An-Najah National University
Faculty of Graduate Studies

Synthesis of Three Dimensional Cellulose Diamine Polymer for Wastewater Purification

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Dedication

To my lovely husband "Talal" and my little daughter "Laian" Thank you for your patience

To my Great parents,

My lovely Sisters and Brothers

My Doctors in the Chemistry Department at An-Najah National University

I dedicate this work to All people in my life who supported me, encouraged me and love me

Acknowledgement

In the beginning, praise and thanks to Allah Almighty, who inspired me on my way, without his help my effort would have gone astray.

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحت عنوان

Synthesis of Three Dimensional Cellulose Diamine Polymer for Wastewater Purification

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي من نتاج جهدي الخاص ، باستثناء ما تمت الاشارة اليه حيثما ورد ، وأن هذه الرسالة ككل أو أي جزء منها لم يقدم من قبل لنيل أي درجة علمية أو بحث علمي أو بحثي لدى أي مؤسسة تعليمية أو بحثية أخرى

Declaration

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

Student's name: **اسم الطالب : باسمة قاسم خليف**

Signature: **التوقيع :**

Date: **التاريخ : 13/2/2018**

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Abbreviations Table

1	CM	Modified Cellulose
2	CDA	Cellulose Dialdehyde
3	CDI	Cellulose Diimine
4	CDAm	Cellulose Diamine
5	OISW	Olive Industry Solid Waste
6	OILW	Olive Industry Liquid Waste

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Abstract

Cellulose is the most abundant natural product; it has unlimited number of industrial applications. It reacts like alcohol and can be converted into various polymers with various functionalities. In this work cellulose extracted from Olive Industry Solid Waste (OISW) was converted to cellulose dialdehyde by oxidation with periodate, then reacted with the bifunctional amine 1,4-diaminobenzene to form cellulose diimine which then reduced to cellulose diamine by reacting it with sodium borohydride. The structure of the prepared polymers were analyzed by FT-IR, NMR (^{1}H and ^{13}C), and other spectroscopic and thermal methods. Produce cellulose diamine has a unique molecular structure, diamine compound holds the cellulose chain together and both form a kind of crown amine. The crown amine cages have several binding sites of nitrogen and oxygen that are distributed though the ring. These sites have high affinity for metals. The prepared cellulose diamine was used to extract toxic metals form wastewater. The metal that were extracted are lead, iron, and copper. The extraction efficiency of the cellulose diamine for these metals was evaluated as a function of pH, adsorbent dosage, temperature and time. The optimum conditions were the temperature was 30 ^{o}C, the time was about 120 min, pH was about 4.0 and the dosage is 0.5 g. Under these conditions a quantitative remove of metals from solutions concentrations 10, 20, 50 ppm was attained. The extraction efficiency for heavy metals were studied by using two type of polymer: powder and fiber polymer, we found powder polymer more efficient in extraction

The kinetic calculations showed that, adsorption rate followed the Pseudo-second-order. The R^2 for Pseudo-second-order equation was 0.9999.

Chapter I

Introduction

1.1 Background

The rapid increase of global industrial activities became the main source of water pollution by toxic heavy metals. Examples of toxic heavy metals have specific concern due to toxicity, accumulation and persistency in nature is Cr, Fe, Se ,V, Cu, Co ,Ni ,Cd, Hg ,Pb ,Zn, As. The issue resulted in a serious environmental problems. The excessive amount of metals entering the water sources may cause sever toxic problems for animals and humans [1, 2, 26]. For instance, mercury with concentration over the permitted limit [3] can cause neurobehavioral disorders, attention deficit hyperactivity disorders, and intellectual retardation. High concentration of cadmium can cause bone damage and a nephrotoxic effects [4]. Lead was also found to causes kidney damage, cognitive impairment, behavioral disturbances, encephalopathy, and anemia [5]. Copper with high concentrations was found to cause damage to the gastrointestinal tract, weakness, lethargy and anorexia [6]. Removal of heavy metal ions from wastewater before they get into water sources became essential from the standpoint of environmental pollution control. Several methods have been developed for this purpose, among these are chemical precipitation, reverse osmosis, ion-exchange, membrane separation, coagulation and flocculation, adsorption, and biosorption [7]. Some of these techniques have limitations, such as less efficiency and sensitive under certain operating conditions. So far the most efficient technology for removing metals from wastewater is adsorption. Adsorbents are available at low cost and very efficient [8-11].

Also, they could be made from plant wastes, requires little processing, selective adsorption of heavy metal ions, good adsorption capacity, low cost, and free availability [8-11].

Recently, the research in this area was directed toward developing natural based materials at low-cost for commercial application.The natural material that received the highest attention is cellulose [8-11].

1.2 Cellulose

1.2.1 Cellulose structure

Cellulose is a natural polymeric material consist of anhydroglucose repeat unit (Figure I.1) that are linked successively through ß-1,4-glycosidic bonds in the β-configuration between C1 and C4 of adjacent units to form a polymeric chain (Figure I.1).

The cellulose chains are linear consist of about 10,000 monomer units, grouped together in bundles called microfibers, which form may be ordered (crystalline) or less ordered (amorphous) regions. Microfibers build up to form finally cellulose fibers.

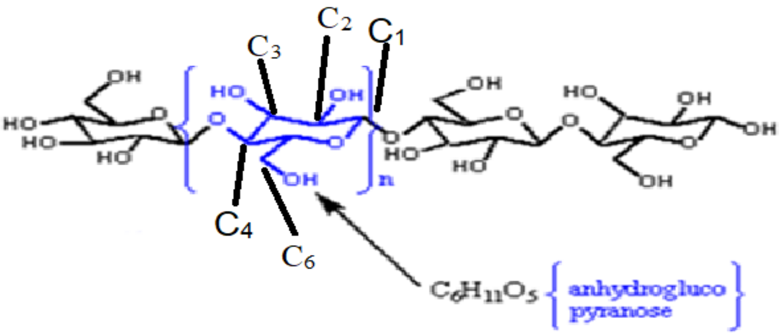


Figure I .1 Molecular Structure of cellulose

As shown in Fig1.1, each anhydroglucopyranose repeat unit possesses hydroxyl groups at C2, C3, and C6 positions, capable of undergoing the typical reactions known for primary and secondary alcohols.

Cellulose is a very stable polymer and insoluble in water. Cellulose is safe, odorless, tasteless, hydrophilic, insoluble in water and in most organic solvents, biodegradable and it is chiral polymer [2,17].

The degree of polymerization, n, is dependent on the cellulosic source, it could be anywhere between 10,000 and 15,000 as shown in Table (1.1).

The strong hydrogen bonding between hydroxyl groups and oxygen atoms of the cellulose chains is the source of the high strength, stability and insolubility of this polymer.

There are regions within the cellulose fibrils where cellulose chains are in a highly ordered structure (crystalline region) and regions that it is disordered and open for reagents (amorphous).

The molecular structure of cellulose has characteristic properties: chirality, hydrophilicity, degradability, and broad chemical variability initiated by the high donor reactivity of the OH groups.

Many of cellulose properties depend on the degree of polymerization. The small chain length molecule resulting from the breakdown of cellulose are known as cellodextrins, cellodextrins are typically soluble in water and organic solvents [20,21]

1.2.2. Sources of cellulose

Cellulose is the most abundant natural polymer, it could be extracted from any plant present on earth. Examples on the content of cellulose in various raw materials is shown below:

- Bushes: 30%
- Woods: 40–50%
- Bast Plants (flax, ramie): 65–70%
- Cotton Fibers: >90% [20,21]

Table 1.1: Degree of polymerization of cellulose from various sources [20,21] :

Source	Degree of polymerization
Acetobacter xylinum	2,000-3,700
Acetobacter cellulose	600
Bacterial cellulose	2700
Bagasse	700-900
Bast fibers	1,000-5,000
Cotton fibers	8,000-14,000
Cotton linters	1,000-6,500
Flax fibers	7,000-8,000
Ramie fibers	9,000-11,000
Pulp cellulose (bleached)	5,00-2,100
Wood fibers	8,000-9,000
Valonia	25,000-27,000

1.3 Cellulose Source Materials:

1.3.1 Wood

It is the primary source of cellulose material, wood abundant and has many advantages. In general, extraction of Cellulose starts with ‘‘purified’’ wood, i.e. wood with most of the lignin, hemicellulose and impurities removed. Typical materials are bleached and Kraft pulping

1.3.2. Plant

Plants are another 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

1.3.3 Tunicate

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

1.3.4. Algae

Cellulose is produced by several species of algae (green, gray, red, yellow-green) within the cell wall. There are considerable differences in cellulose microfibril structure between the various algae species caused by differences in the biosynthesis process [21].

1.3.5 Olive industry waste

Olive mill waste consists of about 44% of olive industry solid wastes (OISW) and 56% of olive industry liquid waste (OILW) [18]. The main component of OISW is cellulose (45%) making it potentially attractive as low cost feed material for cellulose.

The olive industry wastes are acidic, have extremely high biological oxygen demand (BOD) and chemical oxygen demand (COD) values, and also contain high toxic levels of polyphenols [19]. The waste materials pose a challenge in waste management to the olive mills and a concern to environmentalists, that causes a serious disposal problem. In addition to this, olive industry loses economic value by disposing the effluent or selling it for a low price to other industries. In certain countries, the OISW is usually burned or left to rot, thus releasing CO_2 into the atmosphere, while OILW tends to be disposed of via the sewage system, which has implications for water quality. So olive industry waste is a major problem facing by industrialist in view of increasing environmental standards day by day. In addition to this, olive industry loses economic value by disposing the effluent or selling it for a low price. The challenge is to utilize and convert these waste materials into useful and low-cost marketable products, and this is the main objective of this thesis.

Olive Industry is a major industry in Palestine, usually occurs by a conventional batch process where the olive is pressed and oil and water are collected then oil is separated from water by centrifuge and decantation.

In addition to olive oil, solid waste is generated during the press process. The solid waste is known as Jefft, Jefft consists of several components, which consists mainly of three polymers: cellulose, lignin, and hemicelluloses. The main constituent. Cellulose, will be extracted from the olive industry solid waste (OISW), it is a linear homopolysaccharide made of the monomer D-glucose.

Cellulose used in this study was extracted from OISW and purified using pulping and bleaching processes developed at our laboratories (20).

1.4 Cellulose as a metal adsorbent

Removal of heavy metal ions from wastewater is essential from the standpoint of environmental pollution control. Numerous methods have been used to remove heavy metals from wastewater which include chemical precipitation ,membrane separation, ion-exchange, reverse osmosis, coagulation and flocculation, biosorption, and adsorption.

Due to increase the cost and environmental considerations associated with the use of commercial adsorbents, that led to work aimed at developing new low-cost adsorbents derived from renewable resources like cellulose. The advantages of using cellulose is, its high abundance, low cost and can be chemically modified easily.

1.4.1 Chemically modified cellulose for removing heavy metal

- In one study, a chemically modified cellulose bearing pendent methyl benzalaniline chelating group was synthesized. The modified cellulose was used for the removal of Cu^{2+} and Pb^{2+} from aqueous solution. The adsorption kinetic parameters fitted well to the pseudo-second-order kinetic model [12].

- In another study microspheres of cellulose and polyethylene mine were prepared then cross-linked by glutaraldehyde. The cellulose microspheres were used to study Pb^{2+} removal efficiency from aqueous solution on the basis of adsorption kinetics and isotherm equations. The results showed that adsorption capacity on Pb^{2+} of modified cellulose microspheres was 9.46 mg/g.

  In addition it was found that, the adsorption process fit pseudo second order kinetics equation and Freundlich isotherm equation [13].
- Celluloses ester was also used for this purpose, it was prepared by reacting cellulose derived from cheap filter paper was reacted with succinic anhydride in solid state. The prepared cellulose ester was evaluated in extraction of Cu^{2+} from wastewater. The Cu^{2+} removal by the cellulose ester reached 94% at pH = 4.0-5.0 after reaction for 50 min at room temperature [14]. In an invention an amino-modified sawdust adsorbent was also used in purification of wastewater [15].
- Cellulose modified with thiosemicarbazide group was evaluated as adsorbent for Hg(II) from water, the results demonstrated that the thiosemicarbazide modified cellulose possessed high performance for Hg(II) adsorption from water with adsorption capacity of 499.6 mg/g. The sorption model followed Langmuir model and pseudo-second order kinetic model. The fitting coeff. (R^2) was more than

0.98. The enhanced Hg(II) adsorption capability of thiosemicarbazide modified cellulose was related to chelating interaction between Hg(II) and thiosemicarbazide [16].

1.5 Scope of the study

The overall aim of the work described in this thesis is wastewater purification from toxic heavy metals using chemically modified Cellulose extracted from olive industry solid waste.

In this work a 3D cellulose based amine polymer was prepared. The main purpose for use of this polymer is in wastewater purification. The method of making the polymers comprises oxidizing cellulose extracted from olive industry solid waste to dialdehyde using periodate, then cross-linking the dialdehyde with 1,4 diaminobenzene. Produced polymer 3D polymer is expected to have multisite for metal binding.

The primary goal of this project is to prepare cellulose based a 3D polymer for wastewater purification.

The specific objectives for this research are:

To synthesize a 3D cellulose based amine polymer able to strongly bind metals present in wastewater and other contaminated sources.

To Develop a chemical method to oxidize cellulose to dialdehyde polymer.

To Develop a method for cellulose and diamine crosslinking.

To Evaluate the possibility of using the prepared 3D polymer in wastewater purification.

To Characterize the new polymers by various spectroscopic techniques.

Chapter II

Experimental

2.1 General experimental:

All chemicals were purchased from Aldrich Chemical Company and used without any further purification unless otherwise specified. Atomic absorption spectroscopy (AAS) technique used for determination the concentration of heavy metal after purification process completed. Cellulose powder and cellulose fiber used for preparation of 3D polymers.

2.2 Oxidation of cellulose to 2,3-dialdehyde cellulose (1)

2.2.1 Preparation of acetate buffer with pH of 4.7

A 0.1 M of acetic acid was prepared by diluting a 5.7 mL of concentrated acetic acid to 1 L with distilled water. A 0.1 M of sodium acetate solution was prepared by dissolving a 8.2 g of sodium acetate in a 1 L distilled water. A 200 mL buffer solution was then prepared by mixing a 102 mL of 0.1 M of acetic acid with a 98 mL of 0.1 M sodium acetate solution.

2.2.2 General procedure for cellulose oxidation

Powder cellulose (12.0 g, 0.074 mol of anhydroglucose repeat unit) was added to a beaker wrapped completely with aluminum foil containing 900 mL of acetate buffer (pH = 4.7). To the cellulose suspension was added excess potassium periodate (60.0 g, 0.26 mol) was added followed with the addition of isopropyl alcohol (150.0 mL). The reaction was stirred at room temperature for 15 days (in a dark room). Every 48 hour a small sample from the reaction mixture (only liquid) was taken to check for presence of periodate using UV spectrophotometer at wavelength 290 nm. When the concentration of periodate became constant, an indication that the oxidation reaction of cellulose completed, the product was filtered and washed with water several time to remove residual chemicals and side products.

2.3 Crosslinking of cellulose dialdehyde (1)

2.3.1 Preparation of phosphate buffer (pH = 7)

A 1.0 M solution of disodium hydrogen phosphate was prepared by dissolving 8.2 g of it in 100.0 mL distilled water. A 1.0 M solution of sodium dihydrogen phosphate was prepared by dissolving 5.075 g of it in a 100.0 mL distilled water). Then the two solutions mixed and diluted to 1.0 L by dilution.

2.3.2 Preparation of 2,3-cellulose diamine (2)

To a round bottomed flask (100 mL) fitted with a magnet stir bar cellulose dialdehyde was added (1.0 g, 6.17 mmol of anhydroglucose repeat unit). To it was added 20 mL of phosphate buffer (pH = 7). 1,4-diaminobenzene (0.65 g, 6.2 mmol) was added to the round bottom flask. The reaction mixture was stirred for 24 hours at room temperature. Imine product (CI) was filtered, washed several times with water, then was dried at room temperature. The product was analyzed by FT-IR

2.3.3 Preparation of 2,3-cellulose diamine (3)

Imine product obtained before was added to a round bottom flask (100 mL) fitted with a magnet stir bar. The imine was used as is with no purification. 20 mL of methanol was added, followed with the slow addition sodium borohydride (0.1 g each addition, 1.2 equivalent), the reaction mixture was stirred for 4 hours. The excess of sodium borohydride was destroyed by the addition of water. Produced diamine polymer was filtered and washed with water, ethanol, then dried. The product was analyzed by FT-IR

2.4 Purification of wastewater from toxic heavy metal using cellulose diamine

2.4.1 Preparation of lead solutions.

The extraction experiment was carried out on metal solution that were prepared in the lab.

The following diluted solution of Lead(II) nitrate were prepared from a stock solution with 1000 ppm concentration.

- Lead(II) nitrate with 10 ppm concentration
- Lead(II) nitrate with 20 ppm concentration
- Lead(II) nitrate with 50 ppm concentration

2.4.2 Extraction procedure:

A batch extraction process was used, in this process when a known amount of cellulose diamine polymer was added to a lead solution (100 mL) with known concentration in a glass bottle (250 mL), the bottle was capped and placed in a shaker in way that was immersed in a water bath with controlled temperature and mixed at 180 rpm for specific time. Then, the mixture was filtered to remove the polymer. The supernatant fluid was analyzed for its residual concentration. The concentration of Pb (II) was determined using atomic mass spectroscopy analyzer (AAS). The adsorption capacity (q) and removal percentage (E%) were calculated using equations 1 and 2:

Eq. 1: $q = ((C_0-C_e)/m)) * V$

Eq. 2: $E\% = ((C_0-C_e)/Co)) * 100$ [27,28].

Where q is the adsorption capacity of the adsorbate (mg/g), m is the weight of adsorbent (g), V is the volume of solution (L), m is the relative molecular mass of the adsorbate, and C_0 (mg/L) and C_e (mg/L) are initial and equilibrium concentrations of adsorbate in solution [27,28].

2.4.2.1 Effect of polymer (3) dosage on percent of adsorption:

Four solutions (100 mL each) of lead ion were prepared with known concentration (10 ppm). To each was added 0.1 g, 0.5 g, 1.0 g, 1.5 g of cellulose diamine.

The four sample were shaken above at 30.3 ^oC for 35 min using thermostat shaker, then all samples were filtered and the Pb^{+2}, concentrations were determined in the supernatants using AAS at wavelength 217 nm, results are summarized in the following Table II.1:

Table II.1: Effect of polymer (3) dosage on lead(II) extraction (30.3 ºC, 35 min)

Polymer dosage (g)	Conc. of lead (II) after extraction (10 ppm of lead)	% of Extraction
0.1	7.955	20.445
0.5	2.687	73.13
1.0	2.29	77.1
1.5	0.53	94.7

Another four solutions (100 mL each) of lead ion were prepared with known concentration (20 ppm). To each was added 0.1 g , 0.5 g , 1.0 g ,1.5 g of cellulose diamine.

The four samples were shaken above at 30.3 ºC for 35 min using thermostated shaker, then all samples were filtered and the Pb^{+2}, concentrations were determined in the supernatants using AAS at wavelength 217 nm, results are summarized in the following Table II.2 :

Table II.2: Effect of polymer (3) dosage on lead(II) extraction (30.3 ºC, 35 min)

Polymer dosage (g)	Conc. of lead (II) after extraction (20 ppm of lead)	% of Extraction
0.1	18.634	6.83
0.5	4.6228	76.886
1.0	3.2758	83.621
1.5	0.6848	96.5775

Another four solutions (100 mL each) of lead ion were prepared with known concentration (50 ppm). To each was added 0.1 g, 0.5 g, 1.0 g, 1.5 g of cellulose diamine.

The four samples were shaken above at 30.3 ^{o}C for 35 min using thermostated shaker, then all samples were filtered and the Pb^{+2} , concentrations were determined in the supernatants using AAS at wavelength 217 nm, results are summarized in Table II.3 :

Table II.3: Effect of polymer dosage on lead(II) extraction (30.3 ^{o}C, 35 min)

Polymer dosage (g)	Conc. of lead (II) after extraction (50ppm of lead)	% of Extraction
0.1	49.8105	0.379
0.5	5.0328	89.934
1.0	0.457	99.086
1.5	0.5624	99.8752

2.4.2.2 The effect of extraction time on percent of adsorption

Four solutions (100 mL each) of lead ion were prepared with known concentration (10 ppm). To each was added 0.5 g of cellulose diamine.

The four samples were shaken at 30.3^{o}C for 30 min, 60, 100 min and 120 min using a thermostated shaker, then all samples were filtered and the Pb^{+2} , concentrations were determined in the supernatants using AAS at wavelength 217 nm, results are summarized in Table II.4

Table II.4: Effect of extraction time on adsorption (30.3 ºC, 0.5 g polymer(3))

Extraction Time (min)	Conc. of lead (II) after extraction (10 ppm of lead)	% of Extraction
30.0	1.8637	81.363
60.0	1.0653	89.347
100.0	0.3409	96.591
120.0	0.7075	92.925

Four solutions (100 mL each) of lead ion were prepared with known concentration (20 ppm). To each was added 0.5 g of cellulose diamine. The four samples were shaken at 30.3 ºC for 30 min, 60, 100 min and 120 min using a thermostated shaker, then all samples were filtered and the Pb^{+2}, concentrations were determined in the supernatants using AAS at wavelength 217 nm, results are summarized in Table II.5 :

Table II.5: Effect of extraction time on adsorption (30.3ºC, 0.5 g) polymer (3) Four solutions (100 mL each) of lead ion were prepared with known concentration (50 ppm). To each was added 0.5 g of cellulose diamine.

Extraction Time (min)	Conc. of lead (II) after extraction (20 ppm of lead)	% of Extraction
30.0	1.455	92.725
60.0	0.6318	96.841
100.0	0.4337	97.8315
120.0	0.4051	97.9745

The four samples were shaken at 30.3 °C for 30 min, 60, 100 min and 120 min using a thermostated shaker, then all samples were filtered and the Pb^{+2}, concentrations were determined in the supernatants using AAS at wavelength 217 nm, results are summarized in Table II.6

Table II.6: Effect of extraction time on adsorption (30.3°C, 0.5g polymer)

Extraction Time (min)	Conc. of lead (II) after extraction (50 ppm of lead)	% of Extraction
30.0	12.1599	75.6802
60.0	5.1193	89.7614
100.0	1.4988	97.0024
120.0	0.9256	98.1488

2.4.2.3 The effect of temperature on percent of adsorption

Four solutions (100 mL each) of lead ion were prepared with known concentration (10 ppm). To each was added 0.5 g of cellulose diamine. The four samples were shaken at various temperatures 18, 25, 30, 45 °C for 120 min in a thermostated shaker, then all samples were filtered and the Pb^{+2}, concentrations were determined in the supernatants using AAS at wavelength 217 nm, results are summarized in Table II.7

Table II.7: Effect of extraction temp on adsorption (0.5 g polymer (3) , 120 min)

Extraction Temp (C)	Conc. of lead (II) after extraction (10 ppm of lead)	% of Extraction
18.0	1.205	87.95
25.0	0.5307	94.693
30.0	0.38	96.2
45.0	0.5011	94.989

Four solutions (100 mL each) of lead ion were prepared with known concentration (20 ppm). To each was added 0.5 g of cellulose diamine. The four samples were shaken at various temperatures 18, 25, 30, 45 ^{o}C for 120 min in a thermostated shaker, then all samples were filtered and the Pb^{+2}, concentrations were determined in the supernatants using AAS at wavelength 217 nm, results are summarized in Table II.8

Table II.8: Effect of extraction temp on adsorption (0.5 g polymer (3) , 120 min)

Extraction Temp (C)	Conc. of lead (II) after extraction (20 ppm of lead)	% of Extraction
18.0	0.4831	97.58
25.0	0.5575	97.21
30.0	0.4635	97.68
45.0	0.1802	99.099

Four solutions (100 mL each) of lead ion were prepared with known concentration (50 ppm). To each was added 0.5 g of cellulose diamine.

The four samples were shaken at various temperatures 18, 25, 30, 45 ^oC for 120min in a thermostated shaker, then all samples were filtered and the Pb^{+2}, concentrations were determined in the supernatants using AAS at wavelength 217 nm, results are summarized in Table II.9.

Table II.9: Effect of extraction temperature on adsorption (0.5 g polymer (3) , 120 min)

Extraction Temp (C)	Conc. of lead (II) after extraction (50 ppm of lead)	% of Extraction
18.0	1.33	97.34
25.0	1.5235	96.953
30.0	9.3838	81.2324
45.0	1.0953	97.809

2.4.2.4 Effect of pH on adsorption efficiency

Four solutions (100 mL each) of lead ion were prepared with known concentration (10 ppm). To each was added 0.5 g of cellulose diamine.

The pH was adjusted to 2.5, 4.1, 6.3, 11.7, then placed in a thermostat with a shaker and mixed for 120 min. Then all samples were filtered and the Pb^{+2} was concentrations were determined in the supernatants using AAS at wavelength 217 nm, results are summarized in Table II.10

Table II.10: Effect of solution pH on adsorption (0.5 g polymer (3) , 120 min , 30 ^{o}C)

Solution pH	Conc. of lead (II) after extraction (10 ppm of lead)	% of Extraction
2.5	9.8726	1.274
4.1	1.8418	81.582
6.3	1.7603	82.397
11.7	5.1542	48.45

Four solutions (100 mL each) of lead ion were prepared with known concentration (20 ppm). To each was added 0.5 g of cellulose diamine.

The pH was adjusted to 2.58, 3.85, 6.3, 11.4, then placed in a thermostat with a shaker and mixed for 120 min. Then all samples were filtered and the Pb^{+2} was concentrations were determined in the supernatants using AAS at wavelength 217 nm, results are summarized in Table II.11

Table II.11: Effect of solution pH on adsorption (0.5 g polymer (3) , 120 min , 30 ^{o}C)

Solution pH	Conc. of lead (II) after extraction (20 ppm of lead)	% of Extraction
2.58	17.8395	10.8395
3.85	3.8759	80.6205
6.3	3.7023	81.4885
11.4	5.3664	73.168

Four solutions (100 mL each) of lead ion were prepared with known concentration (50 ppm). To each was added 0.5 g of cellulose diamine.

The pH was adjusted to 2.57, 4.18, 6.55, 11.4, then placed in a thermostat with a shaker and mixed for 120 min. Then all samples were filtered and the Pb^{+2} was concentrations were determined in the supernatants using AAS at wavelength 217 nm, results are summarized in Table II.12

Table II.12: Effect of solution pH on adsorption (0.5 g polymer (3) , 120 min , 30 ºC)

Solution pH	Conc. of lead (II) after extraction (50 ppm of lead)	% of Extraction
2.57	42.5128	14.97
4.18	5.7296	88.54
6.55	7.0017	85.99
11.4	8.7187	82.56

2.4.3 Extraction of Fe (III) and Cu (II)

2.4.3.1 Preparation of Iron (III) and Cu (II) solutions

The extraction experiment was carried out on metal solution that were prepared at the lab.

An iron (III) chloride solution with 1000 ppm was prepared and used as a stock solution.

From the stock solution Iron (III) chloride 50 ppm concentration was prepared by diluting a 25 mL of 1000 ppm solution to 500 mL with distilled water.

A copper (II) solution with 1000 ppm was prepared by dissolving a 3.929 g of Copper sulphate pentahydrate in 1 L distilled water. The solution was used as a stock solution.

From the stock solution Copper (II) sulphate pentahydrate 50 ppm concentration was prepared by diluting a 25 mL of 1000 ppm solution to 500 mL with distilled water.

2.4.3.2 percent of Extraction for Copper and Iron ion at optimum conditions:

Four samples of copper ion were prepared with known concentration (50 ppm, 100 mL each), dosage of polymer was weighed 0.5g and put in four samples of copper ion.

These four sample were shaken at 180 rpm, 120 min, 30 ^{o}C using thermostated shaker with changed the pH value, then all samples (metal ion + polymer) were filtered, the concentration of residual ion in supernatant was measured using AAS at wavelength 324.8 nm, results are summarized in table II.13

Table II.13: percent of extraction of copper at optimum conditions (0.5 g polymer (3) , 120 min , 30 ^{o}C)

Solution pH	Conc. of copper (II) after extraction (50 ppm)	% of Extraction
2.88	5.9918	88.01%
4.33	0.8280	98.344%
5.96	1.2750	97.45%
9.55	1.1425	97.715%

Four samples of iron ion were prepared with known concentration (50 ppm, 100 mL each), dosage of polymer was weighed 0.5g and put in four samples of iron ion.

These four sample were shaken at 180 rpm, 120 min, 30 °C using thermostated shaker with changed the pH value, then all samples (metal ion + polymer) were filtered, the concentration of residual ion in supernatant was measured using AAS at wavelength 248.3 nm, results are summarized in table II.14

Table II.14: percent of extraction of iron at optimum conditions (0.5 g polymer (3) , 120 min , 30 °C) :

Solution pH	Conc. of iron (III) after extraction	% of Extraction
2.80	14.0532	71.89%
4.38	0.3781	99.2438%
6.11	0.2410	99.518%
10.89	0.2959	99.40%

2.4.3.3 Comparison between powder cellulose and fiber cellulose for adsorption Iron(III) ion

Two samples of Iron were prepared with known concentration (50 ppm, 100 mL each), then 0.5g of powder cellulose and 0.5g of fiber cellulose were weighed and put in two samples of Iron ion.

Table II.15: Comparison between powder polymer (3) and fiber polymer for adsorption Iron(III) ion

Conc. Of Iron ion 50 ppm	Conc. Of Fe(III) after extraction Using Powder Cellulose	Conc. Of Fe(III) after extraction Using Fiber Cellulose
Iron (III)	0.7233	5.8575
% of Extraction	98.553 %	88.285%

These two samples were shaken at 180 rpm, 120 min, 30 ^oC (optimum conditions) using thermostated shaker, then all samples (metal ion + polymer) were filtered, the concentration of residual ion in supernatant was measured using AAS at wavelength 248.3 nm, results are summarized in table II.15:

As shown from the table powder polymer is more efficient for extraction of iron (III) ion

2.4.3.4 Comparison between powder cellulose and fiber cellulose for adsorption Copper (II) ion

Two samples of Copper were prepared with known concentration (50 ppm, 100 mL each), then 0.5g of powder cellulose and 0.5g of fiber cellulose were weighed and put in two samples of Copper ion.

These two samples were shaken at 180 rpm, 120 min, 30 ^oC (optimum conditions) at using thermostated shaker, then all samples (metal ion + polymer) were filtered, the concentration of residual ion in supernatant was measured using AAS at wavelength 324.8 nm, results are summarized in table II.16:

Table II.16: Comparison between powder polymer (3) and fiber cellulose polymer (3) for adsorption Copper (II) ion

Conc. Of Copper ion 50 ppm	Conc. Of Cu(II) after extraction Using Powder Cellulose	Conc. Of Cu(II) after extraction Using Fiber Cellulose
Copper (II)	1.5622	2.73
% of Extraction	96.87%	94.538%

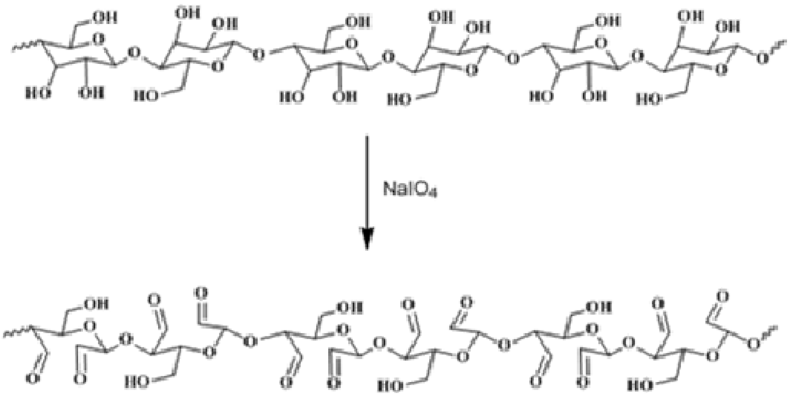
As shown from the table powder polymer is more efficient for extraction of copper (II) ion

Chapter III

Result and Discussion

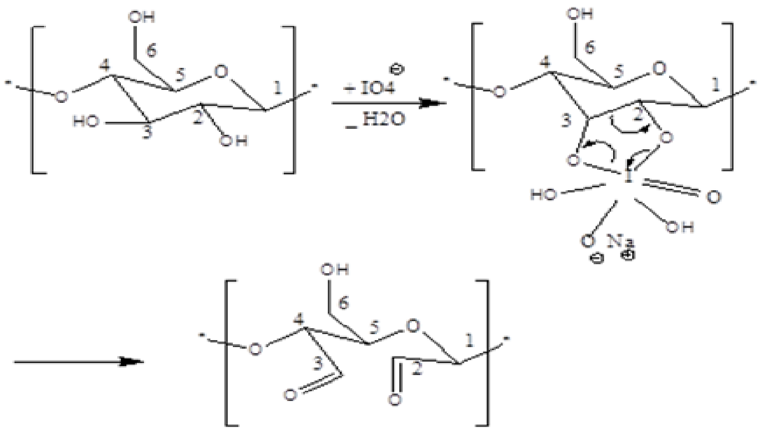
3.1 Oxidation of Cellulose to 2,3- Dialdehyde Cellulose

Periodate oxidation of cellulose was carried out according to a method reported by Jackson and Hudson [34,35]. In this method cellulose is treated with an aqueous solution of periodate in a system completely isolated from light. Periodate complexes to the vicinal hydroxyl group at C2 and C3 which leads to cleavage of C2-C3 bond and oxidation of the vicinal hydroxyl groups to form 2,3-dialdehyde units along the cellulose chains as shown in Scheme III.1 [22,23].



Scheme III.1: conversion of cellulose to cellulose dialdehyde.

First the oxidation starts at the amorphous regions of cellulose structure. Since this region is accessible. The oxidation of the amorphous region and the introduction of the dialdehyde affects the crystalline region which cause it to become more accessible [36].



Scheme III.2: Mechanism for oxidation of cellulose to dialdehyde

Oxidation of cellulose was very slow, it was monitored by UV spectroscopy. After certain period of time, a sample of the reaction mixture was withdrawn, filtered and analyzed by UV. The results are summarized in Table II.1, as shown in the table the periodate band intensity decreased with time. An indication that, the reaction is occurring and the periodate is being consumed. It took about 14 days for the reaction to be completed.

Table III.1: UV spectrophotometer reading for completed oxidation reaction

Number of reading	Reaction Time (Hr)	UV Spectrophotometer reading/Periodate band intensity
1	1	3.9999
2	48	3.6123
3	72	3.3113
4	92	2.8721
5	93	2.7992
6	113	2.7668
7	133	2.6833
8	154	2.6351
9	202	2.1887
10	220	2.0750
11	223	2.0626
12	241	1.9451
13	265	1.8638
14	270	1.8029
15	289	1.6704
16	292	1.6464
17	313	1.3176
18	319	0.9591

3.1.1 Determination of aldehyde content

The percentage of aldehyde in cellulose dialdehyde produced by the periodate oxidation reaction was determined using the hydroxylamine-hydrochloride method [40]. In this method, a known amount of DAC was converted to oximes by reacting it with hydroxylamine-hydrochloride. The HCl released from the reaction was back-titrated with a NaOH solution of known concentration. A known weight of DAC sample was suspended in a solution of isopropanol (40 mL) and water (20 mL). The pH of the slurry and the hydroxylamine hydrochloride solution (5 wt.%) were adjusted to 3.5 with

HCl. The two mixtures were mixed for 30 min at room temperature and the released HCl was titrated with 0.5N NaOH to the end point pH of 3.5

Cellulose content of aldehyde was then calculated using Eq 3:

$[Ald] = V_{NaOH}.\ N_{NaOH}/W_{CDA}$ Eq. 3

Under the reaction condition presented in the experimental part, the degree of substitution was about 1.92/ anhydroglucose repeat unit.

3.1.2 FT-IR of Cellulose dialdehyde

The FTIR spectra of the untreated cellulose is shown in Fig.3. The spectrum shows a broad peak at 3310 cm^{-1} is due to the stretching of the O-H, the peak at 1300 cm^{-1} could be related to the -OH bending vibration [18]; the bands at 1053 cm^{-1}, 1435 cm^{-1} and 2903 cm^{-1} correspond to are to C-O-C stretching, $-CH_2$ scissoring and C-H vibration, respectively [29].

The FT-IR spectrum of CDA is shown in Fig.3. The spectrum shows a band at 1730 cm^{-1} cross bonding to the aldehyde carbonyl groups [30]. The aldehyde peak is not very sharp which could be due to hydration and formation of hemiacetals [31]. Since remove of water completely from cellulose required drying it at high temperature (about 120 ^{o}C) which might cause degradation or oxidation to aldehyde functional group.

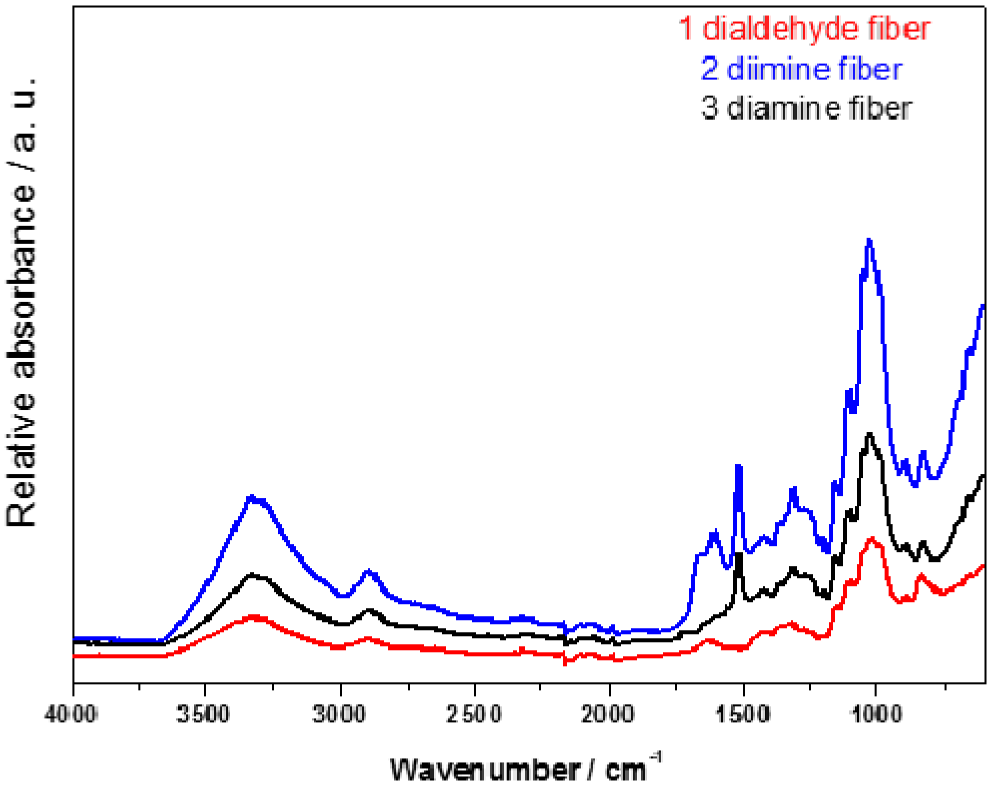


Figure III.3: FT-IR spectra of cellulose CDA, CDI and CDAm

3.1.3 Solid ^{13}C NMR of CDA

The aldehyde carbonyl signal of CDA is expected to show at 175-180 ppm. The absence of this peak could be attributed again to the conversion of the carbonyl group to hemiacetals or it could be hydrated [40]. The rest of the spectrum is for typical for cellulose.

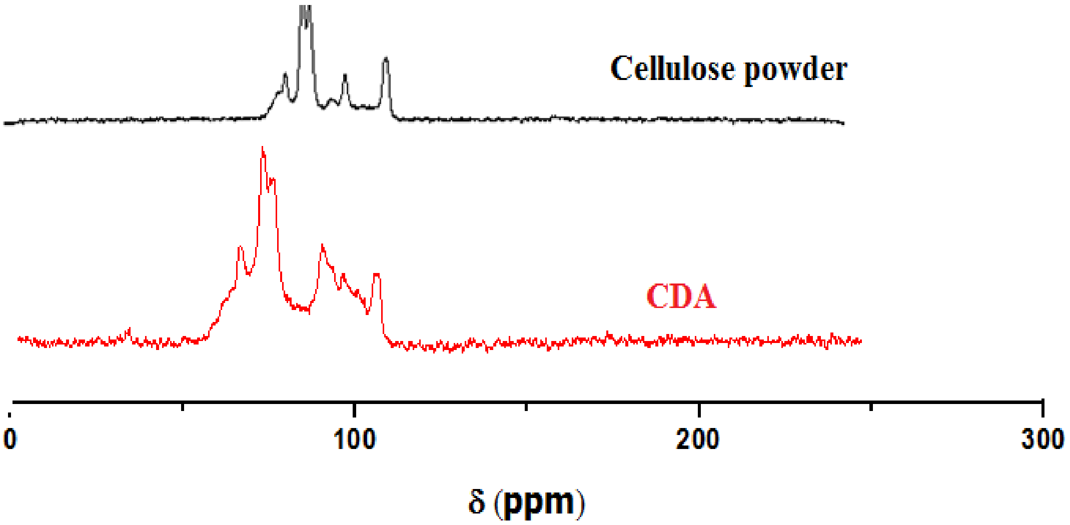


FIG. III.4: ^{13}C NMR of cellulose powder and CDA

3.1.4 Crystallinity of oxidized cellulose

The X-ray diffraction patterns of cellulose powder extracted from OISW and oxidized cellulose are shown in Fig.5 . As shown in Fig.5 , the intensity of the crystalline peaks for the oxidized is lower and became almost amorphous. This could be attributed to the oxidation by periodate and the loss of crystallinity [32, 40, 33]. The loss of crystallinity could be because the glucopyranose ring undergoes be ring opening which disruption and loss of H-bonding which lead loss of the cell structure.

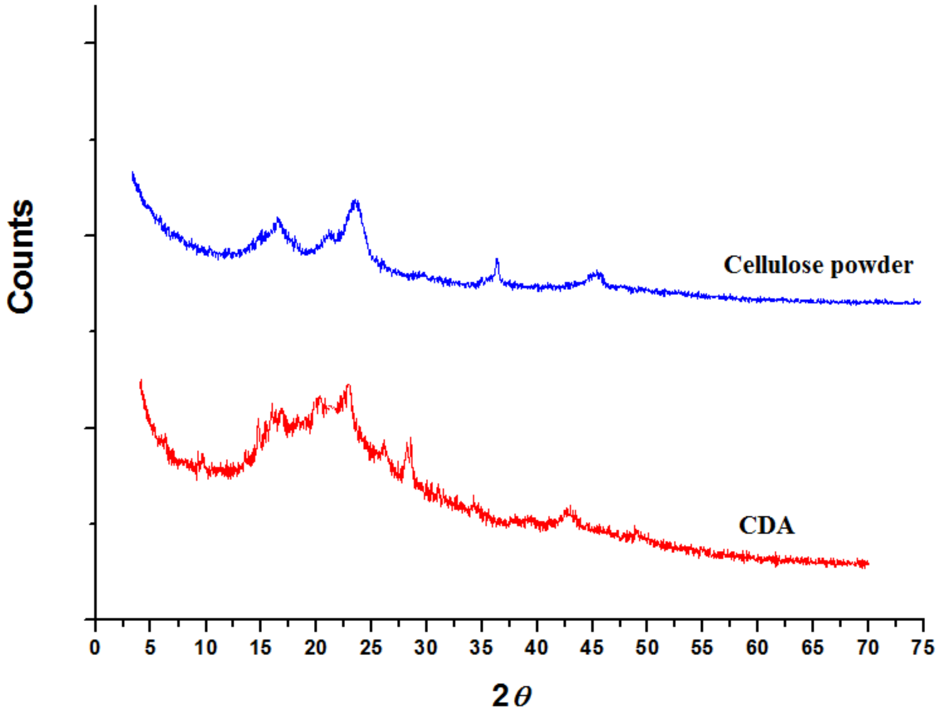


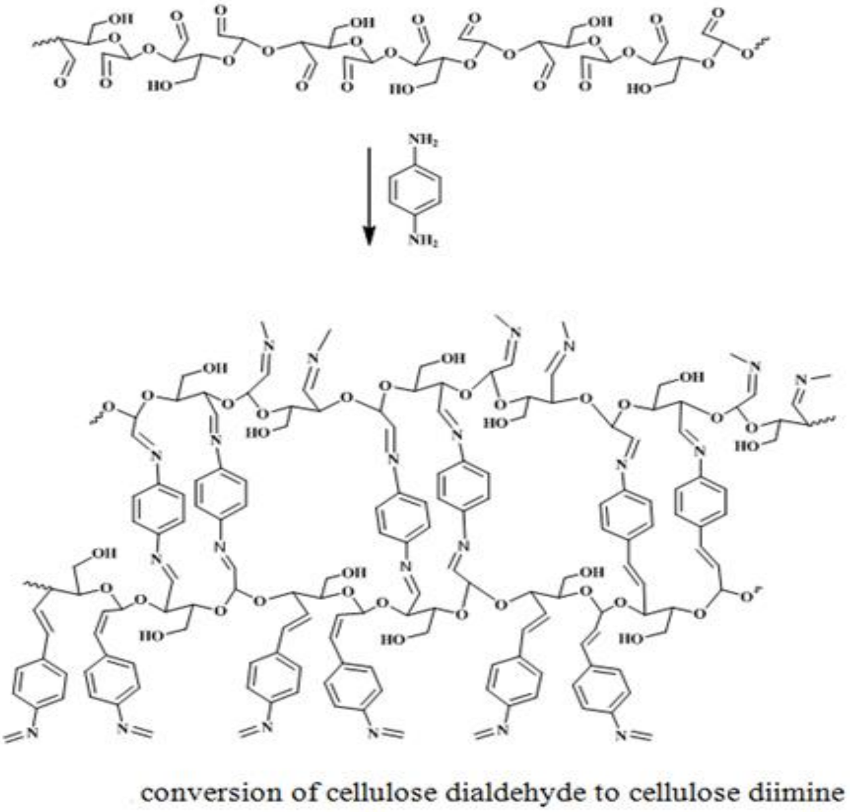
FIG. III.5: X-ray diffraction profiles of cellulose

3.2 Reaction of Dialdehyde Cellulose with Diamine:

The aldehyde groups are known to be versatile, it is very reactive and could be converted to various function group. For example, it can be further oxidized to carboxylic groups [37] or reduced to primary alcohols [38], or reacted with amine to form imine [39]. The imine then could be reduced to an amine. Amine is known to have tendency to complex with metal due to its lone of pair of electrons. In this study it was chosen to be converted to an imine then reduced to an amine

The carbon of the carbonyl group of the aldehyde is an electrophilic carbon it undergoes condensation reaction with amine as shown in Scheme III.6 to form an amine after the loss of a water molecule. Figure shows the reaction between cellulose dialdehyde and 1,4-diaminobnezene. The nucleophilic addition of the amine to the carbonyl compound of the molecule gives rise to a hemiaminal intermediate, followed by transfer of a proton from nitrogen to oxygen, then a loss of water is lost in an elimination reaction to give an imine with excellent yield (>95%).

This diamine was chosen because it bridges to cellulose aldehyde chains and form a kind of crown amine. A circle with multi coordination site for metals.



Scheme III.6: conversion of cellulose dialdehyde to cellulose diimine

3.2.1 FT-IR of cellulose diimine (CDI)

The FT-IR spectrum shown in FIG III.3, shows peak similar those of cellulose in addition to the following: the disappearance of the aldehyde band at 1730 and the presence of the imine group C=N at about 1660 and the C=C of the aromatic group at about 1560.

3.3 Reduction of cellulose imine to amine.

The reduction of cellulose imine was carried out with sodium borohydride, the reaction is a straight forward reaction and usually carried out in methanol. The reduction of the arylimine into an amine.

1,4-diaminobenzene was chosen, because it crosslinks the cellulose chains to form a crown amine with high affinity for metal.

3.3.1 FT-IR of CDAm

The obtained FT-IR spectrum of is shown in FIG. III.3 , the spectrum shows the disappearance of the imine band at 1660 cm^{-1}. The aromatic C=C stretching shows at about 1560 cm^{-1} as before with the CDI spectrum. The N-H band which should show up at about 3200 cm^{-1} is covered with the strong and broad O-H band.

3.3.2 ^{13}C of cellulose diimine and cellulose diamine

The NMR spectrum of CDI and CDAm shown in FIG. III.7 clearly show the aromatic carbon which extend from 115 ppm to 145 ppm. Some differences could be noticed between the two spectra in the aromatic region. The peak at 165 ppm in the CDI spectrum could be attributed to C=N, which is absent from the CDAm spectrum.

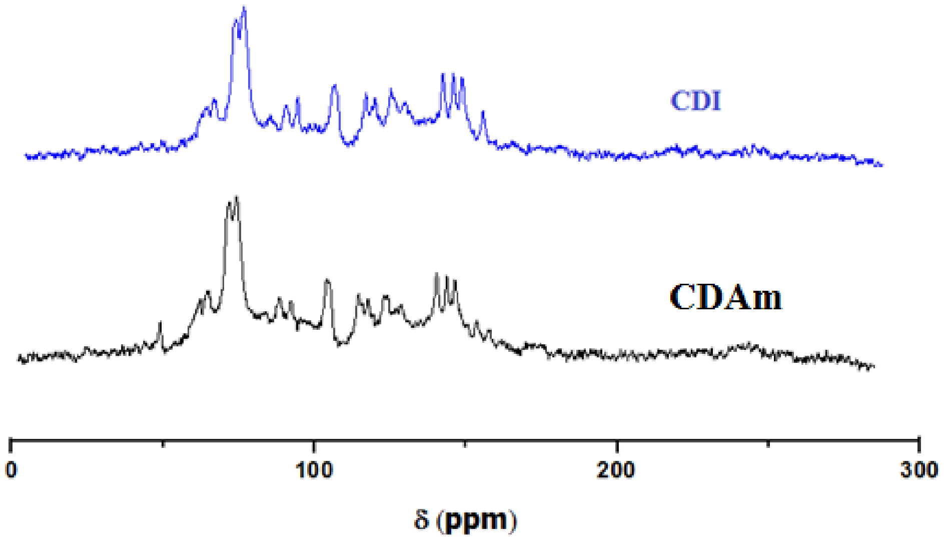
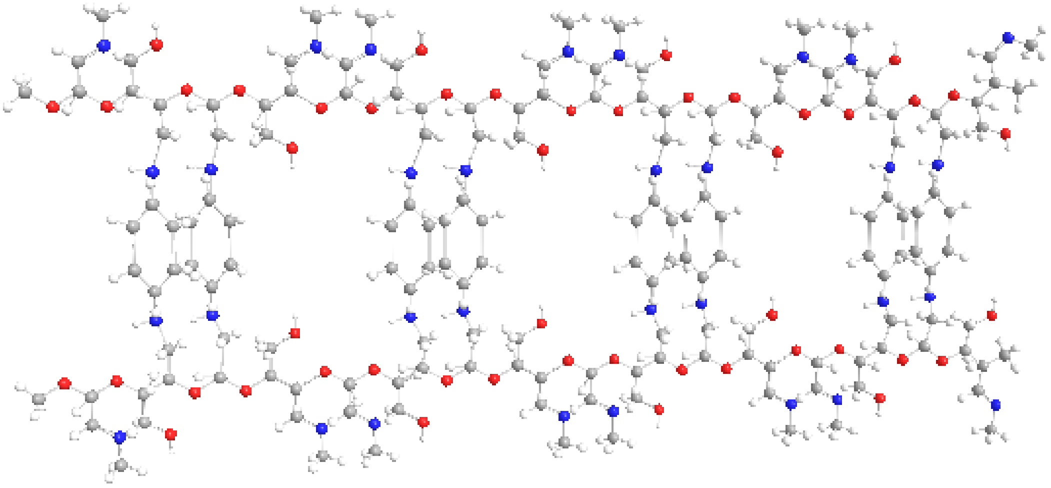


FIG. III.7: ^{13}C NMR of CDI and CDAm

Cellulose diimine shown in scheme III.6 was reduced to cellulose diamine using sodium borohydride. The structure shows a good distribution of amines and oxygen all over the structure. The structure properties make this 3D polymer unique for metal coordination (12, 24, 25).



3.4 Extraction of metals from Wastewater Using Cellulose Based Diamine

In this part of this study, heavy metal ions with different concentration was shaken with different amount of polymer. The effect of other variables such as extraction time, temperature and pH were evaluated to determine optimum conditions for the highest adsorption efficiency.

The extraction was carried out using a batch adsorption process which included suspension then filtration. The analysis was performed on the supernatant to determine the concentration of free unextracted ions

Lead, Copper and Iron ions were evaluated.

3.4.1 Effect of polymer (3) dosage on percent of adsorption of lead:

Four solutions of Lead with known concentration (10 ppm, 100 mL) were prepared, various amount of polymer 0.1 g, 0.5 g, 1.0 g ,1.5 g was added to each solution. The mixtures were shaken at 180 rpm and 30.3 C for 35 min in a thermostat bath.

The solutions were then filtered and the concentration of residual ion in supernatant was measured using Atomic Adsorption Spectroscopy (AAS) at wavelength 217 nm, results are shown in Figure III.8. As shown in Figure III.8, the amount of metal extracted increases by increasing the polymer dosage. The sharp increase occurred at the beginning by increasing the dosage form 0.1 g to 0.5 g, then slow increase was noticed.

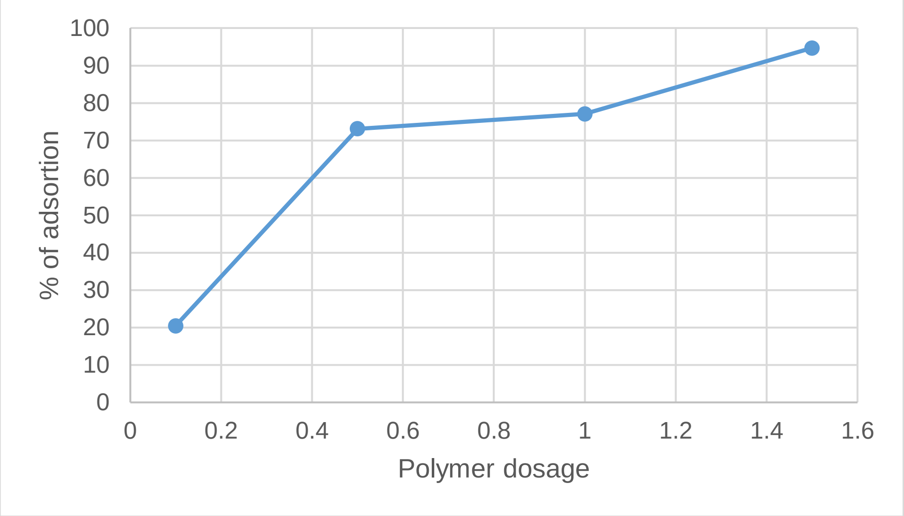


Figure III.8: **Effect of polymer dosage on extraction efficiency, experiment carried out on a solution of lead with 10 ppm.**

In a second experiment the concentration of lead was increase to 20 ppm. Four solutions of Lead with known concentration (20 ppm, 100 mL) were prepared, various amount of polymer 0.1 g, 0.5 g, 1.0 g ,1.5 g was added to each solution. The mixtures were shaken at 180 rpm and 30.3 C for 35 min in a thermostat bath.

The solutions were then filtered and the concentration of residual ion in supernatant was measured using Atomic Adsorption Spectroscopy (AAS) at wavelength 217 nm, results are shown in Figure III.9. As shown in Figure III.9. Similar results were obtained, the amount of metal extracted increases by increasing the polymer dosage. The sharp increase occurred at the beginning by increasing the dosage form 0.1 g to 0.5 g, then slow increase was noticed.

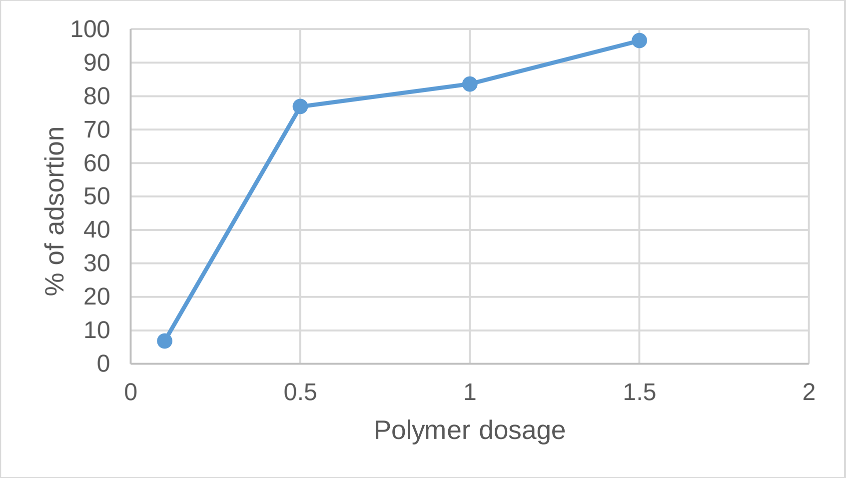


Figure III.9: Effect of polymer dosage on extraction efficiency, experiment carried out on a solution of lead with 20 ppm.

To confirm the previous results, the above experiment was also repeated on a lead solution with 50 ppm concentration. Results are shown in Figure III.10.

From the results of the three experiments it could be concluded that, 0.5 g polymer could be enough to extract more than 80% of the lead ions.

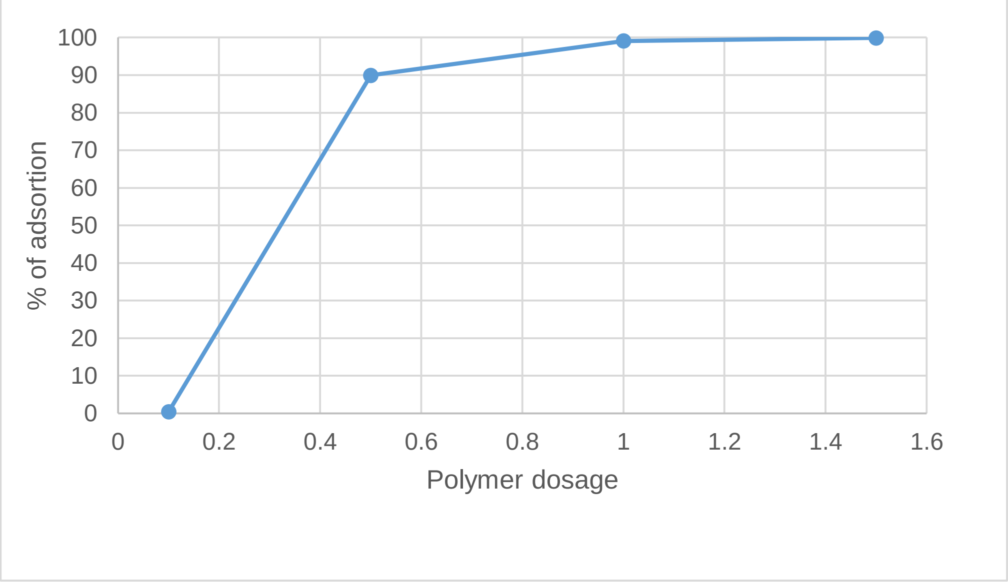


Figure III.10: Effect of polymer dosage on extraction efficiency, experiment carried out on a solution of lead with 50 ppm.

3.4.2 Effect of time on percent of extraction of lead by polymer (3) :

The effect of time was studied on three solutions of lead ions to ensure reproducibility of the results. Three solution of lead with concentrations of 10ppm, 20 ppm, and 50 ppm each with a 100 ml volume were prepared. The polymer dosage was 0.5 g in all experiments. The extraction was carried out for period of time ranges from 30 to 120 min.

The solutions were shaken at 180 rpm and 30.3 C, using thermostat shaker for various period of time. The solutions were then filtered and the concentration of residual ion in supernatant was measured using Atomic Adsorption Spectroscopy (AAS) at wavelength 217 nm. Results are shown in Figures III. 11, 12 and 13. As shown in the figures, after 30 min over 80% of the lead were removed, at a 120 min quantitative extraction was observed.

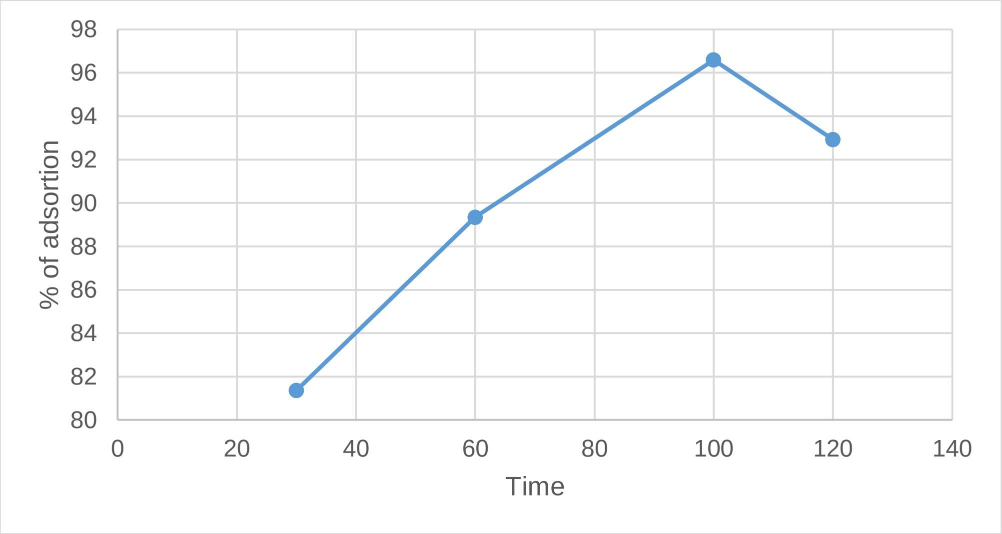


Figure III.11: Effect of extraction time on extraction efficiency of solution with 10 ppm of lead.

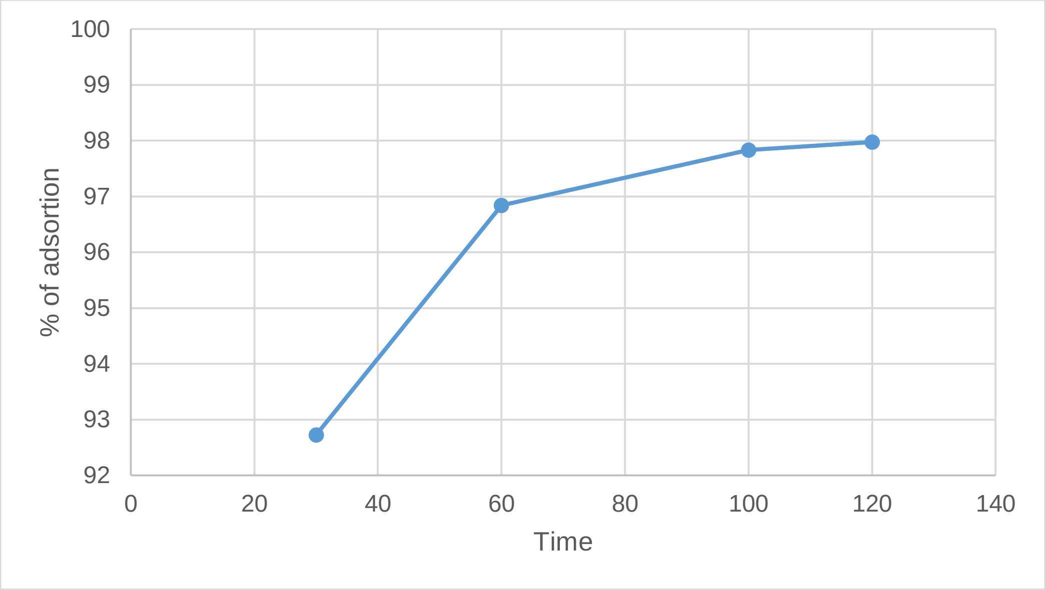


Figure III.12: Effect of extraction time on extraction efficiency of solution with 20 ppm of lead.

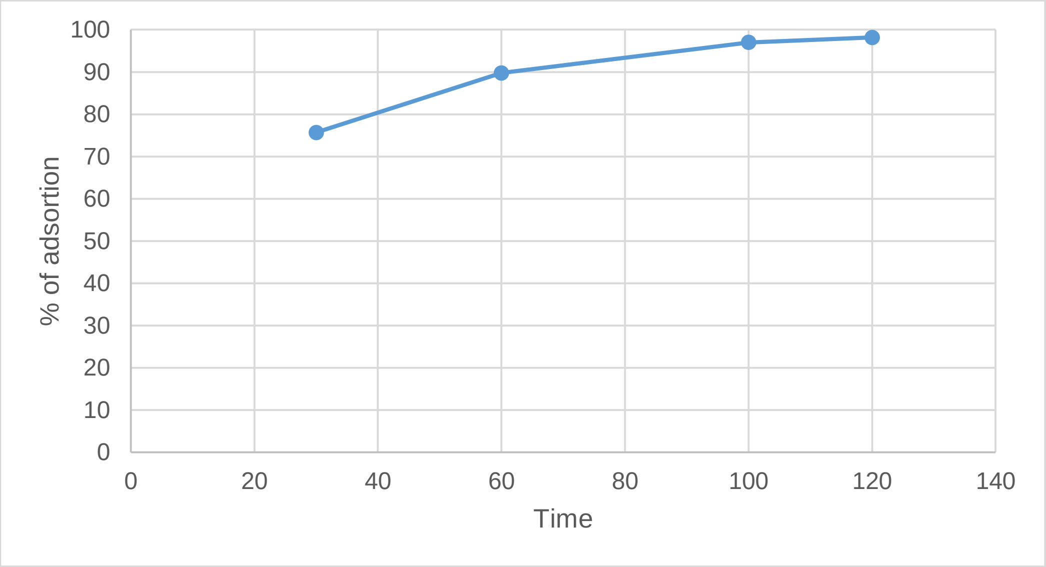


Figure III.13: Effect of extraction time on extraction efficiency of solution with 50 ppm of lead.

3.4.3 Effect of temperature on percent of extraction of lead by polymer (3):

The effect of temperature was studied on three solutions of lead ions to ensure reproducibility. Three solutions of lead with concentrations of 10 ppm, 20 ppm, and 50 ppm each with 100 ml volume were prepared. A polymer dosage of 0.5 g was used in all experiments. The extraction was carried out for period of 120 min at various temperatures ranged from room to 50^{o}C.

As above the solutions were shaken at 180 rpm, using thermostated shaker for various Temp degree. The solutions were then filtered and the concentration of residual ion in supernatant was measured using Atomic Adsorption Spectroscopy (AAS) at wavelength 217 nm. Results are shown in Figures III. 14, 15 and 16. As shown in the figures, an increase in the extraction efficiency was noticed as the temperature increased from room temperature to 45^{o}C. At temperature over 45 ^{o}C the extraction efficiency dropped in in the first case (10 ppm solution), increased in the case of 20 ppm solution, and didn’t change in the case of 50 ppm solution. So mixed results were obtained. Generally, the extraction efficiency enhanced slightly at a temperature over 45 ^{o}C.

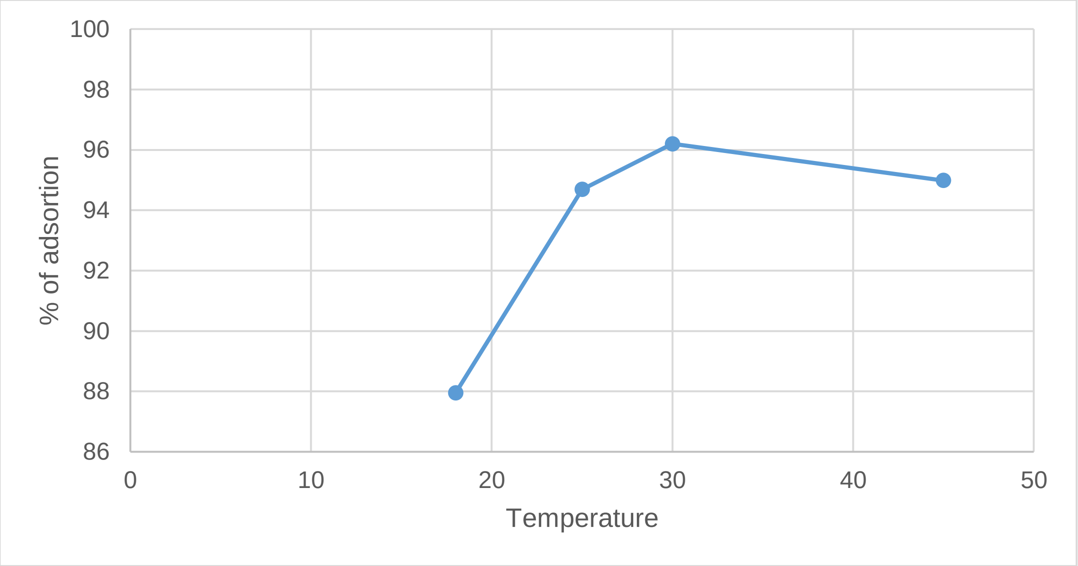


Figure III.14: Effect of temperature on extraction efficiency on solution with 10 ppm of lead.

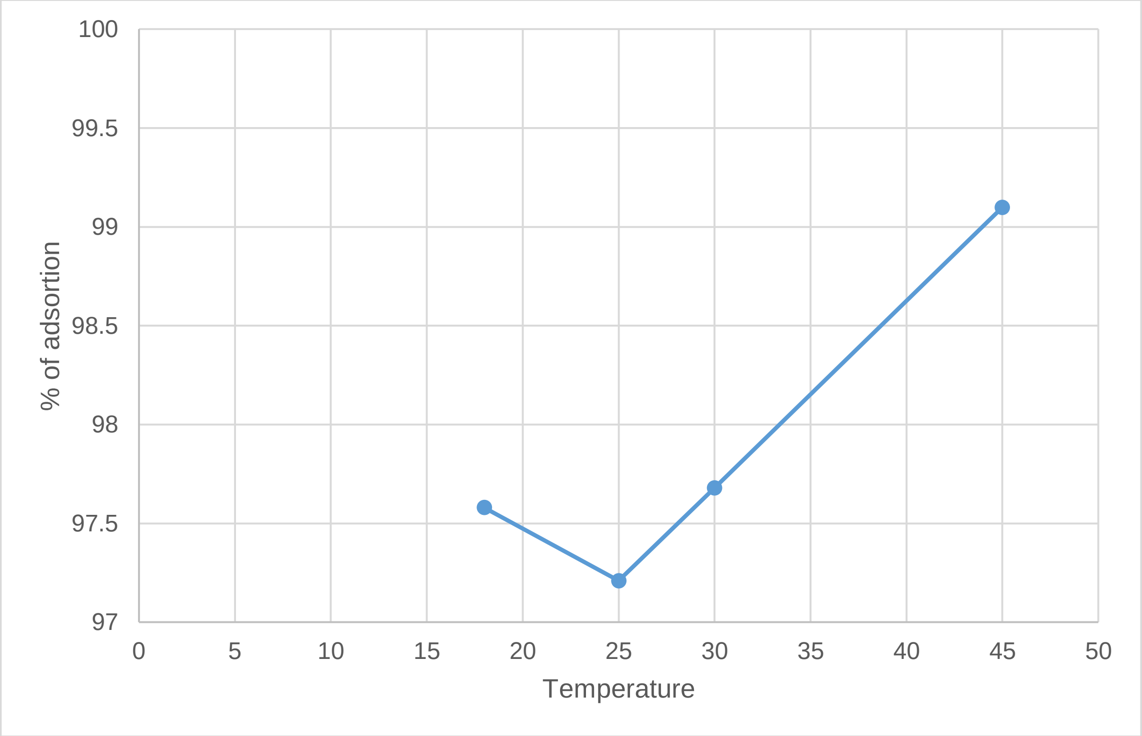


Figure III.15: Effect of temperature on extraction efficiency on solution with 20 ppm of lead

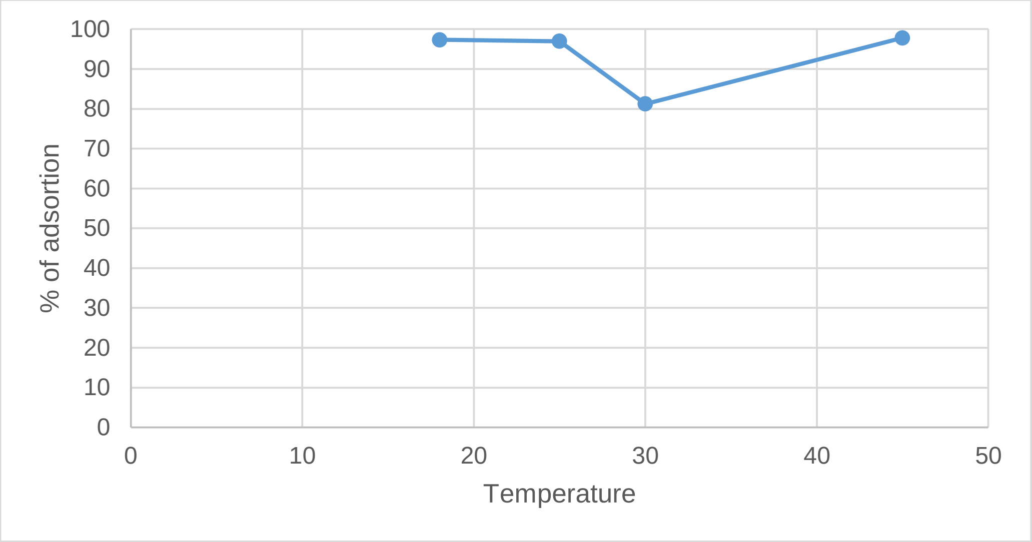


Figure III.16: Effect of temperature on extraction efficiency on solution with 50 ppm of lead

3.4.4 Effect of pH on percent of extraction of lead by polymer (3):

The effect of pH on extraction efficiency was also evaluated. The study was carried out s on three solutions of lead ions to ensure reproducibility. Three solutions of lead with concentrations of 10 ppm, 20 ppm, and 50 ppm each with a 100 mL volume were prepared. A polymer dosage of 0.5 g was used in all experiments. The extraction was carried out for period of 120 min at 30 ^{o}C and various pH ranged from acidic to alkaline.

As above the solutions were shaken at 180 rpm, using thermostated shaker for various pH value. The solutions were then filtered and the concentration of residual ion in supernatant was measured using Atomic Adsorption Spectroscopy (AAS) at wavelength 217 nm. Results are shown in Figures III. 17, 18 and 19. As shown in the figures, an increase in the extraction efficiency was noticed as the pH increased from 2 to 4. The results show that an effective pH for extraction of metal ions is 4 and over. The results are expected since at pH lower than 4, the amine is in the ammonium form, it carries a positive charge. The nitrogen lone pair are not available for binding the metals.

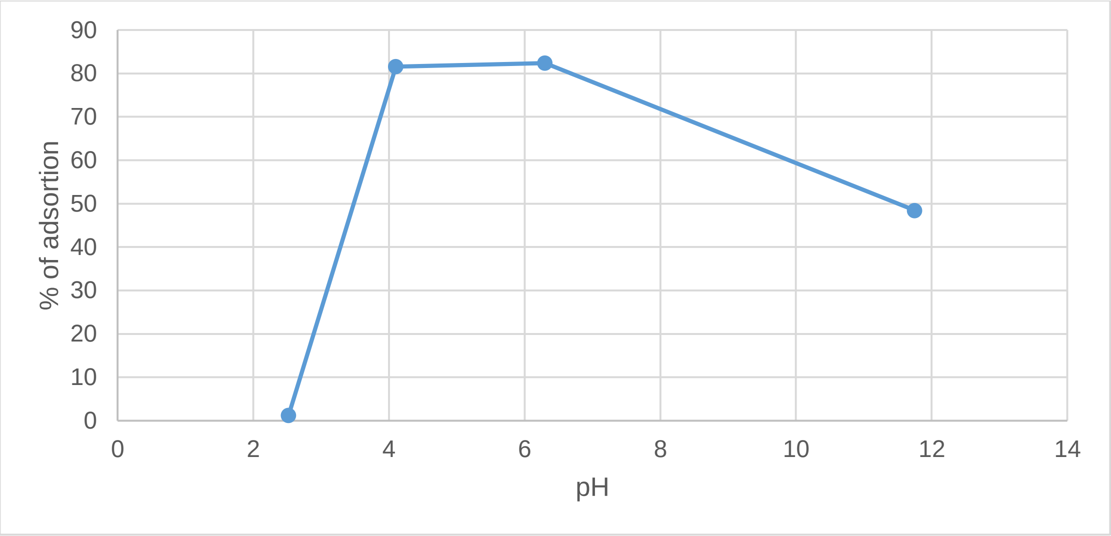


Figure III.17: Effect of pH on extraction efficiency on solution with 10 ppm of lead

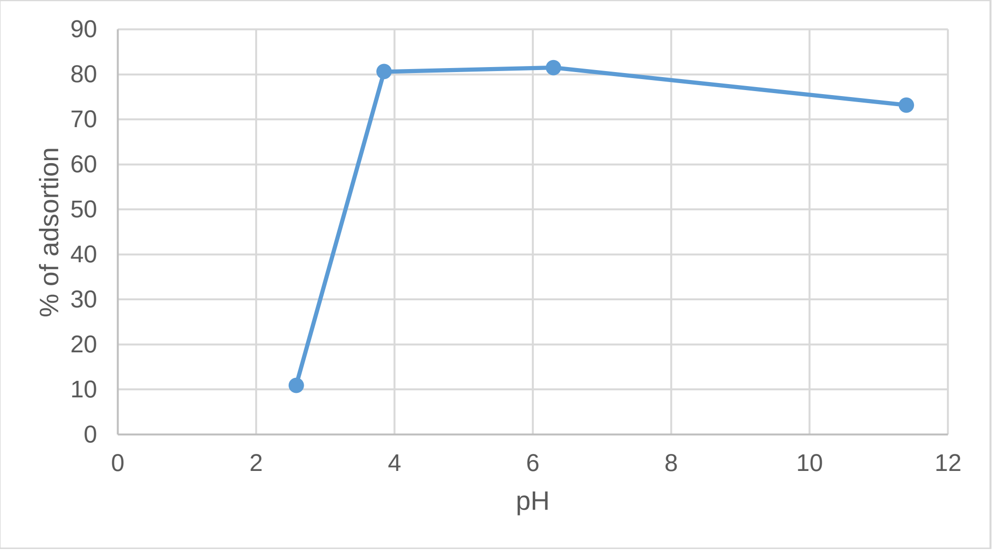


Figure III.18: Effect of solution pH on the extraction efficiency on solution with 20 ppm of lead

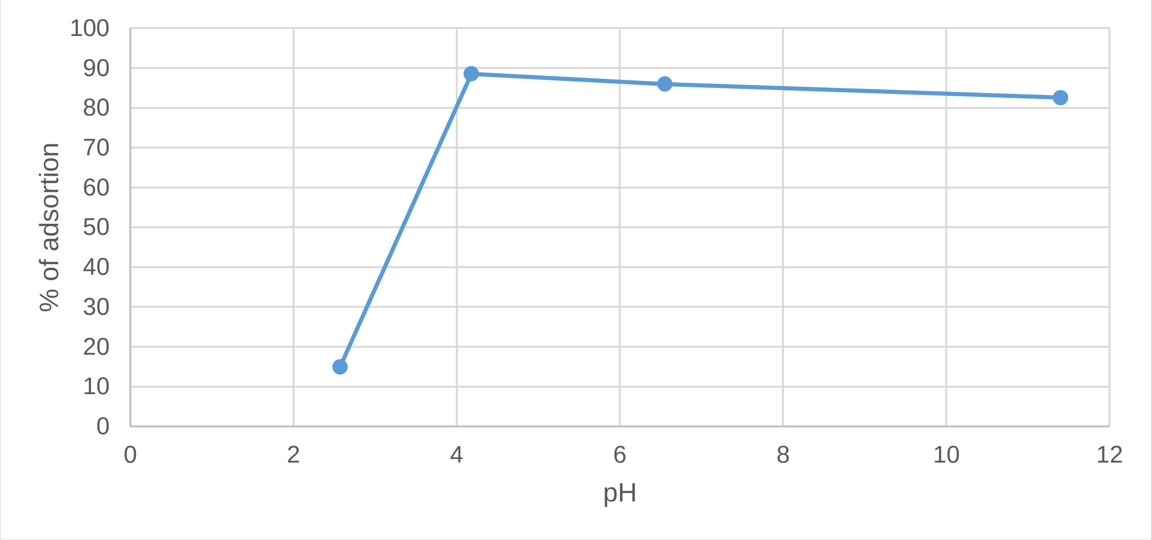


Figure: III.19 Effect of pH on extraction efficiency on solution with 50 ppm of lead

3.5 Comparisons Study on the adsorption of lead, iron and copper ions

A comparison study was conducted on adsorption of various ions by the cellulose based diamine polymer. The adsorption conditions are listed in Table III.2 and in Figure III.20.

Table III.2: Comparison between Lead, Iron and Copper ions adsorption

Solution pH	% of Extraction of copper	Solution pH	% of Extraction of iron	Solution pH	% of Extraction of lead
2.88	88.01%	2.8	71.89%	2.57	14.97%
4.33	98.34%	4.38	99.24%	4.18	88.54%
5.96	97.45%	6.11	99.52%	6.55	85.99%
9.55	97.72%	10.89	99.40%	11.4	82.56%

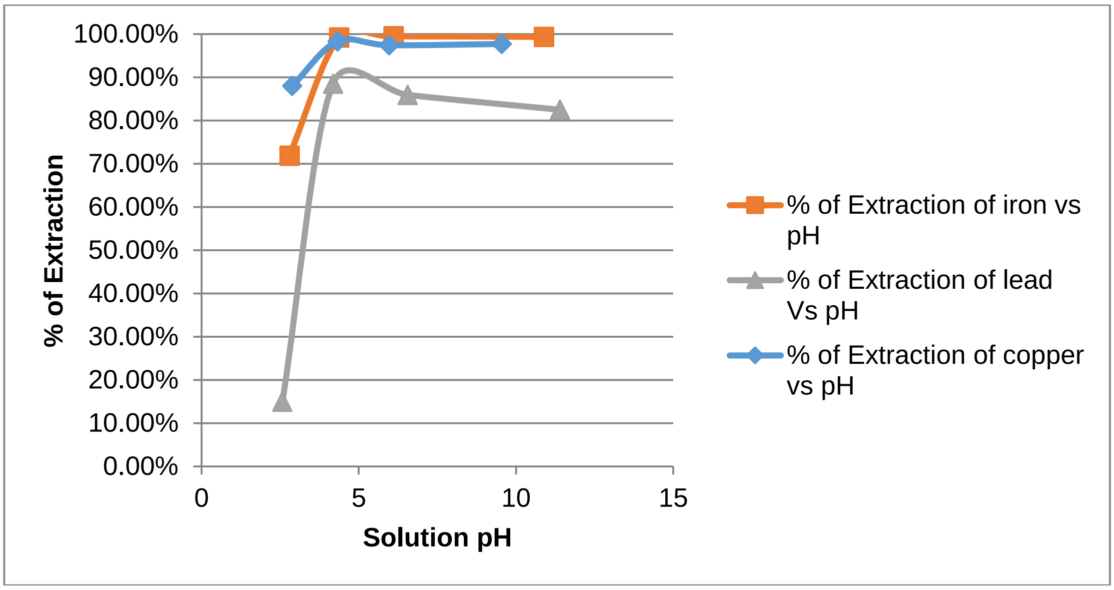


Figure III.20: Percent of metals extraction with pH solution, concentration 50 ppm, polymer weight 0.5 g

As shown in figure III.20, adsorption efficiency for Iron was the highest, copper then lead.

3.6 kinetic studying

The kinetics, which its important physical–chemical aspects of the process, used to evaluate the process of adsorption.The rate equation was used to analyze the adsorption kinetics, pseudo-second-order reaction kinetics

Pseudo-second-order kinetics can be used to assess the process of pb(II) concentration.

3.6.1 Pseudo-second-order adsorption kinetics of adsorbate on CM adsorbent (50 ppm of lead) according to the equation 4, results are summarized as shown in table III.3

$$\text{Eq. 4:} \qquad t / q_t = 1 / (K_2 q_e^{2)} + t / q_e$$

where k_2 ($dm^3\ mg^{-1}\ min^{-1}$) is the rate constant of the adsorption process, q_e ($mg\ g^{-1}$) is the equilibrium amount of adsorbate, and q_t ($mg\ g^{-1}$) is the amount of adsorbate at any time t.

Table III.3: Pseudo-second-order adsorption kinetics

Extraction Time (min)	Conc. Of pb after extraction	% of Extraction	q(mg/g)	t/q
30	12.1599	75.6802	7.56802	3.96404872080148
60	5.1193	89.7614	8.97614	6.68438772122538
100	1.4988	97.0024	9.70024	10.3090232818982
120	0.9256	98.1488	9.81488	12.2263338930277

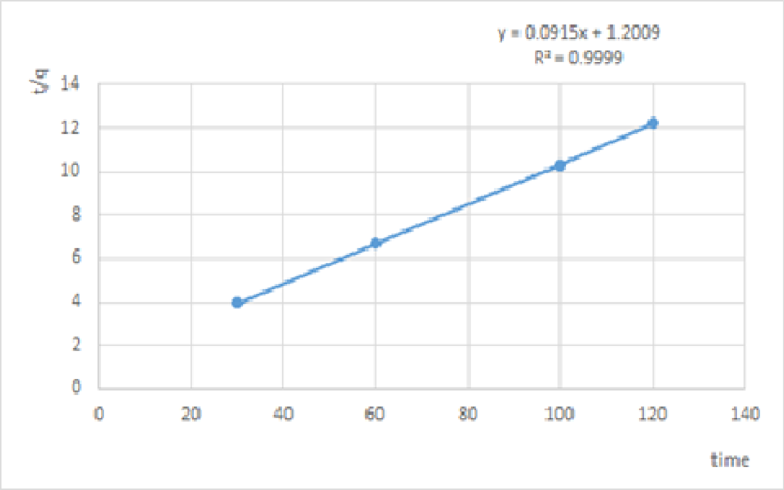


Figure III.21: Pseudo-second-order adsorption kinetics[27]

An adsorption isotherm can be used to characterize the interaction of adsorbate with adsorbents. The isotherm provides a relationship between the concentration of adsorbate in solution and the amount of adsorbate adsorbed on the solid phase when both phases are in equilibrium. In this study, according to the effect of temperature on the adsorption, the equilibrium condition was kept at the optimum temperature of the adsorbate, and the adsorption isotherms were analyzed by the two most commonly used model equations, which were Langmuir and Freundlich.

The adsorption isotherm models of Langmuir and Freundlich can be expressed as Eq. (5,6) and (7) respectively.

The Fig. III.22 and Fig III.23 shows the linear plots of adsorption isotherm for the adsorbate adsorption on CM at the optimum temperature.

3.6.2 Linear plot of Langmuir adsorption of of pb(II) at 30 °C according to the equations 5 and 6, results are summarized as shown in table III.4

Eq. 5: $q_e = (Q^0 \; b_L \; C_{e)} \;/\; (1 + (b_L \; C_{e)})$

Eq. 6: $C_e \;/\; q_e = C_e \;/\; Q^0 + 1 \;/\; (Q^0 b_{L)}$

where C_e (mg L^{-1}) and q_e (mg g^{-1}) are the concentration and adsorption capacity at the equilibrium, respectively. Q_0 (mg g^{-1}) and b_L (L mg^{-1}) are adsorption capacity and binding energy of adsorption of Langmuir, respectively.

Table III.4: Langmuir adsorption of of pb(II) at 30 °C

Conc. Of pb ion (ppm)	q (mg/g)	c/q	1/C	1/q
10	1.6479	6.068182	0.1	0.606818209
20	3.2595	6.135835	0.05	0.306791756
50	8.8541	5.647114	0.02	0.112942282

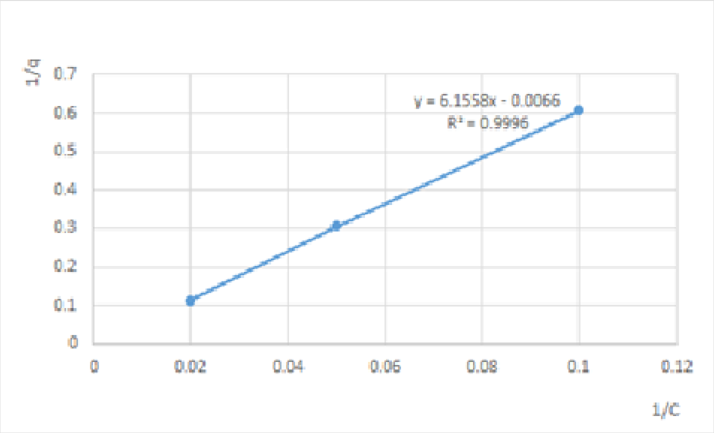


Figure III.22 : Langmuir adsorption of of pb(II) [27]

3.6.3 Linear plot of Freundlich adsorption isotherm of pb(II) at 30 °C according to the equation 7, results are summarized as shown in table III.5

Eq. 7: $\ln q_e = \ln K_F + (1 / n_F) * \ln C_e$

Table III.5: Freundlich adsorption isotherm of pb(II) at 30 °C

Conc. Of pb ion (ppm)	q (mg/g)	c/q	ln C	ln q
10	1.64794	6.068182	2.302585	0.499526
20	3.25954	6.135835	2.995732	1.181586
50	8.85408	5.647114	3.912023	2.180878

where C_e and q_e are the same meaning as noted previously. K_F and n_F are Freundlich constants measuring the adsorption capacity and the adsorption intensity, respectively.

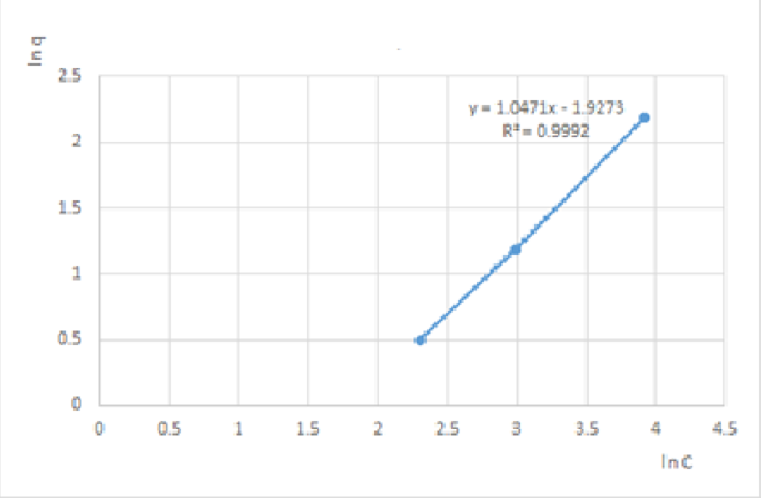


Figure III.23 : Linear plot of Freundlich adsorption isotherm of pb(II) [27]

The adsorption data conformed to the Pseudo-second-order, Langmuir and the Freundlich isotherms but fitted best into the Pseudo-second-order model. The R^2 for Pseudo-second-order equation was 0.9999, R^2 for Langmuir was 0.9996, and R^2 for Freundlich isotherms was 0.9992.

References

[1]: Sud, D., Mahajan, G., & Kaur, M. P. (2008). ***Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review.*** **Bioresource Technology**, 99(14), 6017–602.

[2] Ngah, W. S. W., & Hanafiah, M. (2008). **Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. Bioresource Technology,** 99(10), 3935–3948.

[3] Weiss, B., & Landrigan, P. J. (2000). ***The developing brain and the environment: Anintroduction. Environmental Health Perspectives,*** 108, 373–374.

[4] Friberg, L. T. (1985). ***The rationale of biological monitoring of chemicals – With special reference to metals.*** **American Industrial Hygiene Association Journal,** 46(11), 633–642.

[5] Pagliuca, A. and Mufti, G.J. (1990). ***Lead Poisoning: An Age-Old Problem.*** **British Medical Journal,** 300, 830-832.

[6] Theophanides, T. and Anastassopoulou, J. (2002). ***Copper and Carcinogenesis. Oncology/Haematology,*** 42, 57-64.

[7] Qaiser, S., Saleemi, A.R. and Umar, M. (2009). ***Biosorption of Lead from Aqueous Solution by Ficusreligiosa Leaves: Batch and Column Study.*** **Journal of Hazardous Materials,** 166, 998.

[8] Marchetti, M., Clement, A., Loubinoux, B. and Gerardin, P. (2000). ***Decontamination of Synthetic Solutions Containing Heavy Metals***

Using Chemically Modified Sawdust Bearing Polyacrylic Acid Chains. **Wood Science and Technology,** 46, 331-333.

[9] Maekawa, E. and Koshijima, T. (1990). ***Preparation and Characterization of Hydroxamic Acid Derivatives and Its Metal Complexes Derived from Cellulose.*** **Journal of Applied Polymer Science,** 40, 1601-1613.

[10] Saliba, R., Gauthier, H. and Gauthier, R. (2005). ***Adsorption of Heavy Metal Ions on Virgin and Chemically-Modified Lignocellulosic Materials.*** **Adsorption Science & Technology,** 23, 313-322.

[11] Aoki, N., Fukushima, K., Kurakata, H., Sakamoto, M. and Furuhata, K. (1999). ***6-Deoxy-6-mercaptocellulose and Its S-Substituted Derivatives as Sorbents for Metal Ions.*** **Reactive and Functional Polymers,** 42, 223-233.

[12] Saravanan, R, Ravikumar, L. (2015). ***The Use of New Chemically Modified Cellulose for Heavy Metal Ion Adsorption and Antimicrobial Activities.*** **Journal of Water Resource and Protection,** 7, 530-545.

[13] Gu, Jun; Zhou, Guan-cheng; Wu, Wei-bing; Gong, Mu-rong; Dai, Hong-qi From Xianweisu Kexue Yu Jishu (2014), **22(3),** 8-13.

[14] Wang, Xiaofen; Wei, Wanxing; Zhang, Xiaoxia; Zhou, Min; Liu, Sheng From Huanjing Gongcheng Xuebao (2015), ***9(4),*** 1553-1558.

[15] Zhou, Shukui; Liu, Yingjiu; Xie, Shuibo; Deng, Wenjing; Jiang, Haihao; Kang, Li; Fang, Liang From Faming Zhuanli Shenqing (2015), ***CN 104772123 A*** Jul 15, 2015.

[16] Shi-yong; Xiong, Qi-zhong; Zhao, Hui-jun From Gongneng Gaofenzi Xuebao (2015), **28(2),** 165-171.

[17] Sjostrom, E., Wood Chemistry. ***Fundamentals and Applications. Second edition ed.*** 1993, San Diego: Academic press. 292. b) Nevell, T. P. ; Zeronian S. H.: ***Cellulose chemistry fundamentals in Cellulose Chemistry and its Applications,*** Wiley & Sons, New York, 1985. c) Gray, D. G. J. Appl. Polym. Sci., Appl. Polym. Symp., 37, 179-192, 1983. d) Kubota, T. ; Kusano, T. ; Yamamoto, C.; Yamashita, E. ; Okamoto, Y., Chem. Lett., 7, 724-725 (2001). e) Matsuzaki, K.; Yamamoto, I. ; Sato, T. ; Oshima, R. Macromol. Chem., 186, 449-456, 1985. f) Klemm, D.; Philipp, B. ; Heize, U. ; Wagenknecht, W. ***Comprehensive Cellulose Chemistry, volume Functionalization of Cellulose, Wiley-VCH, Weinheim,*** 1998. g) Trejo-O'Reilly JA, Cavaille JY, Gandini A. Cell.4:305–20, 1997. h) Kuruvilla, J.; Varghese, S.; Kalaprasad, G.; Thomas, S. Prasannakumari, L.; Koshy, P. Eur Polym J 32:1243–50 (996). i) Trejo-O'Reilly JA, Cavaille JY, Paillet M, Gandini A, Herrera-Franco P, Cauich J. J Polym Compos (2000), 21:65–71.

[18] Ayrilmis, N., and Buyuksari, U. ***"Utilization of olive mill sludge in the manufacture of fiberboard,"*** **BioResources** 5, 1859-1867, 2010a.

[19] Azbar, N., Bayram, A., Filibeli, A., Muezzinoglu, A., Sengul, F., and Ozer, A. ***"A review of waste management options in olive oil production," Crit. Rev. Environ. Sci. Technol*** (2004), 34, 209-247.

[20] Othman A. Hamed, Yusra Fouad,a Emad M. Hamed, and Nisreen Al-Hajj ***“Cellulose Powder From Olive Industry Solid Was” BioResources*** 7(3), 4190-4201, 2012. (b)Yusra Salameh MS Thesis. (2009). ***“Method of extracting cellulosic Materials From Olive pulp” An Najah National University***.

[21] Robert J. Moon,*abc Ashlie Martini,d John Nairn,e John Simonsenf and Jeff Youngblood*c. (2011).***"Cellulose nanomaterials review: structure, properties and nanocomposites"*** **Birck and NCN Publications , Chem. Soc.** Rev., 40, 3941–3994

[22] Toshiro Morooka, Misato Norimoto, Tadashi Yamada. (1989). ***"Periodate Oxidation of Cellulose by Homogeneous Reaction***" **Journal of Applied Polymer Science**, Vol. 38, 849-858.

[23] Susanne Hansson, Stora Enso & Gunilla Carlsson. (2015). ***"Production of Dialdehyde Cellulose and Periodate Regeneration: Towards feasible oxidation processes "*** Karlstad University.

[24] Murray M. Sprung. (1940). ***"A Summary of the Reactions of Aldehydes with Amines " ACS Journals, Chem. Rev.,*** *26* (3), pp 297–338

[25] ROBERT W. LAYER . (1966).***"THE CHEMISTRY OF IMINES " B. F. Goodrich Co., Research Center,*** Breckuville, Ohio , December 7

[26] M.A. Barakat. (2011). ***"New trends in removing heavy metals from industrial wastewater " Arabian Journal of Chemistry*** 4, 361–377, King Abdulaziz University (KAU).

[27] Yanmei Zhou, Qiang Jin, Xiaoyi Hu, Qingyou Zhang, Tongsen Ma. (2012). ***"Heavy metal ions and organic dyes removal from water by***

cellulose modified with maleic anhydride" Journal of Materials Science , June, Volume 47, Issue 12, pp 5019–5029

[28] Mambo Moyo, Linda Chikazaza, Benias Chomunorwa Nyamunda, and Upenyu Guyo**.** (2013). ***" Adsorption Batch Studies on the Removal of Pb(II) Using Maize Tassel Based Activated Carbon" Journal of Chemistry,*** Volume 2013, Article ID 508934, 8 pages

[29] Sahin, HT. RF-CF4. (2007). ***plasma surface modification of paper: chemical evaluation of two sidedness with XPS/ ATR-FTIR. Appl.*** **Surf. Sci.** 253 (9), 4367–4373.

[30] Daoud, W.A.; Xin, J.H.; Zhang, Y.H.; Mak, C.L. (2006) ***Pulsed laser deposition of superhydrophobic thin teflon films on cellulosic fibers.*** **Thin Solid Films,** 515, 835–837.

[31] Bayer, I.S.; Steele, A.; Martorana, P.J.; Loth, E.; Miller, L. (2009). ***Superhydrophobic cellulose-based bionanocomposite films from Pickering emulsions.*** Appl Phys Lett. 94 (16), 163902.

[32] Klemm, D.; Heublein,B.; Fink, H.P.; Bohn, A. (2005). ***Cellulose: Fascinating Biopolymer and Sustainable Raw Material. Angew. Chem.,*** Int. Ed. 44, 3358.

[33] Heinze, T.; Liebert, T. (2001). ***Unconventional methods in cellulose functionalization. Progr.*****Polym. Sci**. 26, 1689.

[34] Jackson, E.J.; Hudson, C.S. (1937*). **Application of the cleavage type of oxidation by periodic acid to starch and cellulose.*** J. **Am. Chem**. Soc. 59, 2049.

[35] Jackson, E.J.; Hudson, C.S. (1938). ***The structure of the products of the periodic acid oxidation of starch and cellulose***. J. **Am. Chem**. Soc. 60, 989.

[36] Varma, A.J.; Chavan, V.B. A. (1995). ***study of crystallinity changes in oxidised celluloses.*** **Polymer Degradation and Stability,** 49, 245.

[37] Hofreiter, B. T.; Wolff, I. A. and Mehltretter, L. (1957). ***Chlorous acid oxidation of periodate oxidized cornstarch.*** J. **Am. Chem**. Soc. 79, 6457.

[38] Casu, B.; Naggi, A.; Torri, G.; Allegra, G.; Meille, S. V.; Cosani, A.; Terbojevich, M**.** (1985). ***Stereoregular acyclic polyalcohols and polyacetates from cellulose and amylase.Macromolecules.*** 18, 2762.

[39] Maekawa, E.; Koshijima, T. (1991). Preparation and structural consideration of nitrogencontaining derivatives obtained from dialdehyde celluloses. J. Appl. Polym. Sci. 42, 169.

[40] Kim, U. J.; Kuga, S.; Wada, M.; Okano, T.; Kondo, T. (2000). ***Periodate oxidation of crystalline cellulose. Biomacromolecules,*** 1, 488.

جامعة النجاح الوطنية

كلية الدراسات العليا

تصنيع بوليمر ثنائي أمين السليولوز ثلاثية الأبعاد لتنقية مياه الصرف

إعداد

باسمه قاسم احمد "رضوان خليف"

إشراف

أ.د.شحدة جودة

د.عثمان حامد

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

2018

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الملخص

المعادن الثقيلة السامة، تؤثر على صحة الإنسان، ومن الأمثلة على هذه المعادن: الرصاص والكادميوم والزئبق والزرنيخ. وقد تم دراسة تأثير المعادن الثقيلة على صحة الإنسان بشكل منتظم من قبل المنظمات الدولية مثل منظمة الصحة العالمية

وقد استخدمت المعادن الثقيلة من قبل البشر منذ آلاف السنين، استخدامها يتزايد في بعض المناطق في العالم

العديد من المعادن الثقيلة مثل الكادميوم المستخدم في إعادة تحميلها بطاريات النيكل والكادميوم ومصدر آخر للكادميوم هو دخان السجائر، التي تؤثر على صحة الجسم

الزئبق هو مثال آخر على المعادن الثقيلة والبشرية يمكن أن يتعرض لها من المواد الغذائية والأسماك والمياه على شكل ميثيل الزئبق

التعرض الطويل الأمد لهذه المعادن الثقيلة كما هو الحال في مياه الشرب الملوثة تسبب أمراض مثل سرطان الجلد وبعض أنواع السرطان الأخرى

في بحثي الهدف الرئيسي هو إيجاد حل لهذه المشكلة باستخدام المواد الطبيعية منخفضة التكلفة.

في هذه الدراسة أولا تم استعمال مسحوق السليلوز و الياف السليلوز ، في الخطوة الأولى تمت أكسدة السليلوز باستخدام بريودات الصوديوم لإنتاج ثنائي الدهايد السليلوز في غرفة معتمة بعيدا عن الضوء

في الخطوة الثانية تمت مفاعلة ثنائي الدهايد السليلوز مع ثنائي أمين البنزين لإنتاج ثنائي أمين السليلوز ثلاثي الابعاد.

.في الخطوة الثالثة تم استعمال البوليمر في تنقية مياه الصرف الصحي من الرصاص

لقد تمت دراسة عملية استخلاص الرصاص مع تغيير كمية البوليمر ، تغيير تركيز المعدن وتغيير الزمن ودرجة الحرارة ودرجة الحموضة للحصول على الظروف المثالية .

تمت المقارنه في عملية استخلاص كل من الرصاص والنحاس والحديد(+3) باستعمال المسحوق وكذلك الألياف من البوليمر.

حيث كانت النسبة المئوية لاستخلاص الرصاص بواسطة مسحوق البوليمر هو أفضل من الألياف لنفس المعدن.

تم الحصول على نسبة 88.54٪ لاستخلاص الرصاص عند درجة حموضة 4.18 لتفاعل استمر 120 دقيقة

النتائج تشير في هذه الأطروحة إلى أننا نجحنا في استخدام مسحوق البوليمر و ألياف البوليمر المنتجة من مخلفات الزيتون الصلبة في تنقية مياه الصرف الصحي من المعادن الثقيلة السامة .