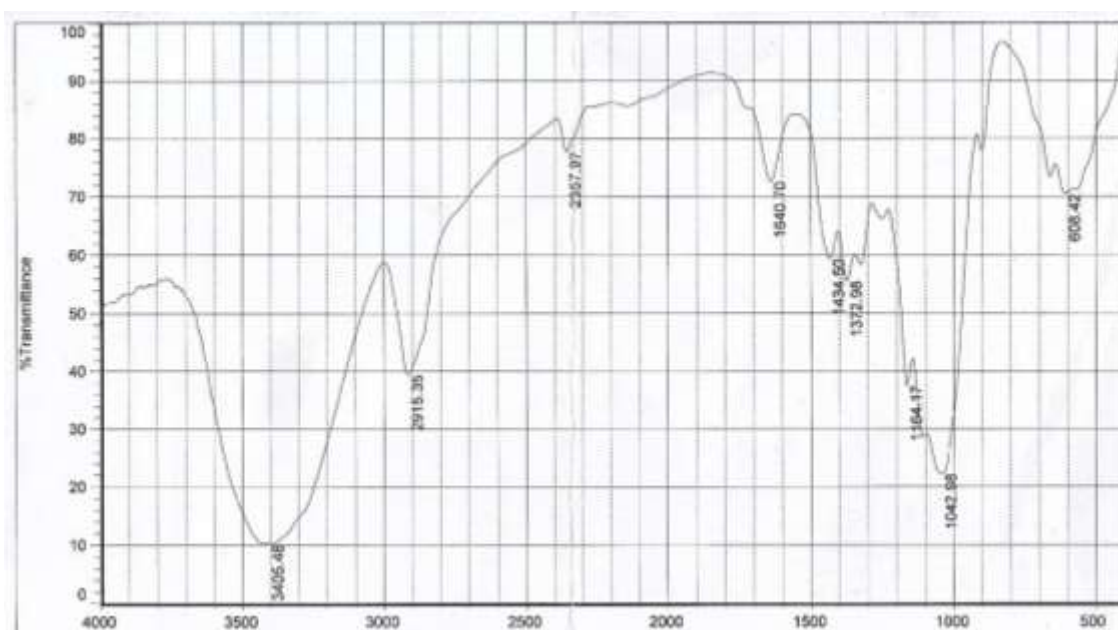
No	Wt. of cellulose (g)	Wt. of AA (g)	Wt. of APS (g)	Wt. of grafted copolymer (g)	G (%)
1	0.5	0.22	0.7	0.01	2%
2	0.5	0.22	1.4	0.04	8%
3	0.5	0.44	0.7	0.03	6%
4	0.5	0.44	1.4	0.086	17%
5	0.5	0.66	0.7	0.05	10%
6	0.5	0.66	1.4	0.14	28%

\*Wt = Weight, AA = Acrylamide, APS = Ammonium persulphate, G=grafting

### 3.4 Fourier Transform Infrared (FT-IR) analysis of cellulose grafted polyacrylamide

One way to evaluate the success of grafting of acrylamide onto cellulose is by comparing the functionality of the original cellulose with that of the grafted

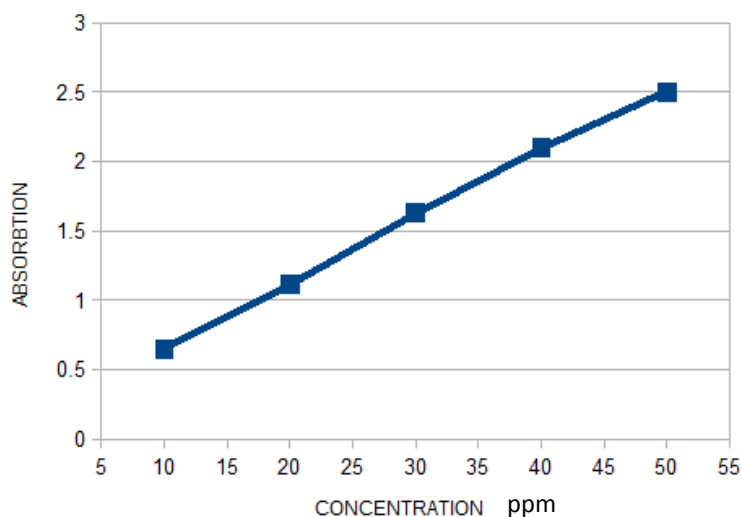
cellulose using FT-IR spectroscopic technique. The FT-IR of grafted cellulose is given in Figure 3.2. The spectrum of grafted cellulose also shows broader band at 3405 and 1640  $\text{cm}^{-1}$ . The bands 1434, 1372  $\text{cm}^{-1}$  indicate the N-H stretching and the N-C stretching of the amide bands, which are characteristic of the  $-\text{CONH}_2$  group present in the acrylamide. The most obvious characteristic of the grafted cellulose spectrum which distinguished it from the spectrum of the original cellulose is the presence of absorption band at 2357  $\text{cm}^{-1}$  which indicate the presence of amide secondary amine group. These changes provide strong evidence of the grafting of acrylamide onto cellulose.



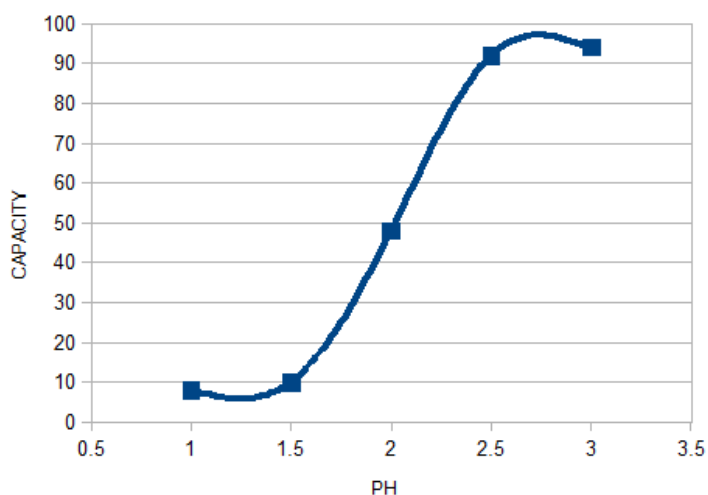
**Figure 3.2: FT-IR spectrum of cellulose grafted polyacrylamide**

### **3.5 Determination of ferric ion by UV/Visible spectroscopy**

Standard solutions of ferric ions were prepared, followed by complexation with ammonium thiocyanate in acidic medium then the absorbance of each solution was recorded by UV/ Visible spectrophotometry and the standard curve is displayed on Figure 3.3.



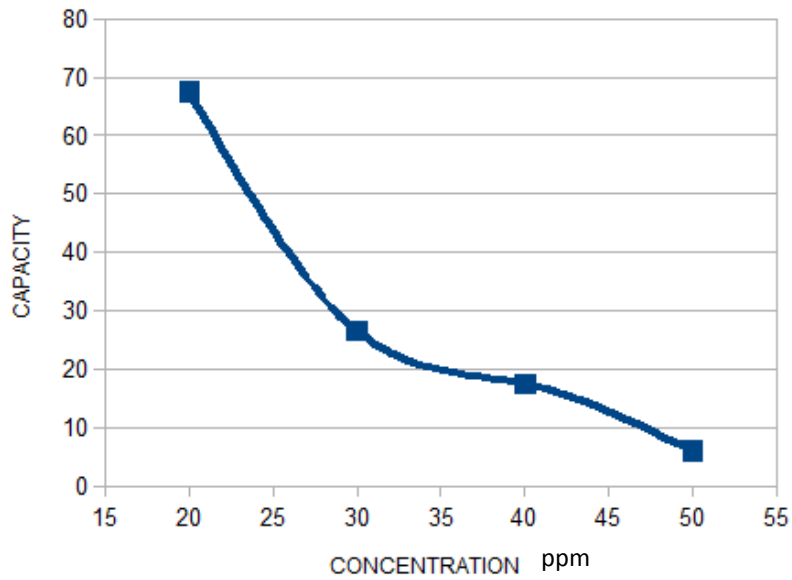
**Figure 3.3: Calibration curve for standard solution of ferric ion**



**Figure 3.4: Effect of pH on the removal of ferric ions at room temperature with cellulose grafted polyacrylamide**

### 3.5.1 Effect of pH

Figure 3.4 shows the dependence of ferric ion removal capacity on the pH in the range between 1 and 3. The initial and final concentrations of ferric ion were determined using UV/Visible spectrophotometry. It is obvious from Figure 3.4 that the removal capacity reaches its maximum value at pH3 (94%) then decreases sharply from pH 2.5 to 2. Another sharp decrease was observed from pH 2 to 1.5 and then remained almost unchanged from pH 1.5 to 1. These results show that the removal capacity of ferric ion is greatly influenced by pH variation and could be achieved at pH range between 3 and 2.5.



**Figure 3.5: Effect of concentration on the uptake of ferric ions at room temperature.**

### **3.5.2 Effect of concentration**

Figure 3.5 shows the dependence of ferric ion removal capacity on the concentration of ferric ions (in the range of 20-50ppm). The initial and final concentration of ferric ions were determined using UV/Visible spectrophotometry. As can be noticed from Figure 3.5 that the removal capacity decrease with the increase of concentration until it reached the minimum value at 50ppm and the maximum value was at 20ppm. These results show that the removal capacity of ferric ions in low concentrations is better than high concentrations.



## **3.6 Conclusion and Recommendations**

### **3.6.1 Conclusion**

-Copolymers of cellulose and acrylamide were successfully synthesized from cellulose purified from corn cob leaves fiber and acrylamide using free radical generation methods at various reaction conditions.

-Grafted copolymer having 28% grafting yield was achieved.

-Removal efficiency up to 94% towards ferric ions from its aqueous solutions was obtained which was found to depend on pH, contact time and initial concentration.

### **3.6.2 Recommendations**

-Further studies which consider the effects of reaction temperatures and reaction time as well as various mole ratios of cellulose to monomer are important.

-Other characterization techniques such as <sup>1</sup>HNMR, TGA, DSC could give better understanding of the structure and properties of the copolymers.

-Study of the biological activity of synthesized cellulose grafted acrylamide.

-Application of the grafted polymer to treat real samples of wastewater to uptake toxic heavy metals.

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