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Preparation of Nanocellulose from rice husks and paper waste and its using in eosin dye removal

A Thesis Submitted to the
Council of the College of Science, University of Diyala
In Partial Fulfillment of the Requirements for the Degree
of Master of Science in Chemistry
by

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بسم الله الرحمن الرحيم

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We certify that this thesis ***(Preparation of nanocellulose from rice husks and paper waste and its using in eosin dye removal)*** was carried out under our supervision in Chemistry Department, College of Science, Diyala University in partial fulfillment of the requirement for degree of master of science in chemistry by student **(HANEENLATEEF KHALEEL)**.

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I certify that the thesis entitled ***(Preparation of nanocellulose from rice husks and paper waste and its using in eosin dye removal*** , presented by ***(HANEEN LATEEF KHALEEL)*** has been evaluated scientifically, therefore, it is suitable for debate by examining committee.

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DEDICATION

To the vow of his age and tired for me ... who encouraged me throughout my scientific career.

To who is the cause of my success .... To who taught me to ascend the ladder of life with wisdom and patience ..

My dear father (My Allah lengthens his life)

To the flower that does not wither ... to the smile of life the spring of tenderness ... which supported me and stood beside me

Until this stage has reached ... to which words are unable to describe her. *(My beloved mother)*

To the companion of the path ….who supported me and stood by my side in the days of good and bad .... to the permanent friend and the faithful husband who lived with me this difficult period

(My husband is loyal)

To my little angel ..... which was born this year and filled my life with hope and light.. was like a star in the darkness of grief.

(My little baby Deema)

To their I will greatest with them and I have to rely .. to the candle that illuminates the darkness of my life .. To those who I have acquired power and love without limits beside them……..

(My brothers and sisters)

Dedicate this humble effort ..

HANEEN

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Many thanks to my family ***(father and mother, my husband and his family for all helps , sisters and brothers)*** *who Keep encouraging me all the time in good times and bad*

I extend my thanks to Assistant Lecturer Zaid Hameed, Assistant Lecturer Noor Sabah, M.sc ***Sally*** *Kamil and all my colleagues at the college of Science in the Department of Chemistry****(Aseel , Zahraa ,Esraa, Rusul ,saleema ,Whadah ,Abdul-Ellah Abdullah ,Ali, Huda , Mahmoud ,Reham)*** *and I extend my thanks to colleagues in the Department of physics****(Anwar*** *,Assistant Lecturer* ***Marwa Rashed, Rusul)*** *for their help and support .*

For all of them, I said " Thank you all "…….

Haneen….

ABSTRACT

The current study aims to prepare nanocellulose (NC) from agricultural waste (rice husks) and industrial waste (paper residue) rather than throwing it into waste and increasing pollution of the environment and thereby reducing environmental pollution to some extent.

In this study ,the nanocellulose was prepared by the acid hydrolysis using sulfuric acid at different concentrations (15,25,35,45)% for agricultural waste (rice husks) and at concentration 50 % for industrial waste (paper residues) to dissolved the raw materials by sulfuric acid and extract cellulose and convert it to nanocellulose by used renewable and advanced method by using ultrasonic processor for different times at (30-180) min .

The techniques for characterization of nanocellulose are Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM), X-ray diffraction (XRD) , and Fourier Transform Infrared spectroscopy (FT-IR) . The surface structure diagnosed using AFM and (SEM) techniques . Nanocellulose was obtained in small sizes and in distinctive forms as indicated by the measurements. The results of the atomic force microscope (AFM) showed the particle size and the accuracy of the distribution of Nanocellulose diameters produced from the rice husks ranges from 20-50 nm . while NC prepared from the paper residues ranged from 65-80 nm , conclude that the NC produced from the agricultural waste is better than the NC of the industrial waste as the nanoparticles size is smaller and therefore there is a larger surface area.

Scanning electron microscope (SEM) offers important information about the morphology of nanoparticles of cellulose with ability analytical pixel (1,5,10,50) µm, where SEM images show differences in the shape of the sample, showing the presence of regular crystalline and other amorphous and irregular regions. This indicates that the resulting nanoparticles are not stable due to deposition of aggregates in nanoparticles, and sulfuric acid has been used to dissolve and dissolve the non-crystallized region .

X-ray diffraction showed the crystallite size of the NC produced from rice husks and paper residues. This technique proved that nano-cellulose is crystalline and has a high crystalline Index and the crystallite size D (determined from the Deby-Sherrer equation) of the nanocellulose produced from the rice husks is smaller than that of the nanocellulose from the paper residue and therefore has the highest crystallization . Fourier Transform Infrared spectroscopy (FT-IR) showed the purity of cellulose by removing lignin and hemicellulose completely from samples.

After obtaining the nanocellulose from the agricultural and industrial waste, an industrial application was applied to it by adsorption of the eosin dye from the aqueous solution . In this field, the effect of the factors affecting on adsorption (equilibrium time, the amount of the adsorbent, the Initial concentration, the temperature and pH) have been studied which are affecting percentage removal of eosin dye onto adsorbents (NC of rice husks and paper residues), it was found that the time needed to reach the equilibrium state was (20) min for NC of rice husks and (30) min for NC of paper residues . In general, the percentage of dye removal from a dilute aqueous solution using NC from rice husks and paper residues decreased by increasing the amount of the adsorbent , this is due to the surface was saturated by dye molecules.

While studying the adsorption of dye into adsorbent surface of NC of husks and residues at different values of pH (3,7 and 9) indicated that the best adsorption of dye on two surfaces prepare at pH 3. The effect of temperature on dye adsorption on the surface of nanocellulose for both types indicated that the decreased by increasing the temperature. It was shown by adsorption process that the percentage removal of dye from aqueous solution using NC product from the rice husks was more efficient in removing dye than NC obtained from the paper residues.

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Symbols or abbreviations	*The meaning*
NP	**Nanoparticles**
NC	**Nanocellulose**
CNF	**Cellulose Nano-fibers**
MFC	**Micro-fibrillated cellulose**
CNC	**Cellulose Nano-crystals**
BC	**Bacterial cellulose**
EHS	**Environmental, health and safety aspects:**
AFM	**Atomic Force Microscope**
SEM	**Scanning Electron Microscope**
XRD	**X-ray Diffraction Spectroscopy**
FT-IR	**Fourier transform infrared spectroscopy**
µm	**Micrometer**
min	**Minute**
rpm	**Revolution per minute**
Qe	**Amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium**
C_t	**Concentration of adsorbate after any time**
C_o	**Initial concentration of adsorbate**
C_e	**Equilibrium concentration of adsorbate**
m	**Weight of adsorbent**

V	**Volume of solution**
R%	**Percentage removal of adsorbate**
pH	**Power of hydrogen**
UV- visible	**Ultraviolet - visible spectroscopy**
λ max	**The wavelength of maximum absorbance**
A	**Absorption**
ε	**Molar absorptivity coefficient (M^{-1} cm^{-1})**
b	**The path length (cm $^{-1}$)**
c	**The concentration (M)**
Avg	**Average**
R^2	**Correlation coefficient**
JCPDS	**Join committee on power diffraction standards**
D	**Crystallite size (nm) .**
λ	**wave length of radiation.**
θ	**The Bragg's angle.**
β	**The full width at half maximum (FWHM).**

Chapter One

(Introduction)

1. Introduction

1.1.Nanotechnology

Nanotechnology which is a new and evolving science widely used in recent times .The great evolution of science and technology occurred in the twentieth century in the second half of it, has not created daring and new ideas , but also leads to the creation of tools that enable realization of atoms in the material in the surrounding ,this science is science of technology. Contributed achievements scientific as shown in Figure (1.1), especially which occurred in end of twentieth century input effective in widening of nanotechnology[(1)] .Nano-science defines a set of developments and technologies that are depends on chemical , physical , and biological phenomena occurring at the nano-scale ranging of approximately (1 to 100) nm , the conduct and properties of materials at the nano-scale vary greatly when compared to the others at the micro , macro or bulk levels, this science is taught how to control the material by revealing the physical, chemical and biological characteristics of the materials and this is a distinctive class of this science and this is what distinguishes it from the rest of the modern techniques spread at present [(2)]. The source of word (Nano) is from word of the Greek (Nanos) which is means (dwarf) . When think about Nano-science and nanotechnology , we think of very small objects . This branch of science and technology deals with materials that possess at least one nanometer dimension . The nano is one billionth of a meter with small dimensions (length, width) ranging from 1 to 100 nm[(3)]. Science and technology continues to be oriented towards new materials, advanced processes, sustainable and environmentally friendly cellulose is considered increasingly important at present[(4)].

Nanotechnology is one of the most important innovative scientific and economic fields ,nanotechnology show even greater possibility for the functionality introduction of new and specialized in a wide range of different areas(5) :

1. Electronics and optics
2. Health
3. Energy
4. Construction
5. Environment.

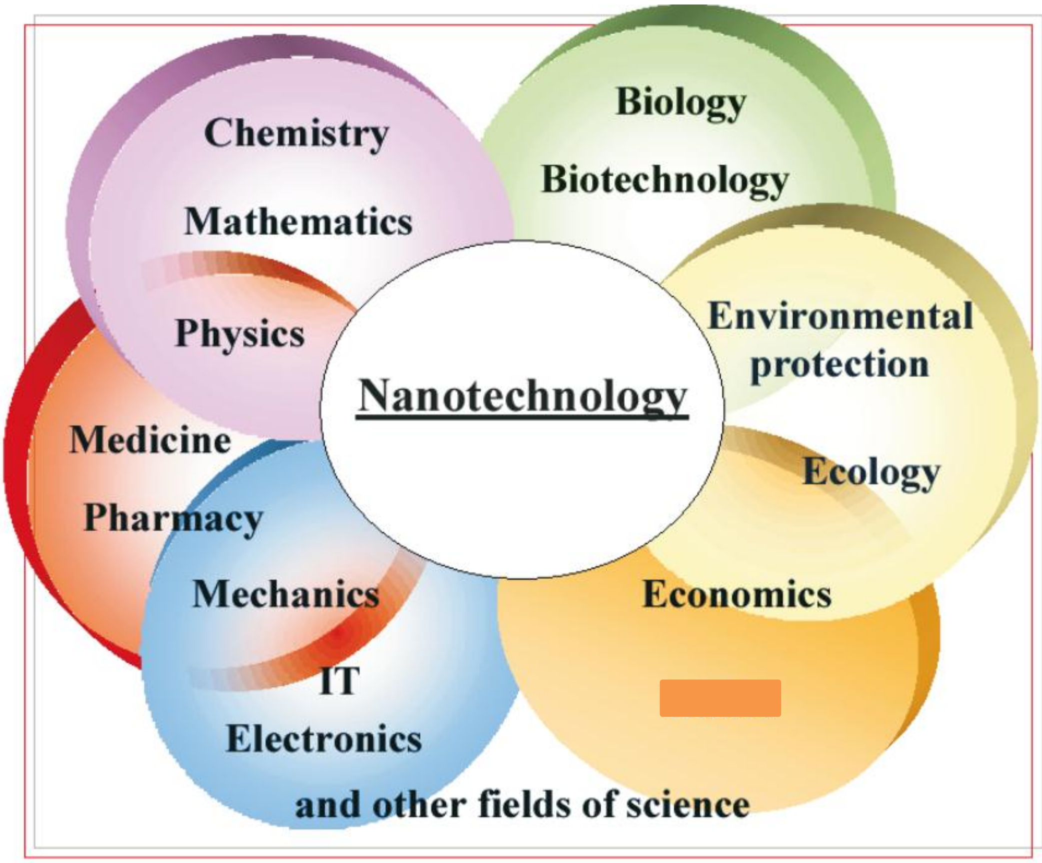


Figure (1. 1) : Interdisciplinarity of nanotechnology

1.2. Nanoparticles

Nanoparticles are tiny particles ranging in size from 1 to 100 nanometers . However, it's may exist as a fraction of a compound ,the nanoparticles are important even if it was are regular in the matrix alone (for example, the role of nanoparticles as a catalyst for acceleration) or diffuse in solution for example, determine the color of the colloidal dispersion of nanotubes of gold in a liquid medium(6).

The lengths and diameters of nanoparticles are different and this depends on the raw materials and the process of extraction and preparation ,and have desirable properties such as high degree of crystallization , have a high surface area that makes them capable of entering many other important reactions in biological applications , all this made these nanoparticles it takes its place in the field of materials science(7).

These nanoparticles are prepared by the initial treatment of samples of cellulose with sulfuric acid at different temperatures, then mechanical degradation, or ultrasonic decomposition of cellulose treated with acid degradation(8) . That nanoparticles generally can be classified as one of two types: engineered or non-engineered

1. Engineered Nanoparticles: It is designed and formed for the physical properties designed to meet the special needs of applications. As in pharmaceutical drugs

2. Non-engineered nanoparticles are unintentionally produced ,or produced naturally, such as nanoparticles in the atmosphere , physical properties as well play an important role in determining Nanoparticles may be known by a number of trade names, including particulate matter, aerosols,

colloids, nanoparticles, and Nano-powders , the increasing use of engineered nanoparticles in industrial and household applications will very likely lead to the release of such materials into the environment , and assessing the risks of these NP in the environment requires an understanding of their mobility, reactivity and persistency(9).

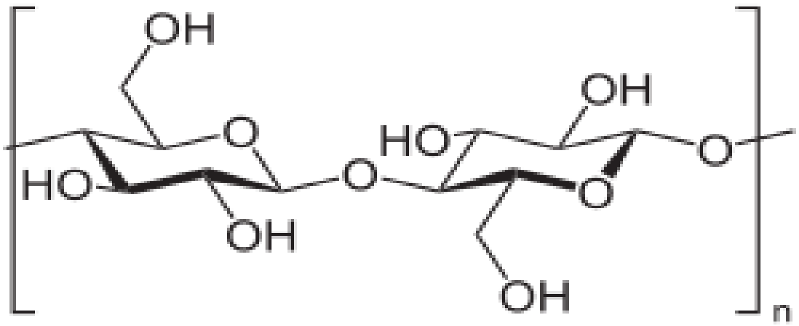
1.3. Nano-cellulose:

Nano-cellulose is a new and widely developed type of cellulose that is found in fibers that can be extracted from trees, plants, some species of bacteria, algae, and some marine organisms. Nano-cellulose is not one type of material . It is a family of substances but it is characterized by its different properties .This difference is due to the variation in the preparation method as well as the source from which nanocellulose was obtained(10).

The nanocellulose crystals preparation from the original cellulose and have nanostructures with small dimensions . The dimensions of the nanocellulose crystal are based on the material from which they were started(11). Nanocellulose refers to isolated cellulose molecules with at least one dimension on the nanometer scale and are less than 100 nm at the same time possessing new properties associated with their nanostructures(12).

1.4. Cellulose : Definition sources and structure of cellulose

Cellulose is the chemical compound which considered the most obtainable regenerate polymer that considered the most common in nature[13,14]. The structure of cellulose is $[C_6H_{10}O_5]n$,as in figure (1.2). At first it was thought the wood was the only source of cellulose , but overtime it was found that other plants such as flax, jute, rice husks, cotton ,corn cobs, etc, also animals such as some bacteria and sea creatures ,they were contained a large quantity of cellulose. Nanocellulose was discovered around 1950 from cellulose fibers by the acid hydrolysis[15]. Cellulose is an important structural component of the essential cell wall of green plants , and other plants. Some types of bacteria excrete it to form biofilms [16] .



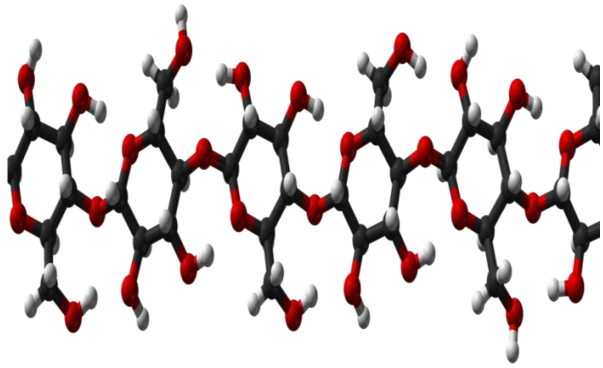


figure (1.2): Cellulose chemical structure[17].

Cellulose is present in many plants and cellulose function in nature is to give hardness and strength to plant structures. Cellulose with lignin and hemicellulose(figure 1.3) helps the plant to stand erect and gives hard branches from outside[18]. The cellulose fibers is non-toxic and can be recycled and is also biodegradable. It is also characterized by strength and hardness of high quality allows the production of composites with low density. However, cellulose fibers have limitations related to thermal stability as well as high moisture absorption . In last years it has been found that the acid degradation of cellulose fibers produces crystalline molecules called cellulose, Although cellulose fibers have excellent chemical and physical properties , it is also characterized by low density and nanoparticles making it one of the best specifications for the reinforcement of nano-components[19].

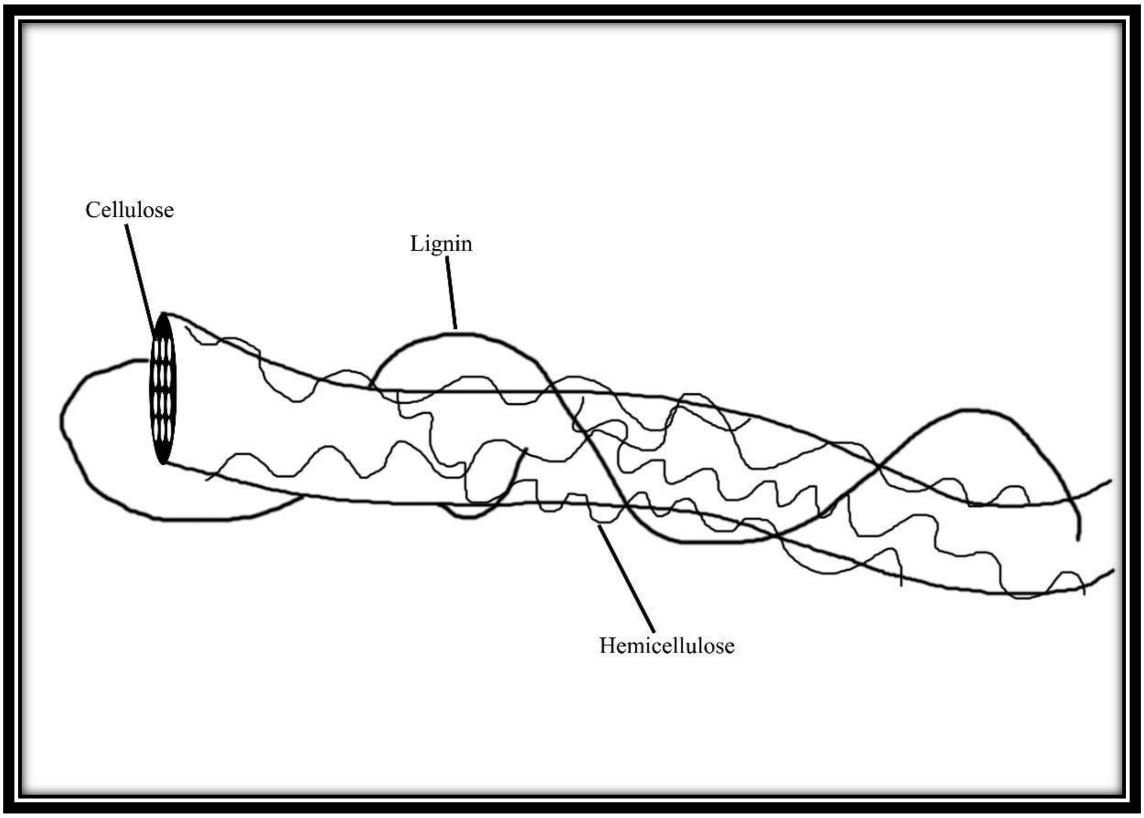


Figure (1.3): Showed image over a plant wall where hemicellulose is entangled and has bonded to cellulose .

In general, cellulose polymer enters the formation of fibers or derivatives of many and extensive products and materials. Nano- fibers consist of both amorphous and crystalline parts (as shown in figure 1.4), which can be distinguished by nanotubes of cellulose which contain small dimensions that can be prepared from acid degradation which produces nanoparticles of crystalline cellulose[20]. Crystals of cellulose and nano fibers are obtained by acid degradation and mechanical treatment of other trace processes[21] . Crystalline cellulose nanoparticles are small nanoparticle particles that are sourced from cellulose. Cellulose nanoparticles are synthesized by acid degradation using a sulfuric acid that dissolves the amorphous chains found in cellulose to be separated from the stronger crystalline particles. Cellulose contains many hydrogen bonds that must be removed For the formation of cellulose nanoparticles[22].

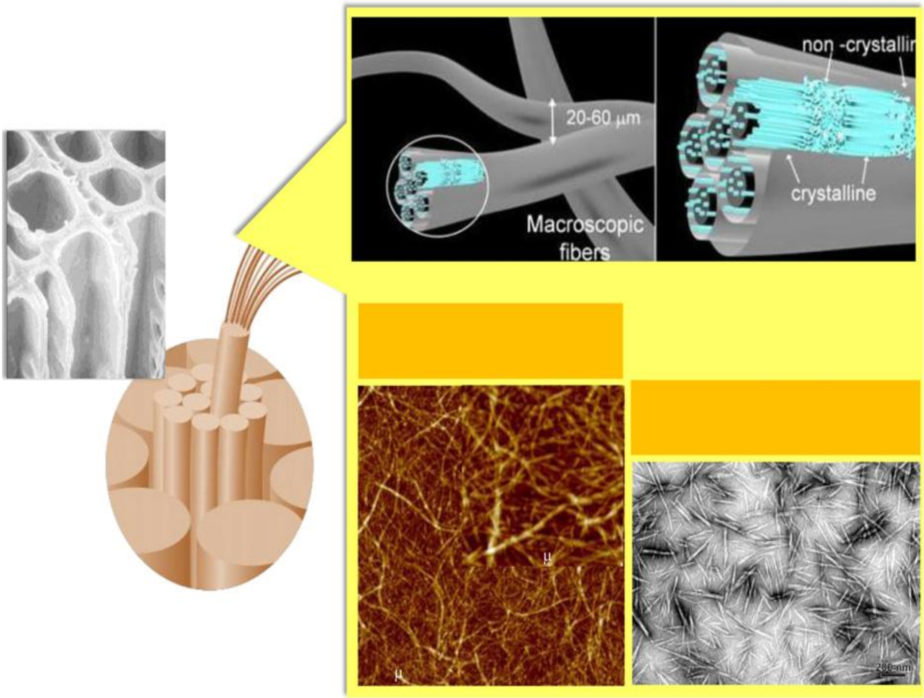
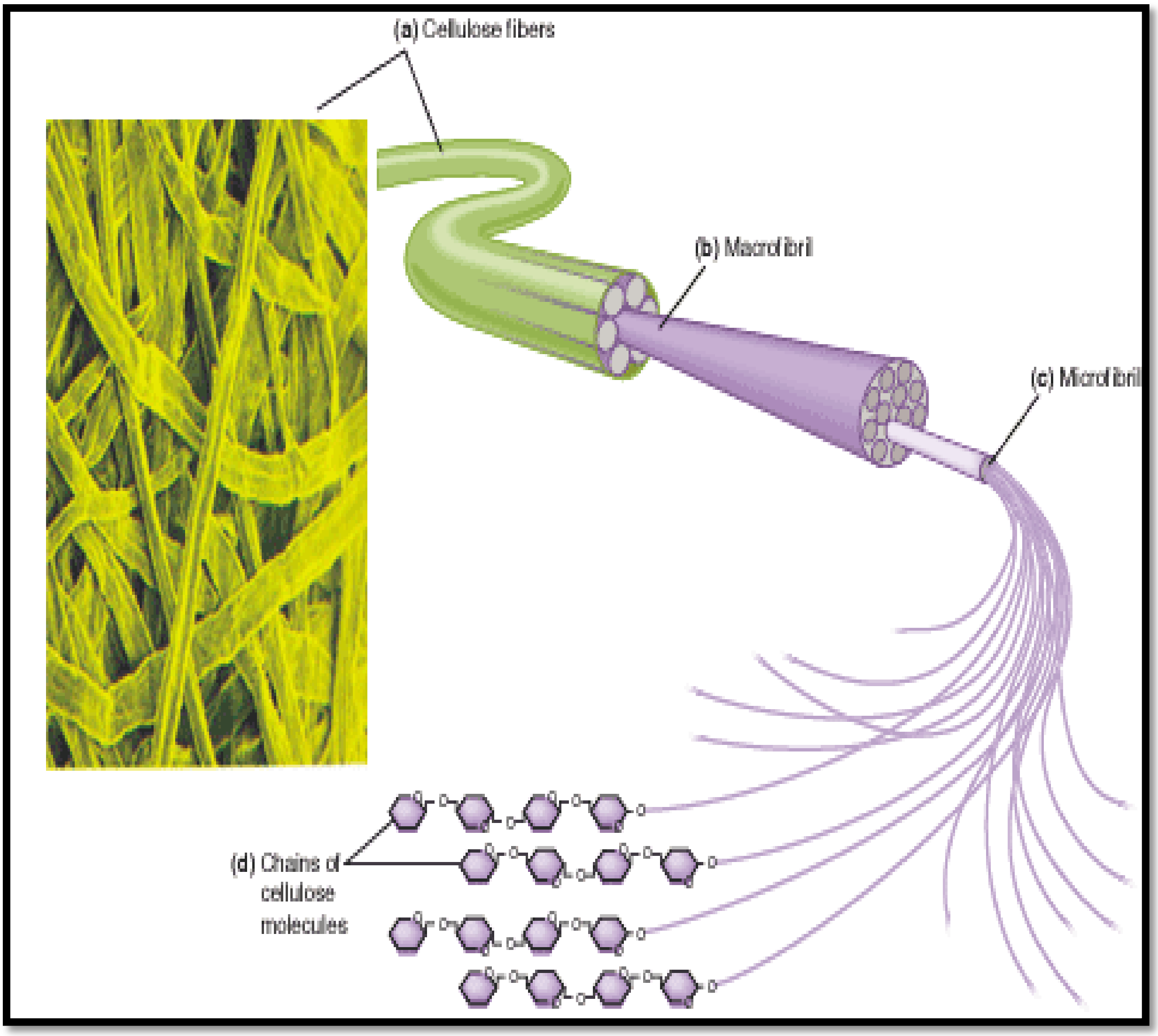


Figure (1.4) :explains of CNF and CNC production from fibers cell walls by chemical and mechanical treatments [20] .

The molecular weight of cellulose depends on the main source of the original cellulose as its sources (either vegetarian (cotton, straws, etc.), animal and marine organisms such as algae or the source of bacteria) and on the way of isolation, and on the method of determining the molecular weight used. Cellulose has a high degree of polymerization being greater than 10000 and a molecular weight of about 200000[23] ,as in figure (1.5):



Figure(1.5) : Showed Cellulose fibrils

1.5. Extraction cellulose from plant fibers

Extraction of Cellulose includes essential treatments and oxidation treatments which can affect the nature of cellulose or acid treatment. This is very important because it can change the crystalline form and cellulose derivatives as well as can change the chemical and thermal stability of the material . Cellulose can be extracted from plant fiber using some chemical treatments which are: Alkaline treatment and bleaching. Alkaline treatment is made with 2% of the sodium hydroxide in a temperature not exceeding 80 degrees Celsius. This process allows soluble sugars to be removed . The purpose of bleaching is to remove most of the remaining phenol molecules such as lignin and polyphenols[24] .

Lignocellulosic fibers is one of the advanced renewable materials that attract scientists to the present time. There are about 2000 types of plant fiber useful in different parts of the world used in many industrial, medical and agricultural applications [25] . Natural fibers when they originate from plants are easily accessible to it and are known as cellulose fibers . Cellulose is the basic chemical compound in this fiber . It is known as lignocellulose fibers because these fibers contain natural polyphenols and lignin in their structure (figure 1.6) . Because of the abundance of fiber and other agricultural waste, it has become the new interest in research in the field of modern advanced technology[26].

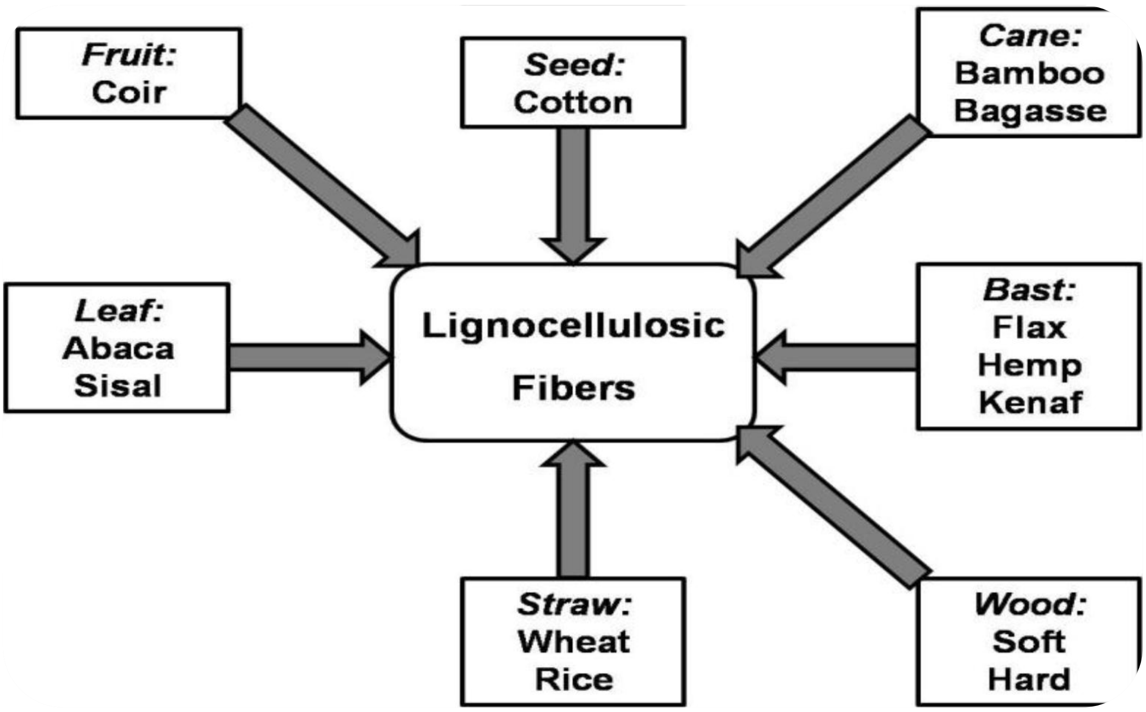


Figure (1.6) :Classifications of Ligno-cellulosic fibers

1.6. properties of Nano-cellulose

Nano-cellulose has been increasingly important in many applications in the fields of science, biomedical engineering and other applications due to its distinctive characteristics including[(27)] :

1- Its constantly renewable nature

2- Have good mechanical properties and distinctive

3-Anisotropic form

4- Have a high importance in optical properties

5-Compatible with life because it is a friendly of the environment

6-Non-toxic

1.7. Shape and Structure of Nano-materials

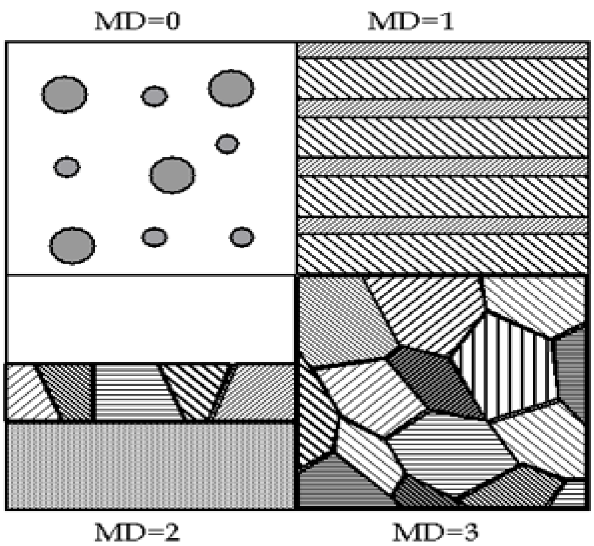
Nano-materials it can be classified according to their dimensions that are : the zero-dimensional nanostructures such as nano-particles , the one-dimensional nanostructures such as fibers , Nano-rods , whiskers and nanowires . In several cases , Nano-tubes and Nano-cables are also considered one-dimensional structures , thin films are considered as two-dimensional nano-structures. The three-dimensional nanostructures are colloids which are bearing complex shapes has been three-dimensional nanostructures(28). Nanoparticles can be classified into four categories(29) :

- Zero dimension (powders) .

- One dimension (multilayer) .

- Two dimensional or two dimensions (nanoparticles with a diameter less than 50 nm) .

-The three dimensions are nanotubes composed of nanotubes of equal size . (As shown in figure 1.7)



Figure(1.7) : Dimensional classification of Nano-materials.

1. 8. Classification of Nano-cellulose

In the past, the term Nano-cellulose was not used in a completely uniform manner. Several MFC, NCC and BNC terms have been used, and the latter for bacterial Nano-Cellulose(30) . Classification of Nano-cellulose structures : different types of Nanocellulose can be categorized into different sub-sections according to form , dimension , the function , the method of preparation and this in turn dependent on cellulose sources and treatment conditions . The various types of Nano-cellulose are currently used. The Nano-cellulose has been classified into six group(31). key forms of cellulose Nano-materials as shown in figure (1.8) : Cellulose Nano-fibers (CNF) , Micro-fibrillated cellulose (MFC) , Cellulose Nano-crystals (CNC) , Bacterial Nano -cellulose (BNC) .

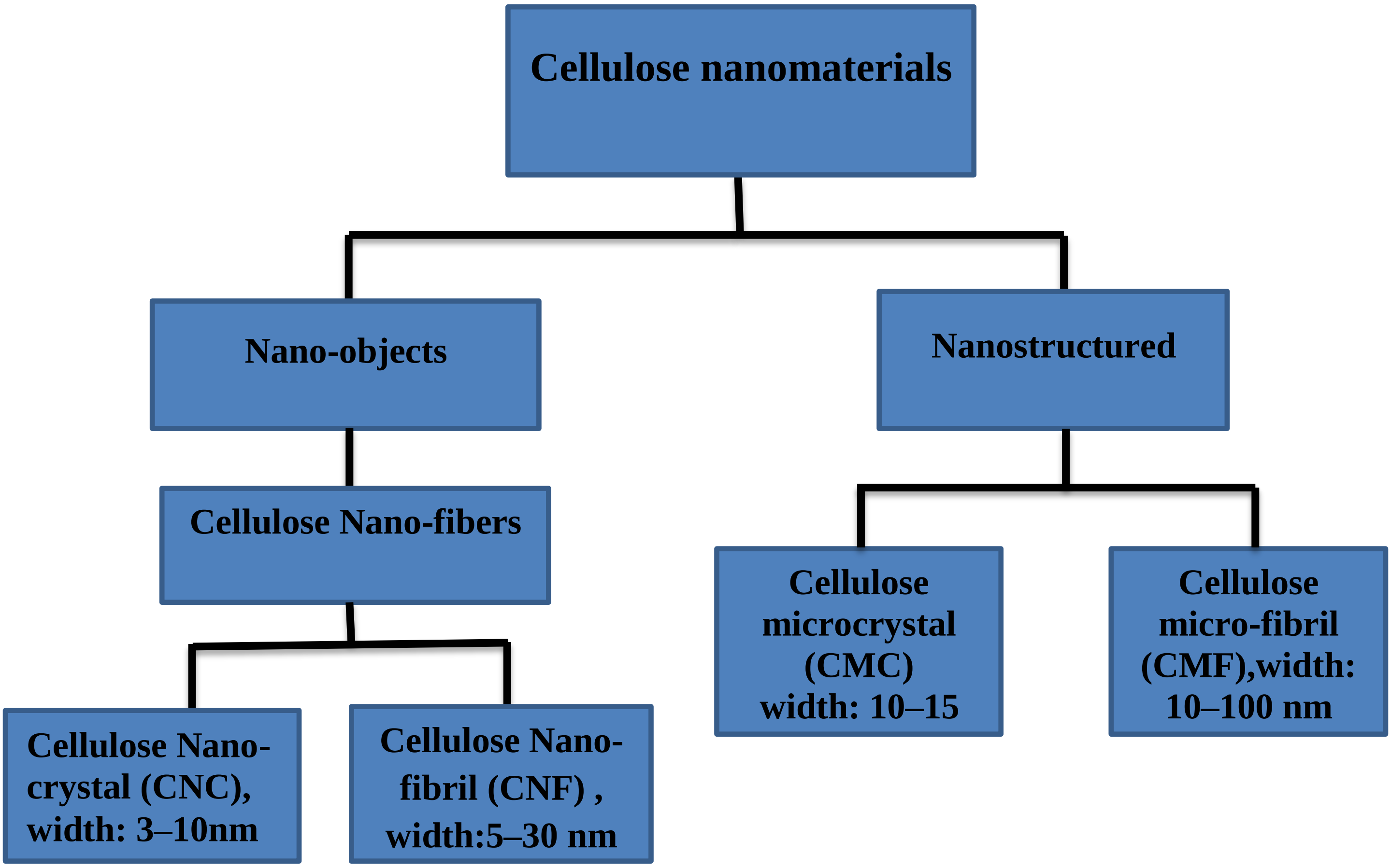


Figure (1.8) : Key forms of cellulose Nano-materials

1.9. Recycling of Agricultural &Industrial Waste

The term "recycling" has become a widely used term."Recycling" is defined as the extraction or separation of useful materials that are intended to be recycled for use in other purposes, such as recycling paper for other purposes, for example recycling paper in the cardboard and newspaper industry[32] .

1.9.1. Agricultural Wastes

Agricultural waste has become a major environmental problem but it used for many useful purposes, Such as chemical adsorption or dye, chemical recovery and feed Stock for energy production , this is done by waste reuses, recycling , waste management , waste treatment and minimization[33]. At present, many fields and their residues contain cellulose in high quantities such as rice residues (rice husks), wheat straw, barley straw, corn cobs and others[11]. It is possible to take advantage of the remnants of raw apple stem instead of throwing it as waste in the extraction of cellulose as well as a high quantity of Nano cellulose , these materials will become a friend of the environment in the province of Aomori in Japan, the highest producing apple, thus forming one of the most abundant biomass resources in this region[34] . Agricultural waste materials are usually composed of cellulose and lignin as the main components(like figure 1.9). Other components are , lipids, hemicellulose, proteins, simple sugars, starches, extractives water, hydrocarbons obtained from various sources [35] .

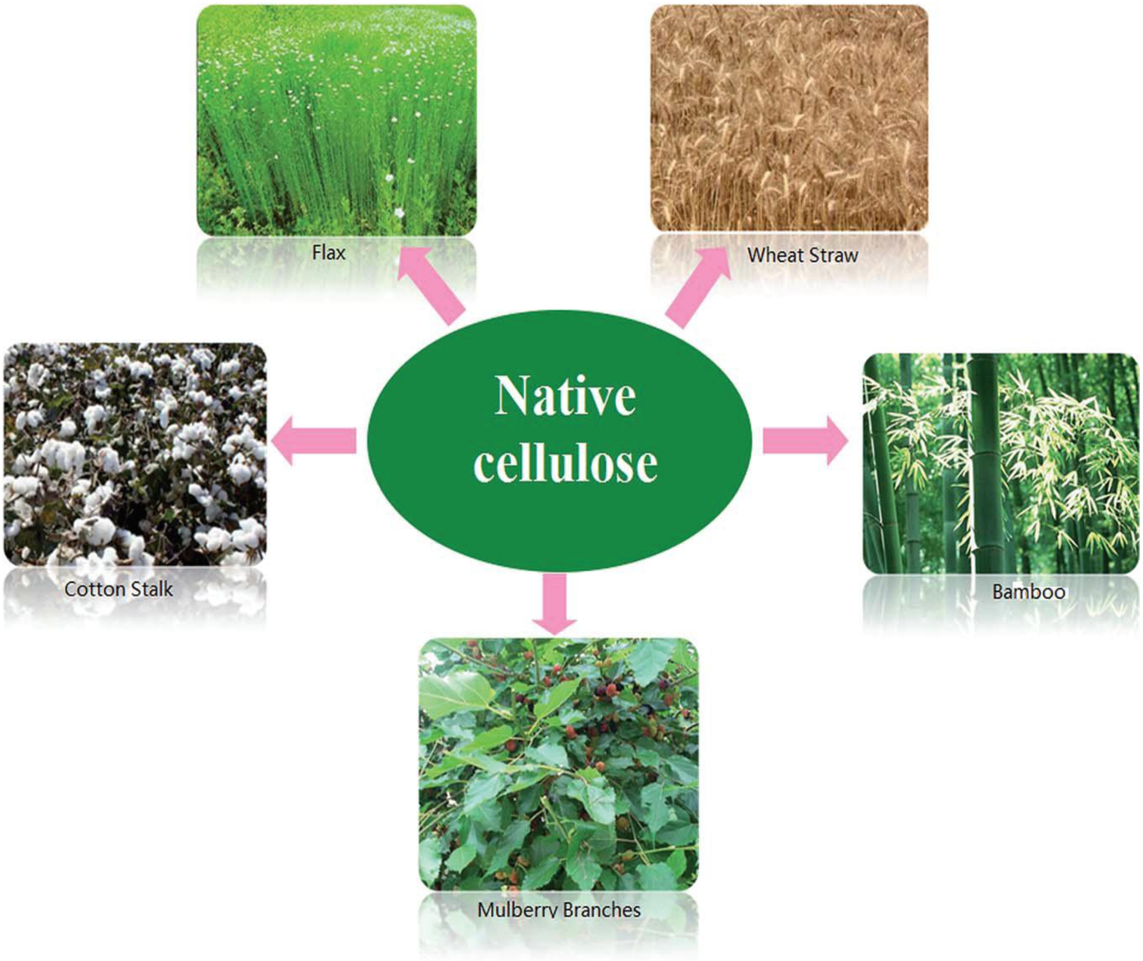
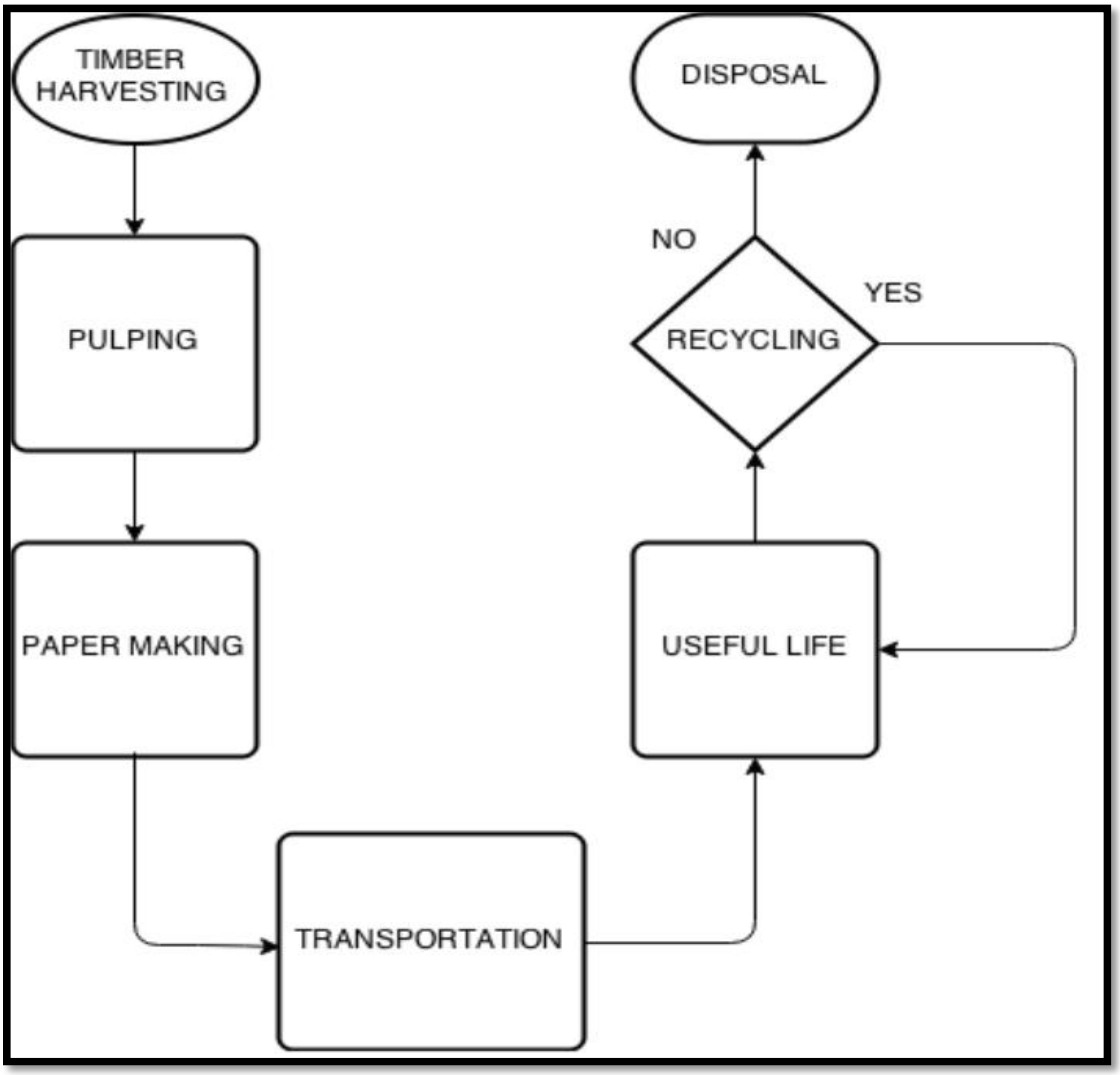


Figure (1.9) :Sources of cellulose

1.9.2. Industrial waste

Almost any type of waste paper can be recycled. However, if the waste paper is in direct contact with the other waste, it is impossible to take advantage of it and hinders recycling. Therefore, the contaminated paper is not acceptable in this area, for example household waste and care waste health and many more, and also if the waste paper contains materials that are difficult to separate(36) . The paper is used as a consumptive material with a high rate of natural origin. It is derived from raw plant fibers such as trees and other types of perennial plants. These fibers, which are included in the paper industry, are rich in cellulose. The paper residue can be used to extract cellulose and Nano-cellulose rather than throwing it as waste ,and causing damage and a large environmental problem . As well as cellulose derived from the remnants of paper can be used in the production of paper, this means that there is sustainability of nature and achieve great economic value[37-40]. Figure (1.10) shows the flow chart of the paper lifecycle [41].



Figure(1.10) : Indicates the paper life cycle

1.10. Nanocellulose applications

There are many applications in the field of Nano-cellulose due to its physical and mechanical properties, Cellulose in its various forms, such as borates, nanoparticles and nanowires, uses in many technical applications because of its desirable properties. Therefore, it is used in a wide range of applications[42] :

1.10.1. Industrial applications :

The nanoparticles of cellulose are used in many industrial applications and are widely used in this field where it are used in the field of electronic and telecommunication industries[43].

A. Manufacture of paper and cardboard:

Cellulose enters the paper industry (paper and cardboard). Since cellulose fibers make paper stronger, especially paper made from wood fiber, it is the strongest paper type where there is an overlap between the molecular forces and fiber. This increases the surface area of the bond and thus increases the strength of the paper. The paper is more effective in terms of cost and production where the process is more production of paper and less expensive[44].

B. Cosmetics products:

The use of nanoparticles in cosmetics is nothing new, and because of the wide development in nanotechnology has embraced the manufacture of cosmetics for the following reasons[45] :

1 - form a protective layer of skin because of its ability to penetrate deeper into the layers of the skin more than skin preparations before the use of nanoparticles in cosmetics, adding to their ability to deliver nutrients useful for skin

2-act as an antioxidant and this advantage benefits in maintaining the youth and vitality and appearance of the skin

3 - because of its small size it helps in the concealment of wrinkles

1.10.2. Environmental, health and safety (EHS) aspects:

All nanoparticles show good properties .These properties make nanoparticles of all kinds increasingly important in the field of technology. However, their effects on the environment and human beings are not clearly understood, but so far studies and research have shown the safety of cellulose and Nano-cellulose, and it is not toxic to humans and the environment, on the professional safety, these materials are friendly to the environment, all of this depends on the source of the nanocellulose, the raw materials used and the way of production(46).

1.10.3. Nano-cellulose for Biomedical Applications

Nano-cellulosic materials can be used as microbial pesticides and can be used as antibacterial agents in wounds as well as used in water purification, in medicines and in the packaging of antimicrobial foods, a water-based emulsion can be prepared from cellulose fibers, which can be used to clean the skin and hair, as well as to remove makeup and to be used in the treatment of dry and sensitive skin(42) .

1.11. The Adsorption

Adsorption is one of the most important technologies for the simplicity of the technology used for this method compared to other methods, in addition to the low economic cost. Many researchers have now resorted to the use of new adsorbent material that is natural, where applications in modern technologies are almost devoid of the use of waste life before putting it into the environment[(47)] .

Adsorption defined as the Accumulation of molecules , Atoms, and ions of a substance called (Adsorbate) on a porous solid surface called (Adsorbent) , the substance to which occurs the adsorption for it is called adsorbate and the surface on which the adsorption occurs is called the adsorbent [(48)] . Adsorption can also be defined as A process that has been occurs when a liquid solute or a gas accumulates on the surface of a solid or a liquid "adsorbent surface" , creating an atomic or a molecular film which is adsorbate [(49)].

The accummenence of adsorption is due to the atoms in any surface being subject to unbalanced forces of attraction perpendicular to the surface plane and these forces possess a certain unsaturation .The contact of immiscible phases result in penetration of bulk of one phase by the other, this is called "absorption" [(50)] .

1.11.1. Types of Adsorption

Adsorption in generally classified into two types physicsorption and chemisorption as follows :

1-Physical adsorption : is also defined physic-sorption. This type of adsorption occurs on the surface of some inert materials in the process of adsorption because of the electronic saturation of their atoms due to the bonds that these atoms are associated with the atoms adjacent to the material itself . Adsorption on such surfaces is carried out by natural gravitational forces ,which are the pattern of forces that cause liquefaction of gases, sometimes called Vander Walls Force. This adsorption is similar in nature and mechanics to the phenomenon of vapor condensation of matter on the surface of the substance itself [(49-51)].

2-Chemical adsorption: the other type of adsorption is chemisorption. This type of adsorption occurs on the surfaces of the active materials in the adsorption process because their atoms are not electronically satiated[(48)] . The atoms of these surfaces remain unsaturated electronically despite their bonds with neighboring atoms. In this type of adsorption, the surface tends to form chemical bonds with atoms or molecules Which adsorb on the surface, and this type of adsorption occurs frequently on surfaces of solids[(52)].

1.11.2. Adsorption mechanism:

The adsorption mechanism is a classic method. It is divided into three steps as in figure (1.11). These steps are as follows[53] :

Step 1: Diffusion of adsorbate to adsorbent surface : Occurs diffusion of adsorbate on the adsorbent surface through intermolecular forces between adsorbate and adsorbent.

Step 2: Migration into porous of adsorbent : The second step involves migration of adsorbate on porous of adsorbent .

Step 3 : In this step the particles of adsorbate are distributed on the surface of adsorbent it full of the volume of porous on the surface ,particles of adsorbate are building up monolayer of interacted (molecules , atoms and ions to the active sites of adsorbent) , it is the last step which is monolayer accumulation of adsorbate on the adsorbent surface [35,54] .

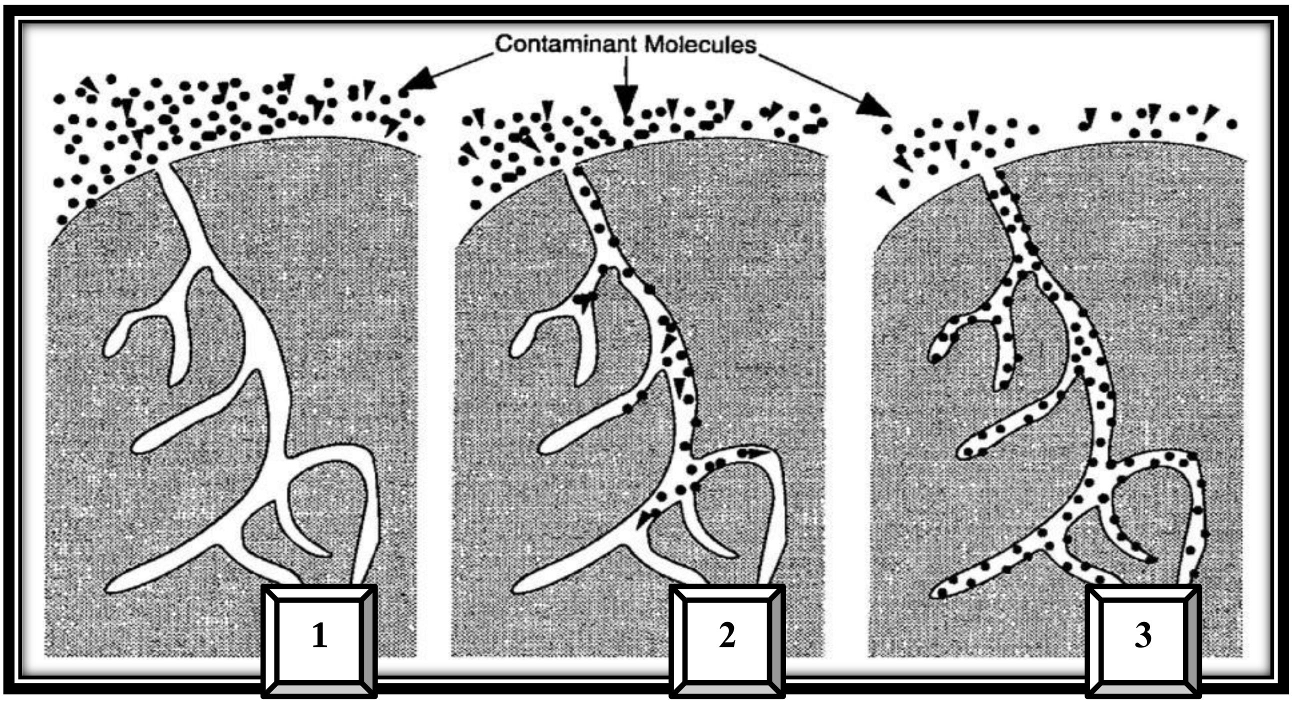


Figure (1.11): Explained steps of the adsorption mechanism

1.11.3. Applications of the adsorption processes

Adsorption has several important applications including the following applications [55,56] :

1. Pollution: Removal of colors from wastewater is so important for solving biological , ecological and industrial problems associated with dyes , different adsorbents were used for purification of wastewater to separate pollutants and toxic gases on suitable substances [57].

2. Industry: Applications of adsorption are important like , decolorization ,color materials removal from vegetable, aqueous solution and oils , deodorization and taste improvement of drinking, by adsorption on adsorbent surface.

3. Chromatographic analysis: The chromatographic analysis is depends on a nominated fact is (solid) may adsorb to varying range of the different constituents of a mixture present in a solution .

4. Catalysis: The adsorption of reactants on the catalytic surface as a first step in the reaction is a requirement to catalyzed reaction.

5. Medicine and pharmacology: The importance of active surface materials is depends on their adsorption properties, which have many applications ,such as purification of widely differing biochemical and vitamins, pharmaceutical products ,enzymes and antibiotics chromatography**.**

6.Protection from pesticides : Using selected adsorbents as a screen for pesticides in order to reduce their migration from other graveyards, stores and contaminated soils and concrete , the manuscript presented the study upon the possibility to removal of pesticide from aqueous solutions by using low-cost adsorbent [58] .

1.12 The Eosin dye

Eosin dye is a pink, heterocyclic acid dye, containing bromine atoms displaying yellow-green fluorescence, water soluble. Because to its bright color, the dye is commonly used in the fields of dyeing, leathers, printing and also fluorescent pigments and for printing inks, etc . The toxic nature of the dye is still not sufficiently known , but its growth in the living systems is proved to be hurtful . Thereby, there is a need for introducing an efficient method for the removal or recovery of eosin generated from industrial waste solutions. Biological methods are also unproductive in degrading Eosin dye due to its stability to oxidizing agents, light, heat and complex aromatic structure(59). As shown in figure (1.12) :

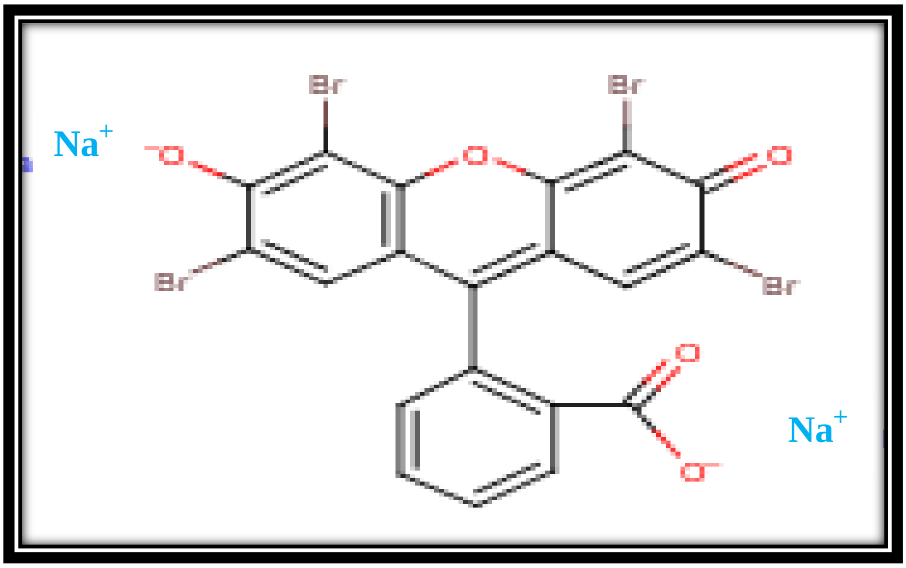


Figure (1.12): Structure of Eosin Dye(60).

The Specification of eosin dye:

1-The formula of eosin dye is ($C_{20} H_6Br_4Na_2O_5$) ,

2-Eosin dye is called by 2,4,5,7 tetrabromo fluorescein,di sodium salt

3- The Molar mass of it (691.88).

4-The Solubility in Water and Alcohol

5- Type of dye: Acid dye .

Because the proton is given to the basial group. It is used in dyeing process illustrated as follows [61] :

$$Dye^- + H^+ + Fiber \rightarrow Dye^- H^+ \_Fiber$$

In general :

Nanotechnology is now become an widely known science which is most commonly used in other fields of science like physics ,electronic and engineering since several decades. Recent exploration of nanotechnology in pharmaceutical science and biomedical results in successful improvement of conventional means of drug delivery system[62] .

Millions of tons of agricultural waste are generated globally every year. Examples are straws and wheat , sugarcane bagasse, and corn cobs. Agricultural waste containing a large amount of cellulose such as wheat straw can contain 30–44% cellulose therefore it can be use agricultural waste in many using and several application [63] .

Nanocellulose are extracted naturally from plant cell walls, can be separated through various chemical and mechanical extraction methods. Depending on the precise nature of the treatment and a range of Nano-cellulose morphologies[64].

Nano-cellulose has distinctive properties such as renewable, nanosize, , low toxicity, availability, low cost of raw material ,biocompatibility and bio-degradation, which allows it to be used in multitude fields . Nano-cellulose largely includes cellulose Nano-crystals ,cellulose nanofibrils and bacterial Nanocellulose(65) . Cellulose is a common substance and is very abundant in nature . Nanocellulose and Nanotechnology is increasing strongly in research and development , and this holds great prospects in sustainable applications(66).

The adsorption technology is used to accomplish many separation processes, especially those that cannot be accomplished or that are accomplished in a non-practical and inefficient manner using traditional methods such as distillation, absorption or even membrane-based systems(51).

1.13 .Literature Survey

Nanotechnology is currently used extensively and renewable because it have enormous potential that can be used in many fields of development, research and application. Nano-cellulose has been used in many studies for the time being because it is safe for the environment . It has been used in many applications in the industry, medicine, agriculture, also pollutant removal and cosmetics .

(Hahn ,2004) , studied various microstructural features such as agglomerated Nano-powders , isolated nanoparticles, Nano-composite materials and consolidated Nano-materials as well as all materials classes are considered . As an important component of modern studies on Nano-materials a section describes the various characterization tools available. Based on these remarks some properties of nanostructured materials was summarized emphasizing the property-microstructure relationships . As well as a summarized outlook on applications and initial industrial use of Nanomaterials is presented. An attempt is made to give an overview of the field of nanostructured materials irrespective of the synthesis process[67] .

(Scalf and West ,2006) , showed preparation of the wood particles scanned with AFM to measure roughness . Paper yields that source from fibers of wood can vary in quality based on the physical properties of the particulates . Nanoparticles is unique subset of the broad field of nanotechnology, include any type of particles with at least one dimension of less than 500 nanometers . Nanoparticles play an important role in a wide variety of fields including advanced materials, pharmaceuticals, and environmental detection and monitoring . The atomic force microscope (AFM) is ideally suited for characterizing nanoparticles. It deals the capability of three dimensions visualization and both quantitative and qualitative information on several physical properties containing morphology, size, roughness and surface texture [68] .

(Abdul Hussein ,et .al ,2007) ,Showed using of Methylene blue dye as adsorbate to study the ability of different surface activities as adsorbents. The adsorbents can be used in removal of specific pollutant materials from solution on solids which is one of the easiest and cheapest separation methods . As well as some of removed materials are economically important . In previous study , the ability of English bentonite to extract methylene blue dye from Aqueous solution was completed . Furthermore this work , Iraqi locally bentonite was used as a cheaper adsorbent for methylene blue from aqueous solution. It has also been make a comparison between English bentonite and Iraqi bentonite in different parameters of adsorption of dye from aqueous solution , some practical factors affecting adsorption process [69].

(Al-Taweel ,et . al ,2007) ,discuss the adsorption of Crystal violet from solution on the surface of kaolin . UV-spectrophotometric technique has been used to produce quantitative adsorption data at different conditions of contact time, ionic strength, pH and temperature. The results obtained show that adsorption process follows the first order rate expression. The adsorption phenomenon was examined as a function of temperature (20, 30, and 55 ˚C). The extent of adsorption of Crystal violet on Kaolin was found to increase with increasing temperature (endothermic process) .The amount of dye adsorbed on the clay at different pH values showed an increase in the following order pH 7> 8.1>10.5>11.9. The adsorption process is affected by the electrolyte concentration [70] .

(Liu ,et.al , 2010) , their research showed the preparation and characterization of nanomaterials for clean fuel production, CO_2 capture, solar cells and solar fuels, energy conversion and storage materials, hydrogen storage materials, and fuel cells. Finally, possible future developments in this important and timely area are discussed [(71)] .

(Arif , 2010) , showed that vegetable fibers obtained mainly from plants is the primary source of raw material for production of paper. To ensure that the forest is not depleted of these woods, there is need to provide alternative source of raw materials, this therefore leads to the invention of the process of recycling. Recycling, which is the extraction and recovery of valuable materials from scrap or other discarded materials, is employed to supplement the production of paper. Basically, the materials are reused, or remanufactured into new products. Some products, such as paper, plastics and glass, can be recycled or reused over and over again[(72)] .

(Nadanathangam and Satyamurthy ,2011) , studied the preparation of spherical nanocellulose from microcrystalline cellulose by controlled hydrolysis using anaerobic microbial consortium .The nanocellulose formed during the degradation of microcrystalline cellulose was separated by ultra-filtration membrane and purified by differential centrifugation. The purified nanocellulose was characterized by nanoparticle size analyzer, atomic force microscopy and Fourier Transform infrared spectroscopy. While the conventional process of nanocellulose preparation using concentrated sulfuric acid hydrolysis resulted in the formation of nanowhiskers [(73)] .

(Duran ,et .al ,2011) , discusses the importance of Nano-cellulose material, as well as relevant topics concerning its technological preparations to obtain versatile new composites materials, and the applications of nanocellulose in different domains . At the present moment , the most common techniques for nanocellulose preparation were found to be acid and enzymatic procedures, oxidation, electrospinning, high pressure homogenization , and steam explosion processes. Concerning nanocellulose composites, several aspects were found in recent patents ranging from simple to complex structures with different properties. As unique materials , nanocellulose can be used in different areas of expertise, such as in biomedical and technical applications [(74)] .

(Krishnamachari, et .al ,2012) , in their research showed the acid hydrolysis of microcrystalline cellulose and were performed on different samples obtained from acid hydrolysis of Microcrystalline Cellulose (MCC). Acid hydrolysis of MCC was carried out using 64% H_2SO_4 at 45 °C for 10, 20, 30 min, 1 and 5 h. Elastic modulus and hardness were assessed for each sample . The samples hydrolyzed for 30 min or more had a considerably lower elastic modulus than those hydrolyzed for 20 min or less [(75)].

(Svensson , 2012) , in his thesis explores how to use the dry Nanoporous structure of cellulosic fibers in new types of composite materials . A large effort was also given on how to correctly characterize the structure of fibers where the wet structure has been preserved also in the dry state . Delignified wood fibers have an open fibrillar structure in their water-swollen state .This open fibrillar structure was preserved in the dry state by performing a liquid exchange procedure and the samples were thereafter carefully dried with Ar(g) .This open structure was also revealed using (FE-SEM) field emission scanning electron microscopy [(76)].

(Hebeish ,et .al , 2013), in their research showed the preparation of cellulose nanowhiskers (CNW) , which were synthesized from native cotton cellulose as per the acid hydrolysis methods. Thus Egyptian cotton slivers, after being purified , were subjected to three sulfuric acid concentrations, viz 55%, 60% and 65% (w/w) at 60 ˚C for 60 min. The yield of CNW attains values of 65%, 57% and 50%, respectively. The amorphous regions along with thinner as well as shorter crystallites spreaded throughout the cellulose structure are digested by the acid leaving CNW suspension . The latter could be freeze-dried and CNW powder could be achieved . A thorough investigation pertaining to nanostructural characteristics of CNW was performed. These characteristics could be monitored using TEM for morphology, sizes and size distribution, XRD for degree of crystallinity and crystalline structure, and FTIR spectra for following the changes in functionality [77] .

(Shokrollah , et .al , 2014) , showed the extraction of eosin dye from aqueous solution using non-ionic surfactant. The enrichment of dye was determined by a spectrophotometric study. The effects of different operating parameters, e.g., salt, temperature, concentrations of surfactant, pH , equilibration temperature , the heating time and time of centrifuge have been studied , and its absorbance was measured at 533 nm[78] .

(Thomas ,et. al ,2014) , showed that both cellulose nanofibrils and nanowhiskers could be used as reinforcing fillers to improve mechanical and barrier properties of different types of polymer systems which include rubbers, thermoplastics and thermosets. This research provides an overview of recent progress made in the area of Nano-cellulose and Nano-whiskers preparation from various natural fibers . The various techniques being currently used for the isolation of cellulose Nano-fibers and Nano-whiskers has been presented. Finally, the emerging applications of these materials in various fields including Nano-composite preparation have been presented[79] .

(Lani , et .al , 2014) , in their research showed that isolate nanocellulose from empty fruit bunch (EFB) fiber and their reinforcing effect on polyvinyl alcohol (PVA)/starch blend films . Aseries of PVA/starch films with different content of nanocellulose were prepared by solution casting method . Nanocellulose fiber with diameters ranging from (4 to 15) nm has been successfully prepared and characterized by using FTIR ,SEM and TEM [80].

(Morsy ,2014) ,discuss mainly for nanoparticle preparation, it is in the last years that direct applications of nano-emulsions in consumer products are being developed, mainly in pharmacy, drugs, personal care, health care, agrochemicals and cosmetics.These recent applications have made that studies on optimization methods for nano-emulsion preparation be a requirement. It is focused on the most recent literature on developments of nano-emulsions as final application products and on the optimization of their preparation [81] .

(Shukla , et .al , 2015) , discussed the extraction of cellulose micro sheets from rice husks. The two step methodology is reported to extract the micro size cellulose from rice husk by chemical treatment. The chemically extracted cellulose is micronised into micro dimensions under ambient conditions through the controlled degradation of amorphous segment present in cellulose chain by acid hydrolysis. The obtained cellulose was characterized by infra-red spectroscopy, X- ray diffraction and scanning electron microscopy. These techniques reveal the crystalline nature of micro size cellulose having particle size in the range from 180- 250 nm [82] .

(Zain ,et .al ,2015) , in their research prepared nano-cellulose from Pomelo (Citrus grandis) peel is one of the under-utilized waste materials that have potential in the production of functional ingredients, due to its high fiber content. This study was conducted to isolate and characterize cellulose and nanocellulose from pomelo peer . Cellulose was prepared via alkali treatment followed by bleaching process, while nanocellulose was produced via hydrolysis using sulfuric acid. The physicochemical and structural properties of the produced materials were characterized using proximate analysis, Fourier transform infrared spectroscopy (FTIR), and cellulose crystallinity index (CrI) by X-Ray Diffractometer (XRD) and water holding capacity (WHC). Proximate analysis showed that pomelo peer contains 72.62% carbohydrate, 16.13% moisture, 6.27% protein, 3.41% ash and 1.56% fat .We conclude that pomelo peer can be a principal source of natural cellulose and nanocellulose materials which can be further manipulated for food ingredient applications (83) .

(Silva ,et .al ,2015) , showed that cellulose is widely used in the synthesis of new materials as well as in the adsorption of dye , and showing the importance of study of effect factors on the adsorption process . This study provides further data to establish the removal rate of the solute solution and how the adsorption takes place (84) .

(Johan , 2016) ,explained that cellulose Nanofibers can be extracted from various plant sources and although the mechanical separation of plant fibers into smaller elementary constituents has typically required high energy input, chemical or enzymatic fiber pre-treatments have been developed to overcome this problem . A challenge associated with using Nano-cellulose in composites is the lack of compatibility with hydrophobic polymers and various chemical modification methods have been explored in order to address this hurdle [85] .

(Iulianelli , et .al ,2016) , discuss the essential concepts about nano-cellulose , such as its production methods , structural aspects , and current trends in classification , and the main aspects of cellulose-based nano-composites , including the progress that has been reached in relation to their compatibility , production , final properties and potential applications . In recent years , several studies have been performed using nanocellulose as a component in polymeric nanocomposites . The attention in studying cellulose-based nanocomposite is due to the abundance, renewable nature, and outstanding mechanical properties of this nanoparticle. However, obtaining nanocomposites based on nano-cellulose, with optimal properties[86] .

(Kermani and Esfandiary ,2016) , studied the preparation of nanocrystalline cellulose (NCC) from whatman No.1 filter paper (consist 98% α-cellulose) . The NCC was obtained via acidic hydrolysis using traditional method . In this work a new nanocomposite based on chitosan/polyvinyl alcohol/nanocrystalline cellulose was synthesized , Cts/PVA/NCC nanocomposites were prepared in different concentrations of NCC (5 ,10 and 15)% .The morphology and particle size of NCC and nanocomposites were characterized by X-ray diffraction (XRD) analysis , scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) spectroscopy. SEM images showed the rod-like shape of NCC whiskers .The average crystallite size was obtained from X-ray diffraction data using Scherrer’s equation [87] .

(Seow and Lim ,2016) ,This research presented the application of adsorption in the removal of dyes from aqueous solution . The paper provides the literature information about the dyes as well as its toxicity and classification . Further, the adsorption factors that will affect the process such as solution pH, initial dye concentration, adsorbent amount and temperature have also been reported. Conclusions have been drawn from the literature review regarding the effects of those adsorption factors toward the dyes adsorption[(88)] .

(Ahmadi , et .al ,2017) , studied the efficiency of nano-sized cellulose obtained from rice husk for Cr(VI) adsorption .The effect of adsorption factors including contact time (0–120min) ,pH(3-10), adsorbent amount (0.2–1.5g/L), and initial Cr(VI) concentration (5–50mg/L) were investigated according to one factor at time method . The results showed , in pH 6, contact time 100min ,adsorbent amount 1.5g/L and 30mg/L initial chromium concentration ,the adsorption efficiency reached to 92.99% in adsorption process [(89)].

(Bekiroglu and Elmas ,2017) ,in their research showed recycling of paper waste , it's one of the best options for sustainable development and reduce waste. Because waste paper recycling supplies significant contributions to the sustainability of forestry resources, to energy saving efforts, to reduction of environmental pollution levels and to effective utilization of raw materials. The economic contribution of waste paper recycling can be much greater if these wastes are collected at the source . Economic realization of this contribution can only be achieved through knowledge of the qualitative and quantitative properties of the recycled waste paper [(90)].

(Madureira , et . al , 2018) , indicated that Pineapple peel be a good source of cellulose for the production of cellulose nanocrystals . Peels from fresh-cut fruit was used as raw material . These residues were purified to remove pigments, lipids and hemicellulose, and a bleaching process for delignification was carried out for 4-6 h. All resulting products were characterised for their lignin, hemicellulose, cellulose and ash contents using standard techniques . The purified cellulose was subject to acid hydrolysis for nanocrystal extraction with two testing times, 30 and 60 minutes. The time of extraction did not affect the nanocrystals chemical and physical properties. The use of 6 h of bleaching treatment during purification was shown to be more effective than 4 h [(91)].

(Hossain , et . al , 2018) , in their work explained the derivation of nanocellulose from an alternative option which is rice husks . The processed rice husks was refined by chemical and mechanical treatments . Nanocellulose was subsequently derived from the refined rice husk through acid hydrolysis followed by centrifugation and ultrasonic treatment. Scanning Electron Microscopy ensured the nanoscale diameter while Fourier transformed infrared Spectroscopy confirmed the removal of noncellulosic materials. It is therefore proposed that the native rice husk can also be utilized for manufacturing nanocellulose reducing its adverse environmental impacts [(92)] .

1.14 The Aim of the study

1.Preparation of Nanocellulose from rice husks instead of throwing it as waste and cause damage to environment .

2. Extract nanocellulose (NC) from paper residues which is isolated from the other wastes (household, industrial, etc.) were completely used , instead of throwing the residues of paper, to achieve a great economic feasibility.

3. To comparison between efficient of product of Nanocellulose prepared from rice husks and NC prepared from paper residues through characterization both type of NC by using techniques for characterization of nanocellulose are (Scanning Electron Microscope , Atomic Force Microscope ,X-ray diffraction, and Fourier Transform Infrared spectroscopy) .

4. Show great potential for nanocellulose ,which have distinctive characteristics .

5. After obtaining the nanocellulose from the rice husks and paper residues , industrial application was applied by adsorption of the eosin dye from the aqueous solution on surface of both type of nanocellulose from rice husks and paper residues .

6. Recycling of agricultural and industrial waste for useful purposes, most importantly chemical adsorption .

7. Management and minimization of agricultural and industrial waste .

Chapter Two

(Experimental)

2.1.Materials Used

2.1.1. The chemicals

The properties of chemicals used in this study are shown in the following

Table (2.1): The chemical materials used.

NO.	Chemicals	Formula	Purity (%)	Phase	Source
1	Sulfuric acid	H_2SO_4	98 %	Liquid	Fluka
2	Sodium hydroxide	NaOH	99 %	Solid	Alpha chemical
3	Hydrogen peroxide	H_2O_2	35%	Liquid	Made in Germany
4	Hydrochloric acid	HCl	37 %	Liquid	J.T. Baker
5	Acetic acid	CH_3COOH	98%	Liquid	USA
6	Sodium hypochlorite	NaOCl	95%	Liquid	Sigma-Aldrich USA

2.2. Instruments and Apparatus

2.2.1. Instruments

The apparatus and instruments that are used in this study were listed below with their details, origin, and place of measurement **as table (2.2).**

Table (2.2): The instrumentation used in this study.

NO.	***Instruments names***	***Details and Origin***	***Place Of measurement***
1	**Hot Plate Magnetic Stirrer**	MS-H280-pro ISO LAB Laboratory GmbH,(Germany)	*The Laboratories Of Chemistry Department College of Science, University of Diyala, Iraq*
2	**Electric Balance**	KERN ACJ/ACS,ACS 120-40, WB 12 AE 0308, max 120 g, d= 0.1 mg, (Germany)	
3	**Oven**	BINDER , Hotline International (20-360), (Germany)	
4	**pH Meter**	PH/Ion Benchtop WTW inoLab PH Meters 7110 Benchtop Meters, (Germany)	
5	**Water Bath with Shaker**	BS – 11, 230 VAC – 50 Hz, (Korea)	
6	**Distillation device**	LUZ DE AVISO AGUA INSUFICICENTE, (Germany)	
7	**Ultrasonic Processor**	MTI MADE IN USA	*The Laboratories Of Chemistry Department College of Science, University Of* Baghdad

2.2.2.Apparatus used in characterization

The apparatus used are inserted in the ***Table (2.3)*** with their details, origin, and place of measurement **:**

Table (2.3): Apparatus used in Characterization.

NO.	*Apparatus names*	*Details and Origin*	*Place of measurement*
1	**Atomic Force Microscope (AFM)**	Scanning Probe Microscope, AA 3000 SPM 220 VAngstrom Advanced Inc, AFM contact mode, (USA)	The Special Laboratory of Dr. Abdulkareem M.A. AL-Sammarraie, Iraq
2	**Scanning Electron Microscope (SEM)**	TESCAN , Vega III, Czech (Republic)	Lab. of Nano, Ministry of Science and Technology, Iraq
3	**X-ray Diffraction Spectroscopy (XRD)**	XRD-6000 Cukα (λ=1.5406 A°), 220/50, HZ, SHIMADZU, (Japan)	Lab. of X-Ray Diffraction in Central Service laboratory, College of Education Ibn- AL-Haitham, University of Baghdad, Iraq
4	**FT-IR Spectrometer**	Perkin Elmer Spectrum 65 (Germany)	The Laboratories of Chemistry Department , College of Science , University of Diyala , Iraq

2.3.Raw materials

1.Agricultural waste is the rice husks collected from Diwaniyah , Iraq as a raw material to synthesis of Nanocellulose product.

2.Industrial waste is the paper residues collected as a raw material to synthesis Nanocellulose product

2.4 .Chemical solutions preparation

The solutions used in this study are:

1.Sulfuric acid with different concentrations (15,25,35,45) % of rice husks , and 50% of paper residues .

2. Sodium hydroxide with a concentration of (1%) for neutralization the mixture of solution acid containing sulfuric acid (with different concentrations) , and the sample (agricultural and industrial wastes separately) .

3.Sodium hypochlorite is used with a concentration of (4%) for the bleaching process and to remove most of the remaining phenols such as lignin and polyphenols .

4.Hydrogen peroxide with a concentration of 30% was used for bleaching process .

5.Acetic acid diluted to (90%) and mixed with sulfuric acid 3.5% for acid hydrolysis of paper residues after refining and washing with deionized water several times .

6. Hydrochloric acid with a concentration of(0.1) M was used to adjust the pH of dye solution at different concentration .

2.5. Chemical Methods

This methods deals the purification of the raw materials used, namely, rice husks and paper residues, and converting these wastes by several chemical experiments into nanocellulose materials.

2.5.1 Preparation of nanocellulose from agricultural waste (Rice husks)

Extraction of cellulose from the rice husks in several steps as follows:

A. Purification step :

In this step the rice husks was washed with distilled water in several times (exactly five times) . After that the husks was dried for one week until the husks became completely dry .

B. Grinding step :

In this step the husks was grinded for several time until the rice husks was grinded well . The grinded sample passed through sieves 75 μm to get a good powder.

C. Bleaching step :

In this step the sample (15 gm) added to sodium hypochlorite (4%) and heated at (70˚C) for 3h , filtered and washed with the distilled water several times , then the sample were dried at (50 ˚C) for 5h . Then the sample grinded to get a fine powder [93].

D. Preparation of NC product :

The product has been prepared by acid hydrolysis[5] .Where the product which from bleaching step has been hydrolysis in 100 ml of sulfuric acid in different concentrations (15,25,35, and 45)% ,when the sample added to each concentration of H_2SO_4 the sample must dissolved under strong stirred until the sample completely dissolved at 35˚C with strong stirring , then to finish reaction , added 150 ml of deionized water to solution . After that the solution coolded to 8˚C .The produce left at room temperature for one day to separate of cellulose until the separation completed well .Then solution was filtered , and it was washed with distilled water many times. After that prepared solution contains (1%) of NaOH for neutralization the sample to pH =7 by adding sodium hydroxide (1%) . After neutralization the solution was filtered and it was collected [94] .

To production nanocellulose (NC) , 200ml of deionized water was added to the sample with stirring. After addition the solution sonicated by ultrasonic processor[95] , for three different times(60, 120, and 180) min for all concentration of H_2SO_4 (15,25,35, and 45)% . When the sonication was completed the solution coolded to 8˚C for one day . After that the sample filtered and kept the sample at 8˚C. Finally the sample dried at 60˚C for 12h ,and get a perfect powder .The fine powder were put in plastic tube and ready to measurement, Figure (2.1) showed all steps .

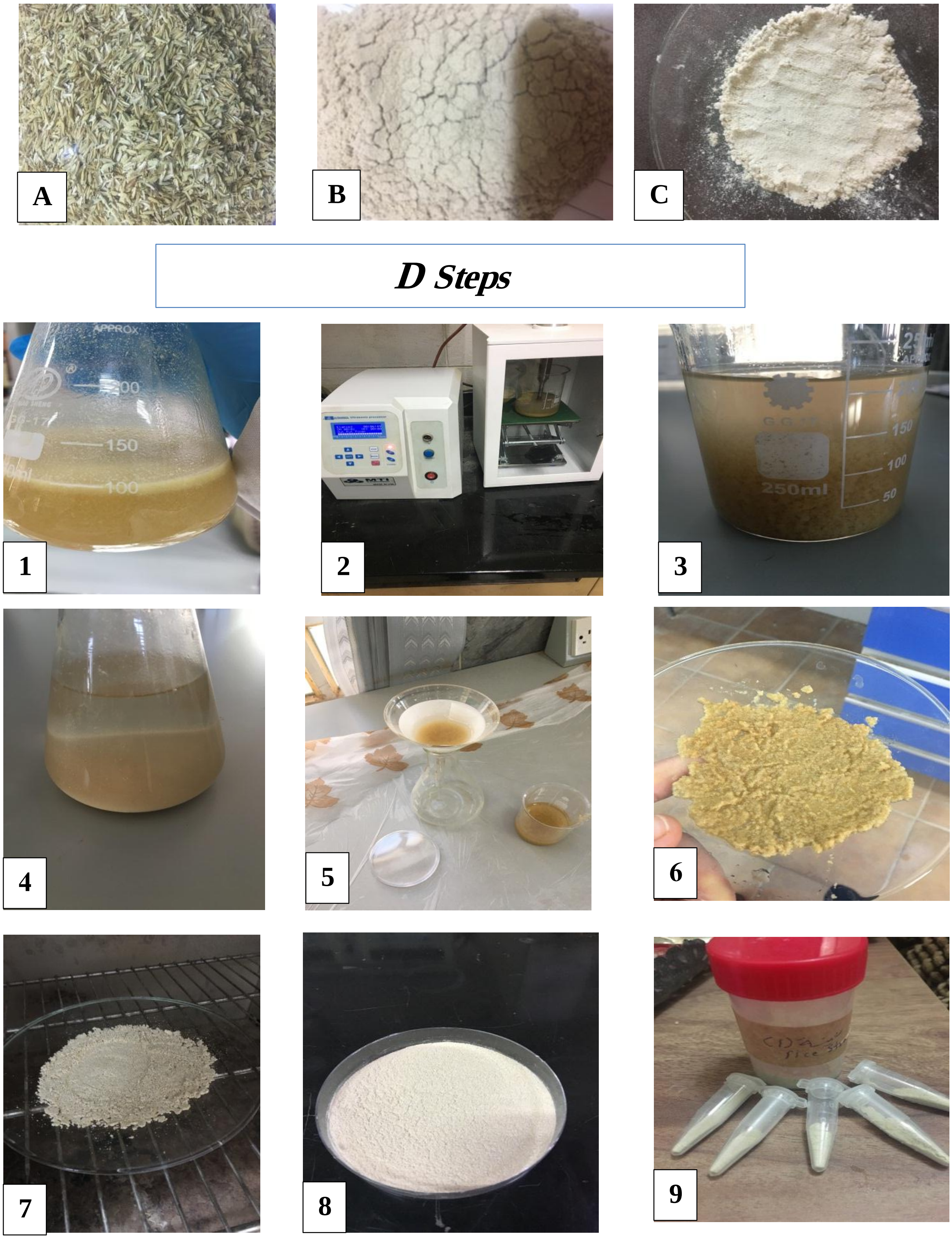


Figure (2.1): Showing steps to prepare nano-cellulose from rice husks .

2.5.2.Extraction the nanocellulose from Industrial waste (paper residues) :

The Nanocellulose (NC) were prepared from paper residues by many steps :

A)Steps of Preparation sample

1.The paper residues were taken ,purified and dried then grinded , the paper residues after grinding became like soft cotton. Then the product was washed with normal water and then with distilled water for several times then the product was dried at 40 ˚C.

2.The sulfuric acid was diluted with a concentration of (3.5%) and the acetic acid with concentration (90%) . After that 4.0 gm of residues were added to 100 ml of the sulfuric acid (3.5%) and acetic acid(90%), then heated it at (80˚C) for 1 h with strong stirring[96] .

Then has been done filtration of the solution and washed with distilled water several times until the smell of acids disappears . At first the filtration was quickly and then became slow and continued for one day . After that the product was dried at 50˚C.

B) Bleaching step :

Bleaching step was done by (30%) of hydrogen peroxide and (5%) of sodium hydroxide . The two solution were mixed together ,and added the sample to mixture for bleaching . After that the solution was heated at 60˚C for 2 h .Then solution was filtered and it was washed with distilled water for several times . After that the product was dried in 70˚C for 3h.

C) Preparation nanocellulose from paper residues :

The product from bleaching step was added to sulfuric acid at concentration 50% with strong stirring [10], then added 150ml of deionized water to end reaction . After that the solution was coolded at 8˚C for 3h ,

then left the solution at room temperature to separate the components . After that the product was filtered and washed with distilled water for several times .Then the product was equated to PH= 7 by sodium hydroxide at concentration 1% . After that the solution was filtered and collected .

The product was added to 100ml of deionized water and it has been done sonicated by ultrasonic device for 60 min , the solution was changed which it became thick ,then the product was coolded at 8˚C . After that the product was filtered and it stored in plastic tube and keep it at 8˚C for 24 h. After that the product was dried at 80˚C for 6 h ,and get a fine powder . By this way the NC was prepared from paper residues , figure (2.2) showed all steps of preparation NC from paper residues.

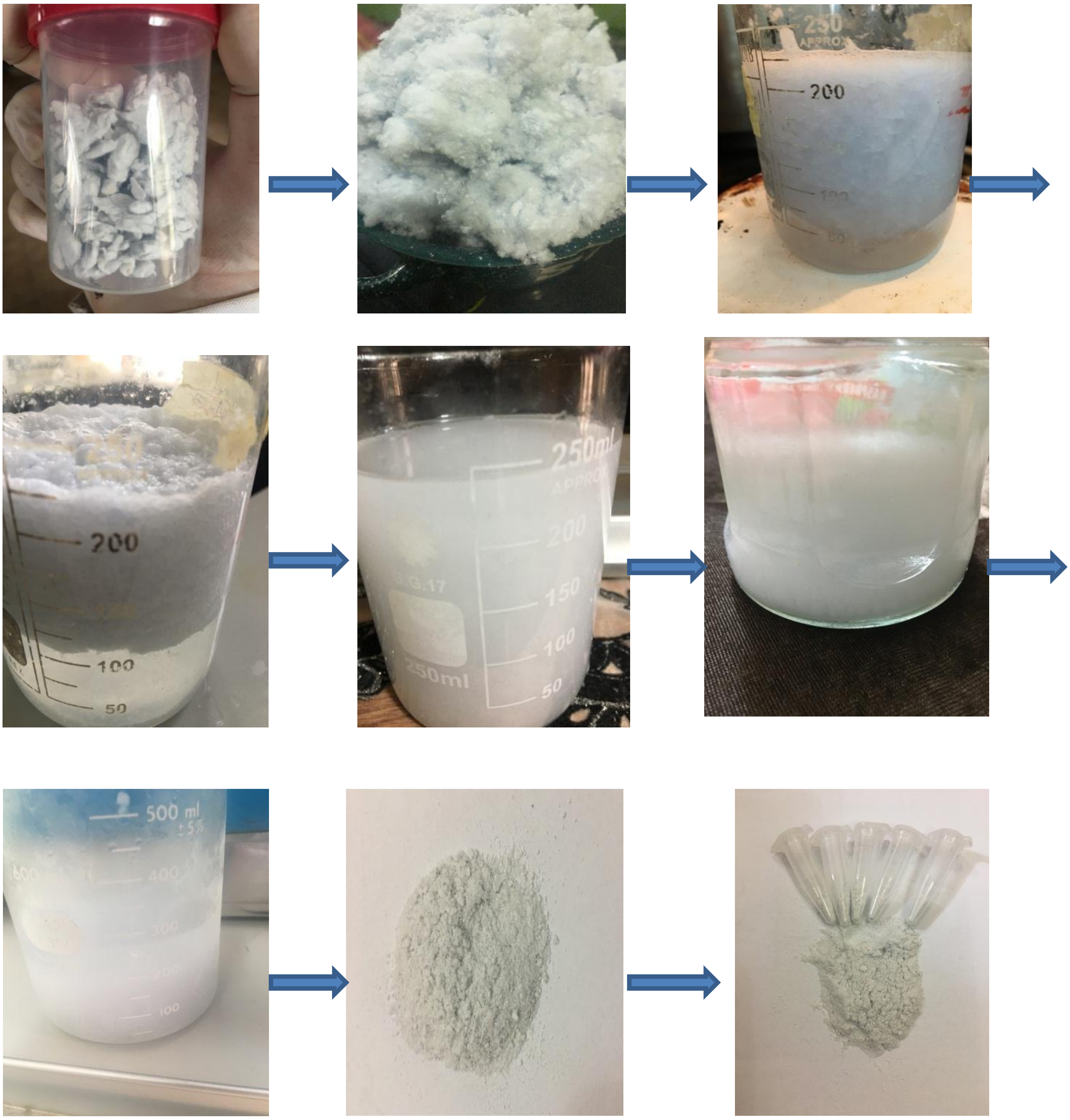


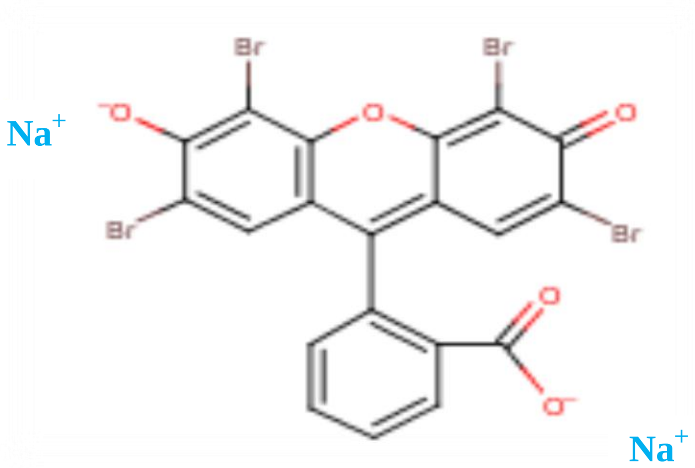
Figure (2.2): Showed steps to prepare nanocellulose from paper residues.

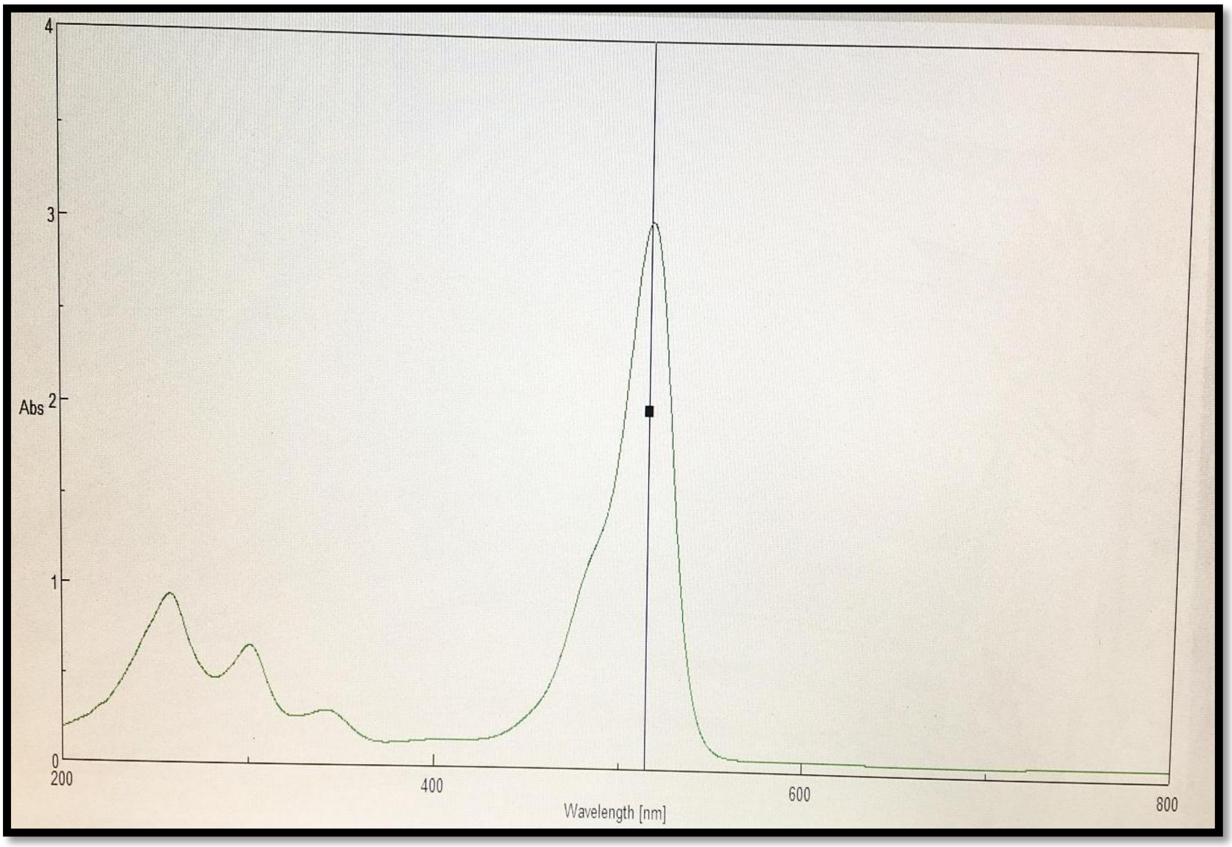
2.6. Adsorption study

2.6.1.Determination of wavelength (λ_{max}) and calibration curve for the eosin dye (at a wavelength λ_{max} 515 nm)

The wavelength of adsorption (λ_{max}) was determined at the highest absorption of the aqueous solutions of the eosin dye by recording spectral absorption by spectroscopy of UV-visible radiation within the range of (200-800 nm) using quartz cells (1 cm) as shown in figure (2.3) , and table (2.4) showed the value of wavelength of eosin dye is 515nm .While calibration curve ,which represents the relationship between absorption and concentrations of the eosin dye, was determined. Five concentrations within the range (10-50ppm) of the dye were prepared based on the Per Lambert law, as in equation (2-1), the relationship showed a straight line as shown in figure (2.4) , which represented the calibration curve of the eosin dye with the above concentrations.

Table (2.4) Value of the maximum wavelength of the Eosin dye

Dye	**λ max**	
Eosin dye $C_{20}H_6Br_4Na_2O_5$ 	***wavelength***	***Absorption***
	515 nm	3.04767
	Phase	***Source***
	solid	BDH



Figure(2.3):UV - Visible Absorption Spectromum for eosin dye .

The Beer-Lambert law (or Beer's law) is:

A = ε * b * c .... (2-1)

Where

A: Is the absorption .

ε : molar absorptivity coefficient with units of M^{-1} cm^{-1} .

b: is the path length cm^{-1} .

c: The concentration (with units M) .

Beer-Lambert law is the linear relationship between absorption which is proportional to the concentration of absorbent molecules in the material [97] .

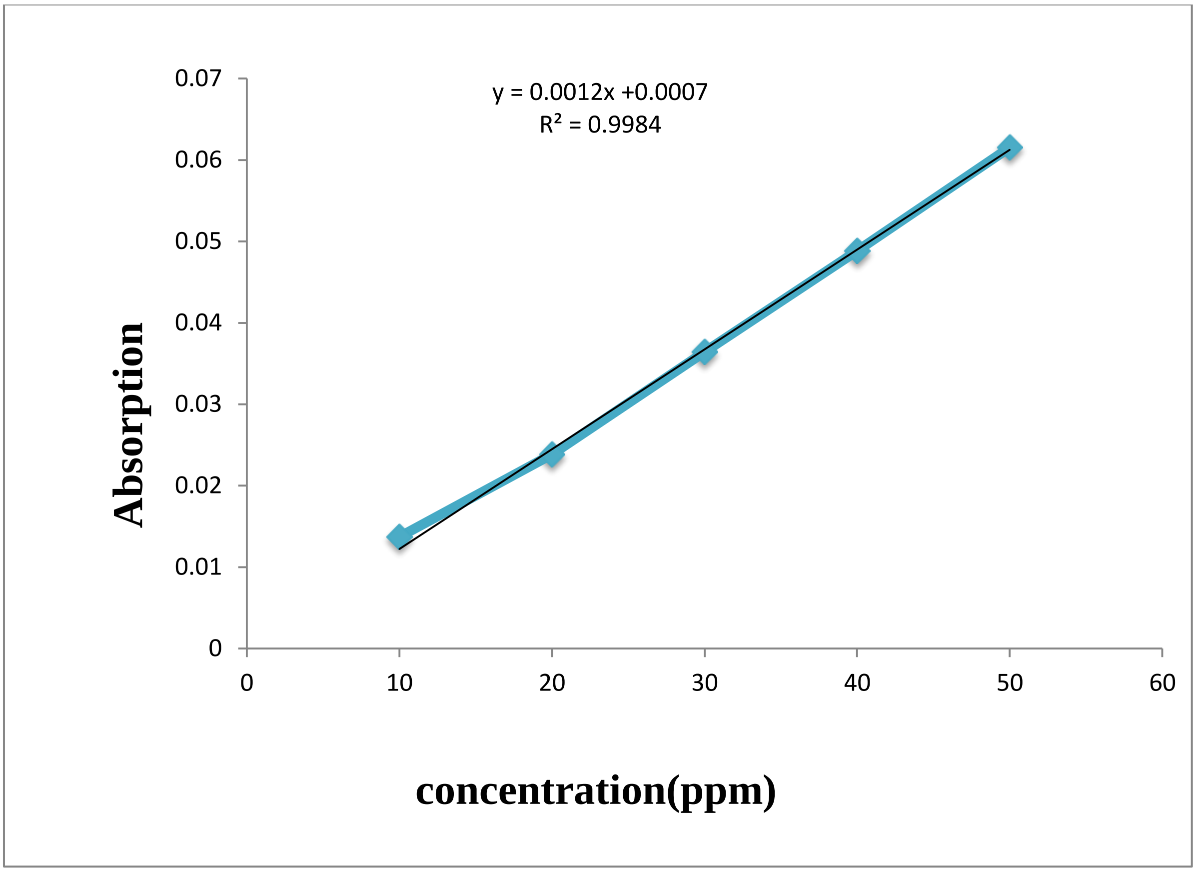


Figure (2.4): Calibration curve for the Eosin dye

The calculation of percentage removal (R %) :

The percentage removal (R %) of eosin dye was a calculated by following equation [98 ,99] :

$$R\% = \frac{(Co-Ce)}{Co} * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2\text{-}2)$$

Where:

R% : The percentage removal of dye

C_o : The initial concentration of dye, **(mg/L)**.

C_e : The concentration of dye after adsorption, **(mg/L)** .

2.6.2 .Effect of contact time

Determination of the time required for the equilibrium between the adsorbate and the adsorbent surface was achieved through the preparation of eight volumetric flasks (100 ml) containing equal volumes of the eosin dye (25 ml) at a concentration of (10 ppm) and the weight of 0.05 g of the nanocellulose prepared from the rice husks and paper residues . The volumetric flasks placed in Water bath with Shaker at a constant temperature (25˚C) and stirring speed (150) rpm ,and after continuous shaking for samples of both types of nanocellulose and at different times (10,20,30,..…80 min) respectively , The samples are then filtered with filter paper twice . The adsorbed quantities were estimated using the spectral methods . Adsorption was followed at the wavelength of the eosin dye (λ_{max} 515 nm) , The results showed that the time of adsorption reach to equilibrium is 20 minutes for nanocellulose from rice husks and 30 minutes for nanocellulose from paper residues .

2.6.3. Effect of adsorbent quantity

Five different quantities were weighed within the range (0.01-0.05) g of nanocellulose both types of rice husks and paper residues, then are placed in five volumetric flasks (100 ml) containing (25 ml) of eosin dye with concentration (10 ppm) . These flasks placed in the water bath with shaker stirring speed (150) rpm , at temperature (25 ˚**C**). Left for (20 min) for nanocellulose from the rice husks and (30 min) for nanocellulose from the paper residues ,and then the samples were filtered with filter paper twice , and measured at the wavelength (515nm) by the UV-visible spectrometer. It is found that the optimum quantity of nanocellulose produced from rice husks was (0.03 g) and (0.01g) of NC from paper residues .

2.6.4. Effect of initial concentration

The effect of the concentrations change of eosin dye was studied by preparing six different concentrations with the range (10-60) ppm to determine optimal concentration of dye. A quantity of adsorbent (0.03)g of NC from rice husks and (0.01) g of NC from paper residues respectively, was placed in volumetric flasks (100 ml) containing (25 ml) of different concentrations of eosin dye , these volumetric flasks were put in a water bath shaker for (20min) of NC from rice husks and (30 min) for NC from paper residues . samples were filtered ,then the adsorption quantity was measured using UV-Visible spectrometer at wavelength (515nm) of the dye . The percentage removal (R %) was calculated , it was found that the best concentration was (10ppm) for both types of NC prepared from husks and residues .

2.6.5.Effect of temperature

The effect of temperature on the adsorption was studied through use of five different temperatures , where five prepared volumetric flasks (100 ml) were placed in each of it (25 ml) of eosin dye , with concentration (10ppm) and the weight of adsorbent surface was (0.03g) of NC from rice husks and (0.01g) of NC from paper residues , these volumetric flasks were put in water bath with shaker for (20min) of NC from rice husks and (30min) for NC from paper residues , Adsorption was occurred at five different temperatures (25,35,45,55,and 65)˚C. Then the samples were filtered , and the adsorption quantity was estimated by the spectral methods. The percentage removal of dye (R %) was calculated ,to find the optimum temperature of both type of NC from rice husks and paper residues was done at 25 ˚C .

2.6.6 Effect of pH

Effect of pH was investigated at pH (3,7 and 9) by the drop addition of (0.1) M NaOH or (0.1) M HCl ; with remained concentration of eosin dye constant (10ppm) ,and then (25 ml) of dye placed in volumetric flasks, added drops of (0.1) NaOH or hydrochloric acid (0.1) M until the pH reached to (PH= 3). Absorption was measured by UV- visible spectrometer before adding the adsorbent , after that added (0.03) g of nanocellulose produced from the rice husks and (0.01) g of NC from paper residues, then the samples were placed in water bath with shaker with stirring speed of (150) rpm at (25 ˚C) . After the equilibrium time for each surface is reached, the samples are filtered and the absorption was measured again by UV- visible spectrometer. Then process was returned at the same conditions but at PH (7 ,9) and the percentage removal (R %) of eosin dye was a calculated . It was observed the highest (R %) at pH 3 .

Chapter Three

(Results &Discussion)

3.1.Conversion of some agricultural and industrial wastes into Nanocellulose

The nanocellulose was prepared in a low cost method, namely, acid hydrolysis, filtration, drying and cooling, where this work was done in a simpler, shorter and lower cost. The work used in this study reduces the use of chemicals used by using aqueous solutions with diluted concentrations of chemicals, In this study, sulfuric acid was used with concentrations of (15,25,35,45)% for rice husks and 50% for paper residues to separate the cellulose from the other components found with cellulose ,where the nanocellulose was extracted from rice husks and paper residues by the ultrasounic technique at different times in which the wastes was transformed into a thick emulsion. The difference between the resultant (NC) from agricultural waste (rice husks) and the industrial waste (paper residues) , that the emulsion produced after sonicated of rice husks was thick emulsion , combined stable manner in two layers at the top was water and in the bottom emulsion of (NC). While the paper residues was transferred to a thick emulsion containing soft white fiber diffused in all over the beaker as shown in figure (3.1).

During work, it was found that lower concentration of sulfuric acid (15%) was needed to more time for hydrolysis compared with the highest concentration 45% of sulfuric acid using to preparation NC from rice husks .

It was found that the acid hydrolysis by using sulfuric acid leads to hydrolysis of raw materials and extraction of cellulose and then ,after cooling and drying and sonicated by ultrasonic processor at different times , produced a fine powder of nanocellulose from both types of wastes (rice husks and paper residues). Good results were obtained from nanocellulose , after that it was identification the product (NC) by using measurements of identification (SEM ,AFM, XRD, and FT-IR) for NC product from rice husks and paper residues.

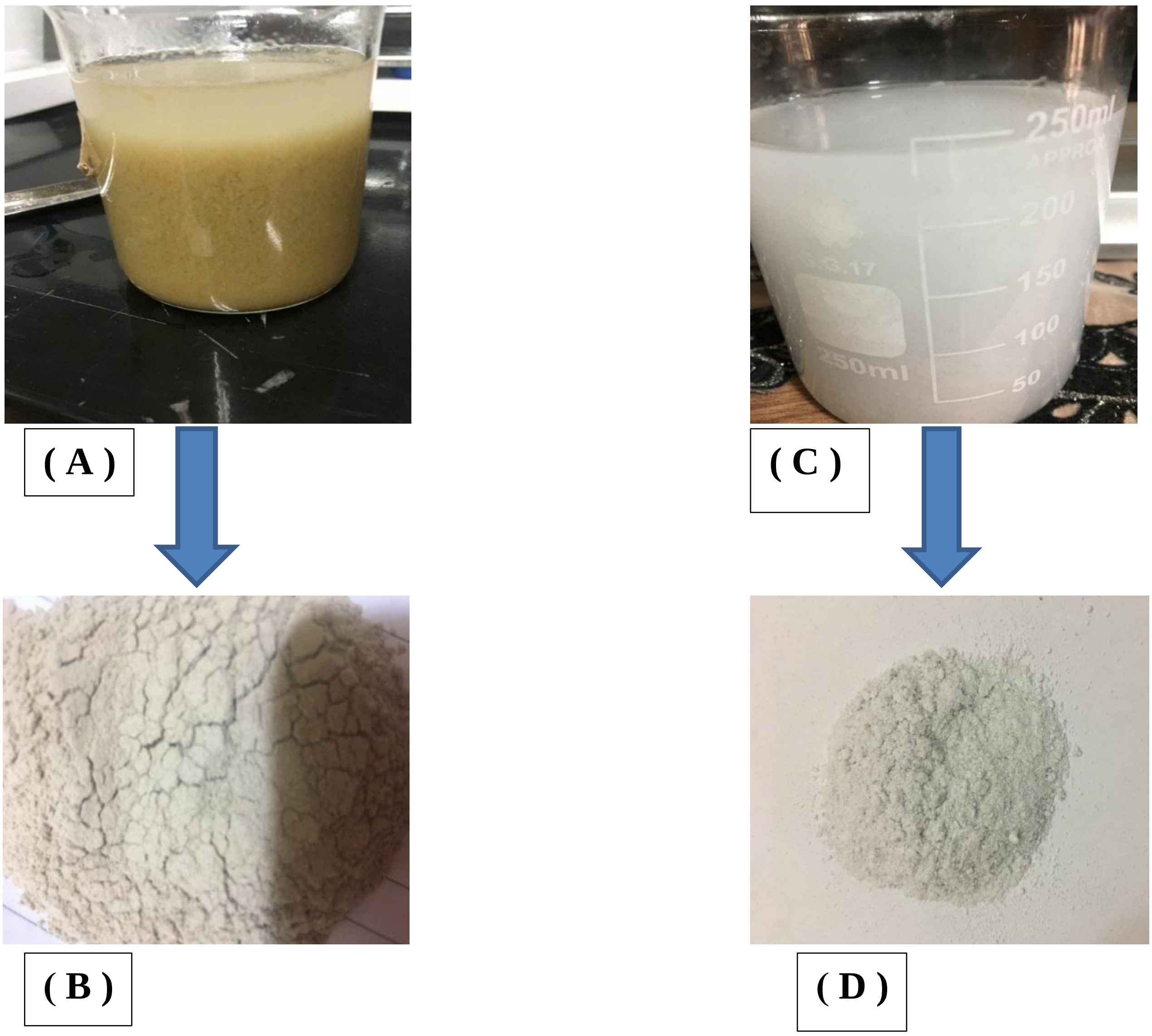


Figure (3.1): Showed NC product from rice husks and paper residues after sonicated in ultrasonic processor .

(A) and **(B)** nanocellulose (NC) produced from rice husks .

(C)and **(D)** nanocellulose (NC) produced from paper residues .

3.2.Characterization of Nanocellulose (NC)

The product of nanocellulose (NC) which prepared from agricultural and industrial wastes was identified by using Scanning electron microscope (SEM) , Atomic force microscope (AFM) , X-ray diffraction (XRD) and Fourier transform infrared spectroscope (FT-IR) :

3.2.1 .Scanning electron microscope (SEM)

Scanning electron microscope (SEM) provides important visual information concerning with the morphology of cellulose . SEM was utilized to check morphology of the nanoparticles of samples[100] . Scanning electron microscope (SEM) shows the morphology of the external side after isolation methods. SEM images show differences in size and shape of the samples . It showed the existence of regular crystalline regions , but also showed non-amorphous areas. Which may be an indication that the resulting nanoparticles are not stable due to deposition of precipitate in the nanoparticle, sulfuric acid was used to dissolve and decomposed the non-crystallized regions [101,102] .

In figure (3.2) ,(3.3) ,(3.4) and (3.5) shows the (SEM) images of (NC) prepared from rice husks at different concentration of sulfuric acid (15,25,35, and 45) % .While in figure (3.6) appeared the SEM image of NC product from paper residues at concentration (50) % of sulfuric acid . The average particles size of NC product from rice husks is (16.22) nm at concentration 15% ,at concentration 25% is (26.36) nm , at concentration 35% is (32.56) nm and at concentration 45% is (28.45) nm , while the average particles size of NC product from paper residues is (65.78) nm , and as was calculated by using program (Image-J) .

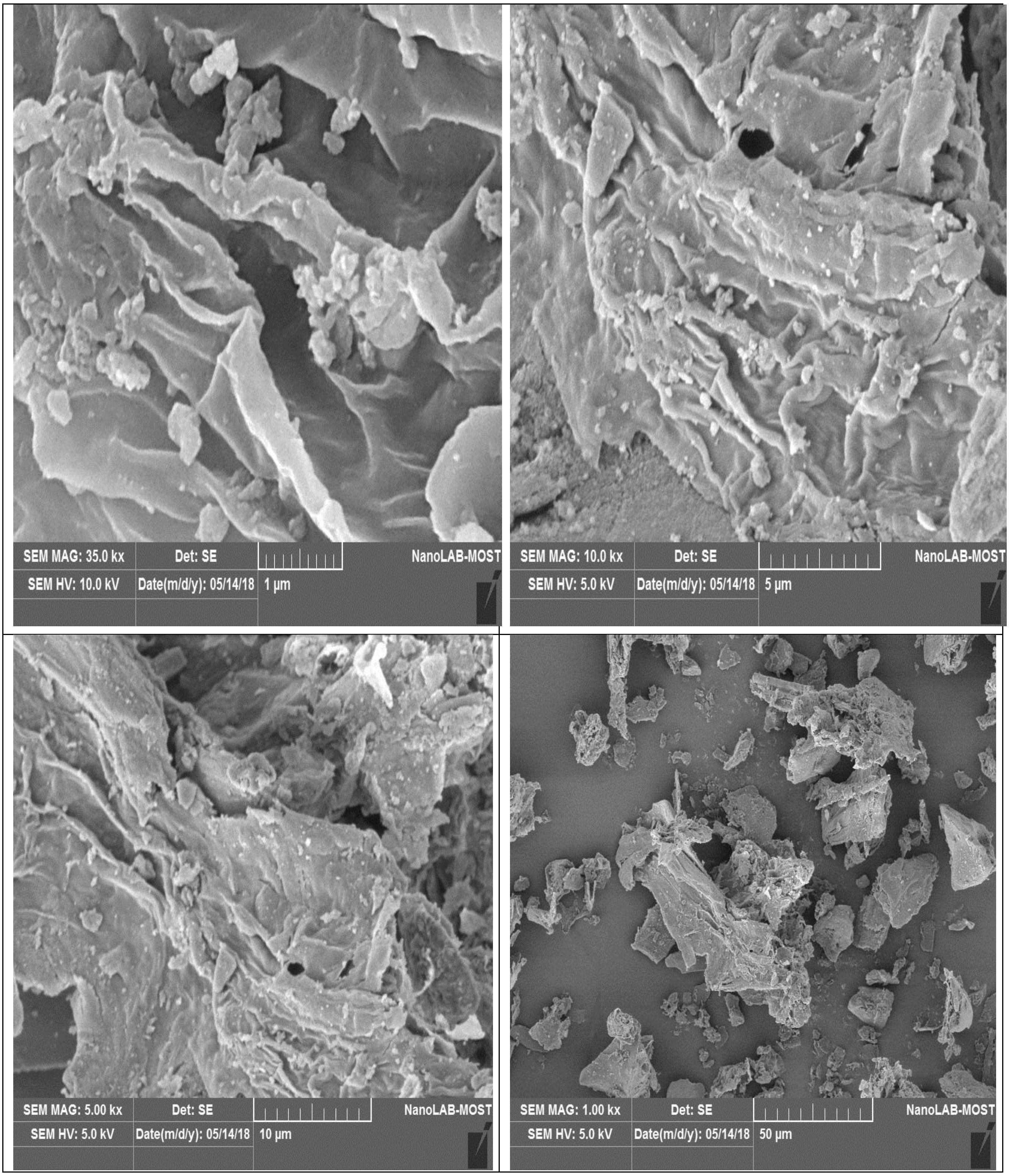


Figure (3.2): The SEM images of (NC) produced from rice husks with concentration (15%) of sulfuric acid .

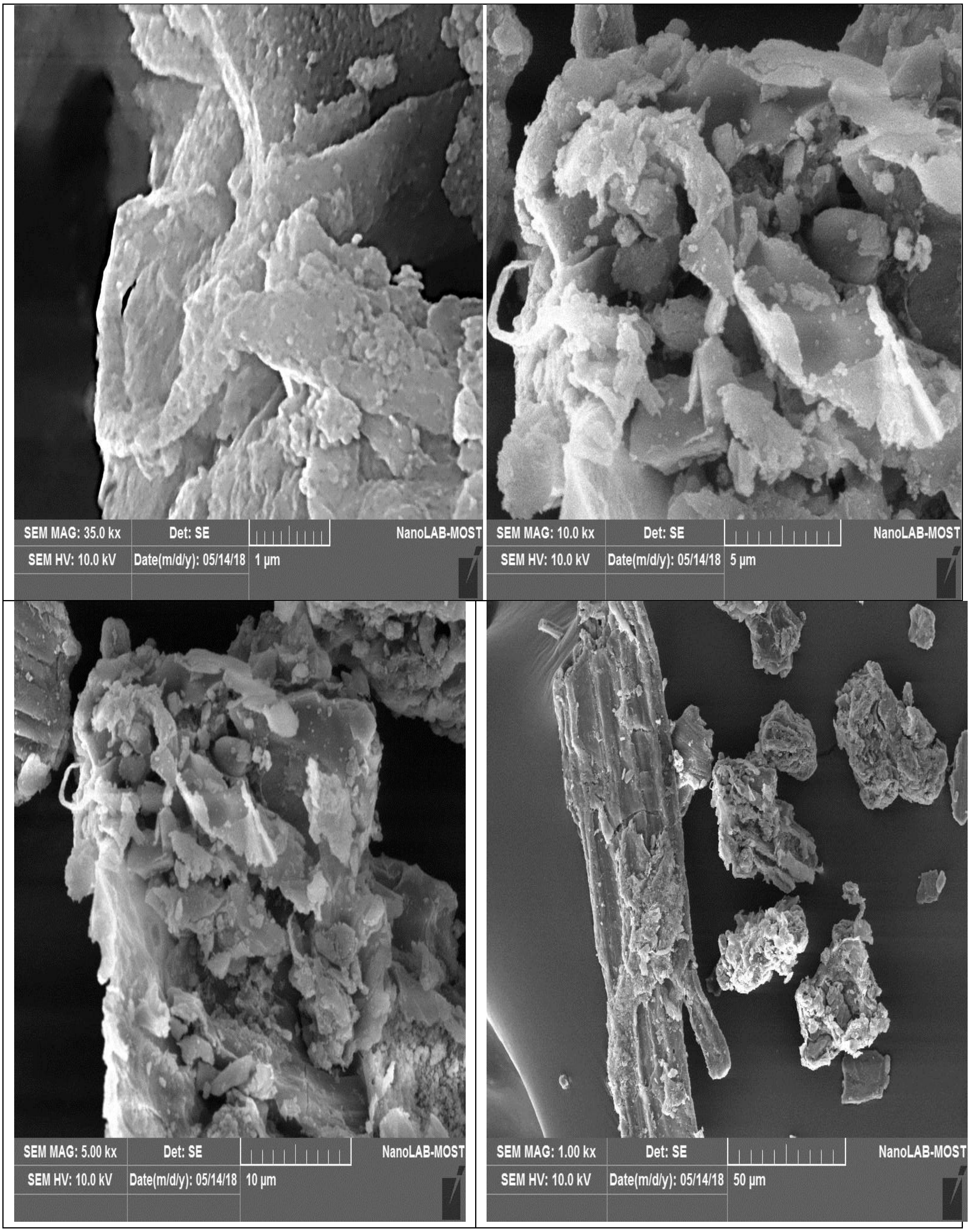


Figure (3.3): The SEM images of (NC) produced from rice husks with concentration (25%) of sulfuric acid .

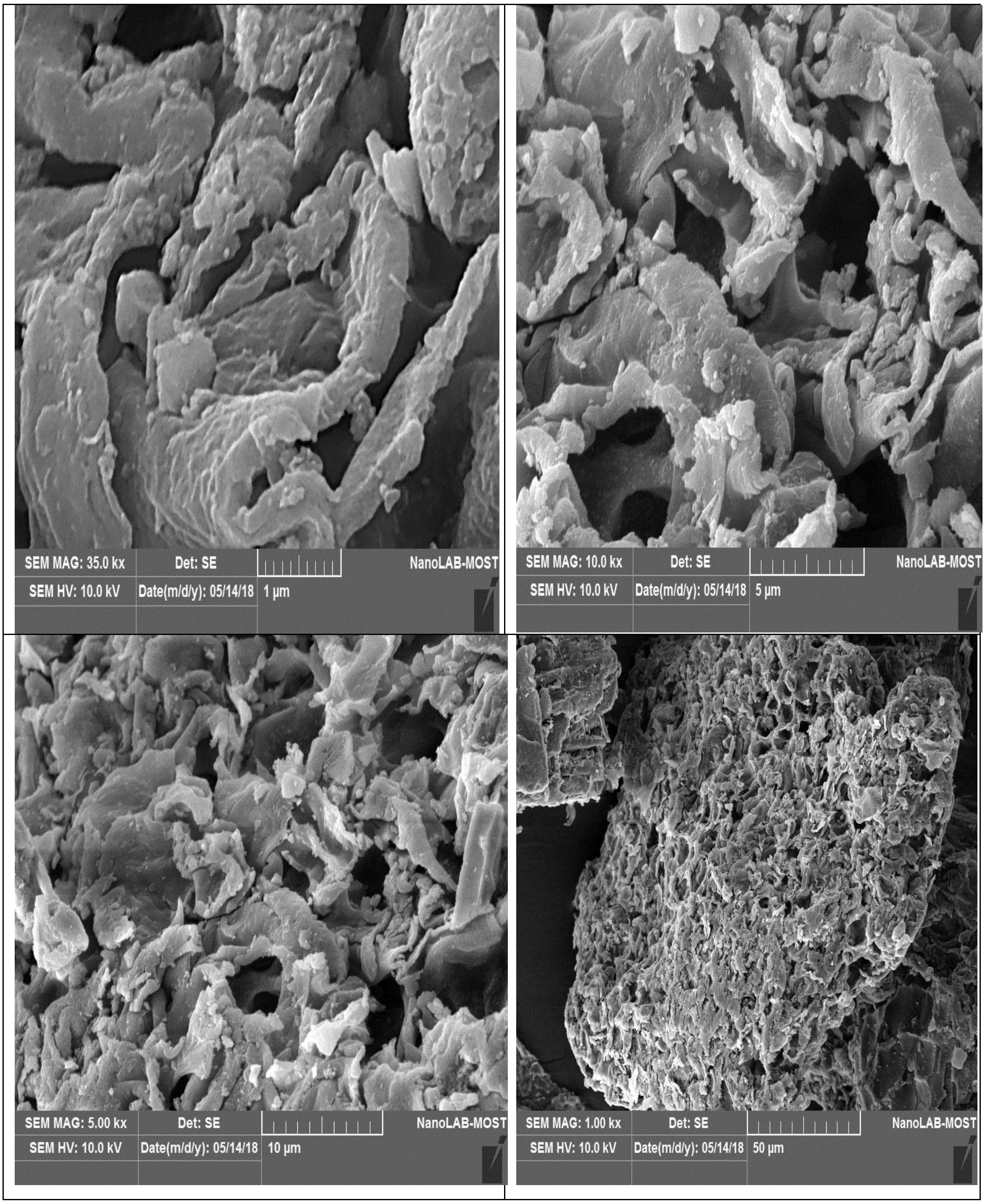


Figure (3.4) :The SEM images of (NC) produced from rice husks with concentration (35%) of sulfuric acid .

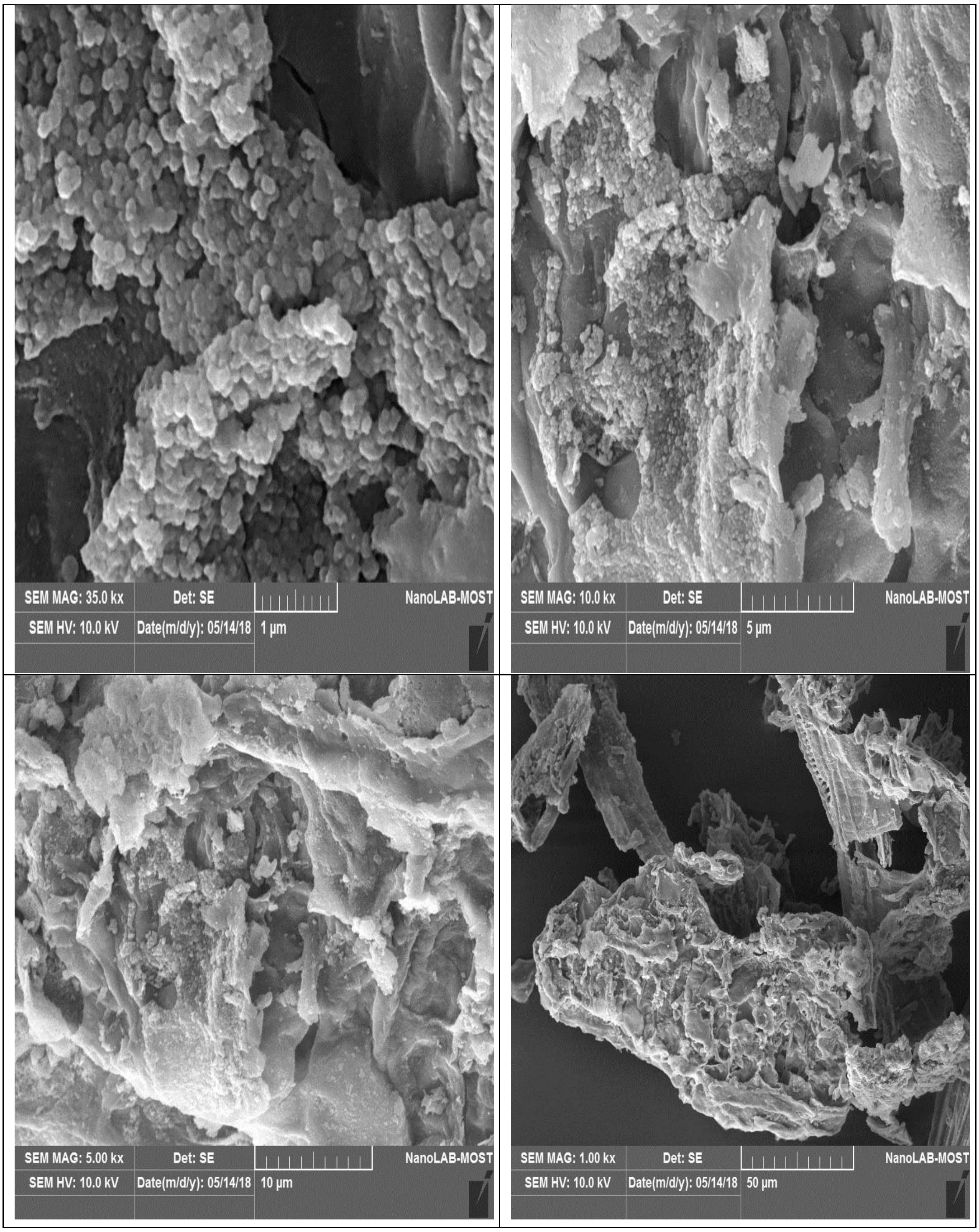


Figure (3.5): The SEM images of (NC) produced from rice husks with concentration (45%) of sulfuric acid .

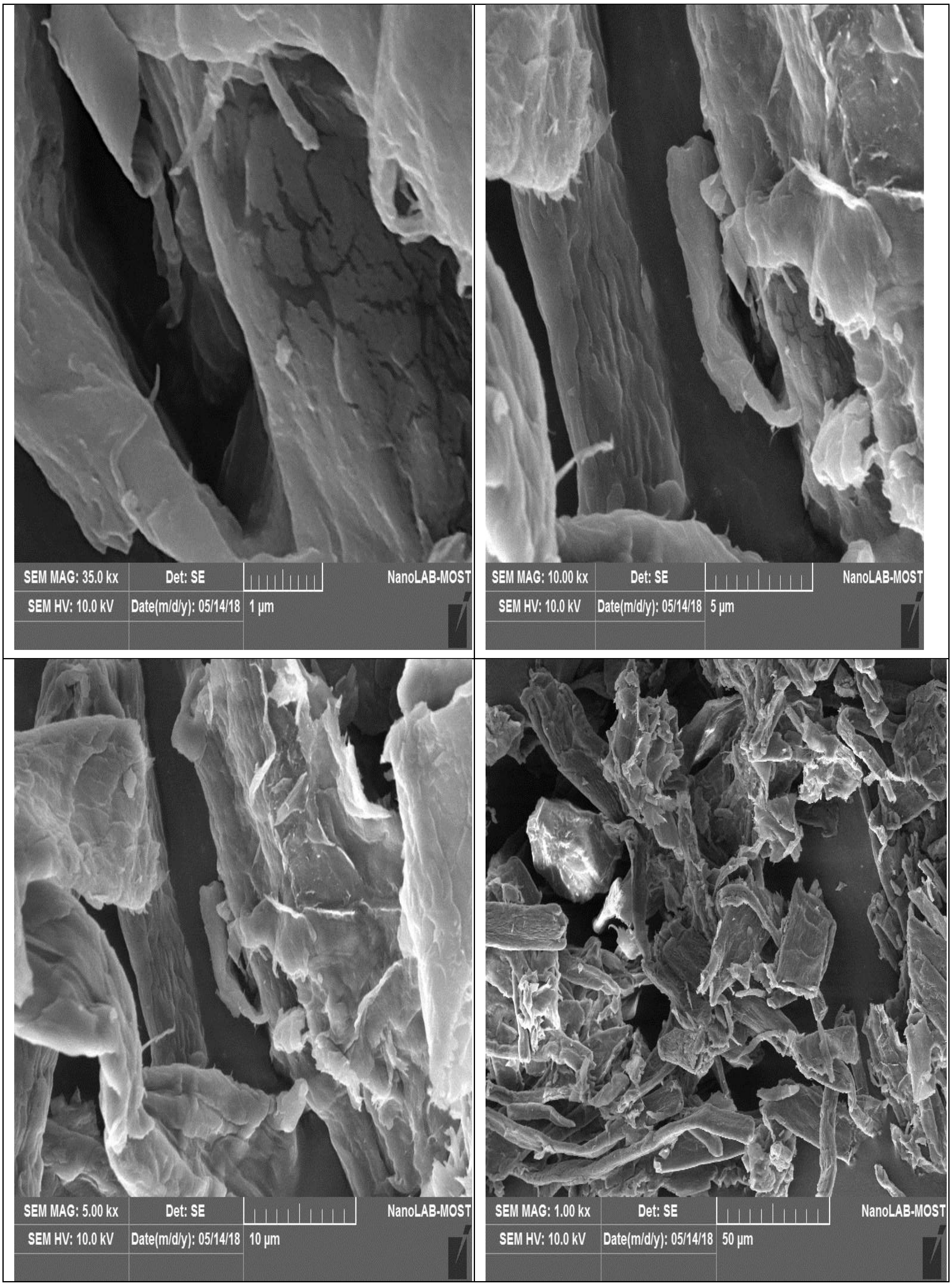


Figure (3.6): The SEM images of (NC) produced from paper residues with concentration (50%) of sulfuric acid .

3.2.2 .Atomic force microscope (AFM)

Atomic force microscope (AFM) was used to know morphological characteristics , particle size diameter determination , and the average granule size of nanocellulose NC [103].

In figure (3.7),(3.8),(3.9) and (3.10) appeared typical AFM images are in two-dimensional and three-dimensional of nanocellulose prepared from rice husks at different concentration (15,25,35, and 45) % of sulfuric acid . While in figure (3.15) appeared the AFM in two-dimensional and three-dimensional images respectively of nanocellulose prepare from paper residues with concentration 50% of sulfuric acid.

Figure (3.7) explains images of AFM for NC of husks at concentration 15% of sulfuric acid with (size = 2020 nm,2074 nm , and ability analytical (pixel = 444,456) , it is found that average roughness is (1.63) nm , and average diameter of NC is (30.66)nm.

In figure (3.8) expounds images of AFM for NC of husks at concentration 25% of sulfuric acid with (size = 2072 nm,2054 nm , and ability analytical (pixel = 448,444) , it is found that average roughness is (3.50) nm , and average diameter of NC is (36.21)nm.

In figure (3.9) explains images of AFM for NC of husks at concentration 35% of sulfuric acid with (size = 2032 nm,2032 nm , and ability analytical (pixel = 448,448) , it is found that average roughness is (2.15) nm , and average diameter of NC is (56.75)nm.

In figure (3.10) expounds images of AFM for NC of husks at concentration 45% of sulfuric acid with (size = 2047 nm,2047 nm , and ability analytical (pixel = 448,448) , it is found that average roughness is (2.45) nm , and average diameter of NC is (45.06) nm .

While in figure (3.15) explains images of AFM for NC of residues at concentration 50% of sulfuric acid with (size = 2004 nm,2045 nm , and ability analytical (pixel = 388nm,396nm) , it is found that average roughness is (2.01) nm , and average diameter of NC is (78.71)nm.

In Tables (3.1) and (3.2), (3.3) and (3.4), and figures (3.11), (3.12), (3.13) ,(3.14) show the granularity cumulating distribution and average diameter data of NC of husks at concentration (15,25,35 , and 45) % respectively of sulfuric acid. Table (3.5) and figure (3.16) show the granularity cumulating distribution and average diameter data of NC of paper residues at concentration 50% of sulfuric acid .

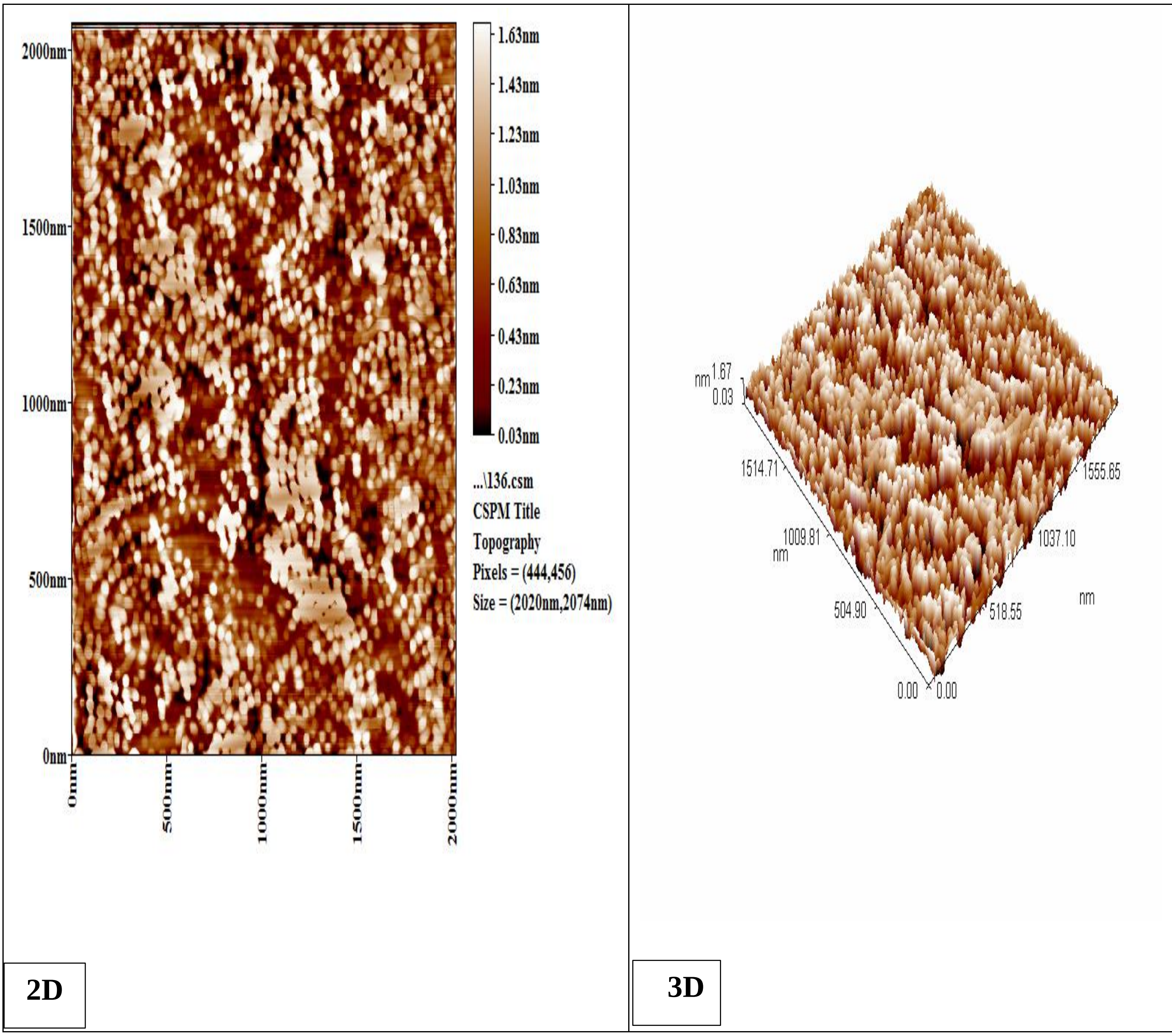
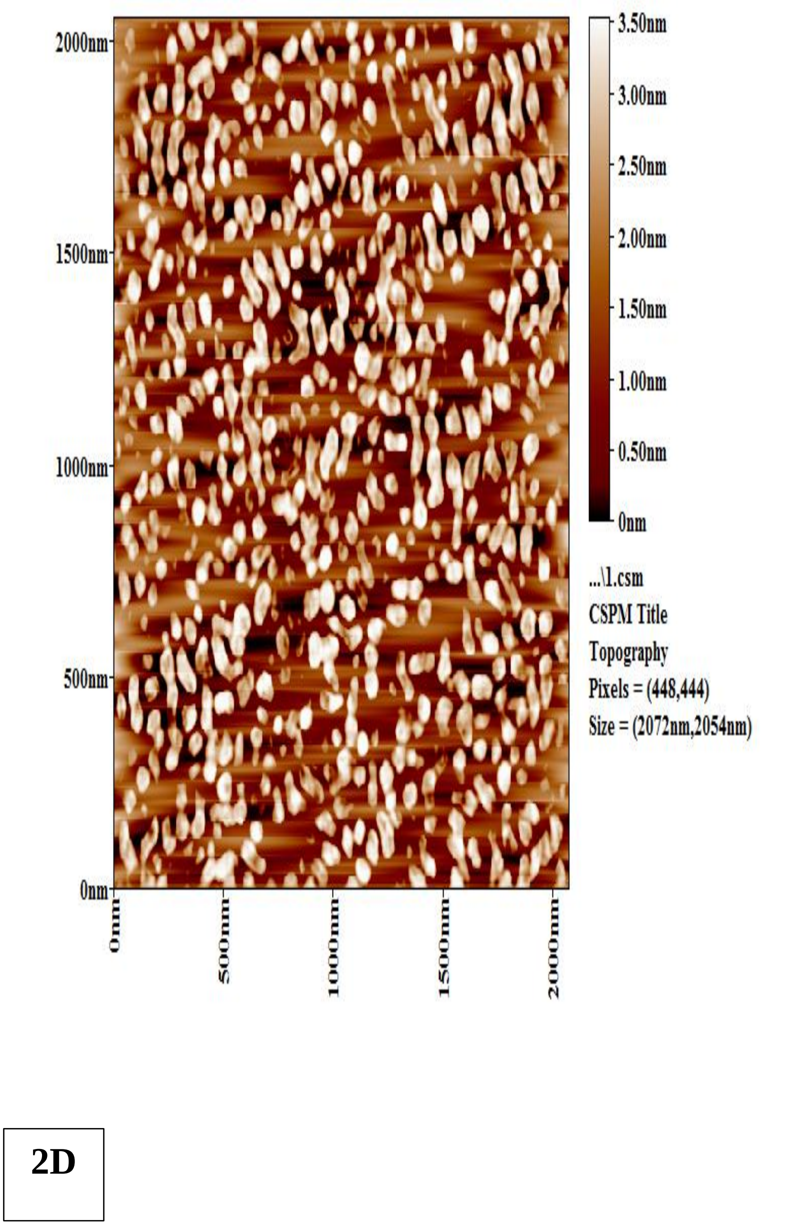


Figure (3.7): Shows AFM image of two-dimensional 2D and three-dimensional 3D of (NC) prepared from rice husks at concentration (15%) of sulfuric acid, sonicated for 180 min.



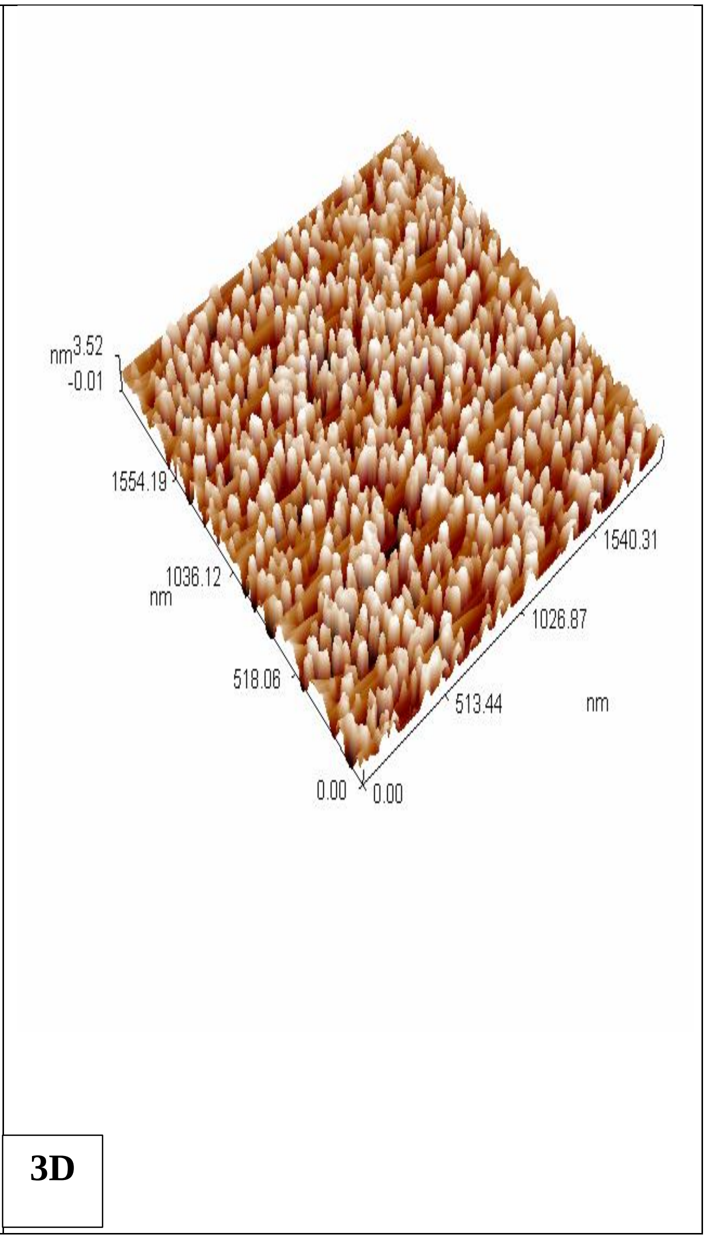


Figure (3.8): Shows AFM image of two-dimensional 2D and three-dimensional 3D of (NC) prepared from rice husks at concentration (25%) of sulfuric acid, which sonicated for 180 min.

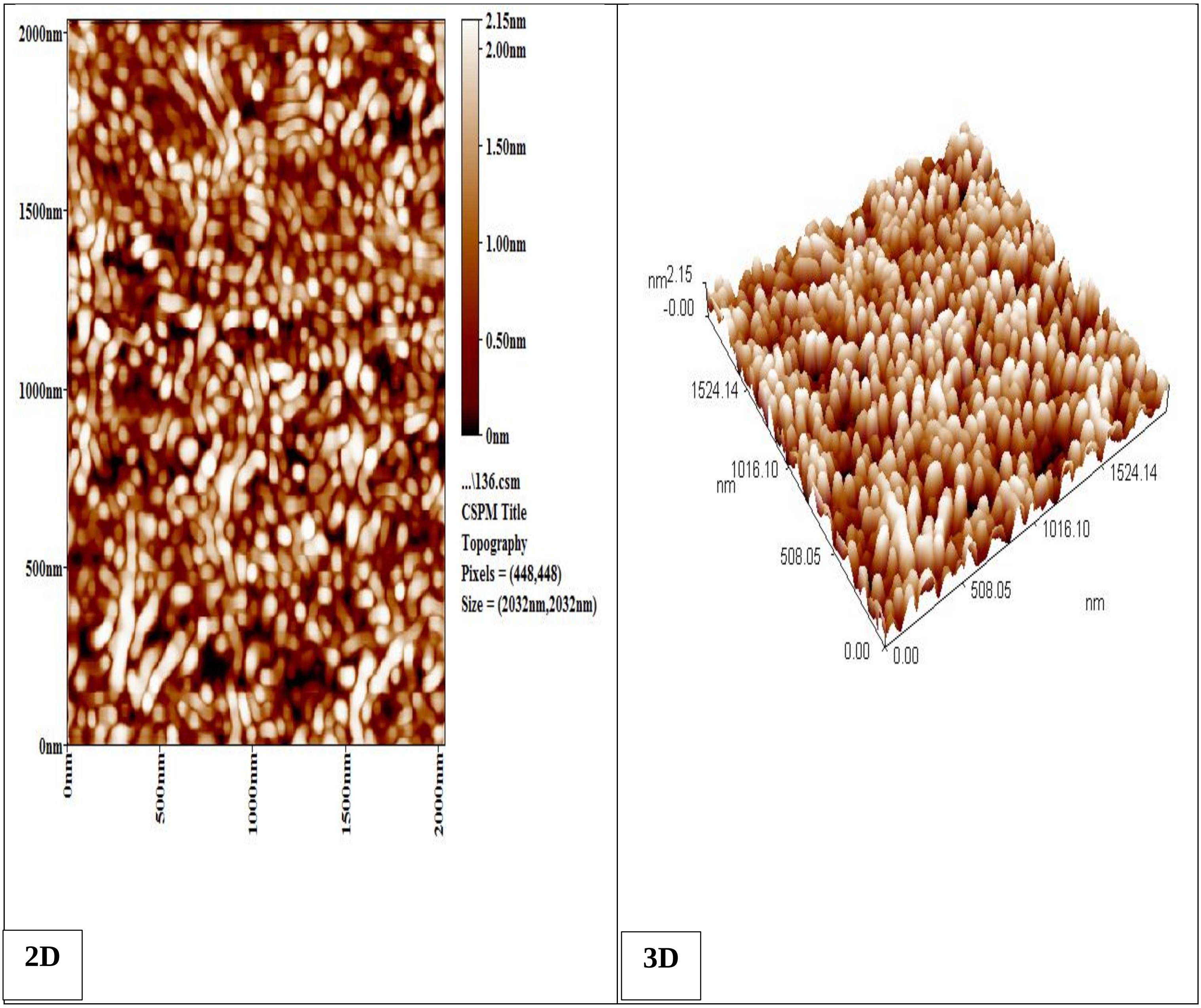
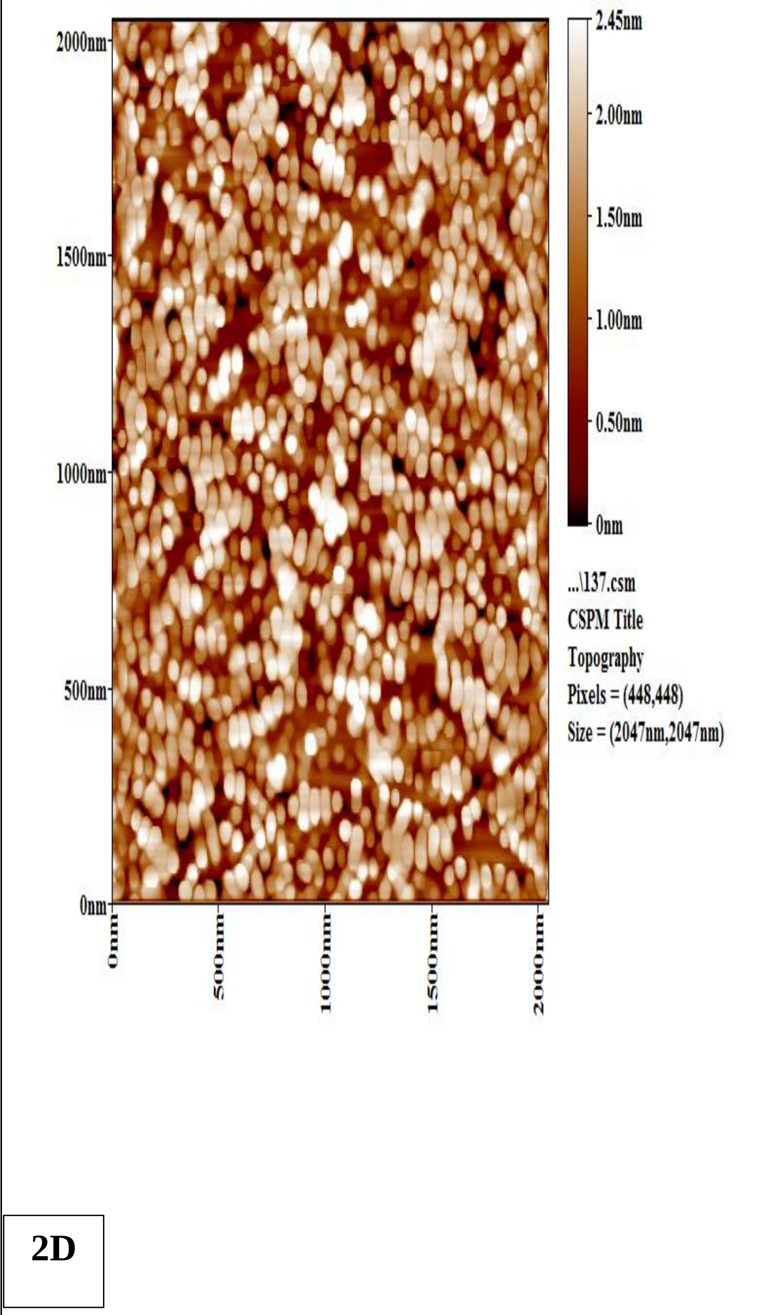


Figure (3.9): Shows AFM image of two-dimensional 2D and three-dimensional 3D of (NC) prepared from rice husks at concentration (35%) of sulfuric acid, which sonicated for 180 min.



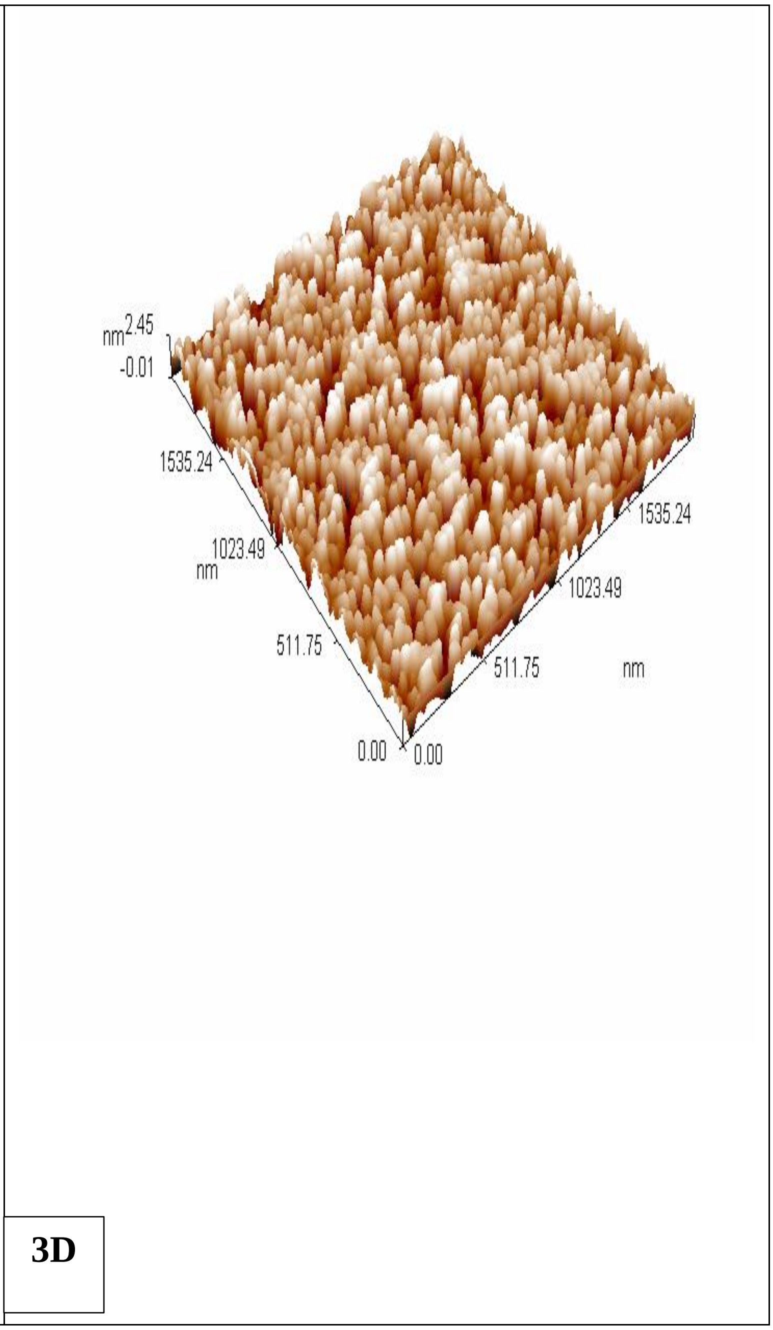


Figure (3.10): Shows AFM image of two-dimensional 2D and three-dimensional 3D of (NC) prepared from rice husks at concentration (45%) of sulfuric acid, sonicated for180 min .

Table (3.1): Granularity cumulating distribution and average diameter of NC prepared from rice husks at concentration (15%) of sulfuric acid, sonicated for180 min .

Avg. Diameter:30.66 nm								
Diameter (nm)<	Volume(%)	Cumulation(%)	Diameter (nm)<	Volume(%)	Cumulation(%)	Diameter (nm)<	Volume(%)	Cumulation(%)
20.00	2.12	2.12	28.00	8.62	31.43	36.00	12.20	78.38
22.00	5.17	7.29	30.00	14.32	45.76	38.00	10.61	88.99
24.00	8.22	15.52	32.00	9.81	55.57	40.00	11.01	100.00
26.00	7.29	22.81	34.00	10.61	66.18			

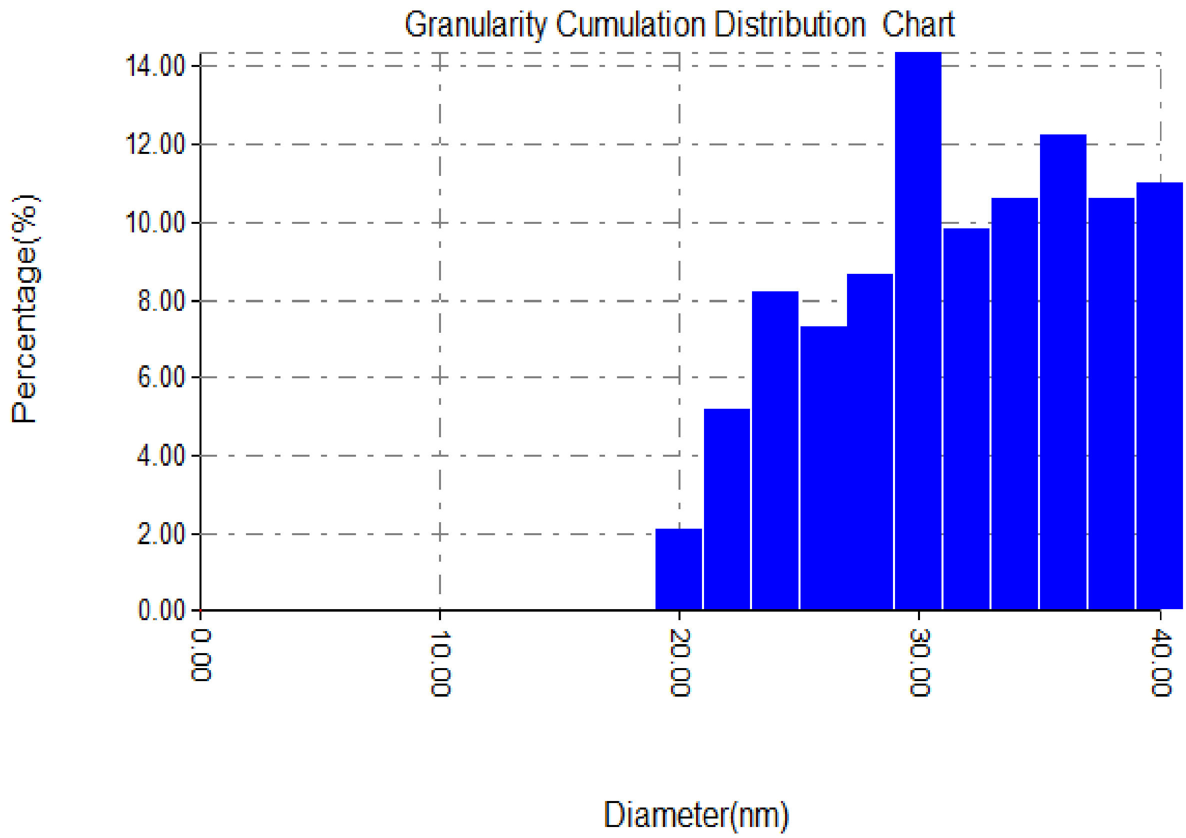


Figure (3.11): Granularity cumulating distribution of NC prepared from rice husks at concentration (15%) of sulfuric acid, sonicated for180 min.

Table (3.2) : Granularity cumulating distribution and average diameter of NC prepared from rice husks at concentration (25%) of sulfuric acid, sonicated for180 min.

Avg. Diameter:36.21 nm								
Diameter (nm)<	Volume(%)	Cumulation(%)	Diameter (nm)<	Volume(%)	Cumulation(%)	Diameter (nm)<	Volume(%)	Cumulation(%)
26.00	4.62	4.62	36.00	8.03	50.60	46.00	6.50	89.23
28.00	8.72	13.33	38.00	10.94	61.54	48.00	5.30	94.53
30.00	13.16	26.50	40.00	6.67	68.21	50.00	3.76	98.29
32.00	7.18	33.68	42.00	6.32	74.53	52.00	1.71	100.00
34.00	8.89	42.56	44.00	8.21	82.74			

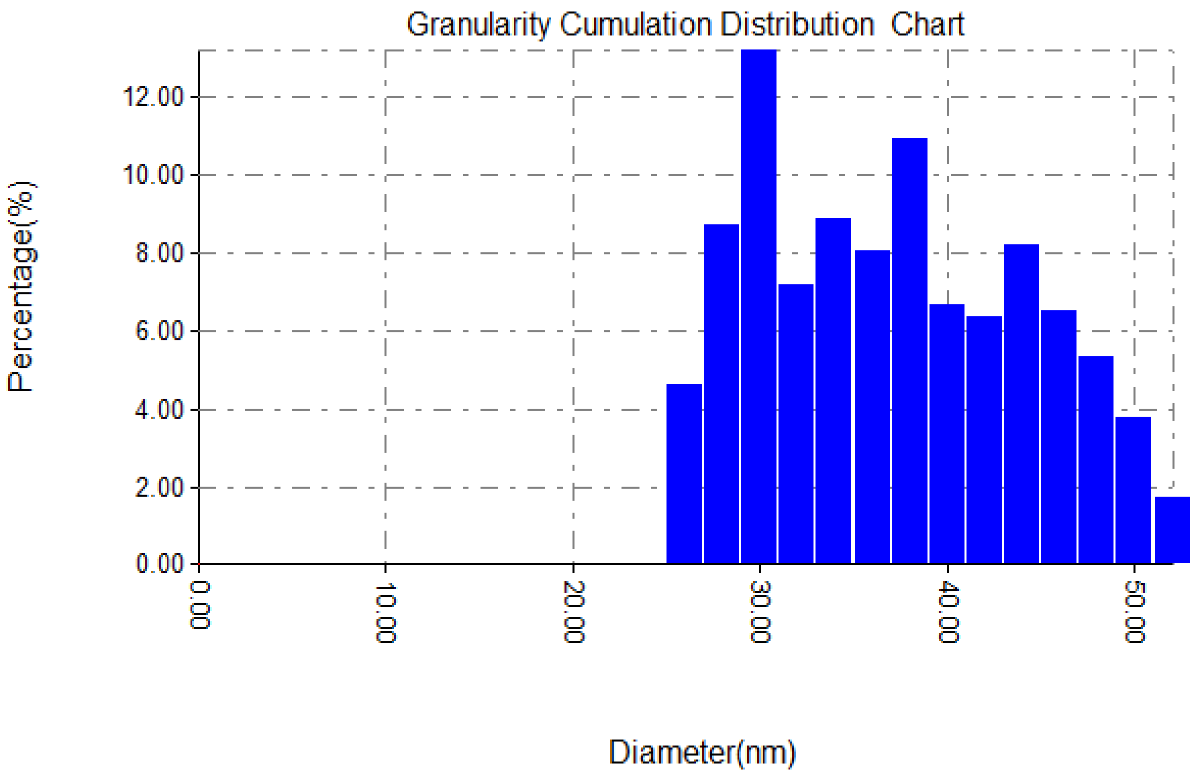


Figure (3.12): Granularity cumulating distribution of NC prepared from rice husks at concentration (25%) of sulfuric acid, sonicated for180 min .

Table (3.3) : Granularity cumulating distribution and average diameter of NC prepared from rice husks at concentration (35%) of sulfuric acid, sonicated for180 min .

Avg. Diameter:56.75 nm								
Diameter (nm)<	Volume(%)	Cumulation(%)	Diameter (nm)<	Volume(%)	Cumulation(%)	Diameter (nm)<	Volume(%)	Cumulation(%)
35.00	3.01	3.01	55.00	14.25	42.19	75.00	11.51	98.08
40.00	6.58	9.59	60.00	15.89	58.08	80.00	1.92	100.00
45.00	8.22	17.81	65.00	15.07	73.15			
50.00	10.14	27.95	70.00	13.42	86.58			

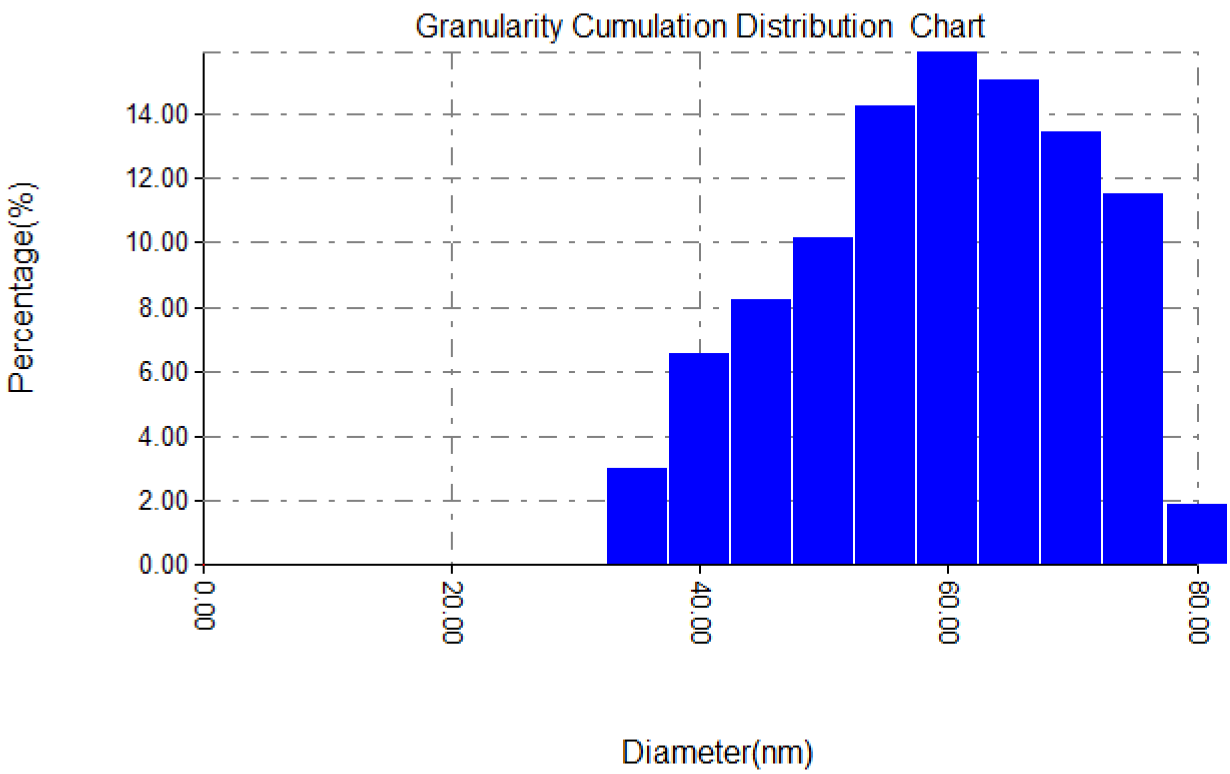


Figure (3.13): Granularity cumulating distribution of NC prepared from rice husks at concentration (35%) of sulfuric acid, sonicated for180 min .

Table (3.4): Granularity cumulating distribution and average diameter of NC prepared from rice husks at concentration (45%) of sulfuric acid, sonicated for180 min .

Avg. Diameter:45.06 nm								
Diameter (nm)<	Volume(%)	Cumulation(%)	Diameter (nm)<	Volume(%)	Cumulation(%)	Diameter (nm)<	Volume(%)	Cumulation(%)
28.00	2.23	2.23	42.00	6.69	40.29	56.00	4.62	82.48
30.00	3.18	5.41	44.00	7.96	48.25	58.00	4.62	87.10
32.00	4.14	9.55	46.00	6.53	54.78	60.00	5.41	92.52
34.00	5.89	15.45	48.00	6.37	61.15	62.00	3.34	95.86
36.00	5.89	21.34	50.00	6.69	67.83	64.00	2.87	98.73
38.00	6.53	27.87	52.00	5.57	73.41	66.00	1.27	100.00
40.00	5.73	33.60	54.00	4.46	77.87			

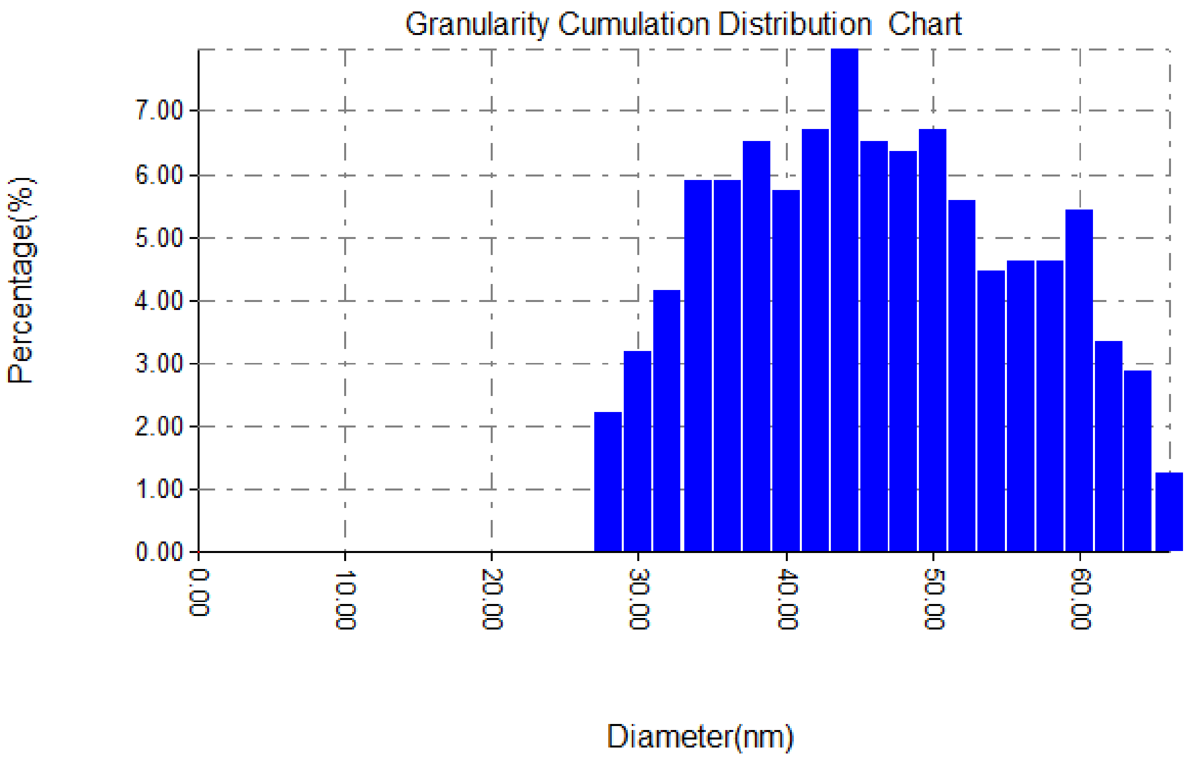


Figure (3.14): Granularity cumulating distribution of NC prepared from rice husks at concentration (45%) of sulfuric acid, sonicated for180 min .

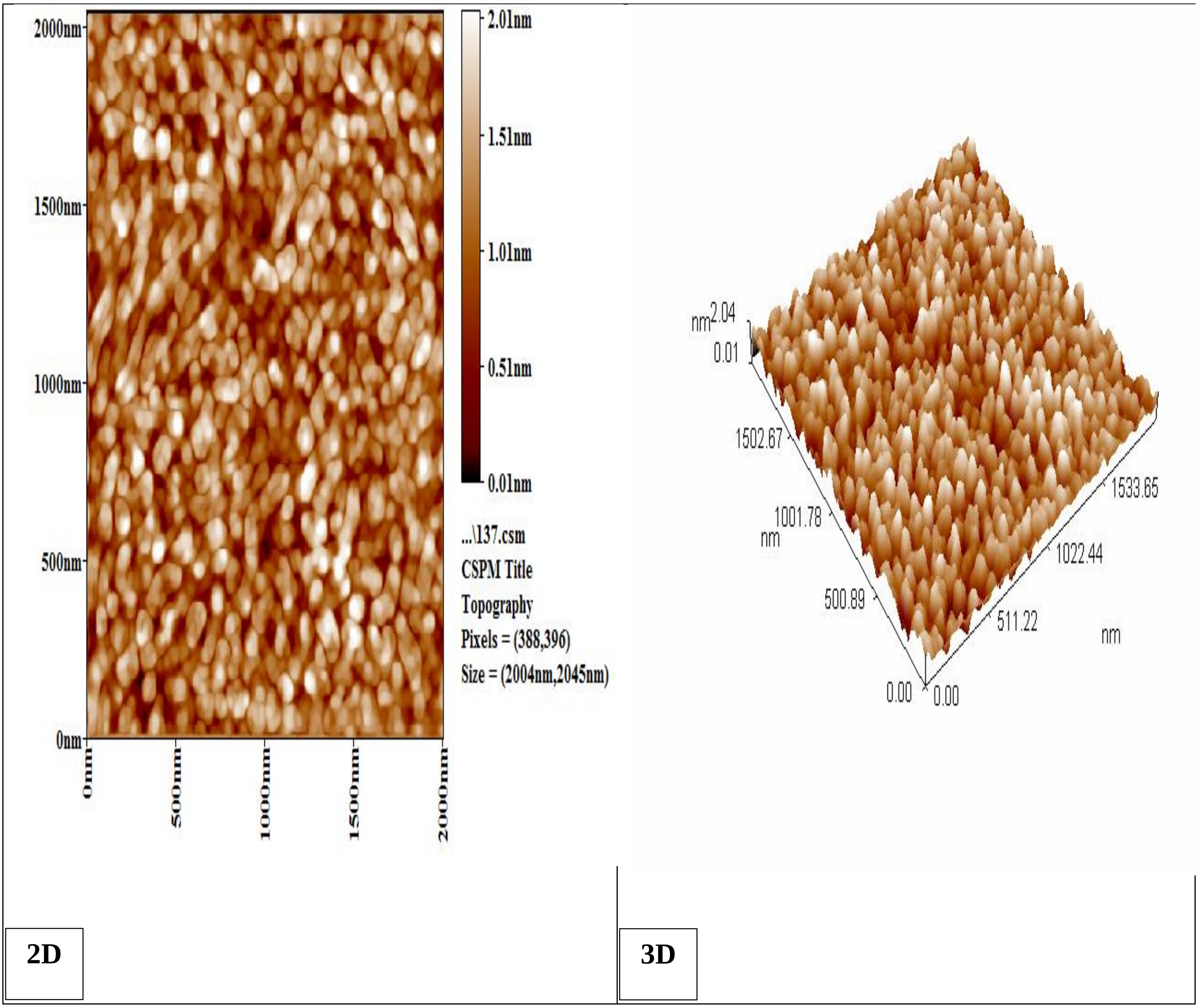


Figure (3.15): Shows AFM image of two-dimensional 2D and three-dimensional 3D of (NC) prepared from paper residues at concentration (50%) of sulfuric acid, which sonicated for 60min.

Table (3.5): Granularity cumulating distribution and average diameter of NC prepared from paper residues at concentration (50%) of sulfuric acid, sonicated for 60 min .

Avg. Diameter:78.71 nm								
Diameter (nm)<	Volume(%)	Cumulation(%)	Diameter (nm)<	Volume(%)	Cumulation(%)	Diameter (nm)<	Volume(%)	Cumulation(%)
65.00	12.97	12.97	85.00	13.39	74.90	105.00	4.18	96.23
70.00	14.23	27.20	90.00	6.69	81.59	110.00	0.84	97.07
75.00	17.57	44.77	95.00	5.86	87.45	115.00	2.09	99.16
80.00	16.74	61.51	100.00	4.60	92.05	130.00	0.84	100.00

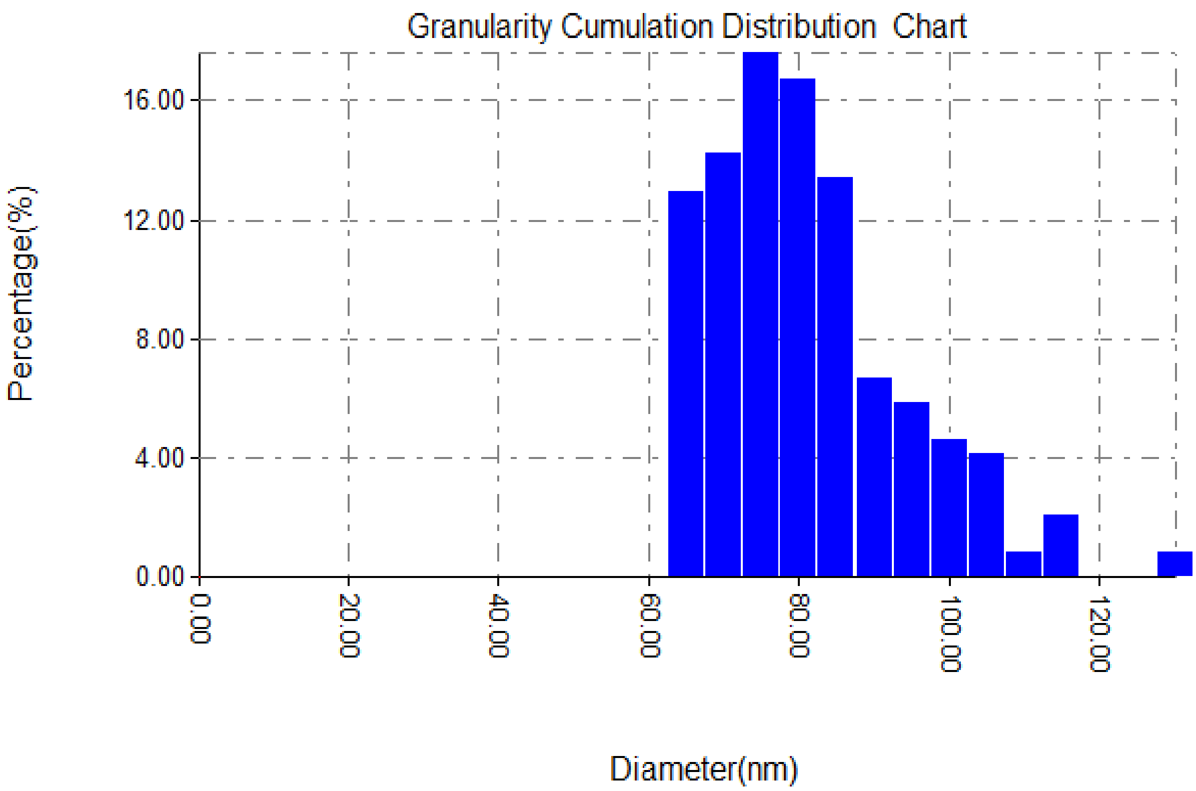


Figure (3.16): Granularity cumulating distribution of (NC) prepared from paper residues at concentration (50%) of sulfuric acid, which sonicated for 60min .

3.2 .3. X-ray diffraction (XRD)

X-ray diffraction (XRD) technique was used for determine and confirm the crystal structure of the nanoparticles . X-ray diffraction pattern of prepared nanocellulose from rice husks by using acid hydrolysis at concentration (15,25,35, and 45) % of sulfuric acid and paper residues with concentration (50%) by using ultrasonic device are shown in figures (3.17),(3.18),(3.19),(3.20) for rice husks and (3.21*)* for paper residues, respectively, with the data of strongest three peaks are shown in tables (3.6) ,(3.7),(3.8), (3.9)and (3.10) .The diffraction peaks indicates that the crystal size is small . Therefore, nanocellulose of rice husks has a smaller nanoparticles size than nanocellulose of paper residues as observed in FWHM (the full width at half maximum) .

In Figures (3.17),(3.18),(3.19),(3.20) for NC rice husks and (3.21*)* for NC paper residues, respectively and Tables (3.6) ,(3.7),(3.8), (3.9)and (3.10). The peaks position of the samples exhibited the monoclinic structure and single phase and are agreements with those reported in JCPDS file **(NO. 50-2242)** , no other impurity peak was observed in the (XRD) patterns. The broading of the diffraction peaks indicates that the crystal size is small .

The particle sizes were calculated from Deby-Sherrer equation [104] **:**

$$\mathbf{D} = \frac{\mathbf{0.9\lambda}}{\boldsymbol{\beta}\ \mathbf{cos\theta}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{(3.1)}$$

Where:

D : Refers to the crystallite size .

λ: The wavelength of radiation.

θ: Is the Bragg's angle.

β: Refers to the full width at half maximum (FWHM) .

crystallite size that has been estimated of the first strongest peaks for NC prepare from rice husks at concentration (15,25,35,45)% is (2.6298) , (4.31527) , (3.2165) , (2.7754) nm respectively and for NC prepare from paper residues is (4.8401) nm. The presence of sharp peaks in XRD samples and particle size of less than (100) nm refers to the nanocrystalline nature of the two surfaces(rice husks and paper residues) .

Table (3.6): The strongest three peaks in XRD of NC prepared from rice husks at 15% of sulfuric acid.

No.	2 θ (deg)	d (Å)	FWHM (deg)	Intensity (counts)
1	22.0373	4.03027	3.08000	59
2	23.1548	3.83823	1.48000	44
3	20.2421	4.38347	1.68000	27

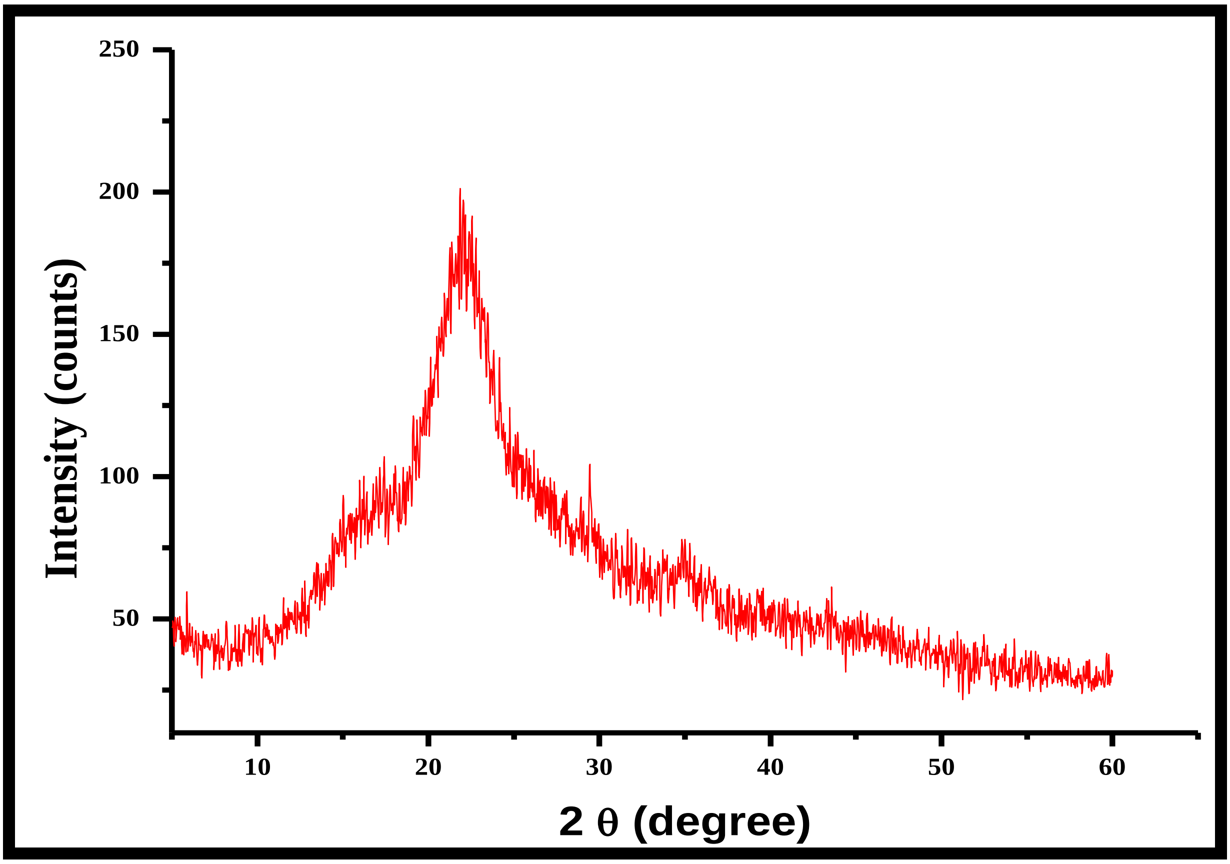


Figure (3.17) : XRD of NC prepared from rice husks at concentration 15% of sulfuric acid .

Table (3.7) : The strongest three peaks in XRD of NC prepared from rice husks at 25% of sulfuric acid .

No.	2θ (deg)	d (Å)	FWHM (deg)	Intensity (counts)
1	21.8777	4.05931	1.88000	50
2	21.2593	4.17597	1.88000	38
3	22.9353	3.87446	1.88000	38

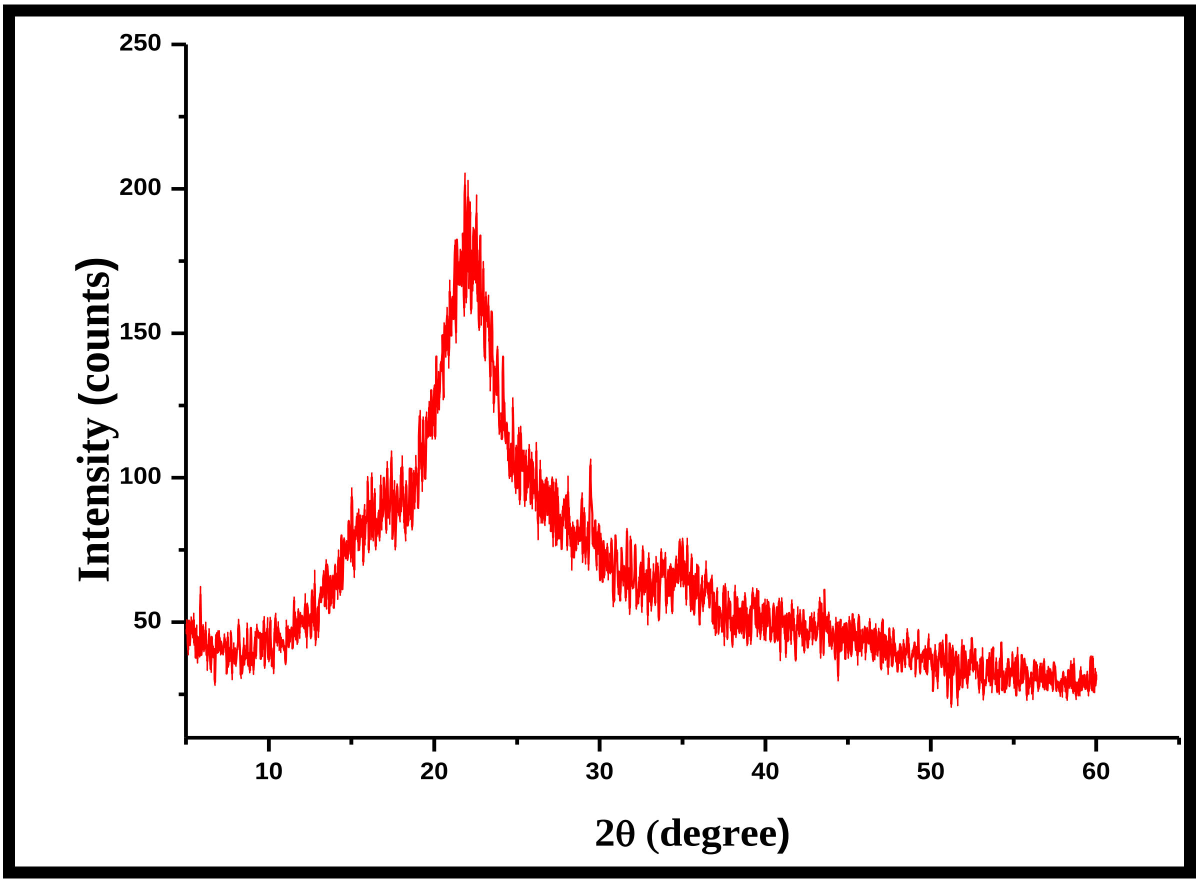


Figure (3.18): XRD of NC prepared from rice husks at concentration 25% of sulfuric acid.

Table (3.8): The strongest three peaks in XRD of NC prepared from rice husks at 35% of sulfuric acid.

No.	2 θ (deg)	d (Å)	FWHM (deg)	Intensity (counts)
1	22.4164	3.96296	2.52000	93
2	21.7381	4.08506	2.25000	84
3	20.6809	4.29144	1.60000	57

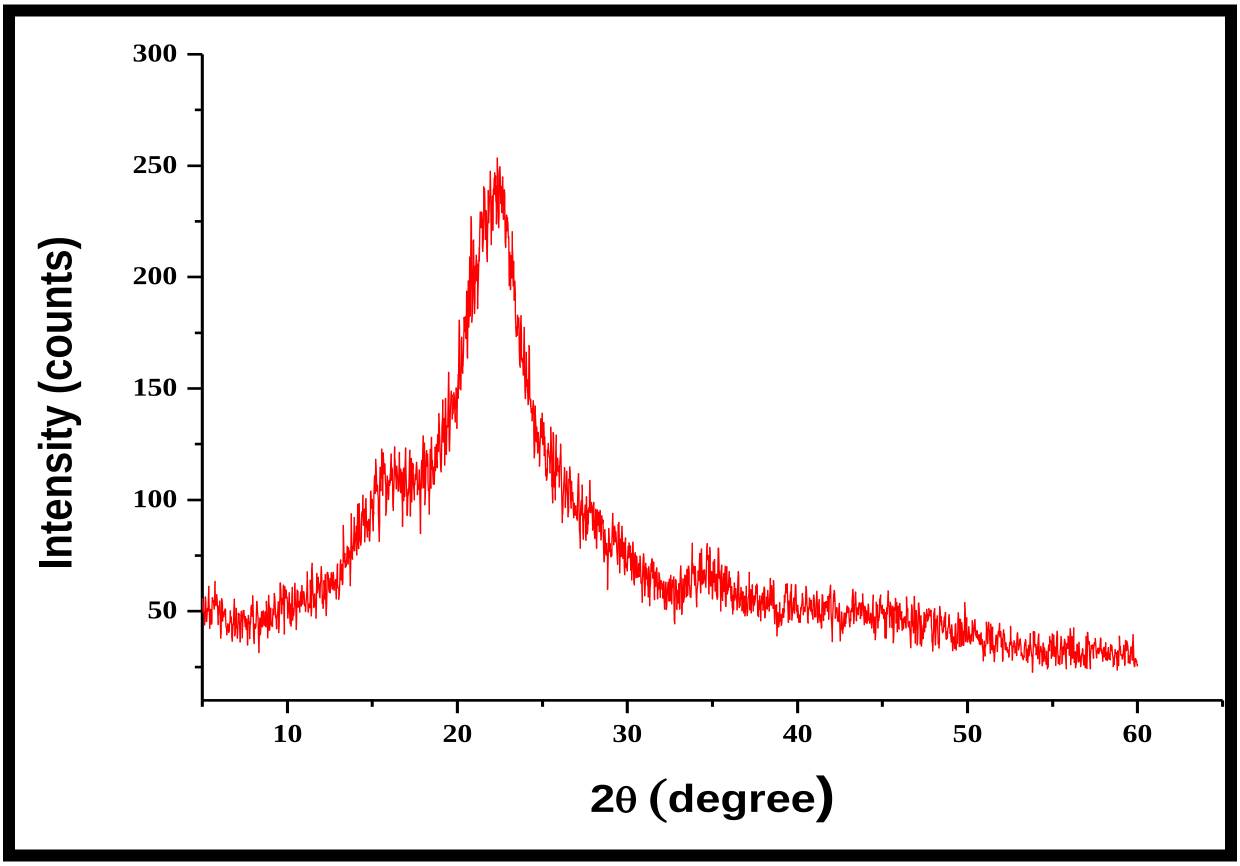


Figure (3.19): XRD of NC prepared from rice husks at concentration 35% of sulfuric acid .

Table (3. 9) : strongest three peaks in XRD of NC prepared from rice husks at 45% of sulfuric acid .

No.	2 θ (deg)	d (Å)	FWHM (deg)	Intensity (counts)
1	22.2967	3.98397	2.92000	84
2	20.5811	4.31203	0.00000	43
3	20.4415	4.34116	0.00000	42

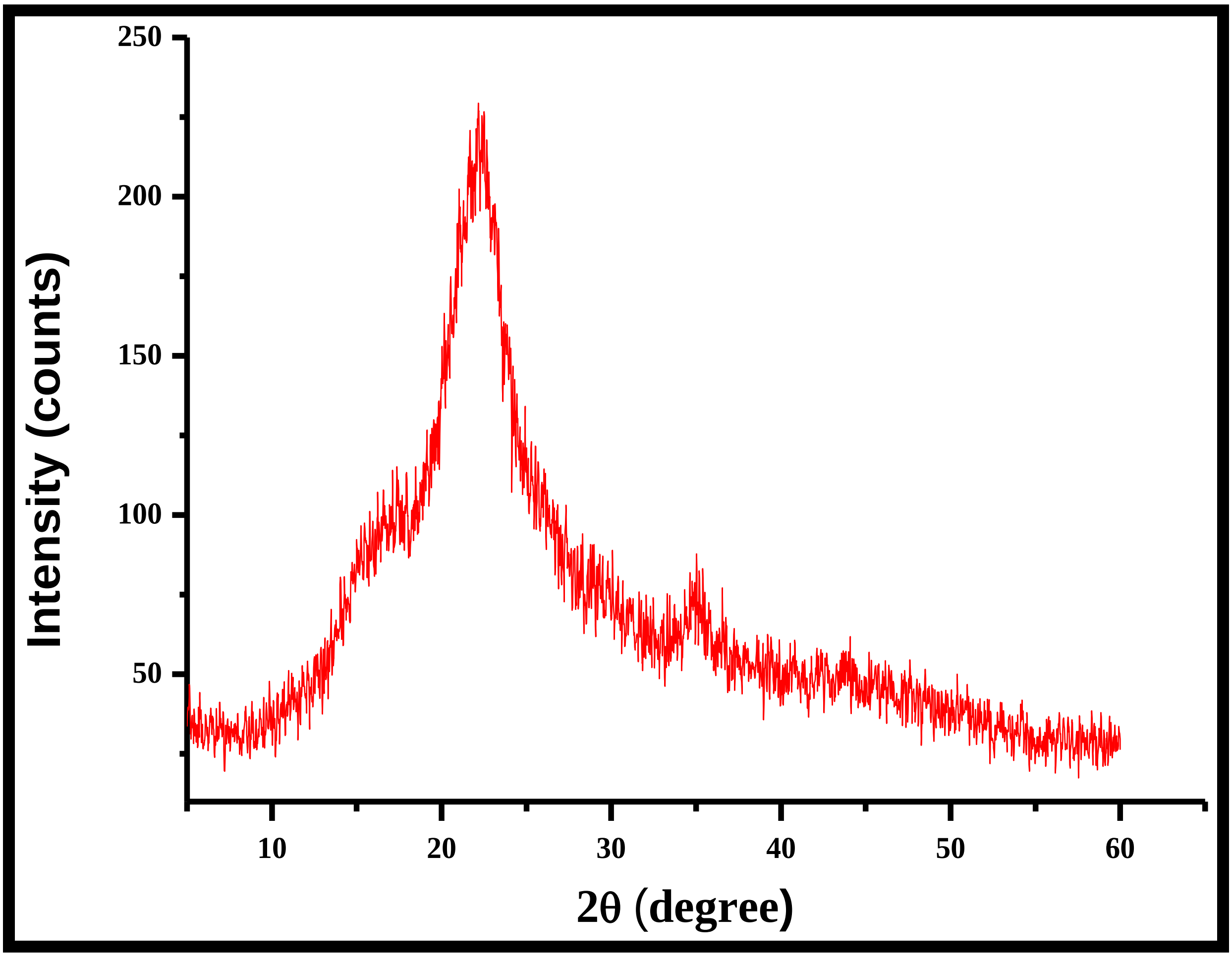


Figure (3.20): XRD of NC prepared from rice husks at concentration 45% of sulfuric acid .

Table (3.10): The strongest three peaks in XRD of NC prepared from paper residues at 50% of sulfuric acid .

No.	2 θ (deg)	d (Å)	FWHM (deg)	Intensity (counts)
1	22.4738	3.95297	1.67500	202
2	20.7606	4.27515	1.56000	50
3	16.0322	5.52379	2.08000	43

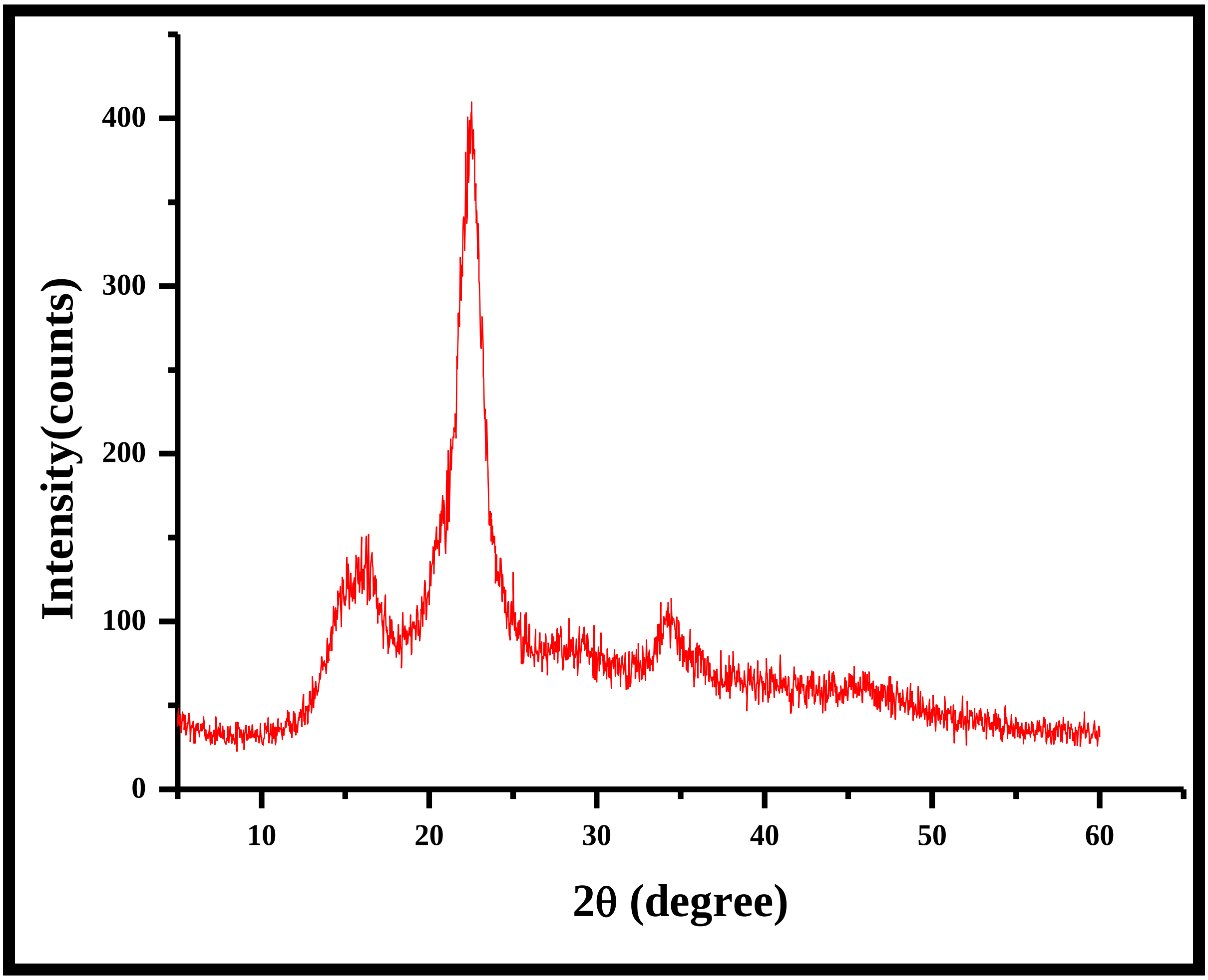


Figure (3.21) : XRD of NC prepared from paper residues at concentration 50% of sulfuric acid .

3.2.4. Fourier transform infrared spectroscop (FT-IR)

FTIR analysis was used to identify the chemical structure of the lignocellulosic components present in the samples . The spectra were recorded in the range of 400-4000 cm^{-1}. It demonstrates the changes in chemical composition of the fibers . The variations relative to the conversion from macro to nano-materials are monitored by the changes in the hydroxyl and carboxyl groups[104] . In Figures (3.22),(3.23),(3.24), and (3.25) shows FTIR spectra of NC prepared from rice husks with concentration (15,25,35,and 45) % of sulfuric acid respectively, and figure (3.26) shows FTIR spectra of NC prepared from paper residue at concentration 50% of sulfuric acid .The peaks at 3340 and 2918 cm^{-1}, present in all the samples, were due to hydroxyl group and to aliphatic saturated (C-H) stretching vibrations of cellulose, respectively. The peak at 1640 cm^{-1} associated with the (O-H) bending vibration[104,105]. It was observed smoothed peaks in the region between 1100 and 1500 cm^{-1}, where it is not possible to attributed signatures for particular vibrations, since, in this region, complex overlap effects may occur. These small peaks could be also from hemicelluloses and proteins which are present in the cellulose fiber walls[106]. The spectra of all samples are typical of cellulose. Presenting peaks at 1060 and 896 cm^{-1} which indicates, according the literature, the purity of the crystalline band of cellulose, with characteristics of C-O stretching vibration and elongation of cellulose typical pulp β-glycoside bonds, respectively, especially in nanocellulose spectra [107] .

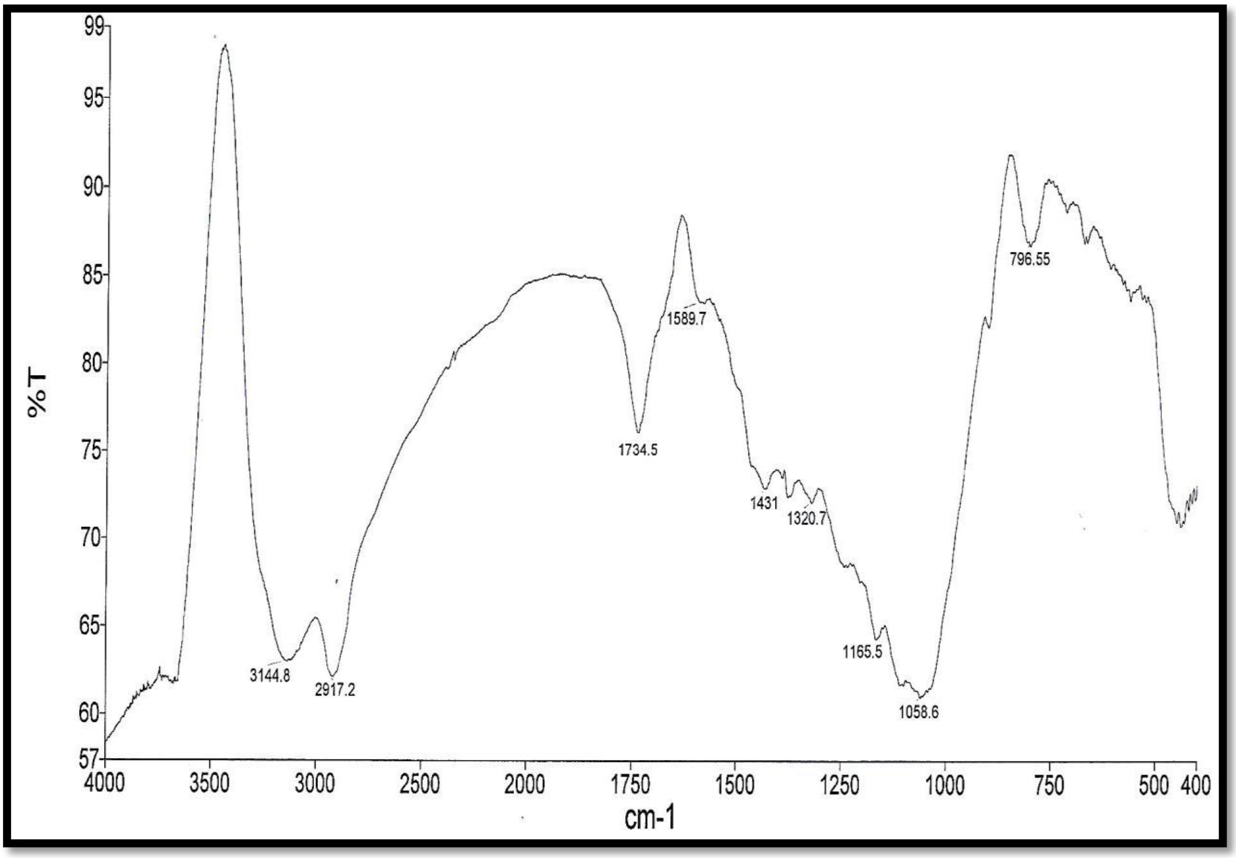


Figure (3.22) : FT-IR spectrum of Nanocellulose produced from rice husks at concentration(15%) of sulfuric acid .

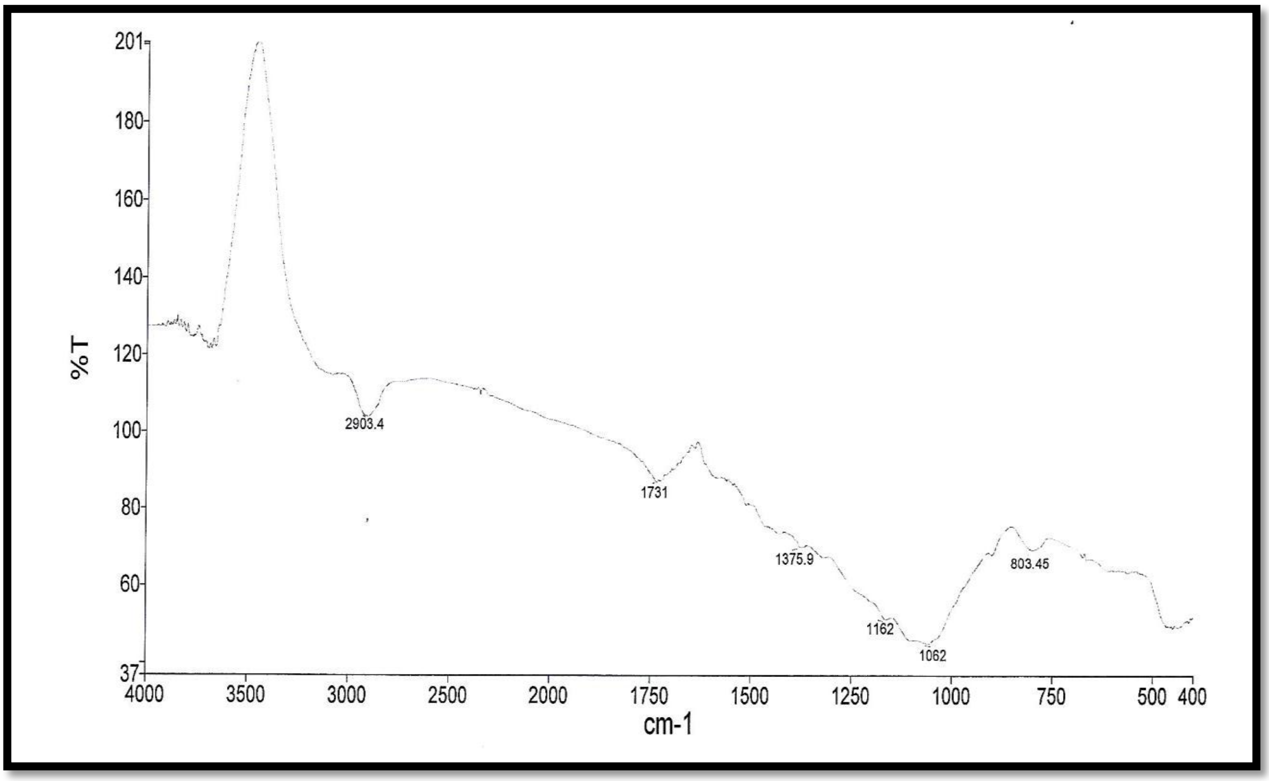


Figure (3.23): FT-IR spectrum of Nanocellulose produced from rice husks at concentration(25%) of sulfuric acid.

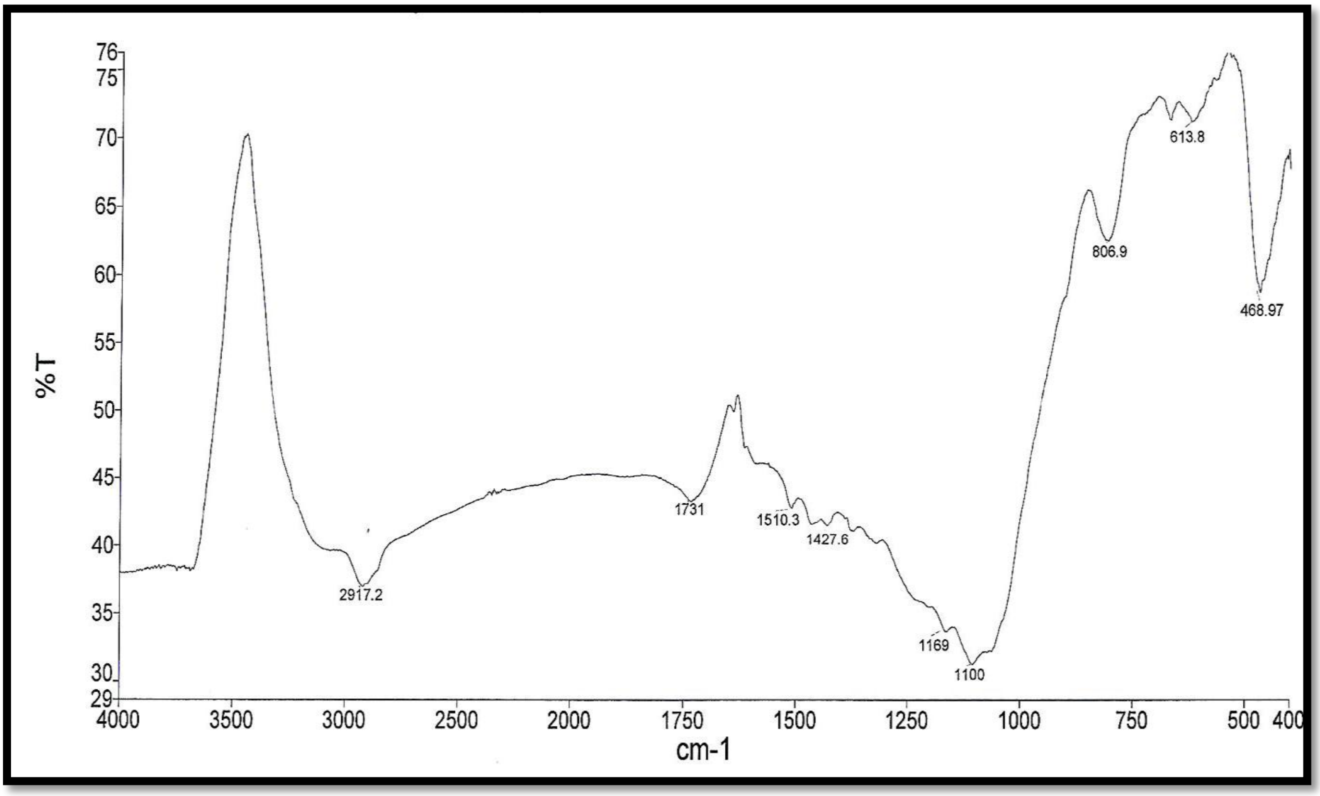


Figure (3.24) : FT-IR spectrum of Nanocellulose produced from rice husks at concentration(35%) of sulfuric acid .

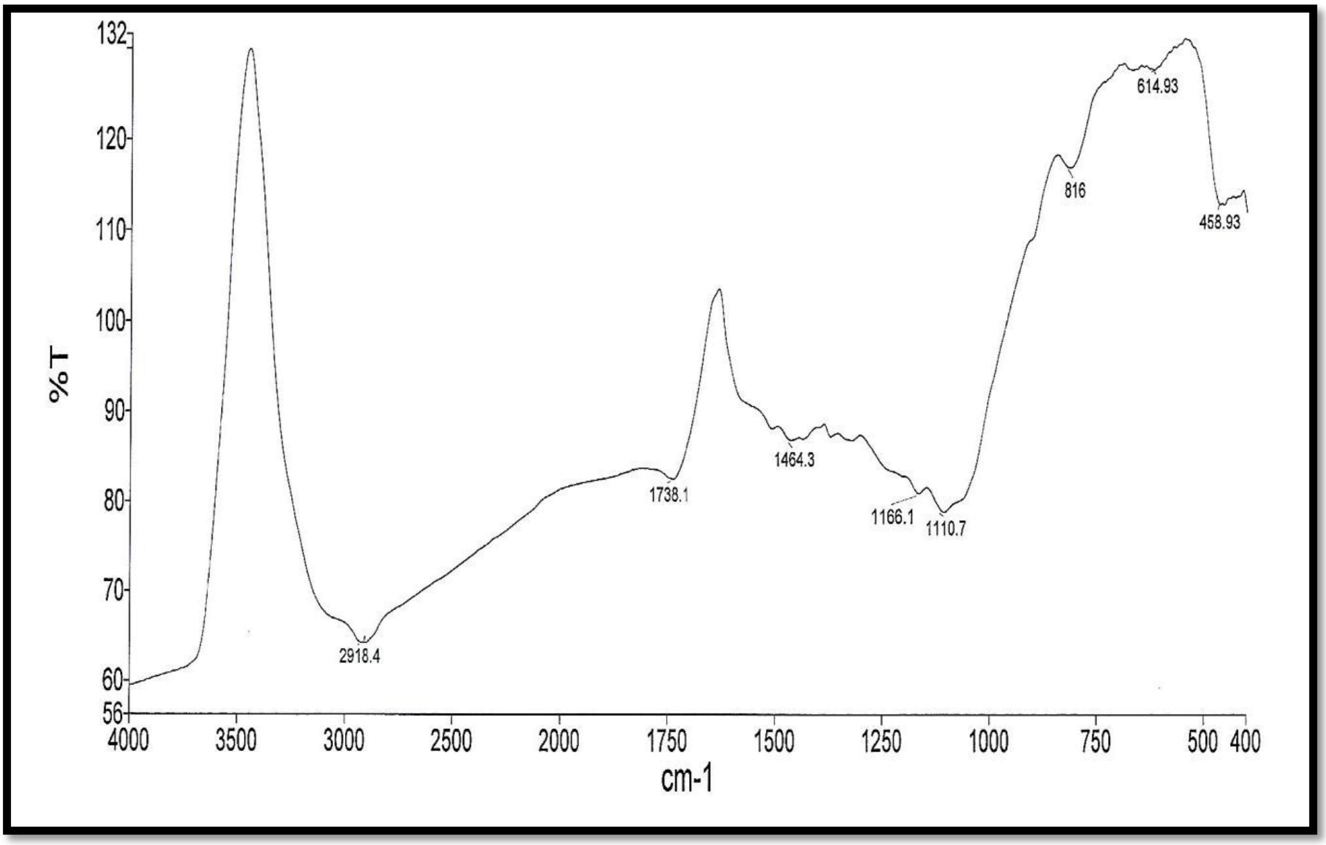


Figure (3.25) : FT-IR spectrum of Nanocellulose produced from rice husks at concentration(45%) of sulfuric acid .

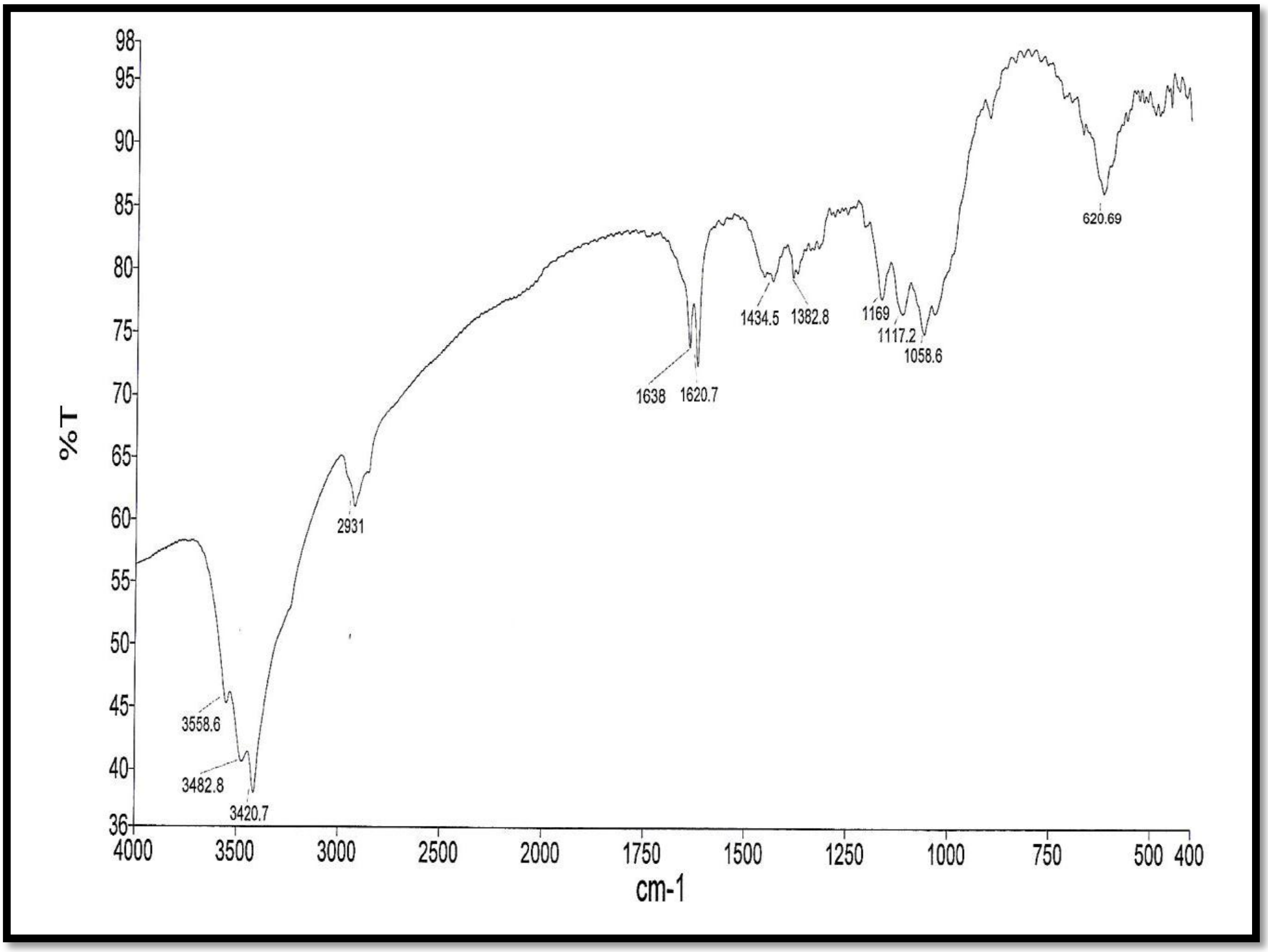


Figure (3.26): FT-IR spectrum of Nanocellulose produced from paper residues at concentration(50%) of sulfuric acid .

3.3 Adsorption study

The Nano-cellulose materials were prepared from rice husks (as agricultural waste) and paper residues (as industrial waste) were used as adsorbent surfaces for eosin dyes (adsorbate), The factors influencing adsorption were then studied in different conditions to study the adsorption behavior with eosin dye.

3.3.1. Determination of contact time of adsorption

This step is important in the research and aims to follow the adsorption of the dye of eosin with time and determine the time necessary to reach the state of equilibrium , These study done with a fixed concentration of dye (10 ppm), and a constant acidic function PH of 7 ,as well as a constant amount of adsorbent surface , which is 0.05 grams of both surfaces . The study showed that the process reaches a state of equilibrium at time 20 minutes for the nanocellulose produced from the rice husks and 30 minutes for the nanocellulose from the paper residue. The results are shown in table (3.12) and figure (3.27) explains change in the percentage of the removal of eosin dye from aqueous solution with change time every 10 minutes for adsorption of eosin dye on surface of NC of rice husks and NC of paper residues.

Table (3.11) Shows effect of contacted time of the adsorption of eosin dye on the surface of the nanocellulose prepared from rice husks and paper residues at 298 K

Time (min)	Nanocellulose of Rice husks		Nano-cellulose of paper residues	
	C_e (mg/L)	R (%)	C_e (mg/L)	R (%)
10	1.62	83.8 %	3.047	69.53
20	1.38	86.2%	2.928	70.72
30	1.72	82.8%	2.705	72.95
40	2.04	79.6%	2.891	71.09
50	2.48	75.2%	2.952	70.48
60	3.09	69.1%	2.980	70.2
70	3.69	63.1%	3.014	69.86
80	4.05	59.8%	3.054	69.46

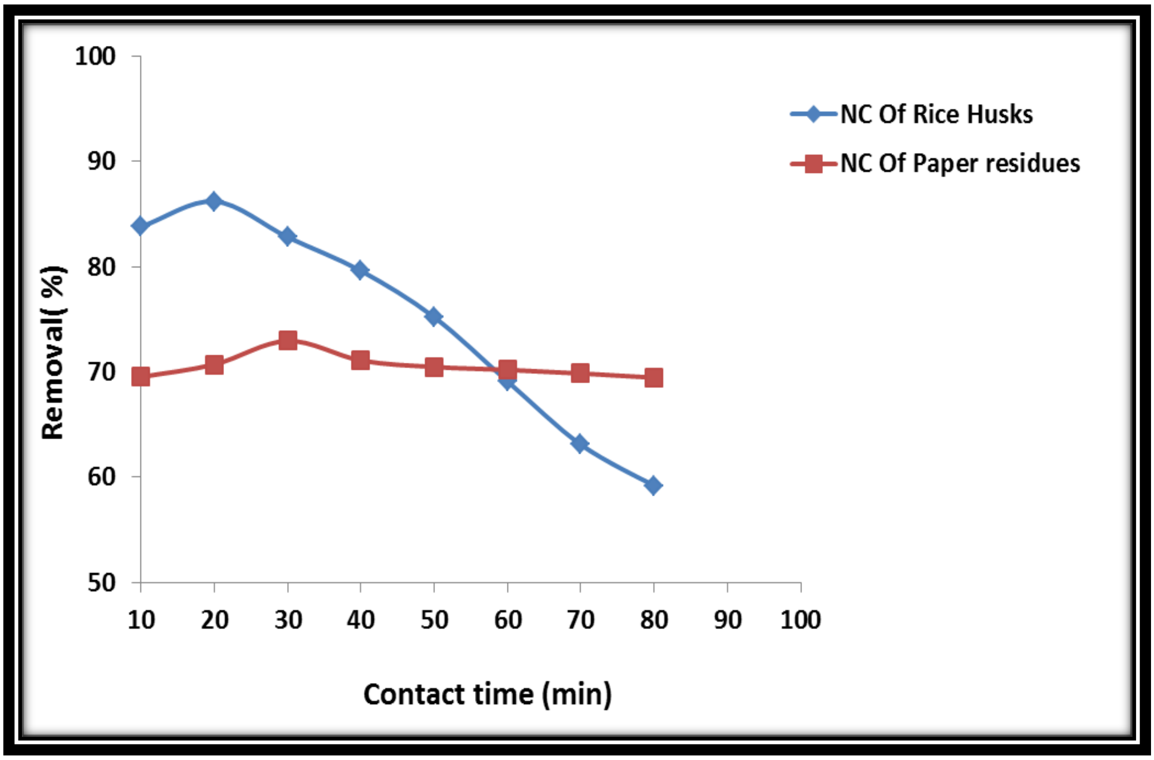


Figure (3.27): explains effect of contact time on adsorption of dye on surface of NC of rice husks and paper residues at 298 K .

The results show that the amount of adsorbate increases after 10 minutes and continues to increase to a certain time and then gradually decrease or stabilize gradually, when the adsorbate to equilibrium with the adsorbent surface it called the equilibrium time, It found that after 20 minutes of adsorption eosin dye on the nanocellulose surface of the rice husks , eosin dye reaches the equilibrium state with the nanocellulose of rice husks . while the nanocellulose of the paper residues after 30 minutes, the dye reaches equilibrium with the nanocellulose of the paper residue . The adsorption was speedy at initial stage due to the initial concentration gradients between adsorbate in solution and the number of free sites available on the adsorbent surface at beginning [109] ,this is because to the beginning of adsorption ,dye molecules begin to enter the adsorbent surface (nanocellulose of rice husks and paper residues). The surface is very active and has a high tendency towards the dye molecules until the surface is saturated with the dye molecules. To resist the spread of these molecules, it can be concluded that the diffusion of dye molecules into the surface pores is the controlling step of adsorption[110].

3.3.2. Effect of adsorbent quantity on adsorption

The effect of adsorbent quantity on adsorption of eosin dye studied by using different amounts of adsorbent for rice husks and paper residues (0.01,0.02,0.03,0.04, and 0.05) g , with remained the concentration of the original dye (10 ppm)and constant PH and constant temperature at 25 C° and constant time 20 min for NC of rice husks and 30 min for NC of paper residues. Results are shown in table (3.13) and figure (3.28).

The percentage of removal was calculated from the following relationship[99]:

$$R\% = \frac{(Co - Ce)}{Co} * 100 \ldots\ldots\ldots\ldots\ldots\ldots (3\text{-}2)$$

Where :

R (%) : Refers to percentage removal of dye

C_o : Is the initial concentration of dye, **(mg/L)**.

C_e : Refers to concentration of dye after adsorption , **(mg/L)** .

Table (3.12) Shows effect of adsorbent quantity on adsorption of eosin dye on adsorbent surface of nanocellulose prepared from rice husks and paper residues at 298 K.

Adsorbent quantity (g)	Nanocellulose of Rice husks		Nano-cellulose of paper residues	
	C_e (mg/L)	R (%)	C_e (mg/L)	R (%)
0.01	0.249	97.51	2.661	73.39
0.02	0.239	97.61	3.102	68.98
0.03	0.205	97.95	3.150	68.5
0.04	0.325	96.75	3.526	64.74
0.05	0.402	95.98	3.700	63

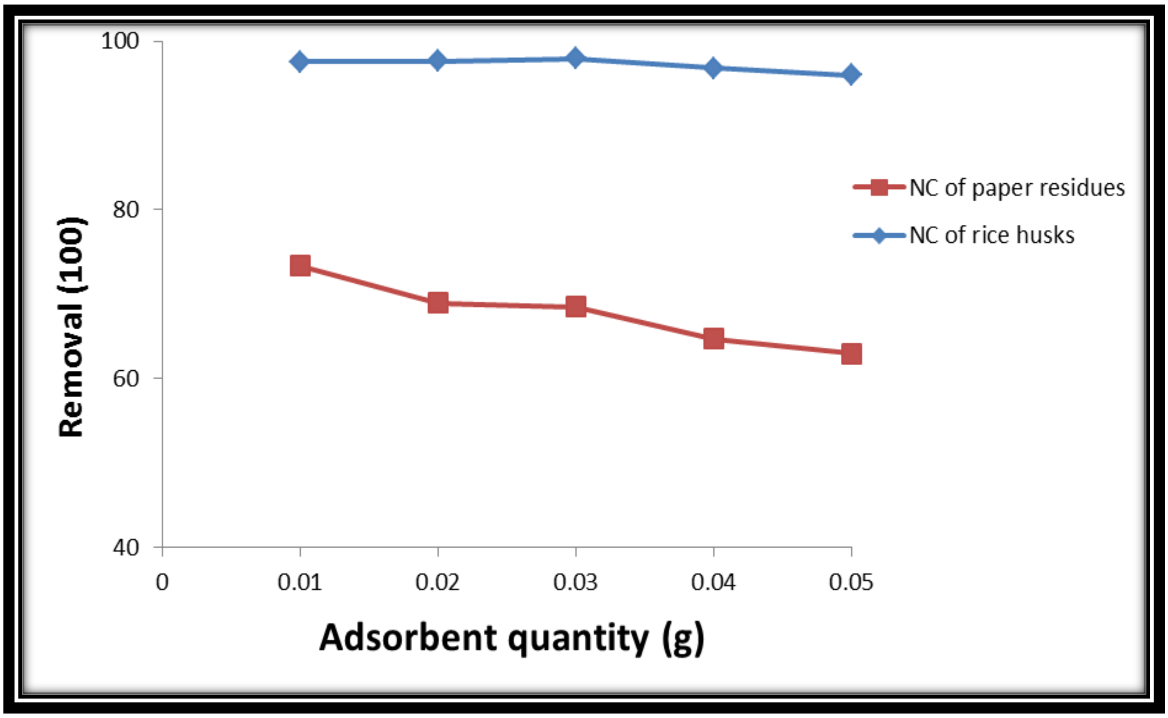


Figure (3.28): explains effect of adsorbent quantity on adsorption of eosin dye on surface of NC of rice husks and paper residues at298 K .

It was found that the percentage of the removal (R%) of dye from aqueous solution through using nanocellulose prepared from the rice husks. It increases with the increase of the amount of the adsorbent surface reach to 0.03g, which we find that the percentage of removal in the maximum case and then begin to decrease gradually and slightly .

The reason for increasing the percentage of removal is to increase the surface area of adsorption and the presence of active adsorption sites , After that, the percentage of removal begins to decrease gradually but slightly, and this is due to the arrival of the surface to the state of saturation of dye molecules . While (R%) of dye from aqueous solution through using the nano-cellulose prepared from the residues of paper, the highest percentage of removal in the maximum case at the minimum amount of use of adsorbent surface which is 0.01 g and the reason for this is because of the availability of a larger surface area, and then begin to decrease gradually with Increase the amount of adsorbent due to surface saturation of dye molecules[111].

3.3.3. Study of the effect of concentration on adsorption

The different concentrations of the Eosin dye to determine the optimal concentration of dye was studied by taking different concentrations are (10 ,20,30,40,50,60) ppm ,at quantity of adsorbent constant is (0.03 g) of rice husks and (0.01g) of paper residues and constant temperature at 25 C ,and constant time 20 min for nanocellulose of rice husks and 30 min for NC paper residues and constant PH. It was found that the best concentration of eosin dye is 10 ppm , which has the maximum percentage of the removal (R%) of the dye from the aqueous solution . Information in the table(3.14) and figure(3.29) below :

Table (3.13) Shows effect of concentration on adsorption of eosin dye on the surface of the nanocellulose prepared from rice husks and paper residues at 298 K.

***concentration* (ppm)**	***Nanocellulose of Rice husks***		***Nano-cellulose of paper residues***	
	C_e (mg/L)	**R%**	**C_e(mg/L)**	**R%**
10	0.351	96.983	0.898	90.698
20	0.598	94.341	0.9312	90.556
30	0.754	93.257	1.069	89.489
40	0.879	92.354	1.239	87.533
50	0.9132	90.019	1.485	85.465
60	1.189	88.5124	1.762	83.452

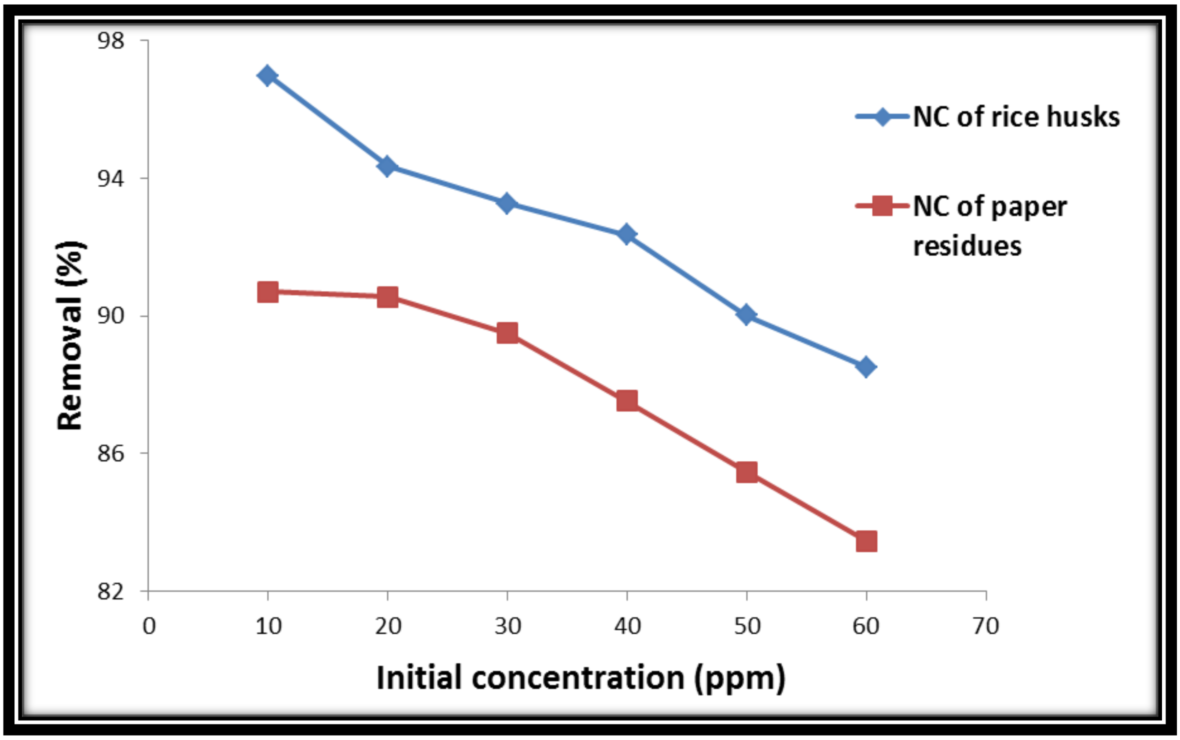


Figure (3.29): Shows the effect of initial concentration on adsorption to eosin dye on surface of NC of rice husks and paper residues at 298 K .

From the above results we note that by increasing initial concentration decreases percentage removal of dye R% as concentration of initial eosin dye is increased there is a decrease in percentage removal of dye from aqueous solution .This can be attributed to the accumulation of molecules of dye on the surface of adsorbent leading to decrease active sites that are necessary for absorption [112,113] .

3.3.4 Effect of temperature on adsorption

The effect of temperature on adsorption of dye was studied at different temperature (25,35,45,55,65)˚C, with remained the concentration of dye constant (10 ppm) and a constant time 20 minutes for NC of rice husks and 30 minutes for NC of paper residues . Results are appeared in table (3.15) and figure (3.30).

In the results indicate that the amount of adsorption (Q_e) and the percentage of removal (R%) to the dye of the eosin on the surface of NC of rice husks and paper residues decrease when the temperature increase where the maximum the percentage removal at 25˚C, then increase in temperature leads to decrease (R%) gradually of this is because the increase in temperature leads to decrease in speed of the spread of molecules on the surface and thus weaken the adsorption of dye molecules on the active sites of the surface where the adsorption occurs(114,115) . It also is the result of the assumption of instantaneous adsorption on adsorbent surface (116).

Table (3.14) : Explains effect of temperature on adsorption of eosin dye on surface of NC of rice husks and paper residues at different temperature.

Temperature (K)	Nanocellulose of Rice husks		Nano-cellulose of paper residues	
	C_e (mg/L)	Removal R%	C_e (mg/L)	Removal R%
298.15	0.162	98.4	0.439	95.61
308.15	0.171	98.3	0.511	92.89
318.15	0.199	98.1	0.6840	91.16
328.15	0.254	97.5	0.751	89.48
338.15	0.492	95.1	0.954	88.2

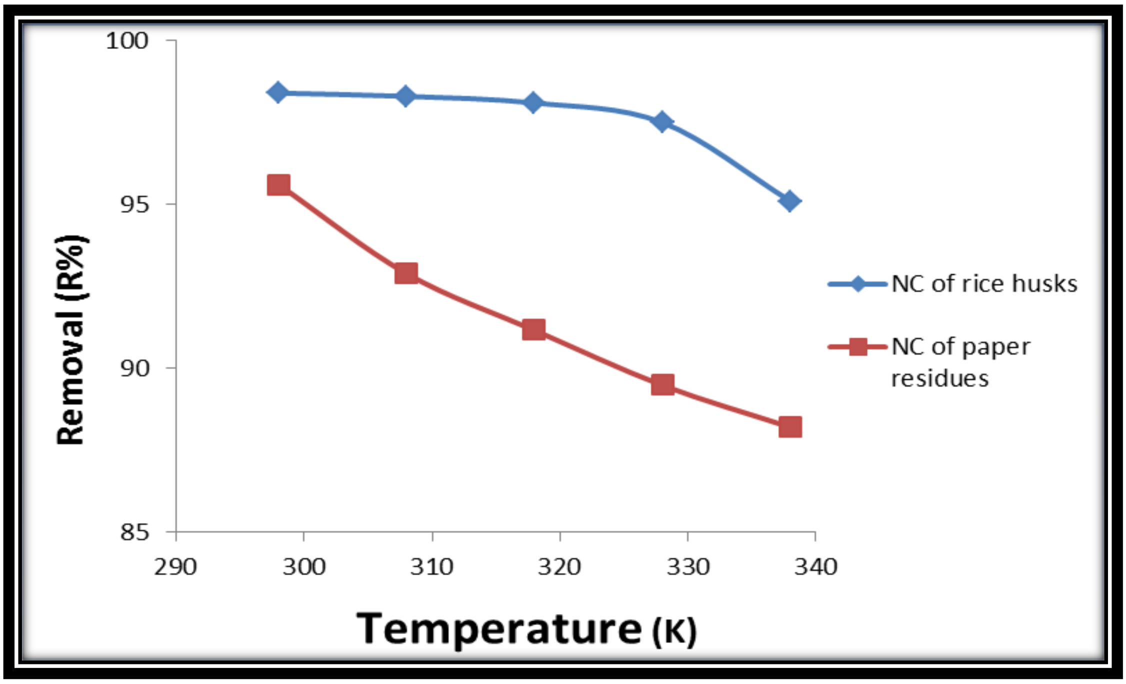


Figure (3.30): explains effect of temperature on adsorption of dye on surface of NC of rice husks and paper residues at different temperature.

3.3.5. Effect of pH on adsorption

The effect of pH on adsorption of dye on nanocellulose produced from rice husks and paper residues was studied by changing the acidic function PH (3, 7 and 9) with a constant concentration of dye (10 ppm) and constant temperature 25C° for 20 min for rice husks and 30 minutes for paper residues and results are shown in table(3.16) and figure(3.31) .

It can be observed that the percentage of the removal (R%) of the eosin dye from the aqueous solution is at its maximum when adsorption on the surface of the substance nano-cellulose of rice husks and paper residues in pH of 3 therefore increase in adsorption at pH of 3 can be attributed to the aggregation of dye molecules , while (R%) decrease when PH increase in pH of 9 .

This study shows that the acid function effects on the adsorbent surface and the adsorbate and the interactions that occur between them . The amount of adsorption of dye on surface of NC from rice husks and paper residues decreases by increasing the acidic function in the following order :

PH=3>7>9

The adsorption capacity was much pronounced at lower pH 3, while as the pH increases adsorption decreases(117,118) . Because ions of hydrogen and hydroxide are adsorbed perfectly strongly ,the adsorption of other ions is influenced by the pH of the solution ,on the other hand , to the extent to which ionization of a basic or an acidic compound affects its adsorption, PH affects adsorption in that it was controlled the degree of ionization .

In general, adsorption of typical organic pollutants from water is increased with decreasing pH (119,120).

Table (3.15): Shows the effect of pH on adsorption of dye on nanocellulose produced from rice husks and paper residues.

PH	Nanocellulose of Rice husks		Nano-cellulose of paper residues	
	C_e (mg/L)	Removal (R%)	C_e (mg/L)	Removal (R%)
3	0.104	98.96	0.375	96.25
7	2.013	79.67	3.184	68.16
9	2.131	78.69	3.085	69.15

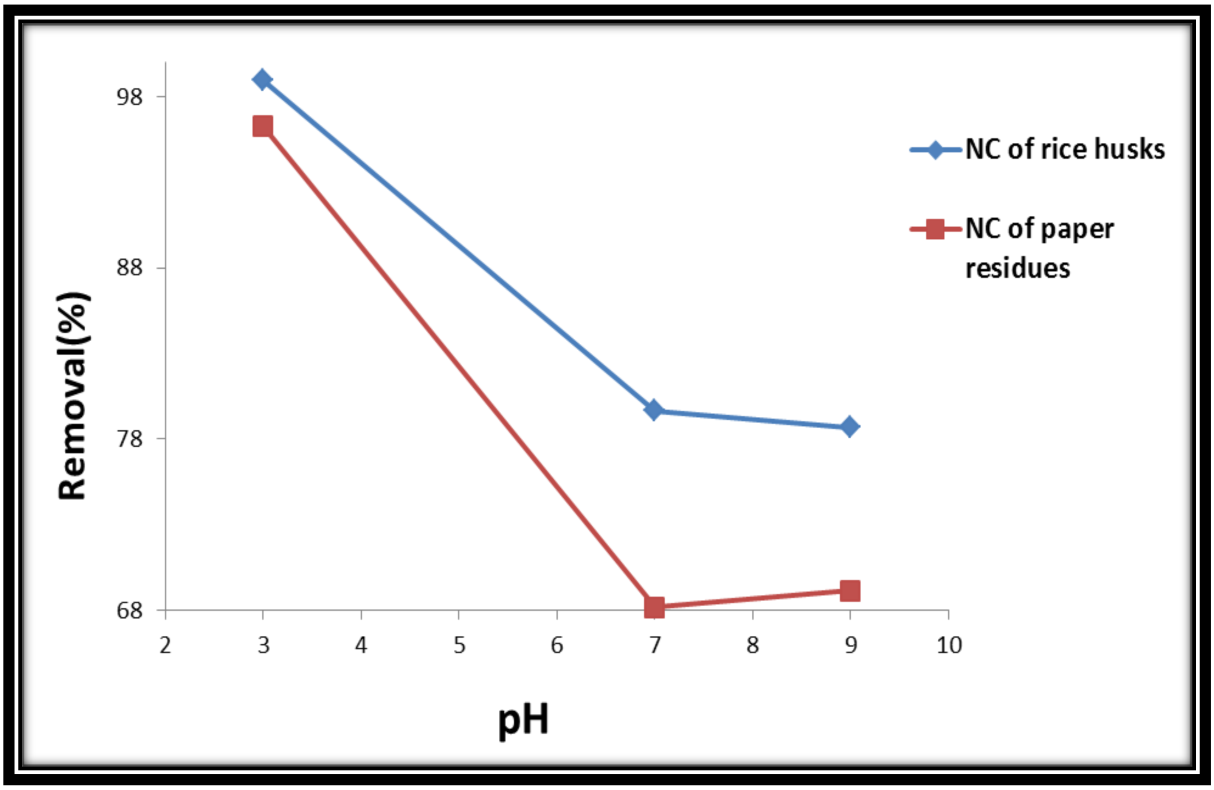


Figure (3.31): explains effect of pH on adsorption of eosin dye on NC of rice husks and paper residues .

3.4 Conclusions

It can be concluded from this study that:

1.Nanocellulose product was prepared from rice husks waste worthless waste and paper residues waste as raw materials .NC product was obtained from cellulose found in the raw materials with simple methods without having an expensive processes such as bleaching , acid hydrolysis ,freeze and drying processes .

2. Ultrasonic device was used to has be done sonication process of the raw materials and it was obtained a powdered with good properties that could have been used in other processes and techniques .NC product was characterized by (XRD ,AFM,SEM, and FT-IR)

3. The Atomic Force Microscope(AFM) images showed that the nanocellulose created from rice husks and paper residues is of small nanoparticle and smooth surface and in two dimensions: 2D and 3D

4. Fourier Transform Infrared spectroscopy (FT-IR) showed the purity of cellulose by removing lignin and hemicellulose completely

5. In this study, an excellent removal of the eosin dye from the aqueous solution by adsorption process using NC as adsorbent surface of dye. Thus, NC can be used to remove pollutants from the environment , therefore NC environmentally friendly.

6. Nanocellulose for rice husks is more efficient than nanocellulose for paper residues in removing eosin dye from the aqueous solution, because percentage of the removal of eosin dye from the aqueous solution by NC of rice husks is higher than the percentage of the removal of eosin dye from the aqueous solution by paper residues. Therefore, nanocellulose for rice husks will be more efficient in removing pollutants from water.

7. The increase in temperature leads to decrease the percentage of the removal gradually of this is because decrease in the speed of the spread of molecules on the surface and thus weaken the adsorption of dye molecules on the active sites of the surface .

8. We believe that in the near future, agricultural and industrial waste containing content High of cellulose is a very promising source of low-cost raw materials for nanocellulose production, as well as other high-value biotransformation processes, thereby minimizing waste which causing significant damage to the environment.

3.5.Future studies

1. Find other renewable and cheap agricultural residues containing high percentage of cellulose such as straws, barley husks and others, rather than throwing it into waste and damaging the environment.

2. Use of other chemical processes and methods that provide the effort and time to extract cellulose and give the output of nanocellulose more efficient to refining polluted water by pollutants such as dyes and metals that cause water toxicity**.**

3. Acid hydrolysis by Using other acid instead of sulfuric acid such as phosphoric acid H_3PO_4 and nitric acid HNO_3, and using different concentrations to observe its effect on the nanoscale size of the substance

4. Use a another adsorbate instead of eosin dye, such as other dyes and other metals that contaminates aqueous solutions .

5. Study effect of adsorption isotherm and thermodynamic process using nanocellulose for both wastes as adsorbent surface .

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الخلاصة

تهدف الدراسة الحالية الى تحضير النانو سليلوز من المخلفات الزراعية (قشور الرز) ومخلفات صناعية (بقايا الورق) بدلا من رميها في النفايات وزيادة تلوث البيئة وبالتالي التقليل من تلوث البيئة الى حد ما .

في هذه الدراسة ، تم تحضير النانو سليلوز بواسطة التحلل الحامضي باستخدام حامض الكبريتيك بتركيزات مختلفة (45،35،25،15)%للمخلفات الزراعية (قشور الرز) وعند تركيز 50% للمخلفات الصناعية (بقايا الورق) لإذابة المواد الاولية بواسطة حامض الكبريتيك واستخلاص السليلوز لتحويله الى نانو سليلوز وذلك باستخدام طريقة متجددة ومتقدمة باستخدام جهاز بالموجات فوق الصوتية وفي أوقات زمنية مختلفة من (30-180) دقيقة.

وقد تم تشخيص ناتج النانو سليلوز المحضر من قشور الرز وبقايا الورق بواسطة عدد من التقنيات والتي هي المجهر الالكتروني الماسح Scanning Electron Microscope (SEM) ، ومجهر القوة الذرية Atomic Force Microscope(AFM)،وجهاز حيود الاشعة السينية X-Ray Diffraction (XRD) ، ومطياف الاشعة تحت الحمراء Fourier transform Infrared Spectroscopy (FT-IR) وبواسطة هذه الاجهزة تم الكشف عن ناتج النانو سليلوز (NC) ، فقد شخص تركيب السطح بأستخدام تقنيات(SEM, AFM).

و تم الحصول على نانو سليلوز بأحجام نانوية صغيرة وبأشكال مميزة كما اوضحته القياسات . فبينت نتائج مجهر القوة الذرية AFM حجم الدقائق ودقة توزيع معدلات اقطار ناتج النانو سليلوز المحضرة من قشور الرز تتراوح من20-50 نانومتر، بينما لناتج النانو سليلوز المحضرة من بقايا الورق يتراوح متوسط القطر من 65-80 نانومتر، و من هذا نستنتج ان ناتج النانو سليلوز المحضر من المخلفات الزراعية افضل من النانو سليلوز المحضر من المخلفات الصناعية حيث ان الحجم النانوي اصغر وبالتالي تتوفر مساحة سطحية اكبر . ويقدم المجهر الإلكتروني الماسح (SEM) معلومات مهمة فيما يتعلق بمورفولوجيا الجسيمات النانوية للسليلوز وبقوة بكسل ability analytical pixel هي µm (1,5,10,50). حيث تظهر صور SEM اختلافات في شكل العينة فقد أظهرت وجود مناطق بلورية منتظمة واخرى غير متبلورة وغير منتظمة . وهذا يدل على ان الجسيمات النانوية الناتجة ليست مستقرة بسبب ترسب المجاميع في الجسيمات النانوية ، وقد استخدم حامض الكبريتيك في إذابة وحل المناطق غير

المتبلورة . اما تقنية الاشعة السينية XRD بينت الحجم البلوري لناتج النانو سليلوز الناتج من قشور الرز وبقايا الورق واثبتت هذه التقنية ان النانو سليلوز ذو شكل بلوري ويمتلك درجة بلورة عالية وان الحجم البلوري D (الذي تم تحديده من معادلة ديباي- شرر (Deby-Sherrer للنانو سليلوز الناتج من قشور الرز اصغر حجما من الحجم البلوري للنانو سليلوز المحضر من بقايا الورق. وأظهر التحليل الطيفي للأشعة تحت الحمراء نقاوة السليلوز عن طريق إزالة اللجنين Lignocellulose و الهيميسليلوز hemicellulose بشكل كامل من العينات

وبعد الحصول على النانو سليلوز من المخلفات الزراعية والصناعية تم اجراء تطبيق صناعي عليه عن طريق امتزاز صبغة الايوسين من المحلول المائي . في هذا المجال ، تم دراسة تأثير العوامل المؤثرة على الامتزاز (زمن الاتزان ، كمية المادة الممتزة ، التركيز الأبتدائي ، درجة الحرارة ودرجة الحموضة) التي تؤثر على نسبة إزالة صبغة الإيوسين على المادة المازة (NC من قشور الرز و بقايا الورق) ، حيث وجد أن الزمن اللازم للوصول إلى حالة التوازن كان (20) دقيقة لـ NC من قشور الرز و (30) دقيقة لـ NC من بقايا الورق. بصورة عامة نجد أن النسبة المئوية (R%)لإزالة الصبغة من محلول مائي مخفف باستخدام النانو السليلوز المحضر من قشور الرز وبقايا الورق تقل بزيادة كمية المادة الممتزة وهذا يعود الى تشبع السطح الماز بجزيئات الصبغة . في حين أن دراسة امتزاز الصبغة على السطح الماز NC لقشور الرز وبقايا الورق عند قيم مختلفة من الدالة الحامضية (3،7 و 9) ظهر أن أفضل امتزاز للصبغة على السطحين عند الدالة الحامضية pH3 . أما تأثير درجة الحرارة على أمتزاز الصبغة على سطح النانو سليلوز لكلا النوعين فقد أشار ان نسبة الإزالة تقل بزيادة درجة الحرارة .وتبين من خلال عملية الامتزاز ان النسبة المئوية لإزالة الصبغة من المحلول المائي باستخدام NC المحضر من قشور الرز انه اكثر كفاءة في الازالة من NC المحضر من بقايا الورق.

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تحضير النانوسليلوز من قشور الرز ومخلفات الورق واستخدامها في ازالة صبغة الايوسين

رسالة مقدمة الى

مجلس كلية العلوم/ جامعة ديالى

وهي جزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

من قبل الطالبة

حـنـين لـطـيـف خـلـيـل

بكالوريوس في علوم الكيمياء 2016

كليـــة العلوم - جامعــة ديالـــى

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