

**An-Najah National University**

**Faculty Of Graduate Studies**

**Synthesize and Characterization of Cellulose  
Derivataized with an Aromatic Amine and Application  
in Waste Water Purification**

**BY**

**Bahia Fared Abu Leil**

**Supervisor**

**Dr. Ahmad Abu Obaid**

**Co-Supervisor**

**Dr. Othman Hamed**

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the Degree of Master of Chemistry, Faculty of Graduate Studies,  
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**This Thesis was Defended Successfully on 14/7/2019 and approved by:**

<b><u>Defense Committee Members</u></b>	<b><u>Signature</u></b>
<b>1. Dr. . Ahmad Abu Obaid / Supervisor</b>	.....
<b>2. Dr. Othman Hamed / Co-Supervisor</b>	.....
<b>3. Dr. Abdal Hadi Deghles / External Examiner</b>	.....
<b>4. Prof. Shehdeh Jodeh / Internal Examiner</b>	.....

## **Dedication**

My mother I hope to dedicate all my achievements to you ,but the stay just for God I wish you mercy and forgiveness. My lovely husband Ammar the first supporter thanks a lot for everything whether incorporeal or monetary, I dedicate this to my little boys Jamal and Bibars also to all my family my father ,my lovely brothers and sisters thanks a lot for support, my mother in law thanks a lot for your help ,to all people and my friends who love and believe me.

## **Acknowledgement**

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My beautiful and greatest doctors in the great university An-Najah national university thanks all , specially doctors in chemistry department ,and to all technicians in chemistry department specially Mr. Omair An-nabulsy you are like a father for me thanks a lot for all help and support .

MEDRC "financial support" I'm grateful to help me in master degree. Thanks my husband ,sisters ,brothers ,friends and all people who support me.

Thank you to everyone help and support me Albeit with a beautiful and encouraging word.

## الإقرار

انا الموقعه ادناه مقدمة الرسالة التي تحمل العنوان:

### **Synthesize and Characterization of Cellulose Derivataized with an Aromatic Amine and Application in Waste Water Purification**

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل، أو أي جزء منها لم يُقدم لنيل أية درجة أو لقب علمي أو بحثي لدى أي مؤسسة تعليمية أو بحثية أخرى.

### **Declaration**

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

**Student's Name:**

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التوقيع:

**Date:**

التاريخ:

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## List of Abbreviations

<b>Symbol</b>	<b>Abbreviations</b>
Cell-o-PADm	Cellulose 1,2-diaminobenzene
CA	Aldehyde content
WHO	World Health Organization
UNICEF	UN Children's Fund
DW	Drinking Water
GW	ground water
SW	Surface water
CNC	Cellulose nanocrystal
XRD	X-ray diffraction
TEM	Transmission electron microscope
$Q_e$ (mg/g)	amount of metal ions adsorbed
$C_o$ (ppm)	initial concentration
$C_e$ (ppm)	equilibrium concentration
$W$ (mg)	weight of the adsorbent
$V$	volume of solution
$Q_{max}$ (mg/g)	theoretical maximum monolayer
	adsorption capacity of the adsorbent
$K_l$ (L/mg)	Langmiur constant
$K_F$	Freundlich constant

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**Abstract**

A cellulose derivative with several coordination sites for metal ions composed of cellulose powder extracted from olive industry waste and 1,2-pheneylnediamine was synthesized and evaluated as an adsorbent for metal ions from sewage. The adsorption efficiency of the cellulose amine polymer toward Fe(III) and Cd (II) was investigated as a function of adsorbent dose, concentration temperature, pH, and time .The adsorption parameters that gives the highest adsorption efficiency were determined. In addition, the cellulose amine polymer showed an excellent efficiency toward approximately twenty metal ions present in the sewage sample. The highest adsorption efficiency was at pH of about 8.3, room temperature and with 2mg/ml of polymer dose.

The cellulose amine polymer has various coordination sites amine, hydroxyl, and aromatic groups. The diversity and frequency of the coordination was the reason for the high efficiency of the cellulose amine polymer toward the metal ions. The thermodynamic analysis results (The Gibbs energy ( $\Delta G_0$ ), enthalpy ( $\Delta H_0$ ), and entropy ( $\Delta S_0$ ) were calculated)

supported the spontaneous adsorption efficiency of the polymer at room temperature. The kinetic study revealed that the metal ion adsorption by cellulose amine polymer **was** pseudo-second-order and followed the Langmuir isotherm model.

# **Chapter One**

## **Introduction**

Purifying the waste water from toxic heavy metals is performed by several reported methods, and among these, adsorption is the most applicable and it receives the most attention because it is highly effective and low-cost. Among the most effective metal adsorbent is activated carbon.

However, it is not optimal in some cases due to the high processing costs. Additionally, natural based materials, such as clay, zeolites, and peat, are among the most evaluated materials as adsorbent for toxic heavy metal ions from waste water. They are the most attractive because they are renewable and available at a relatively low cost. In addition, other natural products, such as cellulosic materials, lignin, chitosan and hemicelluloses, received a lot of attention.

Several cellulosic-based adsorbent such as kenaf, cotton linters, wheat straw, wood sawdust, and rice husk, were prepared and investigated as an adsorbent for toxic heavy metal ions such as those mentioned above. Cellulose nanoparticles are promising adsorbent for heavy metal ions. Despite all of the rapid progress in the study of natural based metal adsorbents, many natural based materials and their derivatives have not been explored as an adsorbent for metal ions.

In this study focused on cellulose powder derivatized with a bidentate chelating agent as a potential new adsorbent for metal ions.

## 1.1 Background

Pollution and water contamination is a serious problem in our world. Water contamination mainly caused by heavy metal ions which became a major problem due to widespread of industry. Examples of these metals ions include  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  ions [1,2].

Heavy metals cause many dangerous diseases if their concentrations in water exceed a certain limit [3] as determined World Health Organization (WHO). For instance, Cd(II) is the main cause of itai-itai disease, which damage kidney and bones [4]. While lead(II) causes anemia and bones damage [5]. Copper(II) causes weakness in body muscles [6]. So, care must take when dealing with these metal ions, and to make sure not to exceed the limit set by WHO[7,8].

## 1.2 Water

Water covers 71% of the Earth's surface, mostly in seas and oceans. Small portions of water occur as groundwater (1.7%), in the glaciers and the ice caps of Antarctica and Greenland (1.7%), and in the air as vapor, clouds (formed of ice and liquid water suspended in air), and precipitation (0.001%) [9]. Billions of people are living without adequate access to safe and clean drinking water (DW) [10]. It is reported by UN that four billion individuals are living in severe water insufficiency circumstances. The UN Children's Fund (UNICEF) and the World Health Organization (WHO) have noted that 663 million people still lack better

quality DW [11]. The World Economic Forum also specified in its annual risk report that water crises are the principal threat facing the world [12]. Several national and regulatory organizations are working on specific goals to detect and reduce the sources of water contamination. The main sources of freshwater are groundwater (GW), well water, river water, lake water, and reservoirs. The reduction of water levels in these sources was recorded on global scale due to drought conditions and high-water usages [10].

Water insufficiency problems are universal and mainly in the developing countries which mainly related to high increase in population growth. It is forecasted to reach over 10 billion people in the year 2050 [13]. Of the total global water, only 2.5% is suitable for drinking and the rest is ocean or other saline water. And only 1% of the freshwater is available for industrial and human needs, and the rest is unusable groundwater, glaciers, and ice caps. Thus, freshwater shortage has become a major global challenge [14]. In addition, the agriculture sector and irrigation significantly depend on water. Seventy percent of available freshwater is currently used for crop watering, whereas the industry consumes 20%, and the rest is consumed by domestic people [15].

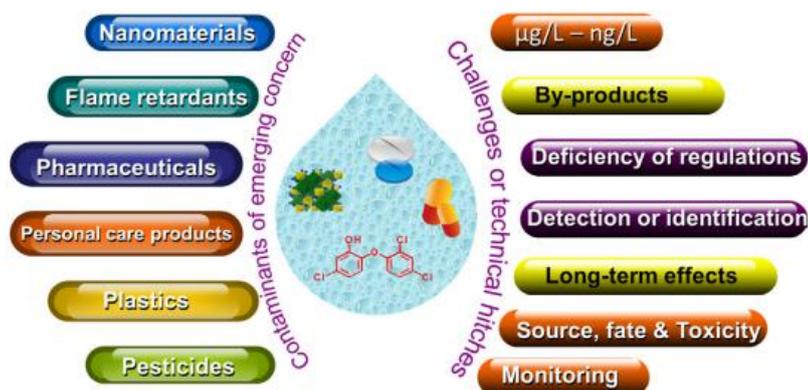
### **1.2.1 Water Pollution**

The major issues in water pollution are (i) detecting the pollutant, (ii) treatment, and (iii) controlling their release into aqueous environment.

Industry and human activities are principally responsible for extreme discharges of toxic contaminants into water resources. With high demand

for drinking water in a rapidly growing third world, many water pollution incidents due to the release of notorious pollutants into drinking water sources are reported all over the world [16,17]. As a result of that, ground water, surface water (SW), and DW are contaminated by numerous metal ions, organic matters, and biological substances.

As mentioned above, the main sources of aquatic environment contamination including (i) industrial, (ii), man-made, (iii) natural disasters, (iv) rainfall, (v) waste treatment plants, and (vi)urbanization [18].



Contaminants of emerging concern and existing challenges in their treatment.

**Figure 1.1:** Contaminants & Challenges

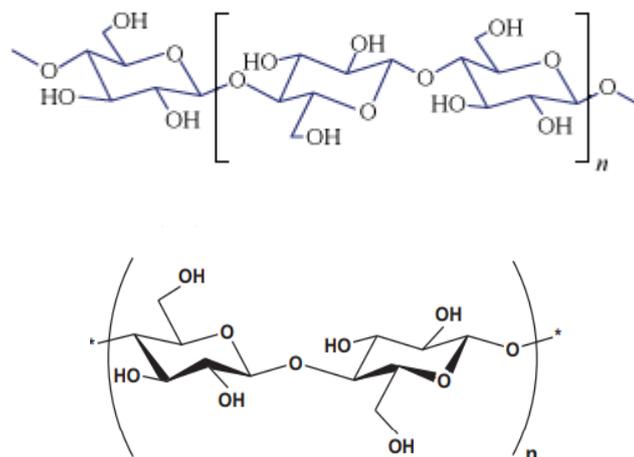
Several methods are reported in the literature for purifying wastewater from toxic heavy metals, among these are: ion-exchange, chemical precipitation, flocculation and coagulation, membrane separation, bio-sorption, and reverse osmosis [7]. Some of these methods have many limitations which makes them not effective such as: working under certain consideration and low sensitivity.

One of the most efficient technology in water purification is adsorption. Since adsorbent could be available from safe and cheap sources, requires little processing, good adsorption capacity. Also, they could be selective for heavy metal ions adsorbent.

Among the natural source of adsorbent is cellulose. Cellulose is very attractive source of adsorbents, since it is natural and requires low costs for operating, so many researches showed attention toward cellulose [8-11].

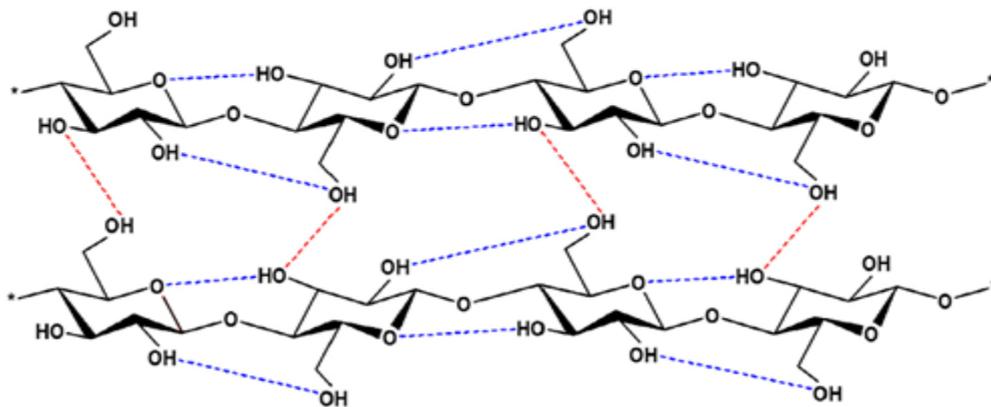
### 1.3 .1 Cellulose

Cellulose is the major component in lignocellulosic biomass which is mainly present in the plant cell wall at about 35–50% [19-21]. It is composed of the linear homo-polysaccharide of b-1,4- linked anhydro-D-glucose units with the repeating unit of cellobiose (Fig.1.2) [22].



**Figure 1.2:** Chemical structures of cellulose and cellobiose

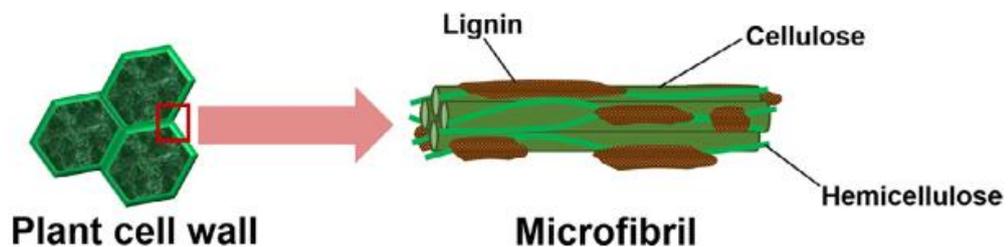
The monomer of cellobiose, is anhydroglucose unit, consists of three hydroxyls, two secondary and one primary. They form strong hydrogen bonding with the adjacent glucose unit in the same chain (intramolecular hydrogen bonding) with adjacent chains (intermolecular hydrogen bonding) (Figure 1.3) [22].



**Figure 1.3:** Intermolecular & intramolecular Hydrogen bonding in cellulose polymer

Cellulose consists of two regions crystalline and amorphous. The hydrogen bonding networks in the crystalline region are strong and tightly packed which lead to the tough, strength, fibrous, insoluble in water, and high resistant to most organic solvents [23–25]. The hydrogen bonding networks in cellulose has wide orientation, resulting in different allomorphs of cellulose [26]. The variation of cellulose allomorphs depends on the source of cellulose biomass and the cellulose extraction treatment method. Generally, there are four types of cellulose allomorph namely cellulose types I, II, III, and IV [24,25].

Cellulose type I is the general allomorph of cellulose in native cellulose which is the parallel packing of hydrogen-bond network. Cellulose type II comes from the chemical regeneration of cellulose I by dissolving in a solvent or swelling in acid or alkaline solution. With these chemical regenerations, cellulose type II is composed of different arrangements of antiparallel packing of hydrogen-bond network. Cellulose type III can be obtained from the ammonia treatment of cellulose I or II, while cellulose type IV is the modification of cellulose III by heating up to 260 °C in glycerol [24,25]. With its plentiful carbon, hydroxyl groups, in the monomer glucose, cellulose is the most natural source for the production of carbon-based materials, valuable chemicals, textiles, papers, and so on [26,27].



**Figure 1.4:** A representative structure of plant cell wall

### 1.3.2 Chemical structure of cellulose

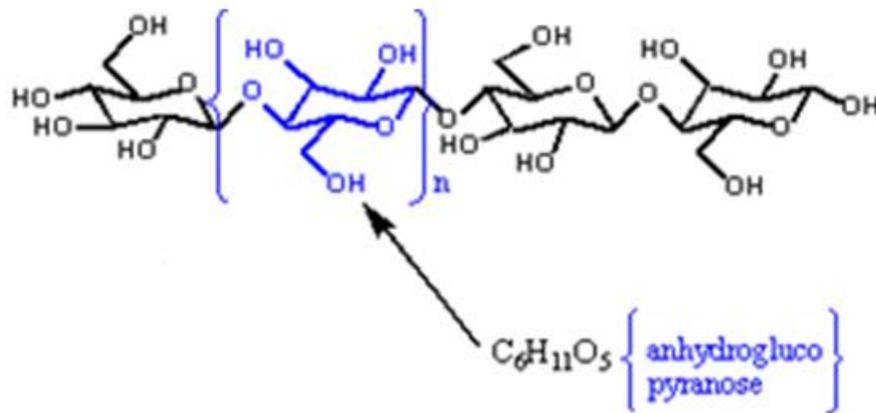
Cellulose chains, are linear consist of about 200 to 10.000 monomers, depends on the source and extraction method. The monomer is anhydroglucose that are linked in cellulose polymer through  $\beta$ -1,4-glycosidic bonds in the  $\beta$ -configuration between C1 and C4 of adjacent units to form a polymeric chain Figure 1.5 .

Microfibers of cellulose be in the form of amorphous or ordered crystalline regions to form fibers of cellulose.

The molecular structure of cellulose has characteristic properties such as: hydrophilicity, chirality, biodegradability, and broad chemical variability initiated by OH groups of cellulose

Strong hydrogen bond between hydroxyl groups and oxygen atoms of the cellulose chains is the source of the high strength, stability and insolubility of cellulose polymer.

However, cellulose fibrils aggregate with the highly ordered regions (crystalline structure) and the disordered regions (amorphous structure) [22]. At the crystalline parts, the chain molecules are of orderly packing which promotes high stiffness and strength of cellulose. In other ways, the amorphous parts contribute to the flexibility of the bulk material [29]. Within the aggregation of ordered and disordered regions, cellulose fibers contain 3–100  $\mu\text{m}$  of size in diameter with 1–4  $\mu\text{m}$  in length for general lignocellulosic biomass [25]. Nanocellulose is the natural fiber which can be extracted from cellulose.



**Figure 1.5:** Chemical structure of and anhydroglucose monomers.

Cellulose is usually extracted from any plant in earth, the contents of cellulose polymer vary one plant to another, like for example: Bushes has about 30% ,Woods has about 20-50%, flax and ramie have about 65–70%, and cotton almost pure

cellulose: >90%

## 1.4 Cellulose Source Materials

### 1.4.1 Wood

Wood is considered the primary source of cellulose polymer. It abundant and has many advantages. In general, extraction of Cellulose starts with “purified” wood, i.e. wood with most of the lignin, hemicelluloses and impurities removed

### **1.4.2 Plant**

Plants are cellulose source primarily because they are abundant. In general, plants can be “purified” similarly to wood.

A wide variety of plant materials have been studied for cellulose sources, including cotton, ramie, flax, potato tubers, sugar beet pulp, banana rachis

### **1.4.3 Tunicate**

Tunicates are the only animals known to produce cellulose micro-fibrils. tunicates are sea animals that have a mantle consisting of cellulose micro-fibrils embedded in a protein matrix. it is thick leathery mantle in their mature phase that is used as a source of cellulose micro fibrils.

### **1.4.4 Algae**

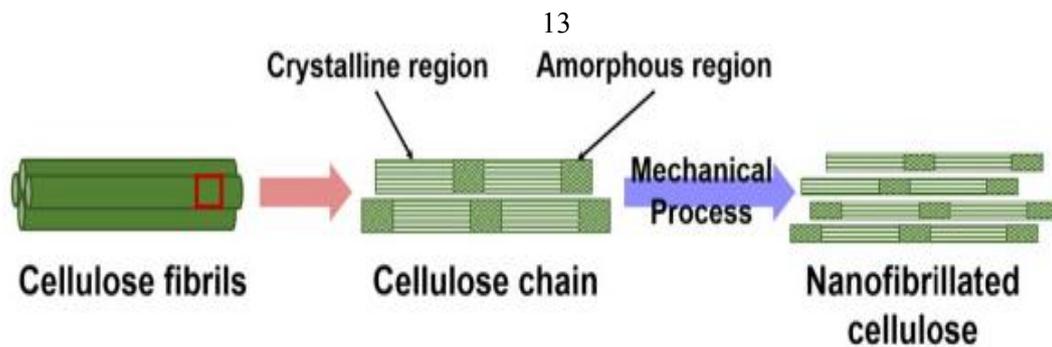
Cellulose is produced by several species of algae (green, gray, red, yellow, green) within the cell wall. there are considerable differences in cellulose micro fibril structure between the various algae species caused by differences in the biosynthesis process.

### **1.5 Nano cellulose**

Recently, the humans become aware of environmental preservation, applications of renewable resources become more and more important for the daily life since they are biodegradable, safe and friendly to human and nature. Nanocellulose is a natural nanomaterial which can be prepared from cellulose by hydrolysis with strong acid such as sulfuric acid. With its

nanometer size in diameter, nanocellulose consists of attractive properties such as high strength, excellent stiffness, and high surface area [28,29]. In addition, nanocellulose contains several hydroxyl groups which are available for surface modification. Nanocellulose can be used in various fields in our life, such as biomedical products, nanocomposite materials, textiles, and other applications. With various hydroxyl groups and strong hydrogen bonding networks, nanocellulose is composed of the outstanding physical and mechanical properties [28,29]. The special attention is the size of nanocellulose fiber which generally contains less than 100 nm in diameter and several micrometers in length. Nanocellulose is a biodegradable nanofiber with light weight, low density (around  $1.6 \text{ g/cm}^3$ ) and outstanding strength property. It has high a stiffness of up to 220 GPa of elastic modulus which is greater than Kevlar fiber. Nanocellulose also has high tensile strength of about 10 GPa which is greater than cast iron and its ratio of strength to weight is 8 times higher than stainless steel. In addition, nanocellulose is transparent and full of the reactive surface of hydroxyl groups as mentioned above, which can be derivatized and add properties to cellulose [28,29,22,27]. Nanocellulose can be classified into three types; nanocrystalline cellulose, nanofibrillated cellulose, and bacterial nanocellulose. Although the three types are similar in chemical composition, they are different in morphology, particle size, crystallinity, and some physical properties due to the difference of sources and extraction methods [22,25].

Nanocrystalline cellulose, also known as cellulose nanocrystals, or cellulose nanowhiskers, it has the short-rod-like shape or whisker shape with 2–20 nm in diameter and 100–500 nm in length. Also, it contains 100% of cellulose that is mainly in crystalline regions (high crystallinity around 88%) [22,25]. The amorphous parts are hydrolyzed and removed by acid while the crystalline parts are still maintained [29,22]. Inference from this extraction method is nanocrystalline cellulose contains high crystallinity with a short-rod shape. Nanofibrillated cellulose, also known as cellulose microfibril, microfibrillated cellulose, cellulose nanofiber, cellulose nanofibril, or nanofibrillar cellulose, is the long, flexible, and entangled nanocellulose which can be extracted from cellulose fibrils by mechanical methods. It has the long fibril shapes with 1–100 nm in diameter and 500–2000 nm in length [30,31]. Also, it contains 100% of cellulose chemical composition with both of crystalline and amorphous regions [28,29]. (Figure 1.6 )shows the schematic of nanofibrillated cellulose which can be extracted from cellulose chains by the cleavage of fibrils in longitudinal axis from the force by mechanical mean [22]. Comparing with nanocrystalline cellulose, nanofibrillated cellulose (Figure 1.6) has the longer length with high aspect ratio (length to diameter), high surface area, and high extensive of hydroxyl groups which is easily accessible for surface modification [25]. Bacterial nanocellulose is the third type of nanocellulose which is different from nanocrystalline cellulose and nanofibrillated cellulose.



**Figure 1.6:** Cellulose fibrils

Nanocrystalline and nanofibrillated celluloses are extracted from lignocellulosic biomass but bacterial nanocellulose is produced from building up of low molecular weight of sugars by the bacteria *Gluconacetobacter xylinus* for a few days up to two weeks [30–32]. Because of that, the bacterial nanocellulose is always in pure form 100%. Other components from lignocellulosic biomass such as lignin, hemicellulose, pectin and so on are not present. Bacterial nanocellulose has the same chemical compositions as other two kinds of nanocelluloses. It is in the form of twisting ribbons with the average diameters of 20–100 nm and micrometer lengths with large surface area per unit [30–32]. Recently, hairy cellulose nanocrystalloid has been reported by van de Ven and coworkers. It can be extracted from cellulose chains by a chemical treatment method without acid or mechanical methods. As a result, the amorphous regions are solubilized but crystalline regions remained similar to the extraction of nanocrystalline cellulose using conventional methods. It is worth noting that hairy cellulose nanocrystalloid consists of some cellulose chains which can be cleaved and protruded from both ends of crystalline region [33–34]. As such, hairy cellulose nanocrystalloid has

high crystallinity and mainly in rod-shaped dimension similar to nanocrystalline cellulose but it also contains both of crystalline and amorphous parts similar to nanofibrillated cellulose [33–35]. Sterically stabilized nanocrystalline cellulose (SNCC) is a derivative of HCNC. It can be produced by oxidation with periodate ( $\text{NaIO}_4$ ) followed by heating treatment. The negative charges of periodate ions can break C2-C3 bonds of glucose units. Meanwhile, it can also convert the C2-C3 hydroxyl groups into aldehydes. As a result, the amorphous regions of cellulose chains can be penetrated while the dialdehyde chains can be created and cleaved at the ends of remaining crystalline regions. With the high reactivity of dialdehyde chains, SNCC can be functionalized with other chemical groups [33,34]. Electrosterically stabilized nanocrystalline cellulose (ENCC) is another kind of HCNC. It can be extracted from cellulose chains by periodate/chlorite oxidation reaction. As a result, the rod shaped crystalline parts are extracted and protruded by the dicarboxylated chains. With dicarboxylated chains, ENCC can be more highly charged, resulting in higher colloidal stability compared to the general nanocrystalline cellulose [33,34,36,37].

### **1.6 Oxidation of cellulose Nano crystalline**

The oxidation of cellulose Nano crystal (CNC) by sodium periodate ( $\text{NaIO}_4$ ) can generate aldehyde functionality for derivatization, crosslinking reactions or for further modification, which can extend the range of applications of CNC.

CNC could be oxidized by sodium periodate and the effects of reaction conditions on the content of aldehyde groups and yield loss of the oxidized CNC were studied. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and transmission electron microscope (TEM) were applied to characterize the oxidized CNC.

## **1.7 Metal Ions**

Pollution by heavy metals is a serious threat to aquatic ecosystems, because some of these metals are potentially toxic, even at very low concentrations. Additionally, heavy metals are not biodegradable and tend to accumulate in living organisms, and they can cause severe problems to both human health and wildlife [57].

Mining and industrial discharges are major sources for the introduction of significant quantities of metal ions into water [38,39,40,41,42,43]. Besides, emerging massive amounts of electronic waste is another major source of toxic metal ions [44,45]. Metal ions are highly toxic pollutants due to their physiological role in human and other living organisms [46].

The significance of metal ions and their interactions in the ecosystem was recently emphasized by “Metallomics” [47,48]. Metals are categorized into three sets: toxic metals (As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sn, Zn, etc.), precious metals (Ag, Au, Pd, Pt, Ru, etc.), and radio nuclides (Am, Ra, Th, U, etc.) [49].

These metals are often denoted as heavy metals described as metallic elements with a high density and are lethal even at trace concentrations [50]. As, Cd, Hg, and Pb are highly toxic [51,52,53] and are on the top 10 of Toxic Substance and Disease Registry (ATSDR) and WHO's toxic substance lists [54,55, Top ten chemicals]. All metals accumulate in human's internal organs, and excessive concentrations result in adverse reactions and diseases [56].

Example on metal toxicity is cadmium .Over the last decades there has been a sharp rise in the global consumption of cadmium (Cd) for batteries and a steady decline in its use for other applications, such as pigments, polyvinyl chloride stabilizers, and plating. cadmium is one of the most toxic heavy metal in the environment. Exposure to Cd can cause kidney damage in mammals and humans [58, 59]. Cd is also known as human carcinogen and may induce lung insufficiency, bone lesions and hypertension [60]. It causes itai-itai disease which is known to damage the joints, causes bones to soften and the body to shrink, while the affected person dies a painful death [61]. According to World Health Organization (WHO) permissible limits of cadmium for portable and drinking water ranges from 0.001 to 0.002 mg/L. Recently, considerable attention has been paid to the adsorption of  $\text{Cd}^{2+}$  ion using natural polymeric materials as adsorbents in wastewater treatment.

## **1.8 Scope of the study**

In this work cellulose based amine polymer was synthesized. The polymer is water insoluble and carries a functional with high affinity for metals. These properties make it excellent candidate for application in waste water purification. The method of making the polymers comprises converting cellulose powder extracted from olive industry solid waste to dialdehyde using periodate, then converting the aldehyde into imine functional groups by reacting it with diaminobenzene. The amine then will be reduced to amine

### **1.8.1 Objectives**

The specific objectives of this work are:

1. Convert the cellulose powder into cellulose based amine polymers able to strongly bind metals present in waste water and other contaminated sources. This comprises:
  - A. Develop a chemical method to oxidize the cellulose powder to aldehyde polymer.
  - B. Develop a method for converting dialdehyde polymer into imine.
  - C. Convert the cellulose based imine into amine.
  - D. Characterize the new polymers by various spectroscopic techniques.
2. Evaluate the possibility of using the prepared cellulose based amine polymer in waste water purification.

3. Evaluate the effect of various factors such as pH, temperature, amount of adsorbent, concentration and contact time on the adsorption of metal ions.

## **Chapter Two**

### **Experimental**

#### **2.1 Materials and Methods**

##### **2.1.1 Materials**

All reagents used in this study were purchased from Sigma-Aldrich (Jerusalem) and used as received. The chemicals include o-phenylene diamine, sodium borohydride, sodium periodate, methanol, cadmium(II) nitrate, Iron(II) nitrate, acetyl chloride, and triethyl amine.

##### **2.1.2 Methods**

#### **2.2 Characterization**

##### **2.2.1. FTIR and XRD**

Infrared spectra were recorded using a Nicolet 6700 Fourier transform infrared (FT-IR) spectrometer equipped with the Smart Split Pea micro-ATR accessory. The smart Split Peak is a horizontal attenuated total reflectance micro sampling accessory. The accessory has a diamond ATR crystal. The following parameters were used: resolution  $4\text{ cm}^{-1}$ , spectral range  $400\text{-}4000\text{ cm}^{-1}$ , number of scans 64. The crystal structures of the prepared cellulose-based polymers were analyzed using X-ray diffraction (XRD, D8 Advance, Bruker, Germany) with  $\text{Cu K}\alpha$  radiation (40 mA) at a scan rate of  $0.02^\circ\text{ min}^{-1}$ . Atomic emission spectrometer and was used to determine adsorption amount of Fe(III), Cd(II). High-resolution  $^{13}\text{C}$  solid-state NMR spectra for the different samples were recorded using the ramp

$^1\text{H}$ - $^{13}\text{C}$  CP-MAS sequence (cross-polarization and magic angle spinning) with proton decoupling during acquisition, respectively. The  $^{13}\text{C}$  CP-MAS experiments were performed at room temperature in a Bruker Avance-IIIHD 600 spectrometer equipped with a 3.2-mm MAS probe. The operating frequency for protons and carbons was 600.09 and 150.91 MHz, respectively. Glycine was used as an external reference for the  $^{13}\text{C}$  spectra and to set the Hartmann–Hahn matching condition in the cross-polarization experiments in  $^{13}\text{C}$  spectra. The contact time during CP was 2000  $\mu\text{s}$ . The SPINAL64 sequence (small phase incremental alternation with 64 steps) was used for heteronuclear decoupling during acquisition. Metal ion analysis was performed using Thermo Scientific iCAP RQ ICP-MS.Analysis.

### **2.2.2. FES-EM analysis**

The surface morphology of the celluloses was studied by field-emission scanning electron microscope (FE-SEM), double beam Helios Nanolab 650 de FEI Company (Oxford, UK) with detector for EDX analysis.

### **2.2.3 Thermal analysis**

Thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed using a TG/DSC 1 Star System (Mettler-Toledo) coupled with a MS-Thermostar GSD320 (Pfeiffer Vacuum) Mass Spectrometer. TG/DSC curves were measured with Pt crucibles, in  $\text{N}_2$  flow ( $20 \text{ mLmin}^{-1}$ ) with a heating rate of  $5 \text{ }^\circ\text{C min}^{-1}$  in the range 25-1600 $^\circ\text{C}$  by a HT1600 oven connected to a MX5 microbalance

(thermostatic at 22 °C). The process was controlled by STARe software v.10.0 (Mettler Toledo). All samples were air dried in an oven at a temperature of 60 °C for one week to remove the excess of water, mainly in the samples subjected to high humidity conditions

## **2.3. Preparation of Cellulose Derivates**

### **2.3.1. Cellulose aldehyde (1)**

A sample of the activated cellulose (5.0 g, 0.15 mol/anhydrous glucose repeat unit) was suspended in a one liter glass beaker with a 300.0 mL of distilled water. The flask was wrapped completely with aluminum foil to isolate it from light as shown in Figure 2.1, then sodium periodate (16.0 g,  $MM= 213.9 \text{ g/ mol}$ , 0.075 mol) was added in two portions 8.0 g each and 6 hours interval. The reaction mixture was mixed at 40 °C for about 12 h. Produced cellulose aldehyde was collected by filtration washed with water (3×250 mL). Aldehyde content (1.89/ anhydrous glucose repeats unit) was determined according to a reported procedure [62]



**Figure 2.1:** Apparatus for oxidation of cellulose

### **2.3.2 Aldehyde content of (CA)**

Cellulose aldehyde (1.00 g) was placed in a flask and add to it 40.0 mL of isopropanol. The mixture was stirred for 10 min, then to it was added 10.0 mL of distilled water. The mixture was mixed well to form a slurry. The pH value of the mixture was adjusted to 3.5 with 10% HCl solution.

A solution of hydroxylamine hydrochloride (5% by weight solution) in water by dissolving 1.0 g hydroxylamine hydrochloride in 20 g water then the pH value was adjusted to 3.5 using 10% HCl solution.

The two solutions were mixed and stirred for 1 hr and titrate with a 0.5 N NaOH solution until the pH reached 3.5 and stayed constant.

The aldehyde content was then calculated using the following equation:

$$[\text{Ald}] = V_{\text{NaOH}} \cdot 0.5/1.0 \text{ g}$$

Here [Aald] is the aldehyde content in mmol per gram of cellulose,  $V_{\text{NaOH}}$  is the volume of NaOH (mL) used in the titration, N is the normality of the NaOH (eq/L) and W the dry weight of cellulose (g) used in titration.

### **2.3.3. Cellulose o-phenyldiamine polymer (2)**

To a round bottom flask (100 mL) fitted with a magnet stir bar and a reflux condenser cellulose aldehyde (2.0 g, 12.3 mmol of anhydrous glucose repeat unit) was added followed with ethanol (40 mL). 1,2-diaminobenzene (2.6 g, 24.8 mmol) was then added and the reaction mixture was refluxed for about 3 h. Then, it was cooled to room temperature, and to it was added excess sodium borohydride (0.3 g). The reaction mixture was stirred at room temperature for 8 hours. Then treated with a solution of ammonium chloride (0.5%) to destroy excess sodium borohydride. Produced cellulose amine polymer was filtered and washed with water, ethanol and dried.

## **2.4. Adsorption study**

The adsorption of all studied solutions was measured by Flame Atomic Absorption at 193.7 nm to determine residual metal ions concentration. All analysis studies were performed in triplicate and the mean of the three runs

was reported. The error range in the experimental data were analyzed using Excel Microsoft software, a certainty interval of 95% was used. The data analysis was performed using the t-test. All variations were considered statistically when  $p < 0.05$  for the analysis of t-test.

The amount of metal ions adsorbed by the cellulose amine adsorbent  $q_e$  (mg/g) and adsorbent efficiency was determined according to Equations. 1 and 2.

$$R (\%) = \frac{C_0 - C_e}{C_0} 100 \quad (1)$$

$$Q_e = \frac{C_0 - C_e}{m} V \quad (2)$$

$C_0$  and  $C_e$  are the initial and equilibrium concentration (ppm) of metal ion in solution,  $q_e$  (ppm) is the equilibrium adsorption capacity,  $W$  is the weight of the adsorbent (mg), and  $V$  is the volume of the solution (L).

#### **2.4.1 Optimum adsorbent dosage for adsorption of Cd(II) & Fe(III):**

Stock solutions:

##### **Cadmium (II)**

A stock solution 1000 ppm Cd(II) was prepared by dissolving 2.7 g of cadmium (II) nitrate (MM = 308.48 g/mol, contains have 1.0 g Cd(II) in a 1L deionized water.

### **(III) Iron**

A stock solution 1000 ppm Fe(III) was prepared by dissolving 7.1 g of iron (III) nitrate .nonahydrate (MM = 404 g/mol, contains 1.0 g Fe(III) in a 1L deionized water.

Several solutions (50 mL each) of Cd(II) and Fe(III) with a concentration of 25 ppm were prepared. Different dosage of cellulose amine varying from (0.01g to 0.15 g) were added to the metal ion solutions at a pH value of 6.3. The solutions were stirred in the presence of cellulose amine polymer 1 for 30 min, filtered through a 0.45  $\mu\text{m}$  syringe filter and analyzed for residual metal ions concentration. The dosage that provides lowest residual concentration was chosen as an optimum dosage.

#### **2.4.2 Optimum contact time for adsorption of Cd(II) & Fe(III)**

Several solutions (50 mL each) of Cd(II) and Fe(III) with a concentration of 25 ppm were prepared. To each solution a 0.1 g sample of cellulose amine polymer 2 was added. The solutions were stirred for various periods ranging from 1 to 60 min, filtered through a 0.45  $\mu\text{m}$  syringe filter and analyzed for residual metal ions concentration. The contact time that provides lowest residual metal concentration was chosen as an optimum contact time.

### **2.4.3 Optimum pH value on metal ions adsorption**

Several solutions (50 mL) of Cd(II) and Fe(III) with 25 ppm concentration were prepared. The pH of the solutions was adjusted to the desired value (2.3 to 10.0) using diluted solutions of HCl (0.1M) or NaOH (0.1M). Then a 0.1 g of the cellulose amine polymer **2** was added to the each of the metal solutions and the mixtures were shaken for 15 min at room temperature, filtered through a 0.45  $\mu\text{m}$  syringe filter and analyzed for residual metal ions concentration. The pH value that provides lowest residual metal concentration was selected as an optimum pH for metal ions adsorption.

### **2.4.4 Optimum temperature for adsorption of Cd(II) & Fe(III):**

Several solutions (50 mL) of Cd(II) and Fe(III) with 25 ppm concentration were prepared. The pH of the solutions was adjusted to 6.3 using diluted solutions of HCl (0.1M) or NaOH (0.1M). Then a 0.1 g of the cellulose amine polymer **2** was added to the metal solutions. The produced mixtures were shaken for 30 min at various temperatures ranging from room to 40  $^{\circ}\text{C}$ , filtered through a 0.45  $\mu\text{m}$  syringe filter and analyzed for residual metal ions concentration. The temperature that provides lowest residual metal concentration was selected.

#### **2.4.5 Optimum initial concentration of metal ions**

Several solutions (50 mL each) of Cd(II) and Fe(III) with various concentrations ranging from 10 ppm to 50 were prepared. The solutions pH values were adjusted to 6.3, then 0.1 of the cellulose amine polymer **2** was added to each solution. Produced mixtures were stirred for 30 min at 25 °C, filtered through a 0.45 µm syringe filter and analyzed for residual metal ions concentration.

#### **2.5. Wastewater purification**

A sample of sewage water collected from the sewage system (Nablus-Palestine) was used in this study. The sample was subject to analysis by ICP-AES (the analysis was performed by the Water Center at An-Najah National University, Nablus, Palestine) to determine the metals content and their concentrations. Two 50.0 mL samples of the sewage water were placed in two Erlenmeyer flasks and their pH values were adjusted 6.3 and 8.3. To each sample was added 0.1 g of the cellulose amine polymer **2**. The mixtures were shaken at room temperature for 30 min. A sample of each mixture was withdrawn with a syringe and pushed through a 0.45 µm syringe filter and subjected to analysis by ICP-AES for residual metal ions concentrations.

## 2.6. Kinetic studies

### 2.6.1. Adsorption isotherm

The adsorption behavior of Cd(II) and Fe(III) molecules on the crosslinked cellulose amine polymer surface was determined by applying the isotherm models Langmuir, Freundlich and Redlich Peterson isotherms [76].

Langmuir isotherm model:

$$\frac{C_e}{Q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max}K_L} \quad (3)$$

Where  $C_e$  is the equilibrium concentration of metal ion (ppm),  $Q_e$  is the amount of adsorbate adsorbed per unit mass of cellulose amine at equilibrium (mg/g),  $Q_{max}$  is the theoretical maximum monolayer adsorption capacity of the adsorbent (mg/g), and  $K_L$  is the Langmuir isotherm constant related to the adsorption energy (L/mg).

Freundlich isotherm model:

$$\ln(q_e) = \ln k_f + \frac{1}{n} \ln C_e \quad (4)$$

where  $K_F$  and  $1/n$  are empirical constants that indicate the relative adsorption capacity and intensity related to the affinity of the metal, respectively [76].

From Langmuir isotherm model, it could be also predicted if the adsorption is favorable or not using the dimensionless constant separation factor shown in Eq.5.

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

Where  $K_L$  is the Langmuir constant and  $C_0$  is the initial adsorbate concentration. If  $R_L$  value greater than 1, means the adsorption is unfavorable. But if the value of  $R_L$  is between 1 and 0, then the adsorption is favorable, and  $R_L = 1$  means linear adsorption.

Freundlich isotherm (Eq. 6) represents the non-ideal adsorption that includes heterogeneous surface energy system.

$$Q_e = K_F C_e^{1/n} \quad (6)$$

Where  $K_F$  ( $L \text{ mg}^{-1}$ ) is the Freundlich constant,  $1/n$  is the adsorption intensity and if  $1/n$  is  $> 0.1$  and  $< 0.5$  then the adsorption is favorable, for  $1/n$  value higher than 2 means unfavorable.

### 2.6.2. Adsorption Kinetics

Pseudo-first-order and pseudo-second-order kinetic models were employed to investigate the adsorption rates to determine adsorption mechanism of the metal ions Cd(II) and Fe(III) on cellulose amine surface. The linearized forms of the rate equations [77], were estimated according to Equations. 7 to 10.

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

$$Q_t = K_{id} t^{1/2} + Z \quad (9)$$

$$\ln \frac{K(T_2)}{K(T_1)} = \frac{Ea}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (10)$$

Where  $Q_e$  and  $Q_t$  are adsorption capacities (mg/g) at equilibrium and at various time (t, min).  $K_1$  is the pseudo-first-order rate constant ( $\text{min}^{-1}$ ),  $K_2$  is the pseudo-second-order rate constant (g/ mg.min). The  $K_{id}$  is the intra-particle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ) and  $Z$  (mg/g) could be used to conclude the thickness of the boundary layer.

The Gibbs energy ( $\Delta G_0$ ), enthalpy ( $\Delta H_0$ ) and entropy ( $\Delta S_0$ ) were calculated according to the following equations:

$$K_c = C_{ads}/C_e \quad (11)$$

$$\Delta G^0 = -RT \ln K_c \quad (12)$$

$$\ln K_s = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (13)$$

where  $K_c$  is an apparent constant of the thermodynamics;  $C_{ads}$  is the adsorbed amount at equilibrium, mg/L;  $C_e$  is the equilibrium concentration in the aqueous solutions of metal ions, mg/L;  $R$  is the universal gas constant, J/mol K;  $T$  is the solution temperature, K [76].

## 2.7 Acetylation of cellulose polymer 2

The reaction was carried out in a round bottom flask fitted with a reflux condenser and a stirrer placed under nitrogen gas. In the flask 1.0 g of cellulose amine polymer was suspended in 20 mL dichloromethane. To it was added 0.5 mL of triethyl amine and 1.0 mL of acetyl chloride. The mixture stirred for 1.0 hr at room temp. The reaction mixture was quenched with water and product collected by suction filtration was washed with a solution of sodium bicarbonate (1%) and water then dried.

## Chapter Three

### Results & Discussion

#### 3.1. Characterization of the cellulose aldehyde and cellulose amine polymer.

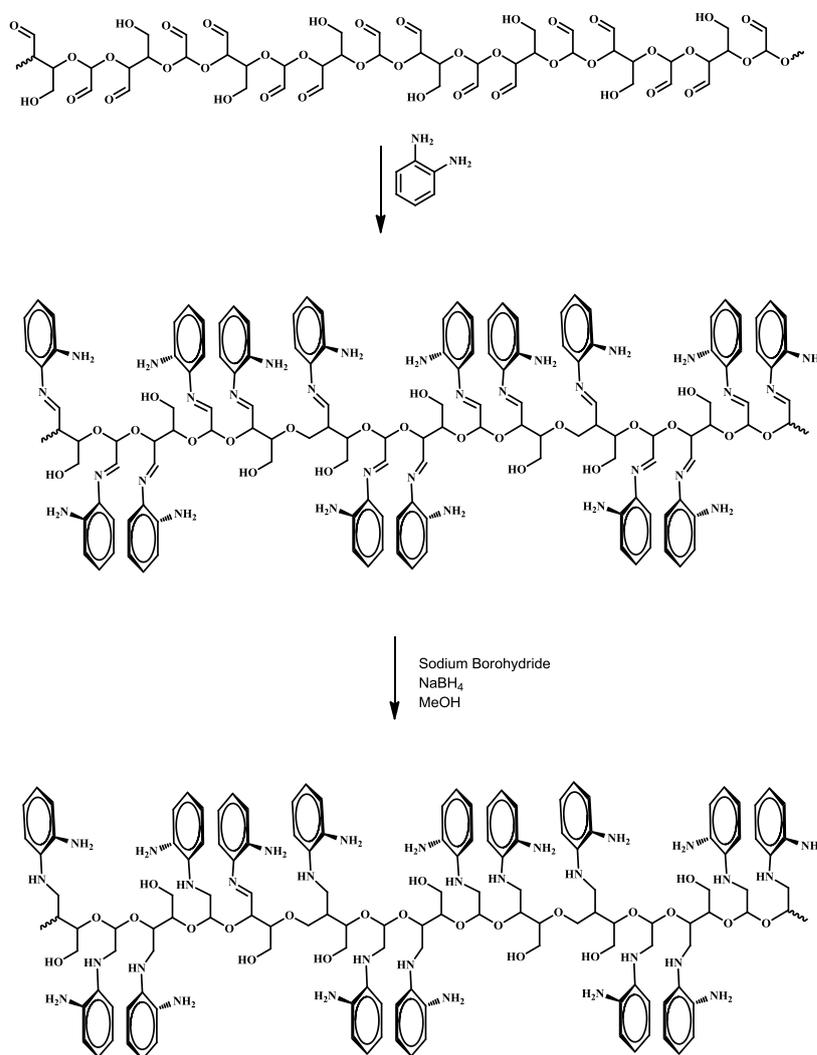
Cellulose powder was extracted from olive industry solid waste following a process of pulping and bleaching reported in the literature [63,64]. The produced cellulose powder was oxidized to cellulose aldehyde by reacting it with sodium periodate (Figure 3.1) following a published procedure [65].

The reaction was performed under neutral condition at 40 °C for 12 hr. The progress of oxidation of cellulose was followed by UV spectroscopy. A certain period of time, a sample of the reaction mixture was withdrawn and its absorbency at 295 nm was measured. Since at this wavelength the periodate absorbs.

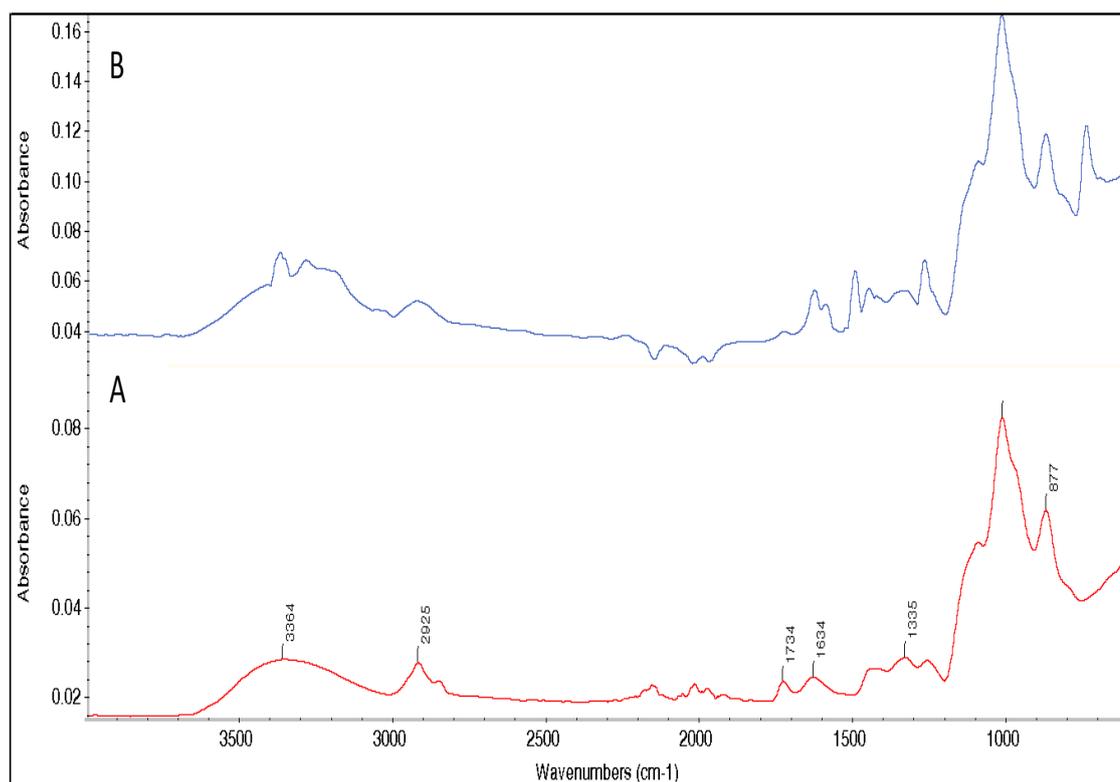
##### 3.1.1 FT-IR Results

The FT-IR spectrum of the oxidized celluloses is shown in (Figure 3.2A). The most significance peaks for CDA were observed at 1732, 1610, 1510, 1425  $\text{cm}^{-1}$  assigned to the typical C=O (aldehyde), C=C (aromatic), skeletal vibrations and with the C-H in plane deformation of the aromatic moiety inserted in the cellulose structure, respectively. The weak band at 1732  $\text{cm}^{-1}$  is due to the hydration and acetal formation [66].

The FT-IR spectra of cellulose amine polymer **2** (Figure 3.2B) shows two peaks at  $1610\text{ cm}^{-1}$ , and  $1635\text{ cm}^{-1}$  corresponding to primary amine and aromatic C=C. The broad adsorption peak at about  $3350\text{ cm}^{-1}$  actually is composed of several peaks originated from O-H or N-H stretching vibrations of primary and secondary amines. The IR spectrum also shows a peak at  $2930\text{ cm}^{-1}$  that could be attributed to the symmetric and asymmetric stretching vibration of the C-H bond



**Figure 3.1.** A representative scheme shows the molecular structures of and products and reaction condition.

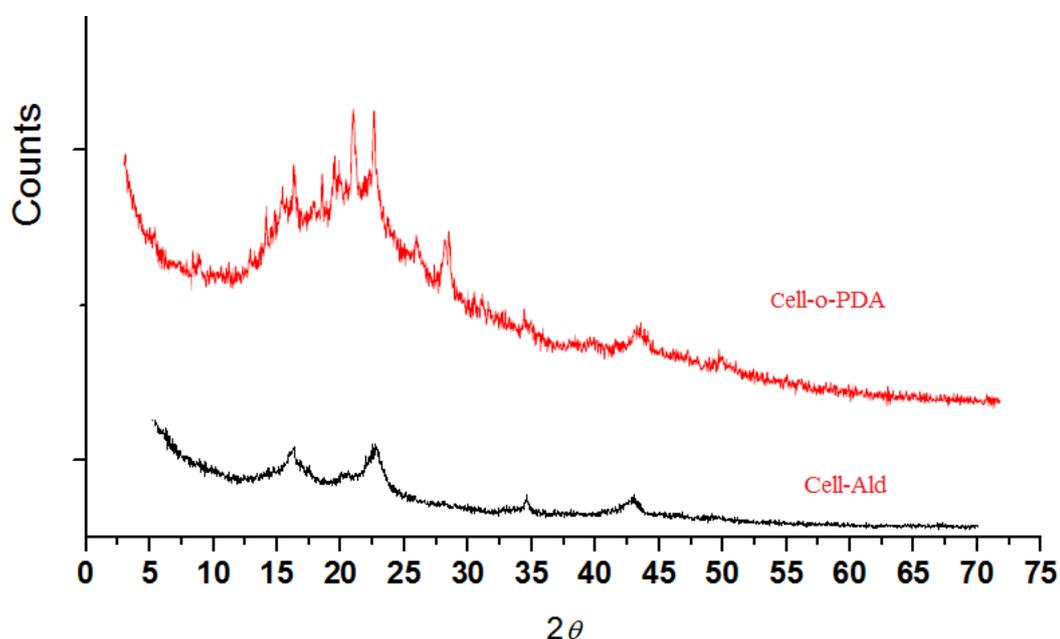


**Figure 3.2**A) FT-IR spectrum of cellulose aldehyde and **B)** FT-IR spectrum of cellulose amine polymer **2**

### 3.1.2 X-ray Diffraction results

The X-ray diffraction patterns of cellulose aldehyde and cellulose amine polymer **2** are shown in Figure 3.3. The intensity of the crystalline peaks at  $2\theta = 16$  and  $32$  in cellulose aldehyde broaden with some shift in their values. This could be an indication for a loss of crystallinity. The loss of crystallinity was attributed to the ring opening of glucopyranose which causes a disruption and loss of H-bonding and consequently a loss of crystallinity [65,67].

The XRD of cell-o-PDA shows the cellulose crystallinity completely change as new compound merged.

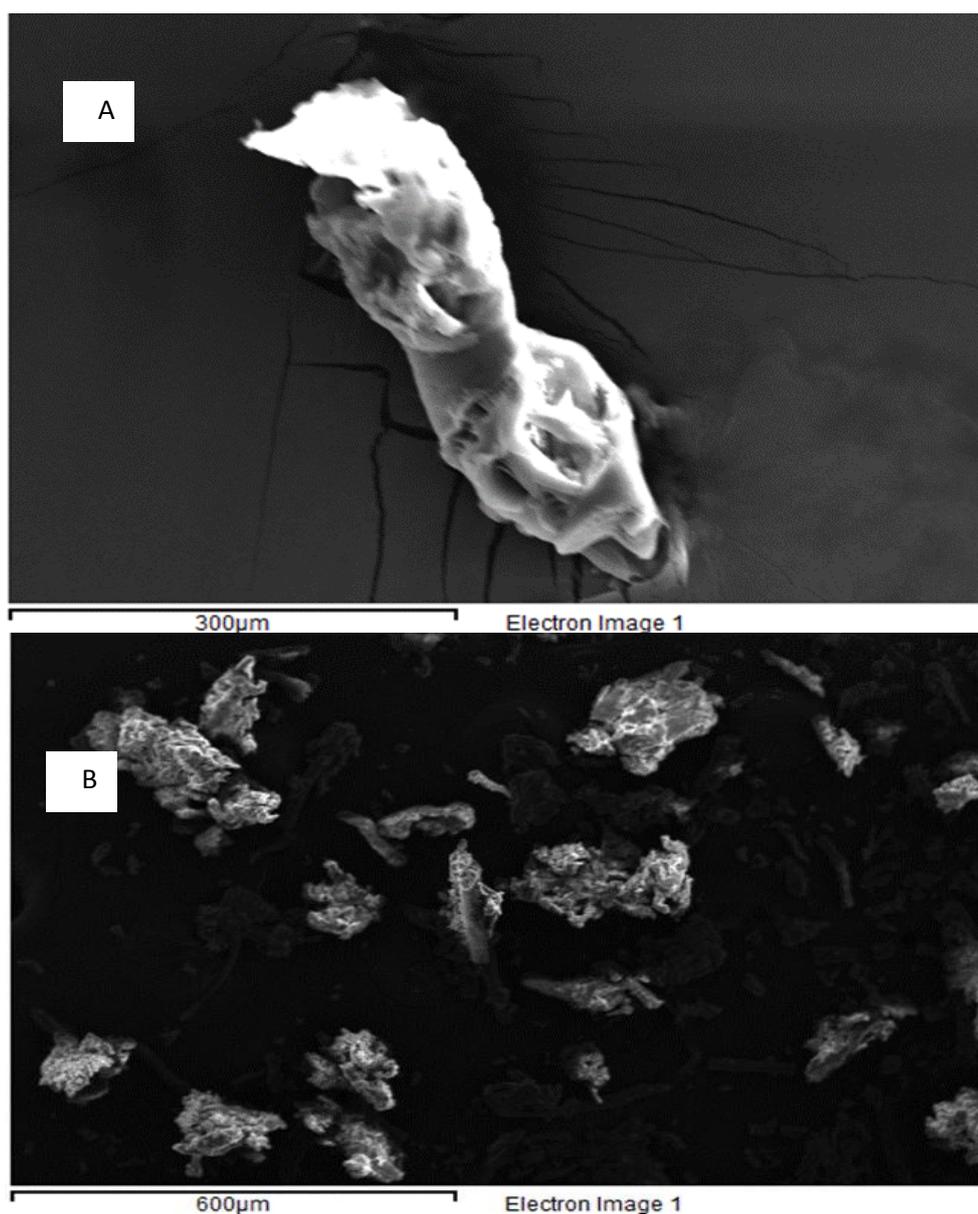


**Figure 3.3:** XRD spectra of cellulose aldehyde and cell-o-phenylene diamine.

The aldehyde carbonyl group has an electrophilic carbon, it undergoes condensation reaction with a nucleophile such as amine to form an imine after the loss of a water molecule. Reduction of the cellulose imine with sodium borohydride produces cellulose amine as shown Figure 3.1. Produced amine has several coordination sites for metal ions including amines, hydroxyl and aromatic functionalities. A representative molecular structure of cellulose amine polymer **2** is shown Figure 3.1.

### 3.1.3 Morphology analysis

SEM images of cellulose aldehyde and cell-o-PDA prepared from it are shown in Figure 3.4, the cellulose aldehyde image shows clearly that, the cell structure has been damaged. The image of cell-o-PDA shows a high porous spongy type of morphology.



**Figure 3.4:** SEM images of A) Cellulose aldehyde and B) Polymer 2 at magnifications of 250× and 50×, respectively.

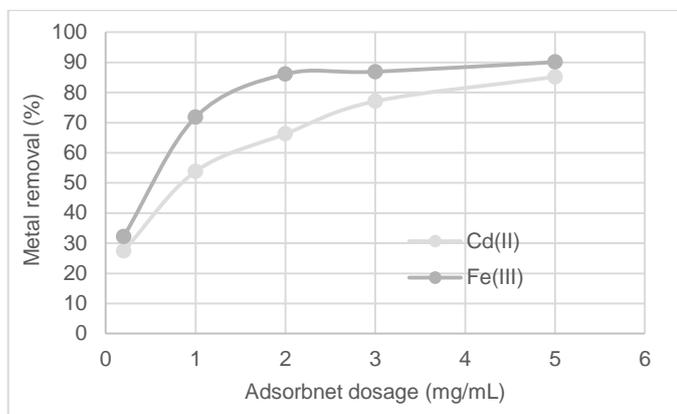
### **3.2. Metal ions extraction**

The extraction was carried out using a batch adsorption process, in this process a known weight of Cell-o-PDAm polymer was suspended in an aqueous solution of metal ions, then filtration and analysis. The analysis was performed on the filtrate to determine the concentration of extracted ions. The effect of several variables such as adsorbent dosage, extraction time, temperature and pH were evaluated to determine best conditions for the highest adsorption efficiency. The adsorption study was performed on cadmium and iron ions.

#### **3.2.1. Optimum adsorbent dosage for adsorption of Cd (II) &Fe (III):**

The dosage that provided the lowest residual concentration of metal ions was chosen as an optimum dosage. This was achieved by performing the experiment on 50 mL of each Fe(III) and Cd(II) with a concentration of 30 ppm, pH value of 6.3, adsorption time of 30 min and at room temperature. The effect of the adsorbent dosage on the removal of Fe(III) and Cd(II) ions is shown in Figure 3.5. As shown in the figure, the amount of metal extracted increased by increasing the polymer dosage. Metal ion removal reached about 67.8 and 88.1% for Cd(II) and Fe(III) respectively at 2.0 mg/ml of dose of cellulose amine polymer, at dose higher than 2.0 mg/mL it became almost constant. This could be because the adsorption process is controlled by two mechanisms, diffusion and surface coordination. As the dosage increase number of available binding sites increase, so the ion removal increases. When all site on the surface are

occupied the diffusion process starts, which is controlled by osmosis, when the concentration of metal ion adsorbed by polymer equal to that in the solution the adsorption stops [68].

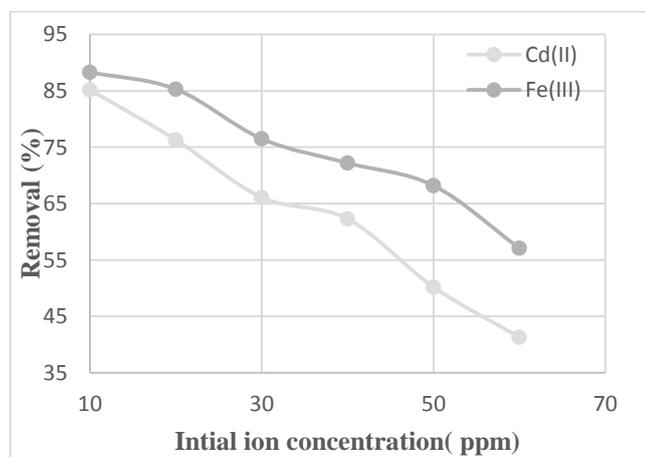


**Figure 3.5.** Effect of adsorbent dose on adsorption of Cd(II) & Fe(III)

### 3.2.2. Effect initial ion concentration

The effect of the initial ion concentration on adsorption efficiency was evaluated under the following adsorption conditions: adsorption time 30 min, adsorbent dose 2.0 mg/mL and pH 6.3. Since at this pH value, the amines functional groups are in Lewis base form. As shown in Figure 3.6, the highest removal was at 10 ppm concentration, at this concentration the % of ions removal reached 88.3% and 83.2% for Fe(III) and Cd(II), respectively. At concentration, higher than 10 ppm starts to decline gradually. The results indicate that, at low concentration of metal ion, the driving forces for adsorption is controlled by the ion diffusion [69]. At high concentration, the availability of the binding sites was the driving force, and they are controlled by the adsorbent dosage. According to the obtained results, at a concentration of about 10 ppm, the binding site are almost

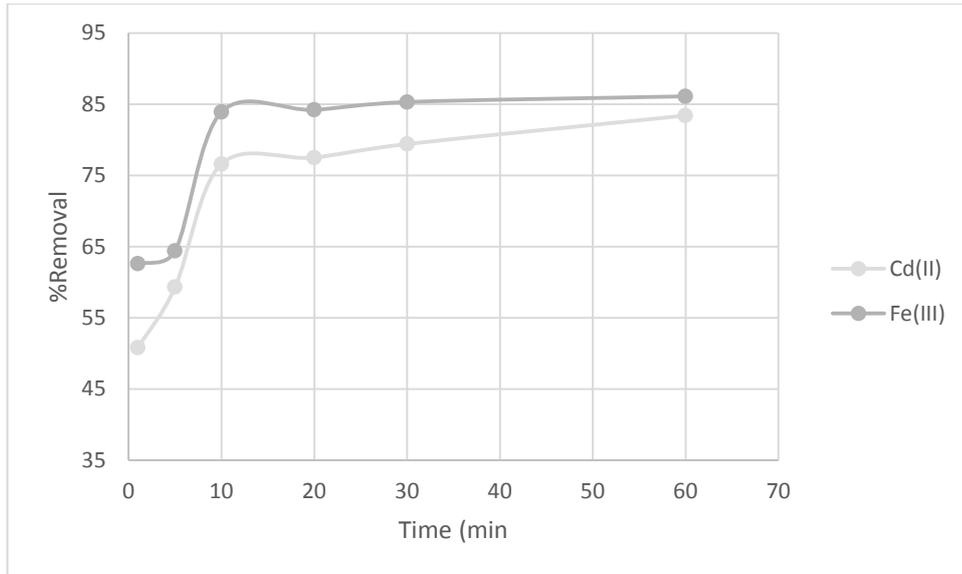
saturated for this reason, at a concentration higher than 10 ppm, the rate of metal removal decreased.



**Figure 3.6:** Effect of initial concentration for adsorption of Cd (II) &Fe (III)

### 3.2.3. Effect contact time on adsorption of Cd (II) &Fe (III)

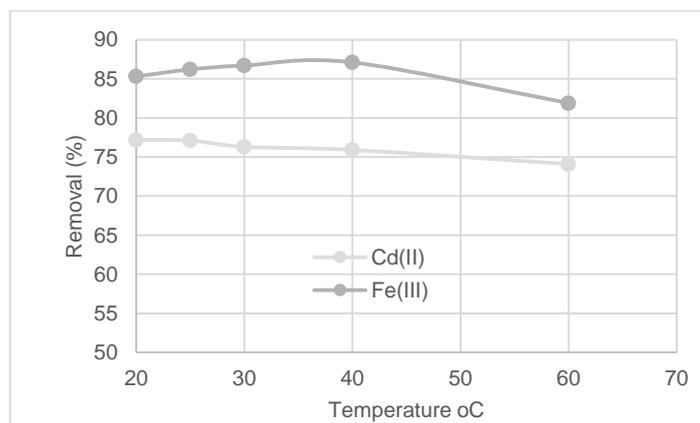
Adsorption of the metal ions Cd(II) and Fe(III) by cellulose maine polymer **2** as a function of time was evaluated under conditions of pH 6.3, initial ion concentration 20 ppm, adsorption temperature 25 °C and adsorbent dose 2.0 mg/mL. Results are shown in Figure 3.7, as shown in the figure, the adsorbed metal ions increased rapidly for the first 40 min due to the availability of the binding sites. Then adsorption rate became almost constant for the next 20 min, so it reached the equilibrium after 40 min. The results indicate that, at this period almost all coordination sites are occupied [70]. A contact time of 40 min was chosen as the optimum contact time. The two ions showed almost similar adsorption behavior with time.



**Figure 3.7:** Effect of contact time on adsorption of Cd (II) &Fe (III)

### 3.2.4. Effect of Temperature on adsorption of Cd (II) &Fe (III)

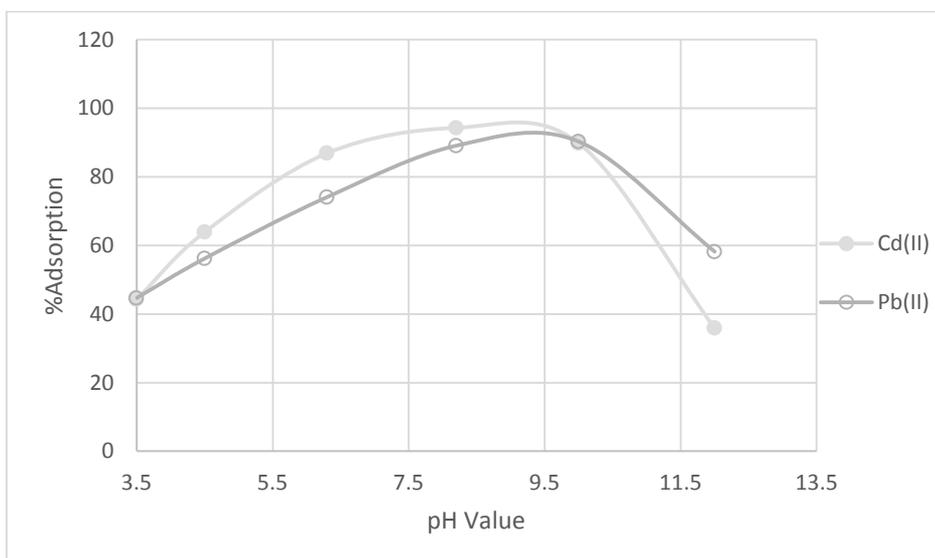
The effect of temperature on adsorption of metal was evaluated under conditions of pH 6.3, initial metal ion concentration 30 ppm, adsorption time 40 min and adsorbent dose 2.0 mg/mL (Figure 3.8). The adsorption efficiency showed no dependence on temperature. Up to about 60 °C, the adoption efficiency was almost constant.



**Figure 3.8:** Effect of temperature on adsorption of Cd (II) &Fe (III)

### 3.2.5. Effect of pH on adsorption of Cd(II) & Fe(III)

The effect of adsorption efficiency as a function of pH value is shown in Figure 3.9. The pH value is critical factor in metal adsorption, since with the pH value, the surface charge of the polymer could be controlled. At low pH value (3.0 or lower) the amine is in the salt form ( $-\text{NR}_2\text{H}_2^+$ ). For this reason, the adsorption efficiency was the minimum (about 20%). However, at pH value higher 3.0 the N lone pair of electron on amine N becomes more available, causing the amine group to behave as a metal binding agent. The highest efficiency was observed at pH 8.6. At higher pH value, the adsorption efficiency started to decline. The formation of metal oxide at pH value higher than 9.0 could be the reason for decreasing in the adsorption efficiency.



**Figure3.9:** pH on the metal removal by cellulose amine polymer 2.

### **3.3. Wastewater purification from metals**

Sewage water is waste water from people living in a community. It is the water released from households after use for various things like washing dishes, laundry, and flushing the toilet, thus the name wastewater. The used water moves from the houses through pipes installed during plumbing. The sewage water then moves into sewers, either constructed by the house owner, or into a sewer facility set up by the municipality.

Mostly, sewage water consists of grey water and black water. Grey water is the waste water from washing either from bathing, dishes or laundry. Black water is the waste water from toilets. It is characterized by debris such as paper wrappings, sanitary products, soap residues, and dirt due to the chemical composition of the various waste materials. Plus, sewage water has a foul smell.

Sewage is generated by residential, institutional, commercial and industrial establishments. It includes household waste liquid from toilets, baths, showers, kitchens, and sinks draining into sewers. In many areas, sewage also includes liquid waste from industry and commerce. The separation and draining of household waste into grey water and black water is becoming more common in the developed world, with treated grey water being permitted to be used for watering plants or recycled for flushing toilet.

Sewage is a complex mixture of chemicals, with many distinctive chemical characteristics. These include high concentrations of ammonium, nitrate, nitrogen, phosphorus, high conductivity (due to high dissolved solids), high alkalinity, with pH typically ranging between 7 and 8. The organic matter of sewage is measured by determining its biological oxygen demand (BOD) or the chemical oxygen demand (COD).

In general, cellulose amine polymer **2** was proved to be a good adsorbent for many metals in sewage water at pH 7 & 10, but it was noticed that results at pH 10 are better than at pH 7 that probably due to adsorption sites are more.

A sample of wastewater collected from sewer was treated with cellulose amine polymer **2**. A photo of the wastewater sample before and after treatment is shown in Figure 3.10. The metal content of the sample before purification and after are summarized in Tables 3.1. The results show that, the polymer **2** has excellent efficiency toward most of the metals present in the wastewater sample, the removal exceeded 90% for several of them.



**Figure 3.10:** Images of waste water sample before and after treatment with cellulose polymer **2**

**Table 3.1: Effect of amine polymer on adsorption metals from sewage water**

Metal	Conc. Before purification	Conc. After purification at pH7	Conc. After purification at pH10	% of extraction at pH7	% of extraction at pH10
Ag	38.158	0.635	0.947	98.34	97.52
Al	4679.423	52.229	129.751	98.88	97.22
Be	0.137	0.029	0.014	78.83	89.78
Bi	1.689	0.644	0.213	61.87	87.39
Cd	0.688	0.070	0.133	89.83	80.67
Cr	522.738	43.036	27.481	91.77	94.74
Co	12.445	1.074	0.979	91.37	92.13
Cs	0.312	0.130	0.277	58.33	11.22
Cu	103.121	2.297	3.491	97.77	96.61
Fe	8156.470	382.911	268.854	95.31	96.70
Ga	2.407	0.480	0.183	80.06	92.4
In	0.025	0.003	0.023	8	8
Li	6.751	5.352	5.441	20.72	19.40
Mn	167.490	25.284	3.905	84.90	97.67
Mo	9.720	2.405	2.681	75.26	72.42
Ni	43.061	10.907	10.846	74.67	74.81
Pb	25.813	1.607	1.573	93.77	93.91
Rb	35.393	20.731	22.204	41.43	37.26
Sr	609.275	231.678	107.354	61.97	82.38
V	16.976	1.361	1.585	91.98	90.66
Zn	696.221	19.347	27.951	97.22	95.99
Ba-1	186.907	54.037	17.432	71.1	93.37

### 3.4. Adsorption analysis

Langmuir (Eq.3.3) and Freundlich isotherm (Eq.3.4) [71,72] were used to evaluate the distribution of metal ions on the surface of cellulose amine polymer **2** after reaching the equilibrium at constant temperature. Langmuir model assumes the formation of monolayer of adsorbate on a homogeneous surface of adsorbent [73]. However, Freundlich model describes the adsorption between adsorbate molecule and the adsorbent with heterogeneous surface.

$$\text{Langmuir isotherm model: } \frac{C_e}{Q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max}K_L} \quad (3.3)$$

Where  $C_e$  is the equilibrium concentration of metal ion (ppm),  $Q_e$  is the amount of adsorbate adsorbed per unit mass of cellulose amine at equilibrium (mg/g),  $Q_{max}$  is the theoretical maximum monolayer adsorption capacity of the adsorbent (mg/g), and  $K_L$  is the Langmuir isotherm constant related to the adsorption energy (L/mg).

$$\text{Freundlich isotherm model: } \ln(q_e) = \ln k_f + \frac{1}{n} \ln C_e \quad (3.4)$$

where  $K_F$  and  $1/n$  are empirical constants that indicate the relative adsorption capacity and intensity related to the affinity of the metal, respectively.

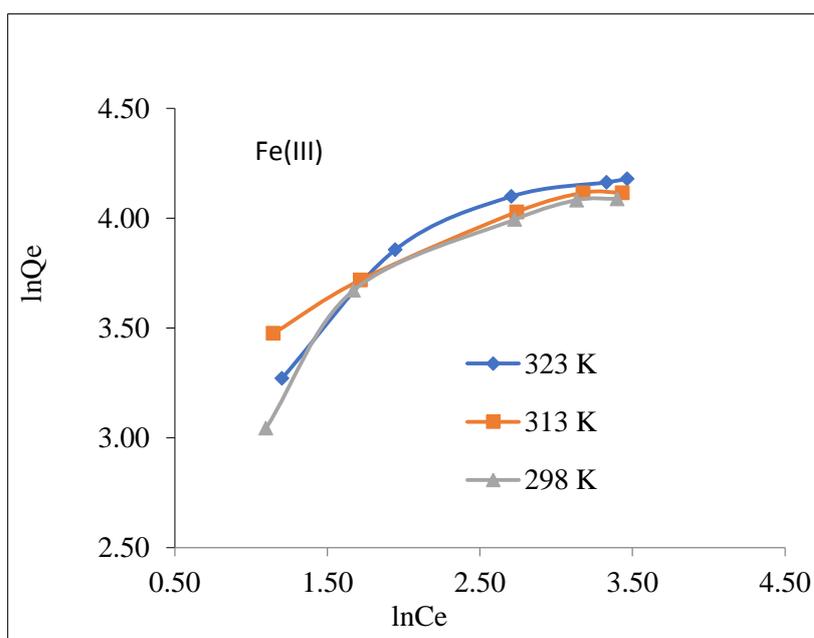
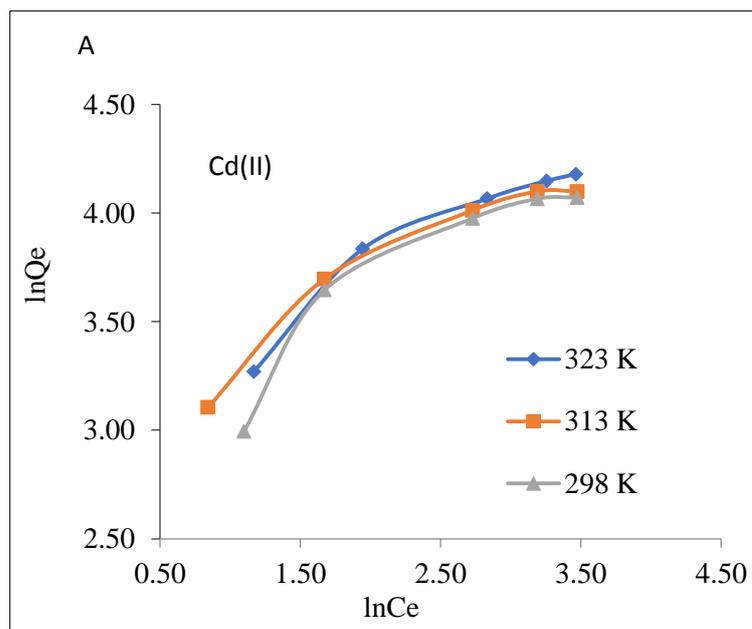
From Langmuir isotherm model, it could be also predicted if the adsorption is favorable or not using the dimensionless constant separation factor shown in Eq. 5.

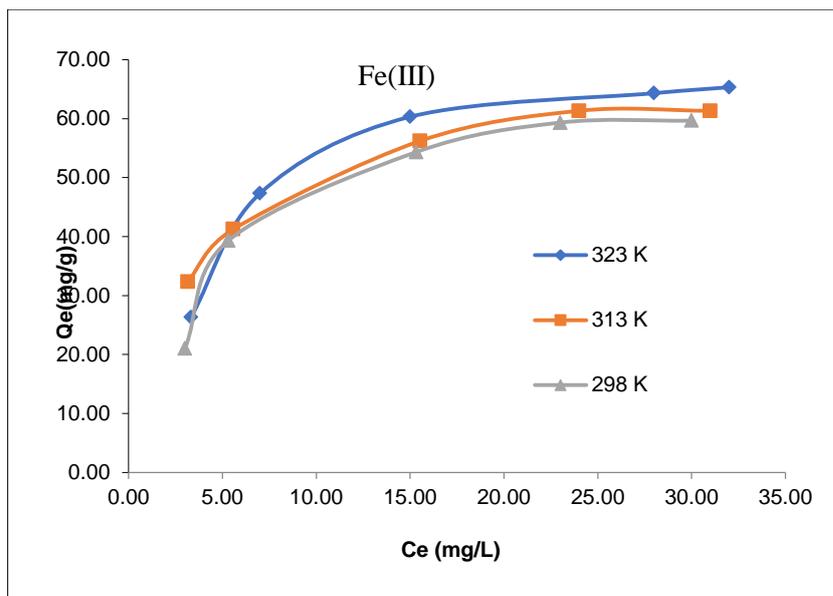
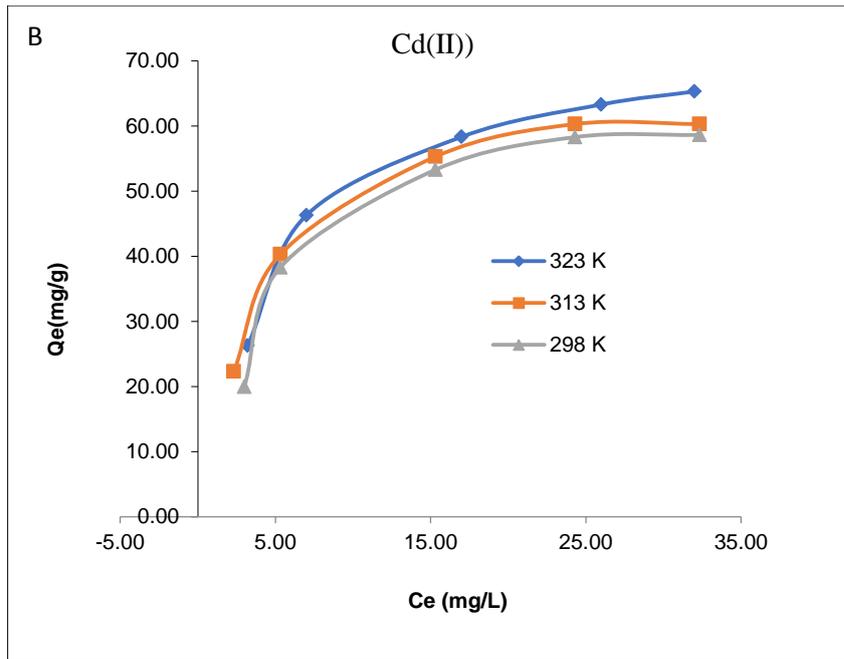
$$R_L = \frac{1}{1 + K_L C_0} \quad (3.5)$$

Where  $K_L$  is the Langmuir constant and  $C_0$  are the initial adsorbate concentration. If  $R_L$  value greater than 1, then the adsorption is unfavorable. But if the value of  $R_L$  is between 1 and 0, then the adsorption is favorable, and  $R_L = 1$  means linear adsorption.

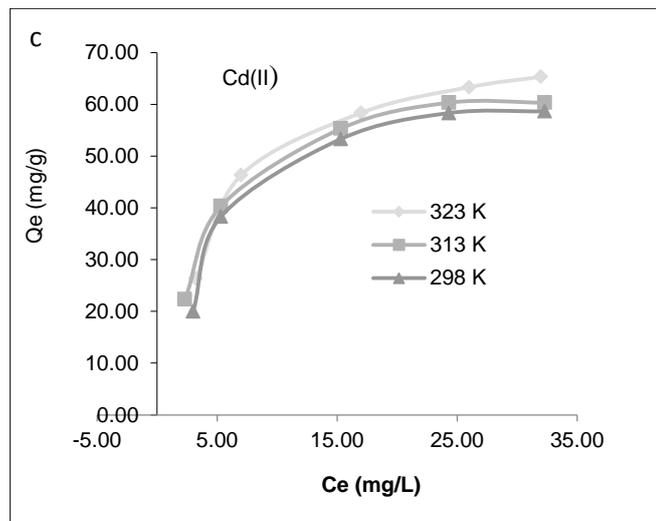
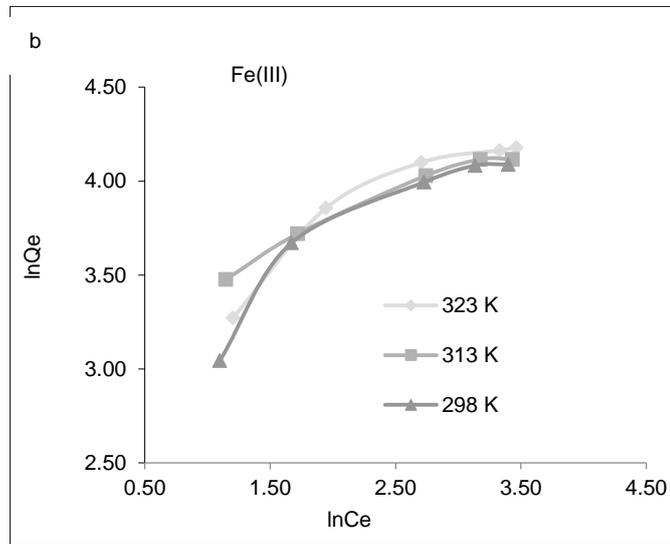
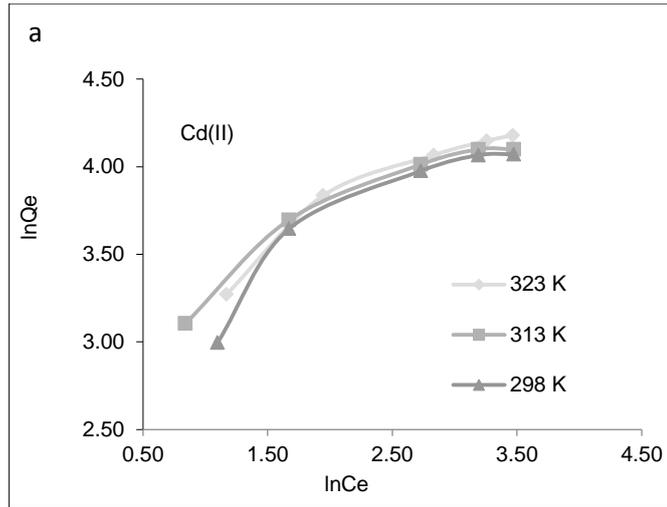
All fitting parameters are summarized in Table 3.2 and Figure 3.11, the correlation coefficients for the Langmuir isotherm model (Table 3.3) are much higher than those for the Freundlich isotherm model, indicating that, the adsorption of Cd(II) and Fe(III) ions follows Langmuir isotherm model

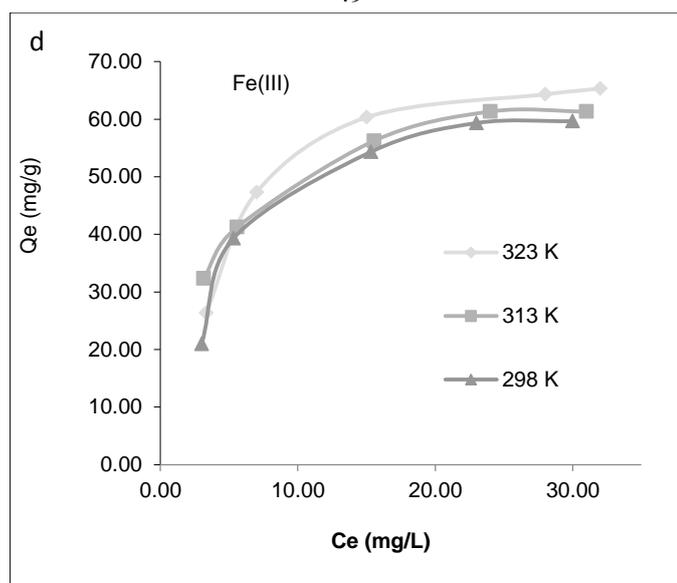
(3.4), where the Cd and Fe ions are equally and homogeneously spread over the cellulose amine polymer **2** porous surfaces. The separation factor  $R_L$  which was calculated for various amounts of adsorbents of polymer **2** polymer was  $0 < R_L < 1$  (Table 3.2). The  $R$  values are much smaller than 1, indicating the high affinity of cell-o-PDAm for Cd(II) and Fe(III).





**Figure3.11:** A) Langmuir and B) Freundlich adsorption model of Cd(II) and Fe(III) ions on polymer 2 at various temperatures.





**Figure 3.11:** Langmuir of (a) Cd(II) and (b) Fe(III); Freundlich adsorption model of (c) Cd (II) and (d) Fe(III) ions on cellulose polymer 2 at various temperatures

**Table 3.2: Langmuir and Freundlich Parameters for the Adsorption of Cd<sup>2+</sup> and Fe(III) Ions by cellulose amine polymer 2**

		Fe(III)			Cd(II)		
Temperature (K)		298	313	323	298	313	323
Langmuir Isotherm	$Q^0$ (mg/g)	2.3792	2.7137	2.6616	2.3873	2.1645	2.3873
	$K_L$ (L/mg)	0.1540	0.1259	0.1274	0.1050	0.1112	0.105
	$R_L$	0.01282	0.01563	0.01545	0.01869	0.01754	0.01869
	$R^2$	0.8705	0.9176	0.9178	0.9607	0.8771	0.967
Freundlich Isotherm	1/n	0.9016	0.6095	0.8466	0.9108	0.7149	0.824
	$K_F$ (L/mg)	21.3427	29.7967	24.229	20.4750	26.222	24.366
	$R^2$	0.9507	0.995	0.9543	0.945	0.9867	0.9762

### 3.5 Kinetics Adsorption

The two kinetic models, pseudo-first-order (Eq. 3.7) and pseudo-second-order (Eq. 3.8), were used to determine the adsorption process, comprising of the adsorption rates and adsorption mechanism of the metal ions Cd(II) and Fe(III) onto the surface of cellulose amine polymer 2:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (3.7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3.8)$$

In addition, the intra-particle diffusion model (Eq. 3.9) was used to determine the rate-determining step during the metal ion adsorption,

$$Q_t = K_{id} t^{\frac{1}{2}} + Z \quad (3.9)$$

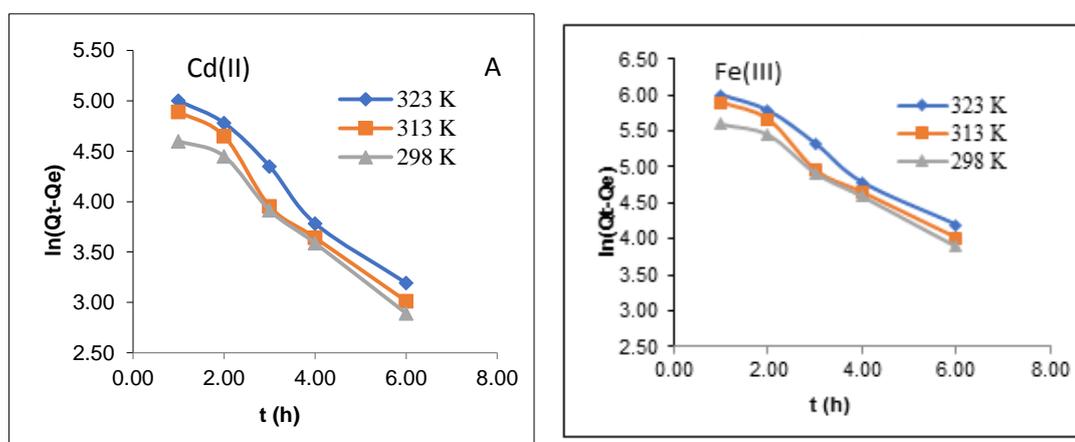
where  $Q_e$  and  $Q_t$  are the adsorption capacities at equilibrium (mg/g),  $t$  is the various times(min),  $K_1$  is the pseudo-first-order rate constant (1/min),  $K_2$  is the pseudo-second-order rate constant(g/ mg min),  $K_{id}$  is the intra-particle diffusion rate constant (mg /gmin<sup>1/2</sup>), and  $Z$ (mg/g) was used to conclude the thickness of the boundary layer.

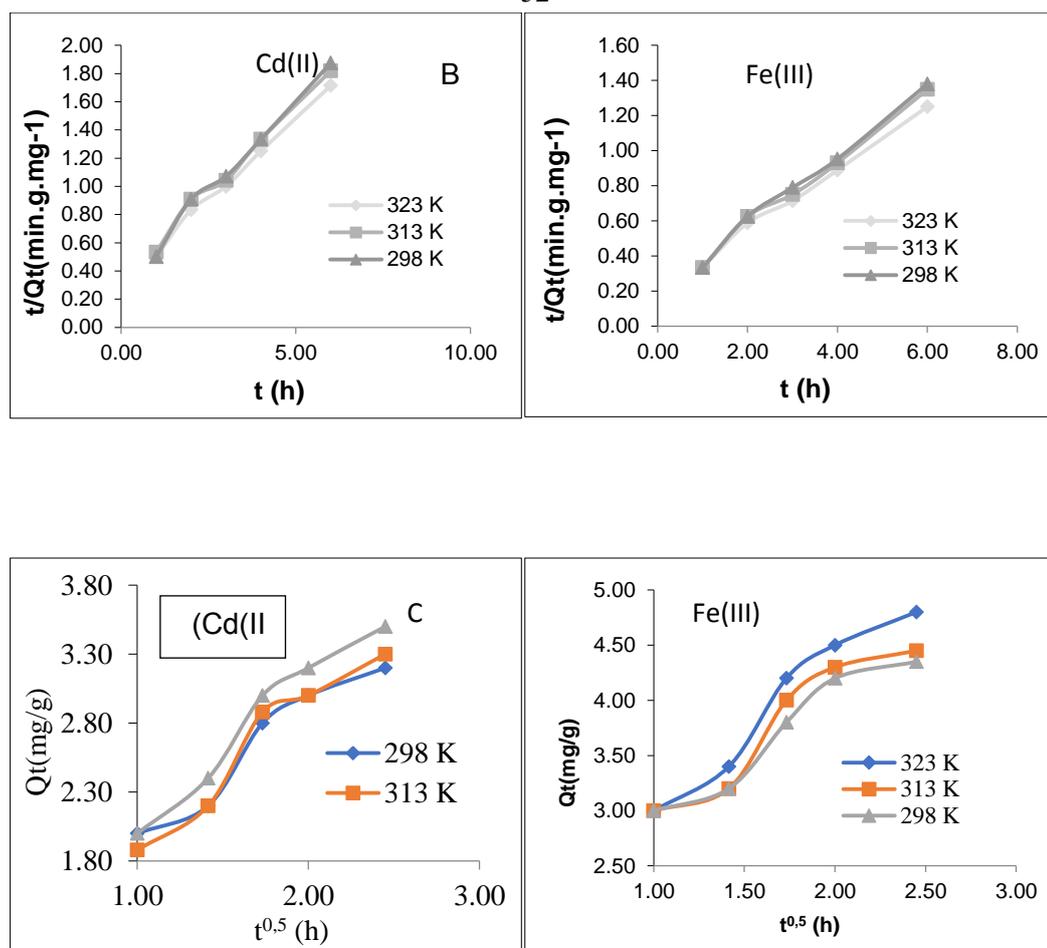
Additionally, the liquid film diffusion model (Eq. 3.10) was employed to investigate if the transport of metal ions from the liquid phase to the solid phase boundary plays a role in the adsorption process,

$$\ln(1 - F) = -K_f dt \quad (3.10)$$

where  $F$  is the fractional attainment of equilibrium ( $F = q_t/q_e$ ),  $q_e$  is the adsorption capacity of the sorbent at equilibrium ( $\text{mg}\times\text{g}^{-1}$ ), and  $K_f$  is the liquid film diffusion constant. A linear plot of  $\ln(1-F)$  versus  $t$  with zero intercept would suggest that the kinetics of the adsorption process was controlled by diffusion from the liquid surrounding the solid sorbent.

The values of all the parameters shown in the above equations are summarized in Table 3.3 and Fig. 3.12. The value of  $K_1$  was obtained by plotting  $\ln(q_e - q_t)$  vs.  $t$  (Fig. 3.12A), while the  $K_2$  values and the adsorption capacity  $q_e$  were calculated from the slope and the intercept of plotting  $t/q_t$  vs.  $t$  (Fig. 3.12 B). The values for  $K_{id}$  and  $Z$  were





**Figure 3.12:** A) Pseudo first-order model for the adsorption of Cd(II) and Fe(III). B) Pseudo-second order model for the adsorption of Cd(II) and Fe(III) ions by cellulose amine polymer 2

obtained from plotting  $q_t$  vs.  $t^{1/2}$  (Fig. 3.12C). When the experimental data was plotted for both the pseudo-first-order and the second-pseudo-order kinetics, the correlation coefficients ( $R^2$ ) for the pseudo-second-order (0.91 to 0.973) were higher than the pseudo-first-order (0.891). The calculated  $q_e$  values (2.675 mg/g, 15.252 mg/g, and 20.856 mg/g) for the pseudo-second-order (see Table 3.3 and Fig. 12B) were close to the experimental  $q_e$  values (2.133 mg/g, 13.91 mg/g, and 18.786 mg/g), indicating that the adsorption process of metal ions on the surfaces of cellulose amine polymer 2 followed the pseudo-second-order.

All plots shown in Fig. 3.12 did not pass through the origin, indicating the presence of more than one rate-determining step in the adsorption processes. From the initial linearity of the graphs shown in Fig. 3.12B, the adsorption process of Cd(II) and Fe(III) ions occurred first *via* an instant adsorption stage (on the exterior surface of cellulose polymer **2**, which resulted in a chemical complexation between the metal ions, amines, and other functionalities [74]. Additionally, the rest of the stages were linear, indicating the gradual adsorption and the intraparticle diffusion rate limiting step of Cd(II) and Fe(III) ions. The values of  $Z$  in Table 3.3 indicate an expansion in the surface layer and a diminished external mass transfer while the potential for internal mass transfer increased.

**Table 3.3:A. The Pseudo-second-order Model for Adsorption of Cd(II) and Fe(III) ions by Cellulose polymer 2.**

T (K)	298			313			323		
	$K_2$ (g/mg ×min)	$Q_{cal}$ (mg/ g)	$R^2$	$K_2$ (g/mg ×min)	$Q_{cal}$ (mg/g)	$R^2$	$K_2$ (g/mg ×min)	$Q_{cal}(m$ g/g)	$R^2$
Fe (III)	0.356	416.	0.986	0.3911	533.5	0.97	0.3814	622.84	0.984
Cd (II)	0.356	152.	0.986	0.3907	196.2	0.98	0.3813	230.67	0.983

**Table 3.3: B.The intra-particle diffusion parameters of Cd(II) and Fe(III) ions onto cellulose amine polymer 2**

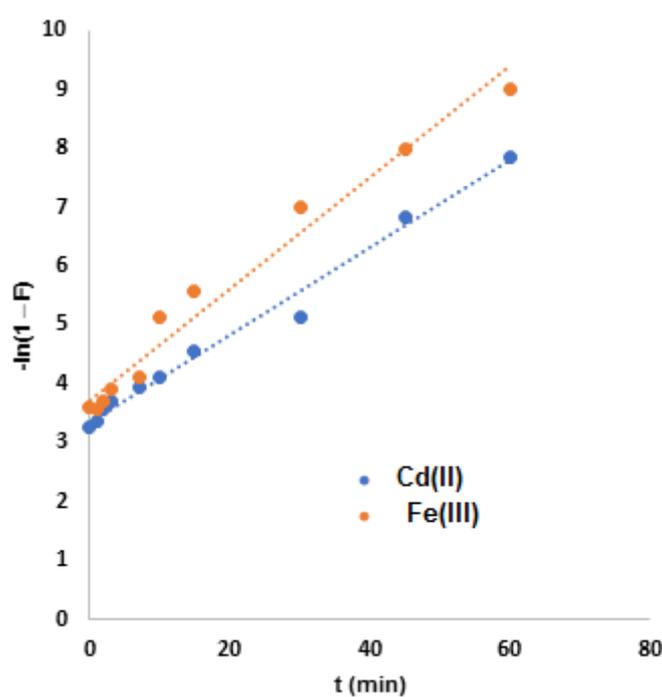
T (K)	298			313			323		
	$K_{id}$	Z	$R^2$	$K_{id}$	Z	$R^2$	$K_{id}$	Z	$R^2$
Fe (III)	1.04	1.92	0.93	1.126	1.851	0.90	1.333	1.68	0.944
Cd(II)	0.90	1.08	0.93	1.036	0.871	0.94	1.083	0.96	0.963

The mechanism for the removal of metals *via* adsorption occurred in several steps. In the first step, the metal ions migrate from the solution to the external surface of the adsorbent. This was followed by the diffusion through the boundary layer to the active sites. Finally, intra-particle diffusion and the adsorption of metal ions in the inner part of the polymer occurred. The valid mechanism in this work was examined by the two models: the liquid-film model and the intra-particle diffusion model. The liquid-film diffusion model (Eq. 3.10) assumed that the flow of the adsorbate molecules through a liquid film surrounding the adsorbent was the rate-determining step. According to Eq. 3.10, a linear plot of  $-\ln(1-F)$  vs.  $t$  (Fig. 3.13) with a zero-intercept suggested that the kinetics of the adsorption process were controlled by diffusion through the surrounding liquid film. As shown in Fig. 3.13, the experimental adsorption data of the metals by cellulose amine polymer **2** from an aqueous solution at different temperatures did not provide straight lines that passed through the origin, and had correlation coefficients of 0.1876 and 0.1578 for Fe(III) and Cd(II) (Table 3.4), respectively. This indicated that the diffusion of the metals through the liquid film around the cellulose-amine was not the rate-

determining step, but may contribute to the adsorption process, especially at the beginning of the adsorption as shown in Table 3.3.

**Table 3.4: Liquid film diffusion model parameters**

	$K_{df}$	$R^2$
<b>Fe(III)</b>	0.1876	0.9735
<b>Cd(II)</b>	0.1578	0.9873



**Figure 3.13:** Liquid film diffusion model plots for the adsorption of composite based of cellulose

### 3.6 Adsorption Thermodynamics

The Gibbs energy ( $\Delta G_0$ ), enthalpy ( $\Delta H_0$ ), and entropy ( $\Delta S_0$ ) were calculated according to the following equations, results are summarized in Table 3.5. These are important when evaluating the behavior of the

adsorption of Cd(II) and Fe(III) ions on cell-o-PDAm. The equations are as follows,

$$K_c = \frac{C_{ads}}{C_e} \quad (3.11)$$

$$\Delta G^\circ = -RT \ln K_c \quad (3.12)$$

$$\ln K_s = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (3.13)$$

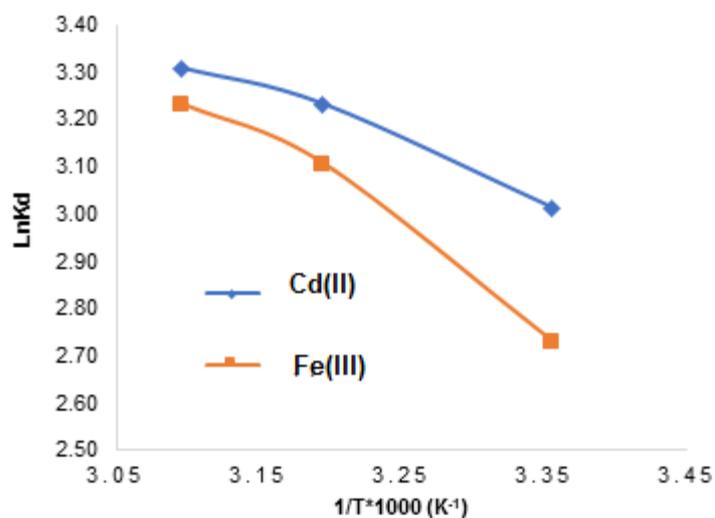
where  $K_c$  is an apparent constant of the thermodynamics,  $C_{ads}$  is the amount adsorbed at equilibrium(mg/L),  $C_e$  is the equilibrium concentration in an aqueous solution of metal ion(mg/L),  $R$  is the gas constant(J/mol×K), and  $T$  is the ions solution temperature (K) .

**Table 3.5: Thermodynamic parameters for the adsorption of Cd(II) and Fe(III) ions onto Cell-oPDAm**

T(K)	Fe(III)			Cd(II)		
	$\Delta G^\circ$ (KJ/mol)	$\Delta H^\circ$ (KJ/mol)	$\Delta S^\circ$ (J/K.mol)	$\Delta G^\circ$ (KJ/mol)	$\Delta H^\circ$ (KJ/mol)	$\Delta S^\circ$ (KJ/mol)
298	-17.144	9.66368	57.562	-18.6156	16.416	77.9326
313	-17.0074			-19.5535		
323	-18.5832			-20.1787		

The  $K_c$  value was calculated according to the Van't Hoff equation (Eq. 3.11) [75]. The standard Gibbs free energy ( $\Delta G_0$ ) ( $\text{Jmol}^{-1}$ ) was calculated using Eq. 3.12. The  $\ln(K_s)$  versus  $1/T$  was plotted as shown in Fig. 3.14. The slopes and the intercept were used to calculate various thermodynamics parameters as shown in Table 3.3. The obtained values of  $\Delta S_0$  and  $\Delta H_0$  were positive, while the entropy increased at the solid/solution interface, driven by the adsorption process. The free energies

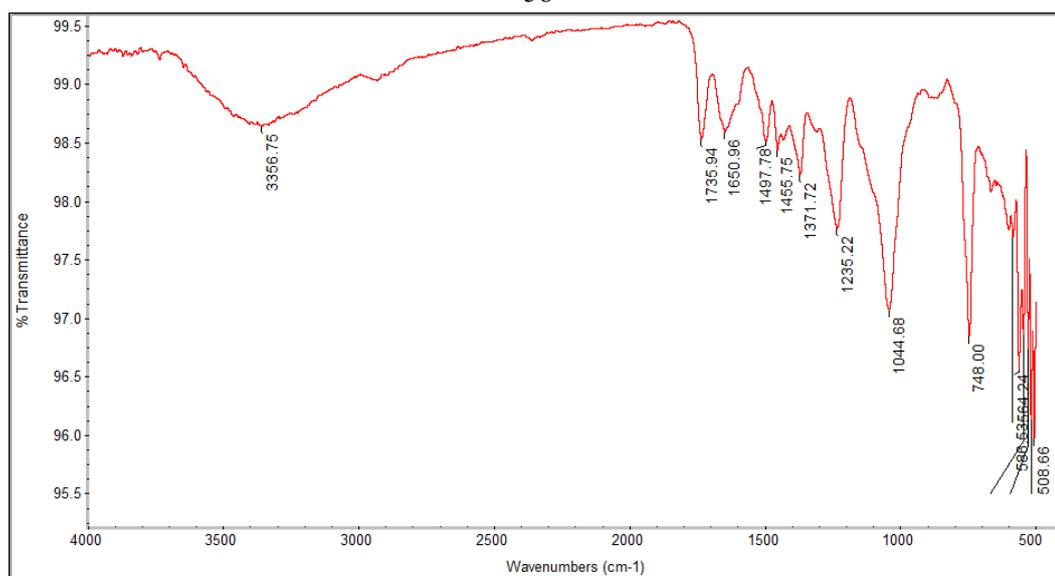
were negative, indicating a spontaneous adsorption process at the tested temperatures.



**Figure 3.14:** Adsorption thermodynamics of Cd(II) and Fe(III) ions by Cellulose amine polymer 2

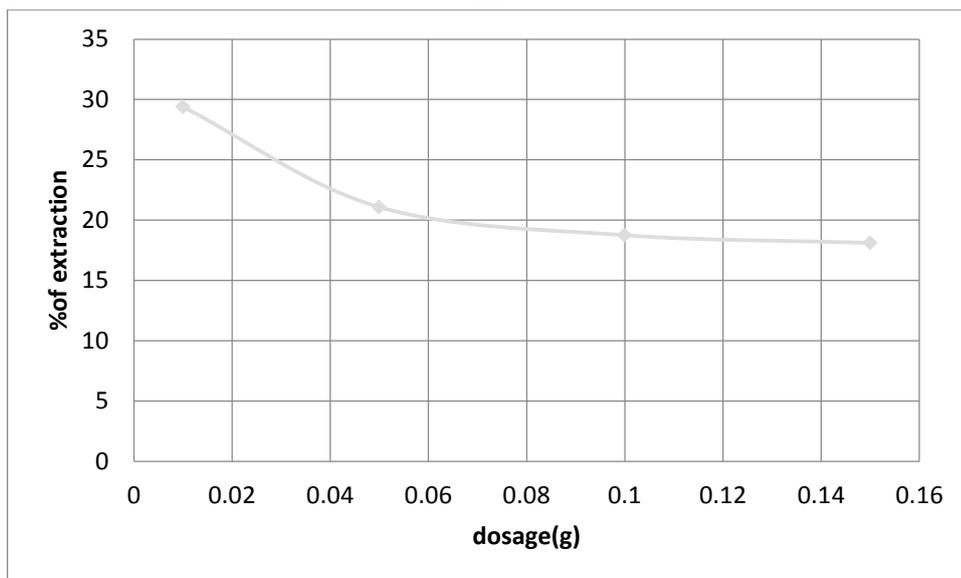
### 3.7 Preparation of amide

The amine group in the cellulose amine polymer 2 was blocked with an acetyl group. The purpose was to determine the binding site in cellulose polymer 2. The acetyl group was added to the polymer by reacting it with acetyl chloride in methylene chloride in the presence of triethyl amine to trap produced HCl. The produced polymer was analyzed by FT-IR, the obtained figure is shown in Figure 3.15. The IR shows clearly the C=O amide at  $1650\text{ cm}^{-1}$ , which is broad with medium strength.



**Figure 3.15:** IR for amide cellulose polymer

The acetylated polymer was used in extraction of Cd (II), the results are as shown in figure 3.15. The extraction efficiency was very low compared to the results obtained using polymer 2 as shown above. This indicate that the amine functional groups is the main binding site for the metal ions.



**Figure 3.16:** Efficiency of acetylated polymer toward Cd (II)

## Conclusions

Cellulose powder derivatized with aromatic amine was prepared and used as an adsorbent for metal ions. The cellulose powder used in this work was extracted from olive industry solid waste, oxidized to cellulose aldehyde, and then reacted with o-phenylene diamine followed by a reduction with sodium borohydride. The produced cellulose amine polymer **2** was subjected to an analysis *via* various spectroscopic methods. The efficiency of the prepared cellulose amine polymer **2** toward adsorbing Fe(III) and Cd(II) was studied as a function of adsorbent dose, temperature, pH, metal ion initial concentration, and time. The polymer showed an excellent efficiency toward both metals, the highest adsorbency was observed at pH of approximately 8.0 at room temperature. The polymer was then evaluated on a real sample of sewage that contained approximately 20 metal ions. The cellulose amine polymer **2** showed excellent efficiency toward most of the metal present in the sewage. The kinetic study revealed that the metal ion adsorption by cellulose amine polymer **2** was pseudo-second-order and followed the Langmuir isotherm model. The thermodynamic analysis showed a negative free energy, indicating spontaneous adsorption process at different temperatures.

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جامعة النجاح الوطنية

كلية الدراسات العليا

تجميع وتوصيف تطبيق مركب الرماد السليلوز أمين المنشط في تنقية مياه  
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إعداد

بهية فريد موسى أبوليل

إشراف

د. احمد أبو عبيد

د. عثمان حامد

قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء، بكلية الدراسات العليا، في جامعة النجاح الوطنية، نابلس - فلسطين.

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ب

تجميع وتوصيف تطبيق مركب الرماد السليلوز أمين المنشط في تنقية مياه الصرف الصحي

إعداد

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إشراف

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د. عثمان حامد

الملخص

المعادن الثقيلة عديدة ومن الأمثلة عليها: الكاديوم، الرصاص، الحديد، الزئبق، النيكل، النحاس، الخارصين، الكوبلت.....الخ. تصبح هذه العناصر تشكل خطراً حقيقياً وأحياناً كارثياً على النظام البيئي بشكل عام والنظام المائي بشكل خاص عند وجودها بنسب وتراكيز تفوق ما هو مسموح به، حيث إن منظمة الصحة العالمية وضعت نسب وتراكيز محددة لما يمكن ومسموح تواجد من هذه المعادن في مياه الشرب وعليه يترتب أخطار عديدة إذا ما تم تجاوز هذه التراكيز ومن الأمثلة على ذلك: فان الكاديوم يسبب وهن وضعف العظام والعضلات وكذلك الرصاص وغيرها من الأمراض العديدة التي قد تفتك بجسد الإنسان وكذلك الثروة الحيوانية والنباتية إلى أن تصل الموت أحياناً وكذلك الزئبق وسميته وتأثيرها على الجسم كأمراض الجلد والسرطانات العديدة والخطرة المميتة في اغلب الأحيان، والعديد من المعادن كالحديد والخارصين وغيرها الكثير من المعادن الثقيلة التي تدخل في العديد من الصناعات التي قد تؤثر على النظام البيئي.

وعليه فاني قد تناولت في هذا البحث العمل على تحضير مركب من السليلوز واستخدامه كمادة طبيعية للتخلص من تلوث المياه حيث تم استخدام السليلوز المستخرج من جفت الزيتون وذلك لتحضير سليلوز أمين عن طريق إتباع الخطوات التالية:

أولاً: العمل على أكسدة السليلوز بواسطة الصوديوم بير ايوديت في جو معتم منعا لتفكك مادة الصوديوم بير ايوديت والحصول على اكبر قدر من السليلوز المؤكسد وهو ثنائي الديهايد السليلوز.

ثانياً: تفاعل ثنائي الديهايد السليلوز مع ثنائي امين البنزين لإنتاج امين السليلوز.

ثالثاً: تم إجراء فحص فعالية المركب الذي تم تحضيره في امتصاص عنصر الكاديوم من المياه الملوثة به وذلك عن طريق دراسة عدة عوامل: التراكيز المختلفة للعنصر، كمية المركب المستخدمة، الوقت، الحرارة، درجة الحموضة.

رابعاً: بعد أن تم دراسة فعالية المركب وتحديد الظروف المعيارية لعمل المركب على تنقية المياه الملوثة تم استخدامه في تنقية مياه الصرف الصحي وقد اظهر نتائج ممتازة.

خامساً: تحويل امين السليلوز لامييد السليلوز ودراسة العوامل التي تم ذكرها سابقاً قد أظهرت التجارب أن السليلوز أمين أكثر فعالية في امتصاص العناصر من الاميد سليلوز حيث تم الحصول على نتائج بنسب امتصاص 94.76% في درجة حرارة الغرفة 25 درجة مئوية وكذلك درجة حموضة 8.6 ووقت وهو 40 دقيقة وتركيز 10 بوحدة جزء لكل مليون وتبين انه المركب قادر على الامتصاص لعدة مرات من خلال استخدامه اكثر من مرة للامتصاص لتصل نسبة الامتصاص ما يفوق 100%.

وعليه فان النتائج قد أظهرت قدرة عالية للبوليمر المحضر في امتصاص العناصر الملوثة السامة بنسب عالية وعليه يمكن استخدامه كمنقي ممتاز للمياه العادمة وإعادة استخدام المياه للعديد من أمور الحياة اليومية.

