An-Najah National University

Faculty of Graduate Studies

CELLULOSE GRAFTED WITH β-CYCLODEXTRIN FOR WASTE WATER PURIFICATION FROM TOXIC METAL IONS

By

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Dedication

To my lovely parents, Thank you for your continuous support, I hope from my Allah to protect you for me.

To my dear brothers, my lovely sister and her sons, to the spirit of my sister (Heba), may ask my Allah to gather you in Paradise.

To my lovely husband and his family, Thanks my Allah for your presence in my life.

To my dear friends who still with me in all my steps of my life.

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To my occupied country Palestine, our teaching is the weapon for us against the Zionist occupation.

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحت عنوان:

CELLULOSE GRAFTED WITH β-CYCLODEXTRIN FOR WASTE WATER PURIFICATION FROM TOXIC METAL IONS

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 the researcher’s own work, and has not been submitted elsewhere for any other degree of qualification.

Student’s Name: **اسم الطالب:**

Signature: **التوقيع:**

Date: **التاريخ:**

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CELLULOSE GRAFTED WITH β-CYCLODEXTRIN FOR WASTE WATER PURIFICATION FROM TOXIC METAL IONS

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Abstract

Three polymers of crosslinked cellulose and β-cyclodextrin (A, B, and C) were designed and synthesized.The cross-linking agent used for this purpose was citric acid. Various proportion of the three materials were used for preparing the polymers. The polymer structures were determined by FT-IR and the polymer morphologies were studied by SEM. The adsorption efficiency of the three cellulose-β-cyclodextrin polymers toward Pb (II) from an aqueous solution was investigated as a function of adsorbent dose, temperature, pH and time, the adsorption parameters that lead to an excellent adsorption efficiency were determined. The high adsorption efficiency of the cellulose polymers could be attributed to the presence of various coordination sites which includes carboxyl, hydroxyl and β-cyclodextrin. Thermodynamic analysis results support the high adsorption efficiency of the polymer. The adsorption process fits well with the second pseudo order model and the adsorption isotherm follows a Freundlich isotherm model. Polymer 2 that contains the largest quantity of citric acid showed the highest efficiency toward lead (II). This could be due to the availability of carboxyl groups.

CHAPTER ONE

INTRODUCTION

1.1 Background

Planet’s water is distributed in the following ratios (oceans and seas contain 97.7% of planet’s water, ice and snow 1.9%, underground 0.4%, lakes 0.009%, atmosphere 0.0013%, rivers and streams 0.0002%) [1-4]. The water on earth is not suitable for drinking except that comes from few sources such as underground water, lakes, rivers and streams. The percentage of drinkable water is about 0.4092% of total earth’s water. Even now a day, it is suffering from pollution.

Because of the life development and spread of industries all over the world, the pollution of water became a threatening issue [5].

Efforts are now directed toward keeping the sources of water clean from metals and toxic organic materials.

Industries are polluting water with many toxic materials like heavy metals, organic materials and others.

Existence of heavy metals in water considered as pollutant if concentrations of these metals exceed the threshold limit value. The threshold limit is defined as the average concentration of metals and toxic organics to that normal person may be exposed for 7-8 hours per week for lifetime without showing adverse effects.

Each metal has its threshold limit value according to its toxicity. Examples on the metals that threats human life are lead (Pb), cadmium (Cd), mercury (Hg) and arsenic (As) [6].

The main source of these heavy metals are industrial wastes and domestic usage, or from acid rain that decomposes soil releasing heavy metals to sources of drinkable water [7].

The danger of heavy metals comes from tendency to bio-accumulates. Bio accumulation defined as; the increase in concentration of chemicals in biological organisms over time, compared to the concentration of chemicals in the environment.

The effect of heavy metals on health could be life threatening, therefore, removal of these metals from water became mandatory. For example, mercury causes nerve damage and death, Arsenic may cause cancer, Cadmium causes cardiovascular disease and hypertension in humans, it is usually interferes with zinc and copper metabolism. Copper may cause liver damage with prolonged exposure and it is toxic to plants. Also, lead can cause brain damage, convulsions, behavioral disorder then leads to death. It usually reaches water from water pipes used in distribution system, auto exhaust (from gasoline), paints, dust and soil containing lead, and plants contaminated with lead.

Purification of water from heavy metals before it reaches the domestic usage is very essential. Several chemical methods are available for this purpose, as for instance chemical precipitation, reverse osmosis, ion-exchange, membrane separation, adsorption and bio sorption [8].

Each method has some limitations such as, low efficiency and sensitivity under certain operating conditions. Researches prove experimentally that, the most efficient method used to remove metals from waste water is adsorption, as adsorbents are available at low cost and with high efficiency [9-13].

Adsorption is one of the most effective, simplest and economical method for waste water purification. There are several solid adsorbents known for this purpose, as natural adsorbents, agricultural waste, industrial wastes, biomass and Nano adsorbents .

Examples on low cost natural adsorbents, that are used for waste water purification are mango peel, cellulose and alisma plantago aquatical [14].

Moringaoleifera, Nirmali, Strychnos, Tamarindusindica in which seeds are used as adsorbents for waste water purification [15]. Also, sand showed some efficiency toward removal metals from waste water [16].

Side products of agricultural and industrial wastes such as, rice husk and fly ash also were a low cost source for removal of heavy metals from waste water [17].

Recently, cellulose received the highest attention as natural product that used in waste water purification. Specially, Nano cellulose-based materials received the most attention [18]. Also, many cellulose derivatives were prepared and used for waste water purification.

1.2 Cellulose

Cellulose is an organic polymer with the formula $(C_6H_{10}O_5)_n$ formed from glucose monomer, polysaccharide consisting of linear chains of several hundred to many thousand of β-(1→4) linked D-glucose units [19,20].

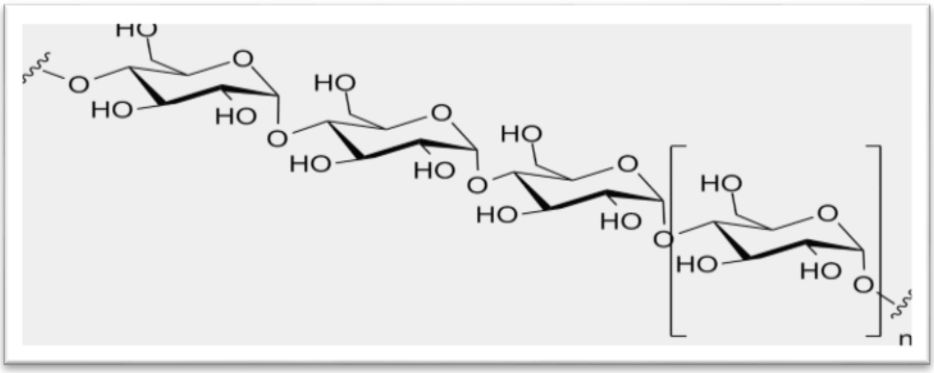


Figure 1.1: Molecular structure of cellulose.

It has a density of about 1.5 g/cm^3, and decomposes at melting point 260-270°c , it is insoluble in water and its molar mass is 162.1406 g/mol per glucose unit [21].

Even it has hydrophilic regions, it is insoluble in water and most organic solvent.

Cellulose is the structural component of the primary cell wall of green plants, many forms of algae and the oomycetes. Some species of bacteria secretes the cellulose to form bio films [22].

Cellulose is the most abundant organic polymer on earth [23] 90% of cotton fiber content is cellulose, and was wood has about 40-50% of cellulose [24].

The number repeat units (degree of polymerization) in cellulose formula differs according to the source of cellulose. The degree of polymerization (ranges from 10000 and 15000 of glucose molecule). As example in cotton fibers is 8000-14000, where as in bacterial cellulose 2700 and in wood fibers is 8000-9000.

Cellulose composed of two regions: crystalline and amorphous. Treating it with strong acids, the amorphous regions can be broken down, thereby producing nanocrystalline cellulose, a novel material with many desirable properties [25].

There are many properties for cellulose that make it a good candidate as a metal adsorbent and other applications, it is nontoxic, biodegradable, stable, high tensile and compressive strength. Each cellulose repeat unit contains three hydroxyl group that can be modified to form many cellulose derivatives for unlimited number of applications [26].

1.2.1 Chemically modified cellulose for removing heavy metals

Several chemically modified cellulose polymers were prepared and used in water purification. Cellulose filter paper modified with ethylenediamine tetra acetic acid (EDTA, Figure 1.2) was prepared by esterification of the paper with EDTA dianhydride and used for the removal of various metal cations, including Ag^+, Pb^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+}, Sn^{2+} and Cu^{2+} with 90%-95% removal efficiency. The cellulose-EDTA material works at a wide range of pH values, also it can be used either as a solid absorbent or a membrane, for waste water treatment [27].

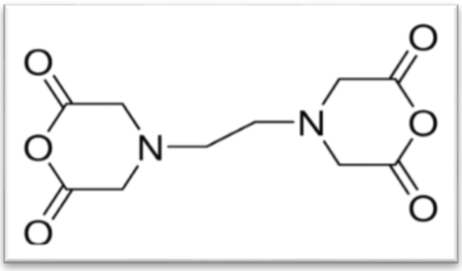


Figure 1.2: Molecular structure of EDTA dianhydride.

Mercerized cellulose usually prepared by treating cellulose with about 16% by weight of sodium hydroxide solution. It was derivatized with succinic anhydride (figure 1.3) and used in the adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} from aqueous single metal solutions. Adsorption isotherms were developed using Langmuir model. Adsorption capacity for Cu^{2+} (30.4 mg adsorbate/g adsorbent), Cd^{2+} (86.0 mg/g) and Pb^{2+} (205.9 mg/g) [28].

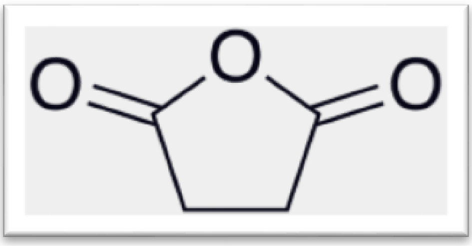


Figure 1.3: Molecular structure of succinic anhydride.

Chemically modified cellulose adsorbent bearing methyl benzalaniline chelating group (figure 1.4) was also synthesized and used for removal of Cu^{2+} and Pb^{2+} metal ions from aqueous solution. In which the kinetic data fitted well to the pseudo-second order kinetic model. Adsorption is spontaneous and exothermic in nature, this resulted from the negative values of ΔG° and ΔH° [29].

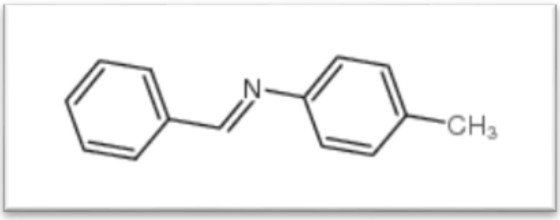


Figure 1.4: Molecular structure of methyl benzalaniline.

The one-step method was developed to synthesize novel supramolecular polysaccharide composite from cellulose and dibenzo-18-crown 6 (Figure 1.5) using ceric ammonium nitrate (figure 1.6) as indicator, and use it in removal of Cd^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+} and Cu^{2+} from waste water [30].

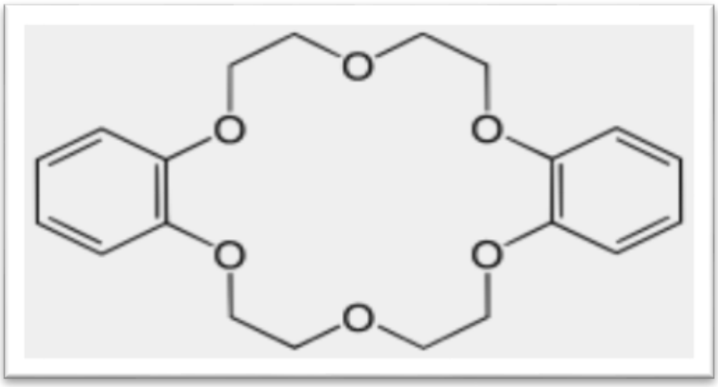


Figure 1.5: Molecular structure of dibenzo-18-crown 6.

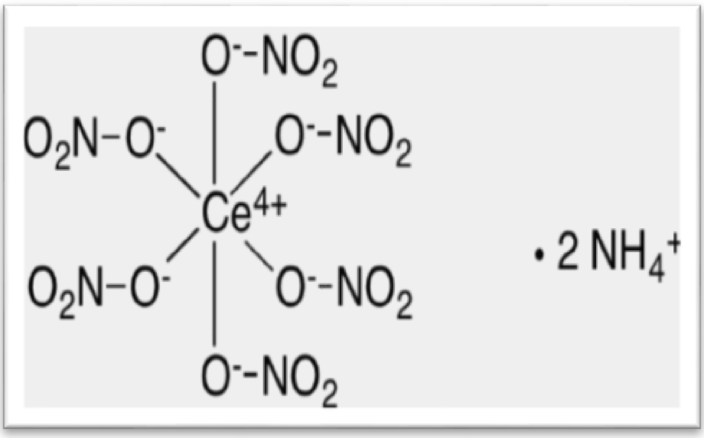


Figure 1.6: Molecular structure of ceric ammonium nitrate.

Novel adsorbent based on cellulose was designed by grafting glycidyl methacrylate (Figure 1.7) monomer on cellulose, then was functionalized by the addition of imidazole. The final product was used in removal of Cu^{2+}, Ni^{2+} and Pb^{2+}. The adsorption capacity for $Cu^{2+}$was found to be 68 mg/g, 45 mg/g for Ni^{2+} and 71 mg/g for Pb^{2+}, the overall kinetic in each case is best described by the pseudo-second order approach, the optimum pH range in all cases ranged from approximately pH=4 to pH=5 since found that absorption capacity significantly influenced by aqueous pH [31].

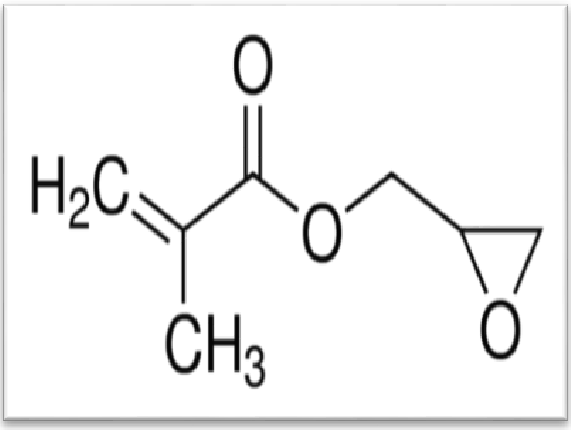


Figure 1.7: Molecular structure of glycidyl methacrylate.

Novel chemically modified cellulose adsorbent using Schiff base tertiary amine-chelating group was synthesized for the removal of Hg^{2+} metal ions from aqueous solution, in this study was found that the pseudo-second order kinetic model and the Langmuir isotherm were well suited for the adsorption of Hg^{2+} ions from aqueous media [32].

1.3 β-cyclodextrin:

Cyclodextrin is a cyclic carbohydrate, its ring composed of several glucose units (similar to cycloamyloses while it is smaller than cycloamyloses which are composed of at least 17 units). The glucose units are bonded together in ring (cyclic oligosaccharides).

Cyclodextrins are produced by enzymatic conversion of starch. It is widely used in food, pharmaceutical, chemical industries, agricultural and environmental engineering [33].

Cyclodextrins are composed of 5 or more of α-D-glucopyranoside units linked 1→4, as in amylose (fragment of starch) as in figure 1.8 [34].

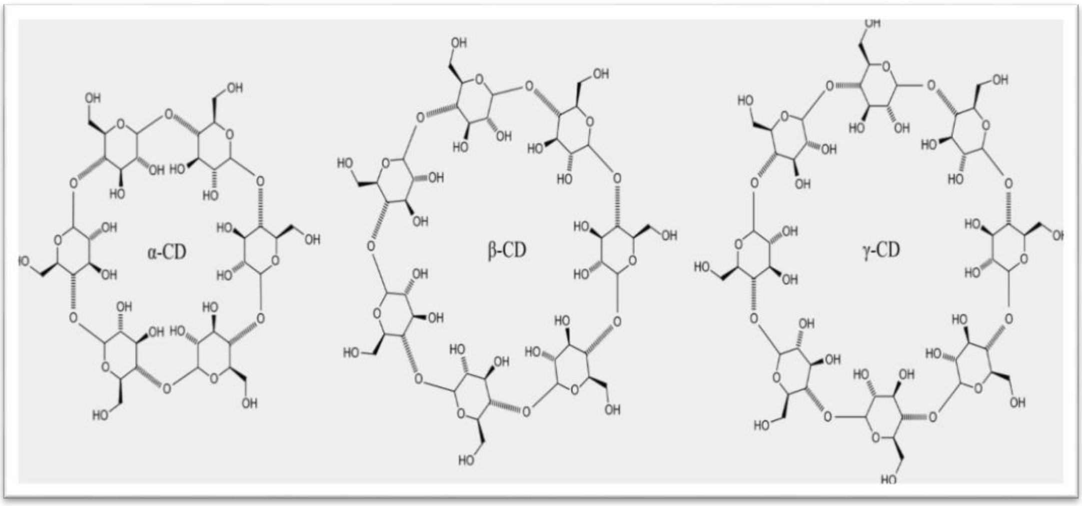


Figure 1.8: Chemical structure of the three main types of cyclodextrins.

Typical cyclodextrins contain a number of six to eight units in the ring, creating a cone shape:

α-cyclodextrin is a 6-membered sugar ring molecule, β-cyclodextrin is a 7-membered sugar ring molecule and γ-cyclodextrin is a 8-membered sugar ring molecule.

There are many applications for these types of cyclodextrins, as:

- Increasing bioavailability: cyclodextrins have hydrophobic areas inside and hydrophilic areas outside, this make cyclodextrin able to form complexes with hydrophobic compounds, this enhance the solubility and bioavailability of such compounds.
- Cholesterol free products, cyclodextrins used in food industry to produce cholesterol free products whereas the bulky and hydrophobic cholesterol molecule lodged inside cyclodextrin rings easily which is then removed.
- Food application: include the ability to stabilize volatile or unstable compounds and reduction of undesirable tastes and odor.
- And β-cyclodextrins can be used with carotenoid food colorants to intensify color, increase water solubility and improve light stability.

Cyclodextrins are able to form complexes with hydrophobic molecules, that make them usable in a number of applications as environmental protection whereas these molecules can effectively immobilize inside their rings toxic compounds like heavy metals or can form complexes with stable substances like trichlorfon (an organophosphorus insecticide) or sewage sludge and this encourage their decomposition.

B-cyclodextrin is white powder and soluble in water.

1.4 Citric acid

Citric acid or 2-Hydroxypropane-1,2,3-tricarboxylic acid, is a weak organic acid with chemical formula $C_6H_8O_7$, and its structural formula shown in figure 1.9.

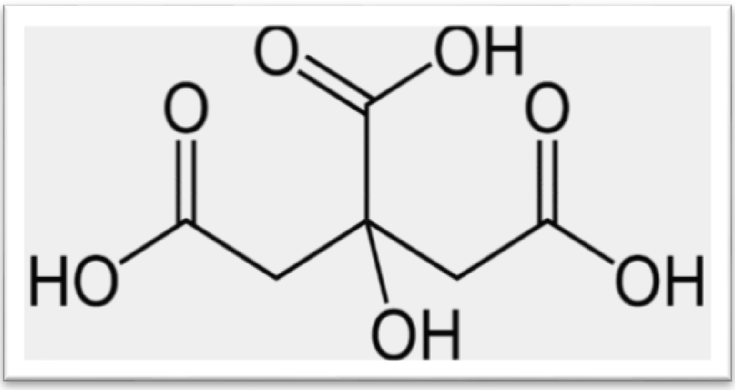


Figure 1.9: Molecular structure of citric acid.

It is a white crystalline solid with no odor, it has a molar mass of 192.123 g/mol as anhydrous compound, and 210.038 g/mol as monohydrated. It melts at point of 156°c and boils at 310°c [35]. It is found naturally in citrus fruits, and in biochemistry, as an intermediate in the citric acid cycle, which occurs in the metabolism of all aerobic organisms.

It is very important as an industrial material, millions of tons of citric acid are produced every year. It used as acidifier, flavoring and chelating agent [36].

Citrate ion is a good chelating agents for metallic cation. The stability constant for the formation of these complexes are quite large.

1.5 Cellulose as a metal adsorbent

Because of water pollution increased, and there is a necessity to remove the wastes from water, and purification from the heavy metals mainly, we focused in this work to develop a new method to remove heavy metals using cellulose complexes as adsorbent.

There are many well known purification ways, such as chemical ways, but these ways have some limitations. So the efforts became direct towards using a low cost and renewable adsorbents on the ground that adsorption is the simplest and most efficient way for purification of water.

Another important point is that cellulose has many advantages make it a good adsorbent, it is natural polymer, renewable, stable, biodegradable but cellulose itself doesn't have the ability to remove heavy metals. It can be modified chemically easily, and to be a good metal adsorbent.

1.6 Scope of the study

In this work, a novel crosslinked polymer with two moieties for waste water purification will be prepared. The polymer is cellulose grafted with β-cyclodextrin. A citric acid crosslinking agent will be used for this purpose. The cross-linking agent adds carboxylic acid groups to the crosslinked product, in addition the polymer contains β-cyclodextrin which is known to have high affinity for organic materials present in waste water. These properties make the target crosslinked cellulose excellent candidate for application in waste water purification from both metals and organic materials. The method of making the polymers comprises reacting cellulose with β-cyclodextrin in the presence of crosslinking agent citric acid in a one pot reaction.

The specific objectives of this proposal are:

1. Synthesize cellulose crosslinked with β-cyclodextrin through the crosslinking agent citric acid.
2. Characterize the new cellulose polymers by various spectroscopic techniques.
3. Evaluate the possibility of using the prepared crosslinked cellulose in waste water purification from metals and organic materials.
4. Develop a process for regenerating the crosslinked cellulose for multi-use.

CHAPTER TWO

EXPERIMENTAL

2.1 General experimental

The chemicals and reagents used in this work were purchased form Aldrich chemical company (USA). All reagents used were analytical grade (Citric acid, β-cyclodextrin), deionized water was used. Cellulose used in this work was extracted from olive industry solid waste.

The metal ion concentrations of all studied solutions were measured by Flame Atomic Absorption Spectrometer at 193.7 nm (ICE 3500 AA System, Thermo Scientific) to determine residual metal ions concertation. 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.

2.2 Polymers preparation

2.2.1 Cellulose based polymer A:

A 1.0 g (5.2 mmol) sample of citric acid and 0.5 g (0.44 mmol) of β-cyclodextrin were mixed in a beaker with 5 ml of deionized water, then 1.0 g (0.88 mmol) of cellulose was ground in a cafe blender, and added to the solution of citric acid and β-cyclodextrin.

The formed mixture was placed in the oven at 110°c until water evaporate completely. After that, the oven temperature was raised to 180 °c, and the mixture kept for a two hours. The mixture was taken out from oven, cooled down to room temperature and grinded. The produced crosslinked polymer was analyzed by FT-IR spectroscopy.

FT-IR spectrum shows the presence of a peak at 1720-1750 cm^{-1}, which corresponding to the C=O of an ester group.

2.2.2 Cellulose based polymer B:

The same procedure used for the preparation of polymer A was followed, the only difference is quantity of citric acid was increased to 2.0 g (10.4 mmol), and amount of cellulose reduced to 0.5 g (0.44 mmol).

FT-IR spectrum shows the presence of a peak at 1720-1750 cm^{-1}, which corresponding to the C=O of an ester group.

2.2.3 Cellulose based polymer C:

The same procedure used for the preparation of polymer A was followed, the only difference is quantity of citric acid was increased to 2.0 g (10.4 mmol).

FT-IR spectrum shows the presence of a peak at 1720-1750 cm^{-1}, which corresponding to the C=O of an ester group.

2.2.4 Polymer solubility in water

A sample of each polymer with known weight (1.0 g) was suspended in water (100 ml) and stirred for about 6 hrs. Then collected by suction filtration, dried in an oven at 100 °C, and weighed. Negligible reduction in the weight was noticed.

2.3 purification of contaminated water from lead metal using Cellulose polymer:

2.3.1 preparation of lead solutions

Stock solution of lead nitrate with (1000 ppm) concentration was prepared in the lab. Then several solutions with various concentrations were prepared from stock solution:

1) Lead nitrate solution with 5 ppm concentration:

0.5 ml of the stock solution and diluted to 100 ml with deionized water.

2) Lead nitrate solution with 10 ppm concentration:

1 ml of the stock solution and diluted to 100 ml with deionized water.

3) Lead nitrate solution with 20 ppm concentration:

2 ml of the stock solution and diluted to 100 ml with deionized water.

4) Lead nitrate solution with 50 ppm concentration:

5 ml of the stock solution and diluted to 100 ml with deionized water.

2.3.2 Extraction process

A batch extraction process was used, whereas known amount of cellulose polymer was added to lead solution with known concentration in a bottle, then the bottle was closed and shaked in the shaker apparatus at constant temperature and at a speed for specific period of time according to the factor which is under study. A sample of each mixture was withdrawn with a syringe, filtered through a 0.45 µm syringe filter and subjected to analysis for residual metal ions concentrations. The concentration of lead metal was determined by atomic absorption spectroscopy.

The adsorption capacity (q) and removal percentage (%E) were calculated using the following equations:

$$q= ((C_0-C_e)/m))*V$$

$$\%E= ((C_0-C_e)/C_0))*100\%$$

Where q is the adsorption capacity of the adsorbent (mg/g), m is the weight of adsorbent (g), V is the volume of solution (L).In the second equation, C_0,C_e in unit of (mg/L) are the initial and equilibrium concentrations of adsorbate in solution, respectively.

2.3.2.1 Effect of polymer dose on the removal efficiency:

Five solutions (10 ml each) of lead nitrate with the same concentration (50 ppm) were placed in five bottles, then different quantities of the polymer were added to each (0.01 g, 0.05 g, 0.1 g, 0.15 g, 0.2 g).

Then these solutions were shaken at room temperature for 30 minutes using thermostat shaker, after the shaking time end, A sample of each mixture was withdrawn with a syringe, filtered through a 0.45 µm syringe filter and subjected to analysis for residual metal ions concentrations. The concentration of lead metal was determined by atomic absorption spectroscopy.

The adsorption efficiency of the prepared three polymers A, B, and C were evaluated in the same manner. The obtained results for three polymers are summarized in the following tables:

Table 2.1: Effect of polymer dose on the lead removal efficiency for polymer A:

Polymer dose (g)	$[Pb^{2+}]$ (ppm)	% of Pb^{2+} removal
0.01	11.2222	77.5556
0.05	10.5751	78.8498
0.1	10.9303	78.1394
0.15	11.6911	76.6178
0.2	11.8788	76.2424

Table 2.2:Effect of polymer dose on the lead removal efficiency for polymer B:

Polymer dose (g)	$[Pb^{2+}]$ (ppm)	% of Pb^{2+} removal
0.01	43.3423	13.3154
0.05	30.6026	38.7948
0.1	18.5085	62.983
0.15	11.9088	76.1824
0.2	5.7965	88.407

Table 2.3: Effect of polymer dose on the lead removal efficiency for polymer C:

Polymer dose (g)	$[Pb^{2+}]$ (ppm)	% of Pb^{2+} removal
0.01	22.8783	54.2434
0.05	15.6457	68.7086
0.1	6.6152	86.7696
0.15	3.9321	92.1358
0.2	3.4767	93.0466

2.3.2.2 Effect of contact time on the lead (Pb^{2+}) removal efficiency:

Five solutions (10 ml each) of lead nitrate with concentration (50 ppm) were put in five bottles, then the polymer dosage that gave maximum removal efficiency (0.05 g for polymer A, 0.2 g for polymer B and 0.2 g for polymer C) was added to each, then the solutions were shaken at room temperature for different times (1 min, 5 min, 10 min, 15 min,30 minutes), A sample of each mixture was withdrawn with a syringe, filtered through a 0.45 µm syringe filter and subjected to analysis for residual metal ions concentrations. The concentration of lead metal was determined by atomic absorption spectroscopy.

The adsorption efficiency of the prepared three polymers A, B, and C as a function of time were all evaluated in the same manner. The obtained results for three polymers are summarized in the following tables:

Table 2.4: Effect of contact time on the lead (Pb^{2+}) removal efficiency for polymer A:

Contact time (min)	[Pb^{2+}] (ppm)	% of Pb^{2+} removal
1	13.0180	73.964
5	9.7913	80.4174
10	8.4254	83.1492
15	6.5672	86.8656
30	13.2266	73.5468

Table 2.5: Effect of contact time on the lead (Pb^{2+}) removal efficiency for polymer B:

Contact time (min)	[Pb^{2+}] (ppm)	% of Pb^{2+} removal
1	19.9442	60.1116
5	5.6077	88.7846
10	2.3320	95.336
15	12.0984	75.8032
30	17.8804	64.2392

Table 2.6: Effect of contact time on the lead (Pb^{2+}) removal efficiency for polymer C:

Contact time (min)	[Pb^{2+}] (ppm)	% of Pb^{2+} removal
1	20.7364	58.5272
5	19.4599	61.0802
10	13.2814	73.4372
15	13.3134	73.3732
30	18.2929	63.4142

2.3.2.3 Effect of temperature on the lead (Pb^{2+}) removal efficiency:

Three solutions (10 ml each) of lead nitrate with concentration (50 ppm) were placed in three bottles, constant quantity of polymer that gave maximum removal efficiency (0.05 g from each polymer) was added to the solutions and shaken using thermostat shaker, for constant time that gave maximum efficiency (15 min for polymer a, 10 min for polymer b and 10 min for polymer c) at different temperatures (room temperature, 30°c and 40°c). A sample of each mixture was withdrawn with a syringe, filtered through a 0.45 µm syringe filter and subjected to analysis for residual metal ions concentrations. The concentration of lead metal was determined by atomic absorption spectroscopy. The adsorption efficiency of the prepared three polymers A, B, and C as a function of temperature were evaluated in the same manner. The obtained results for three polymers are summarized in the following tables:

Table 2.7: Effect of temperature on the lead removal efficiency for polymer A:

Temperature (°c)	[Pb^{2+}] (ppm)	% of Pb^{2+} removal
Room temperature	19.0384	61.9232
30	36.993	26.014
40	39.6421	20.7158

Table 2.8: Effect of temperature on the lead removal efficiency for polymer B:

Temperature (°c)	[Pb^{2+}] (ppm)	% of Pb^{2+} removal
Room temperature	16.9509	66.0982
30	18.977	62.046
40	19.6152	60.7696

Table 2.9: Effect of temperature on the lead removal efficiency for polymer C:

Temperature (°c)	[Pb^{2+}] (ppm)	% of Pb^{2+} removal
Room temperature	9.0535	81.893
30	11.1724	77.6552
40	19.2554	61.4892

2.3.2.4 Effect of lead nitrate concentration on efficiency removal:

Four different lead nitrate solutions were prepared from stock solution (1000 ppm). The solution concentrations (5, 10, 20 and 50 ppm). For each optimized conditions for each polymer were used (For polymer **A**: 0.05 g, 15 minutes shaking at room temperature, For polymer **B**: 0.2 g, 10 minutes shaking at room temperature, and For polymer **C**: 0.2 g, 10 minutes shaking at 30°c). A sample of each mixture was withdrawn with a syringe, filtered through a 0.45 µm syringe filter and subjected to analysis for residual metal ions concentrations. The concentration of lead metal was determined by atomic absorption spectroscopy.

The adsorption efficiency of the prepared three polymers A, B, and C as a function of Lead (II) concentration were evaluated in the same manner. The obtained results for three polymers are summarized in the following tables:

Table 2.10: Lead nitrate concentration effect on lead removal efficiency for polymer A:

Lead nitrate Concentration (ppm)	[Pb^{2+}] (ppm)	% of Pb^{2+} removal
5	1.8595	62.81
10	1.3836	86.164
20	2.3460	88.27
50	6.0288	87.9424

Table 2.11: Lead nitrate concentration effect on lead removal efficiency for polymer B:

Lead nitrate Concentration (ppm)	[Pb^{2+}] (ppm)	% of Pb^{2+} removal
5	2.1004	57.992
10	5.4810	45.19
20	7.9474	60.263
50	17.6463	64.7074

Table 2.12:Lead nitrate concentration effect on lead removal efficiency for polymer C:

Lead nitrate Concentration (ppm)	[Pb^{2+}] (ppm)	% of Pb^{2+} removal
5	2.7100	45.8
10	1.9054	80.946
20	4.0509	79.7455
50	14.7049	70.5902

2.3.2.5 Effect of pH on the efficiency of lead removal:

Five solutions of lead nitrate (50 ppm concentration each) were prepared. Their pH were adjusted to the desired value using diluted solutions of HCl and NaOH.

Then optimized conditions for each polymer were used.

A sample of each mixture was withdrawn with a syringe, filtered through a 0.45 µm syringe filter and subjected to analysis for residual metal ions concentrations. The concentration of lead metal was determined by atomic absorption spectroscopy.

The adsorption efficiency of the prepared three polymers A, B, and C as a function of pH were evaluated in the same manner. The obtained results for three polymers are summarized in the following tables:

Table 2.13: Effect of pH on the lead removal efficiency for polymer A:

pH	[Pb^{2+}] (ppm)	% of Pb^{2+} removal
1.08	25.6264	48.7472
2.08	23.9854	52.0292
4.96	22.6259	54.7482
8.58	19.3114	61.3772
10.25	10.9196	78.1608

Table 2.14: Effect of pH on the lead removal efficiency for polymer B:

pH	[Pb^{2+}] (ppm)	% of Pb^{2+} removal
1.61	46.7763	6.4474
2.08	31.0513	37.8974
4.06	28.1286	43.7428
7.76	18.3363	63.3274
10.05	17.5620	64.876

Table 2.15: Effect of pH on the lead removal efficiency for polymer C:

pH	[Pb^{2+}] (ppm)	% of Pb^{2+} removal
1.51	23.7147	52.5706
2.52	20.7539	58.4922
4.11	19.3091	61.3818
7.3	17.3394	65.3212
10.04	11.5139	76.9722

2.3.2.6 Polymer adsorption cycle

The polymer efficiency was restored by suspending stability of the polymer and its efficiency after using was studied by using the used polymer with optimized conditions and the solutions were decanted and the concentration of lead ion in the supernatant was determined (using atomic absorption spectroscopy) to detect if the used polymer still have efficiency for removal lead ion from contaminated water or not.

The results for three used polymers are summarized in the following tables:

Table 2.16: Reusing for polymer A:

Number of reusing	Concentration of lead (Pb^{2+}) after extraction	% of extraction
1	20.9888	58.0224
2	12.1452	75.7096
3	10.1746	79.6508
4	11.2739	77.4522
5	12.8178	74.3644
6	12.9219	74.1562

Table 2.17: Reusing for polymer B:

Number of reusing	Concentration of lead (Pb^{2+}) after extraction	% of extraction
1	22.0377	55.9246
2	11.9479	76.1042
3	17.2417	65.5166
4	16.5432	66.9136
5	13.8387	72.3226
6	16.3965	67.207

Table 2.18: Reusing for polymer C:

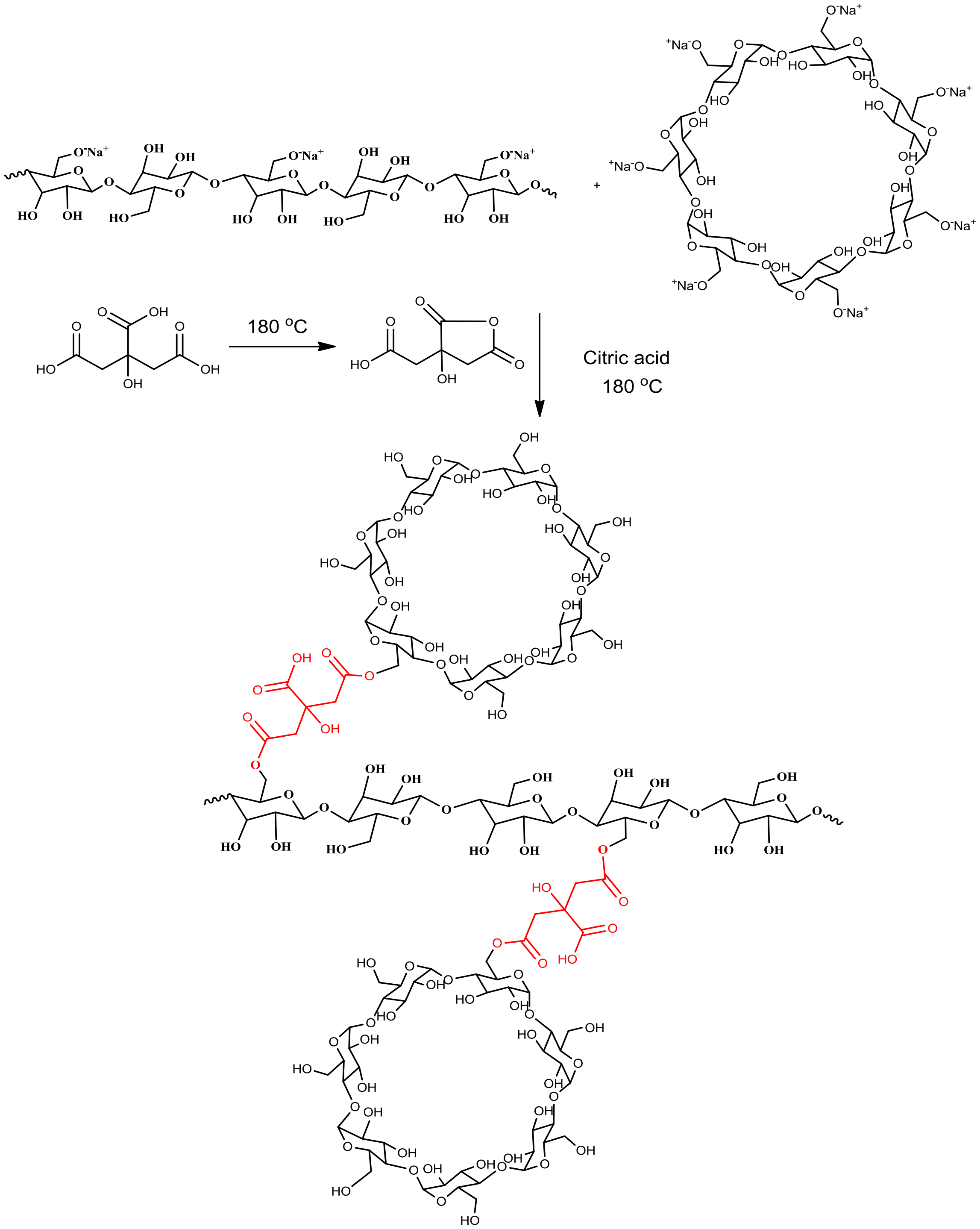
Number of reusing	Concentration of lead (Pb^{2+}) after extraction	% of extraction
1	17.7554	64.4892
2	12.1690	75.662
3	14.7664	70.4672
4	7.9925	84.015
5	15.2339	69.5322
6	14.9161	70.1678

CHAPTER THREE

RESULTS AND DISSCUSION

3.1 Synthesis of Cross-linked cellulose polymers

In this work, a tri component polymer was designed, synthesized and used in waste water purification from toxic metal ions. The three components chosen for this purpose were citric acid, β-cyclodextrin and cellulose. As mentioned previously in the introduction the three components are natural products, safe and commercially available at relatively low price. Citric acid was used in synthesis of the three polymers as crosslinking agent, in order to form two ester linkages between cellulose and β-cyclodextrin, as shown in scheme 3.1. The ester bonds are formed between the carboxyl groups of citric acid and the hydroxyl groups of β-cyclodextrin and cellulose. The reaction was carried in a solid phase at high temperature. Since at high temperature over 170 ^{o}C, citric acid undergoes dehydration and forms anhydride (scheme 3.1), a functionality that undergoes addition reaction with hydroxyl groups to form ester bond



Scheme 3.1: The reaction between cellulose, β-cyclodextrin and citric acid.

Crosslinking agent forms two new covalent bond, between hydroxyl groups of both cellulose and β-cyclodextrin.

The progress of the reaction was monitored by the bond formation of ester linkages between the citric acid (the crosslinking agent) and both cellulose and β-cyclodextrin using FT-IR.

An overlaid FT-IR spectrum of starting materials before curing (crosslinking) and after curing (polymer A) are shown in figure 3.1. The figure also shows citric acid anhydride that was heated at 170 ^{o}C alone for 10 min. The spectrum shows the anhydride carbonyl (1760 cm^{-1}) in addition to the carboxyl carbonyl (1720 cm^{-1}). The results shown by the IR is a proof that citric acid forms anhydride at high temperature with the loss of water molecule as mentioned above. The IR spectrum of the product shows two bands at about 1760 and 1715 cm^{-1} for C=O of ester and carboxyl group, respectively. The presence of the 1760 peak is an indication that the ester linkage is formed. While the starting material shows only one peak at about 1715 cm^{-1} which could be related to C=O of citric acid [37].

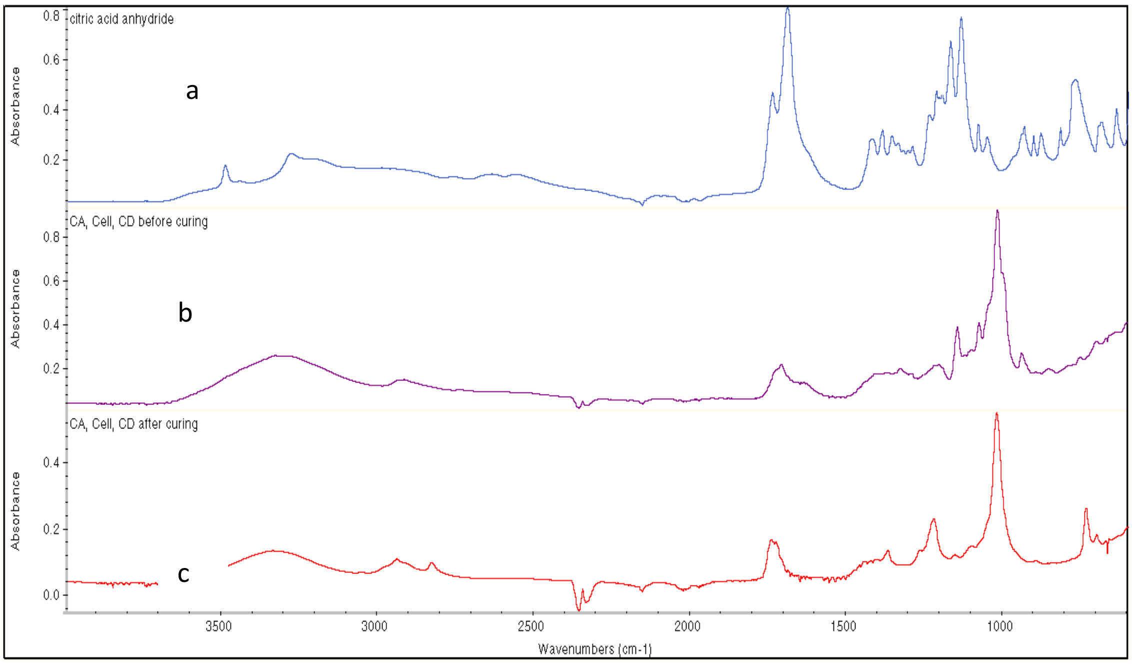


Figure 3.1: FT-IR of a) CA anhydride, b) citric acid, cellulose and cyclodextrin before curing and c) citric acid, cellulose and cyclodextrin after curing.

IR spectra of polymers B and C are shown in figures 3.2 and 3.3. Each show a board strong peak at 1732 cm^{-1} that is composed of severl peaks that overlaped together, which could be attributed to C=O of etser and remaining carboxyl groups of citric acid. The prensce of these carboxyl groups is important for metal ion trapping.

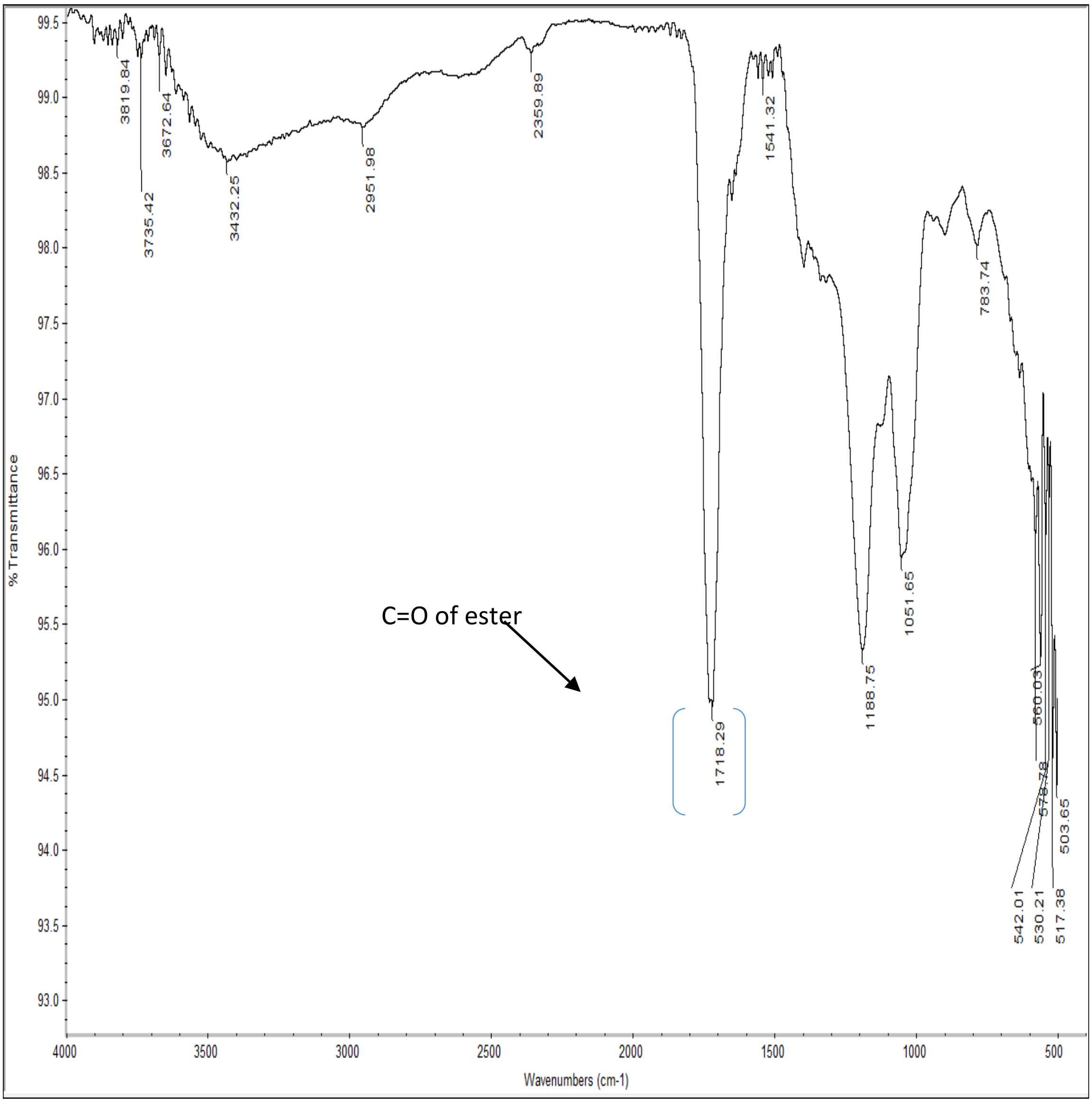


Figure 3.2: IR spectrum for polymer A.

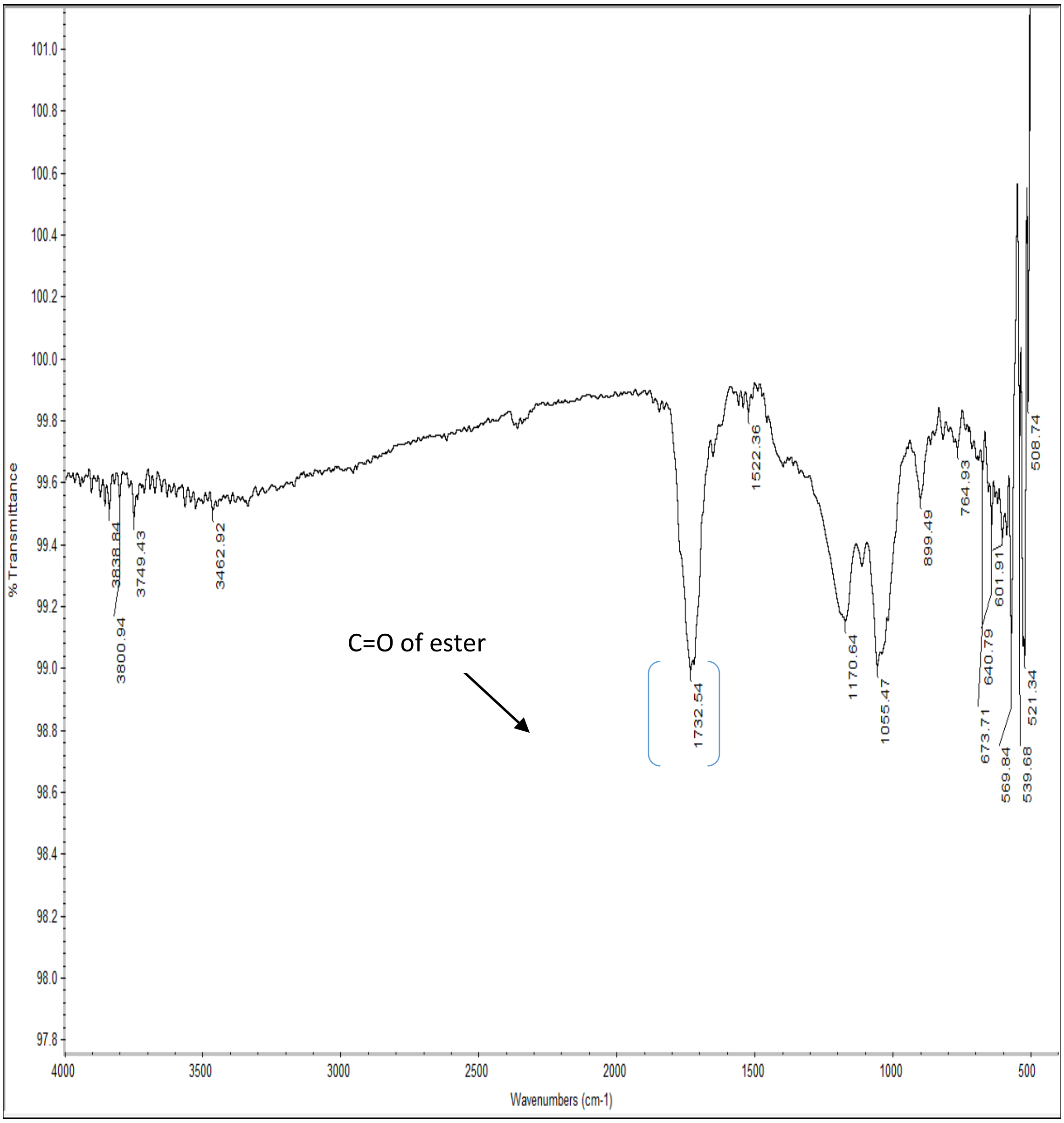


Figure 3.3: IR spectrum for polymer B.

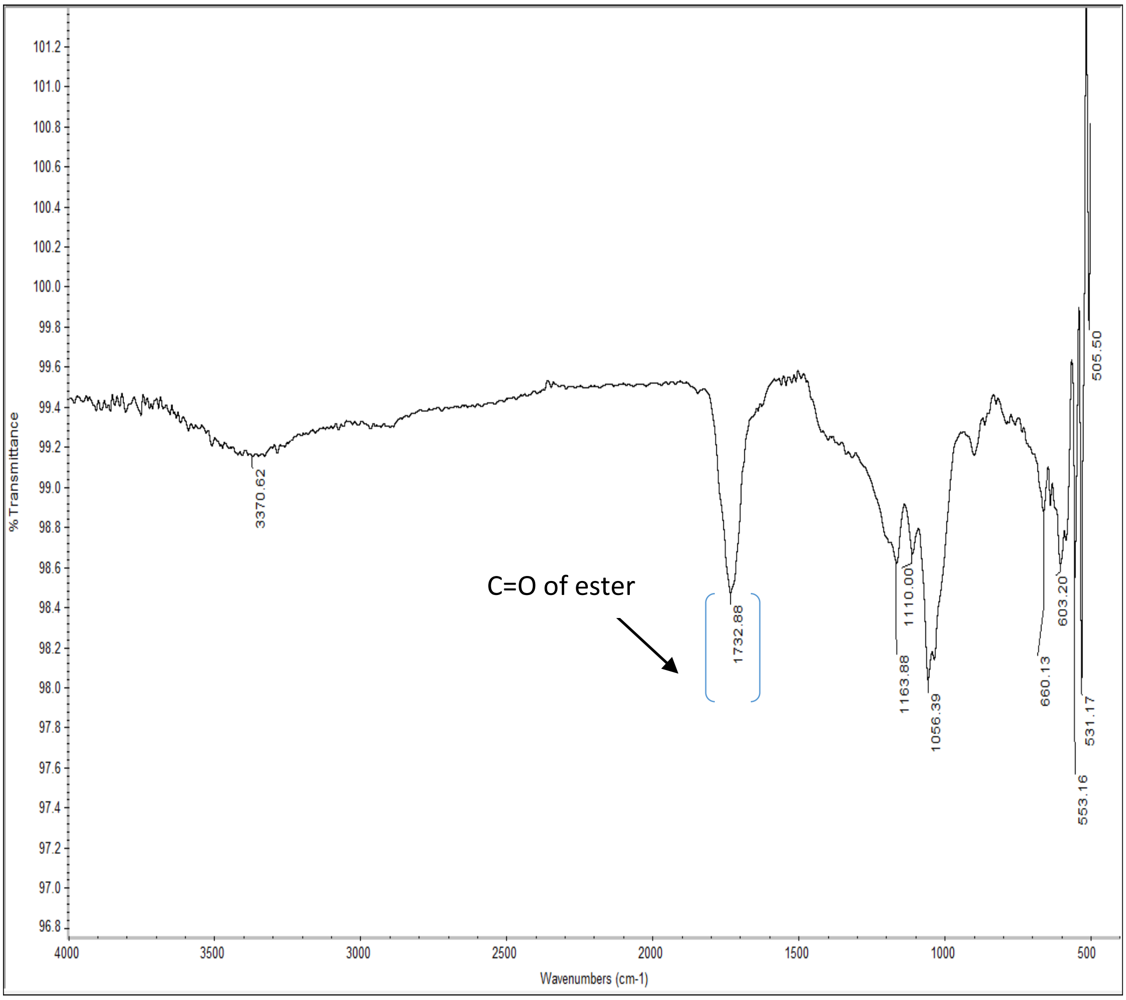


Figure 3.4: IR spectrum for polymer C.

3.2 Polymer Morphology

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

The obtained images show in Figure 3.5. The images show the spongy type of structure. This type of morphology is suitable for filtration.

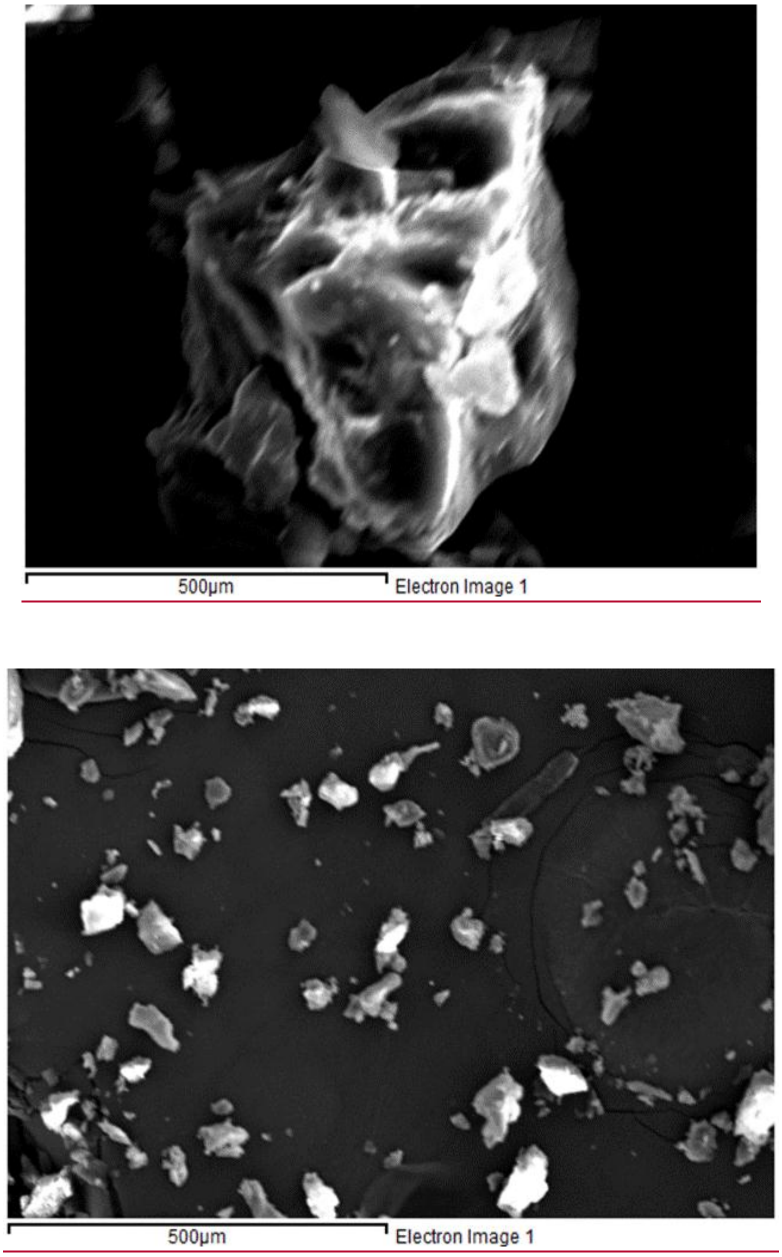


Figure 3.5: The surface morphology of the celluloses.

3.3 Adsorption conditions and procedure

A batch adsorption procedure was followed in this work, all experiments were performed in plastic containers (50 ml), that were placed in a water bath with shaker. The effect of the following variable on polymer adsorbent efficiency were evaluated: metal ion concertation (5 to 50.0 ppm), pH values from 2 to 10, adsorbent dosage (0.01 to 0.2 g), adsorption time (1 to 30 min) and temperature from 25 to 40 ° C. The adsorption study was performed on Pb (II) nitrate. After each adsorption experiment, a sample of each mixtures was filtered through a 0.45 µm syringe filter and analyzed for residual metal ions concentration. The metal ion concentrations of all studied solutions were measured by Flame Atomic Absorption Spectrometer at 193.7 nm (ICE 3500 AA System, Thermo Scientific) to determine residual metal ion 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 based polymers adsorbent qe (mg/g) and adsorbent efficiency was determined according to Eqs. 1 and 2.

$$R\,(\%) = \frac{C_0 - C_e}{C_0}\,100 \quad (1) \qquad\qquad Q_e = \frac{C_0 - C_e}{m}\,V \quad (2)$$

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

3.3.1 Determination of optimum adsorption conditions

3.3.1.1 Optimum adsorbent dosage

The dosage that provided the lowest residual concentration of metal ion was chosen as an optimum dosage. This was achieved by performing the experiment on 10 ml of each Pb^{2+} with a concentration of 50.0 ppm, pH value of 6.3 for 30 min and at room temperature.

Polymer A

The effect of the adsorbent dosage on the removal of Pb(II) ion by polymer A is shown in figure 3.3.1. As showed, the amount of metal extracted was not affected by dosage. Metal ion removal reached about 78.5% for Pb(II) at 0.05 g dose of polymer A. At dose higher than 0.05 it tends to stay almost constant. This could be because the adsorption process is controlled by two mechanisms, diffusion and surface coordination. As the dose increases the number of binding sites on the surface increases, so the removal efficiency increases. When all sites on the surface are occupied the diffusion process starts, which is controlled by osmosis.

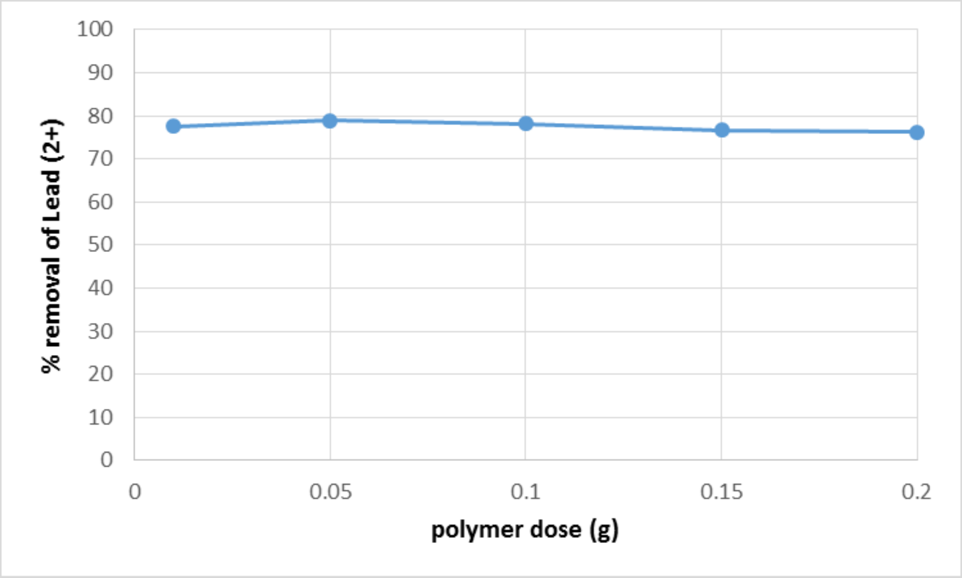


Figure 3.3.1: The effect of polymer **A** dose on the removal efficiency.

Polymer B

The effect of the adsorbent dosage on the removal of Pb(II) ion by polymer B is shown in figure 3.3.2. In preparing polymer B, larger amount of citric acid was used and lower amount of cellulose. This means more carboxyl groups present per polymer repeat unit is higher. So, the number of binding sites is higher. In this case, the adsorption process is controlled by mainly one mechanism, surface coordination. As the dose increases the number of binding sites on the surface increases, so the removal efficiency increases.

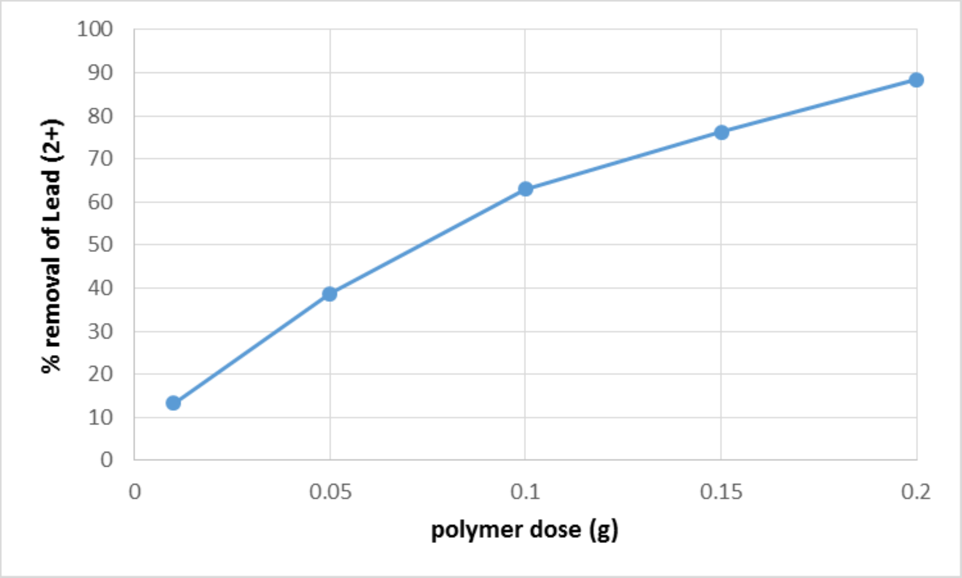


Figure 3.3.2: The effect of polymer **B** dose on the removal efficiency.

Polymer C

The effect of the adsorbent dosage on the removal of Pb(II) ion by polymer C is shown in figure 3.3.3. As shown in the figure, the highest absorbency was at a dose of 0.15 g then it became constant.

In preparing polymer C, larger amount of citric acid was used and the amount of cellulose was same as that used in preparing polymer A. This means lower carboxyl groups are present per polymer repeat unit, it’s like in between of polymer A and B. So, the number of binding sites is lower than that in polymer B, but higher than that in polymer A. In this case, the adsorption process is controlled by major mechanism, surface coordination and a minor mechanism the ion diffusion.

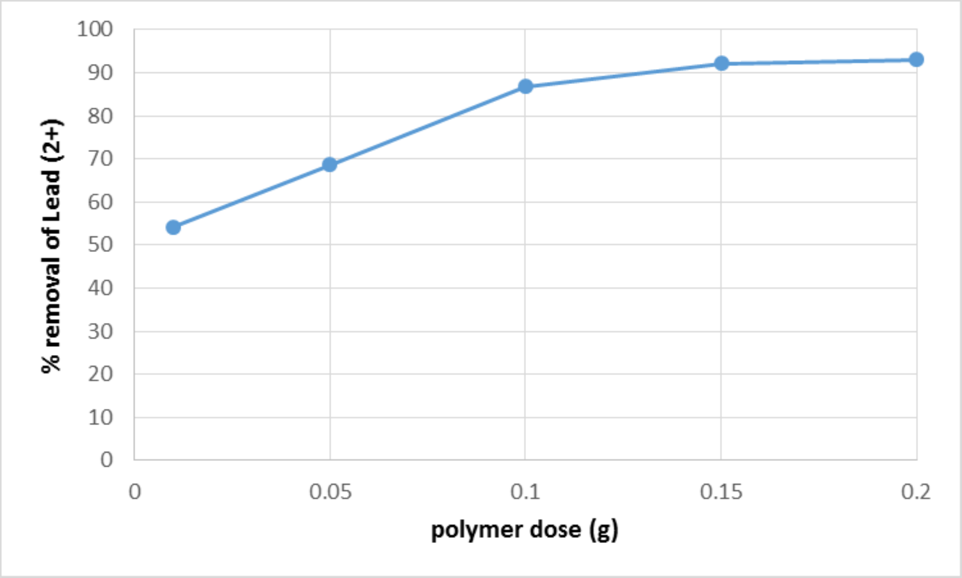


Figure 3.3.3: The effect of polymer **C** dose on the removal efficiency.

3.3.1.2 Optimum contact time

The contact time that provided the lowest residual concentration of metal ion was chosen as an optimum contact time. This was achieved by performing the experiment on a 10 ml of Pb^{2+} with a concentration of 50.0 ppm, pH value of 6.3 for different periods and at room temperature.

Polymer A

The effect of the contact time on the removal of Pb(II) ion by polymer A is shown in figure 3.3.4. As shown in the figure, the adsorbed metal ions increased rapidly for the first 15 min due to the availability of the coordination sites. Followed by a slower adsorption rate for the next 10 min, it reached to the equilibrium after 15 min, so at this period almost all coordination sites are occupied. A contact time of 15 min was chosen as the optimum contact time.

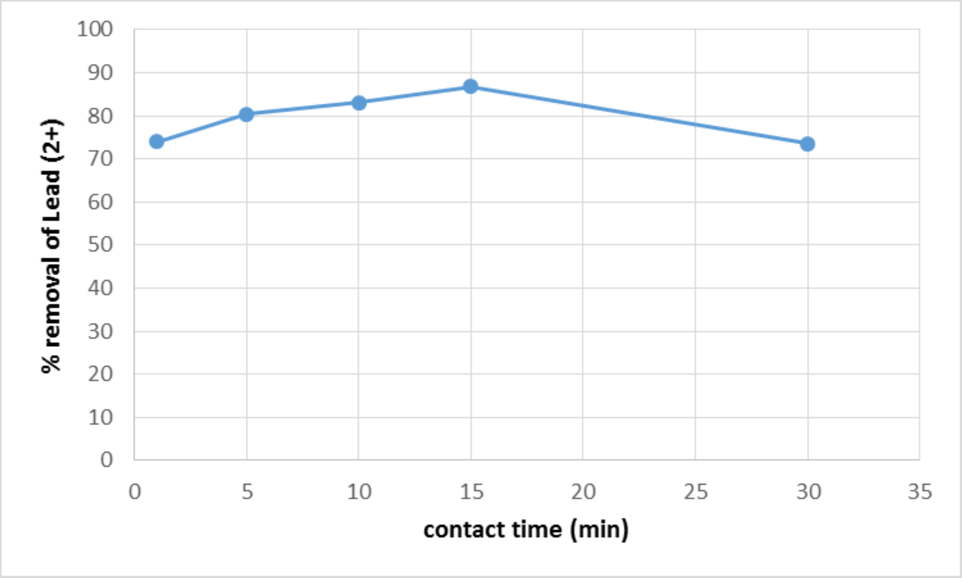


Figure 3.3.4: The effect of contact time on the removal efficiency for polymer **A**.

Polymer B

The effect of the contact time on the removal of Pb(II) ion by polymer B is shown in figure 3.3.5. Polymer B shows similar behavior as polymer A. As shown in the figure, the adsorbed metal ions increased rapidly for the first 10 min due to the availability of the coordination sites. Followed by a slower adsorption rate for the next 10 min, it reached to the equilibrium after 10 min, so at this period almost all coordination sites are occupied. A contact time of 10 min was chosen as the optimum contact time. It reached the equilibrium at lower time than polymer A due to the availability of more carboxyl groups.

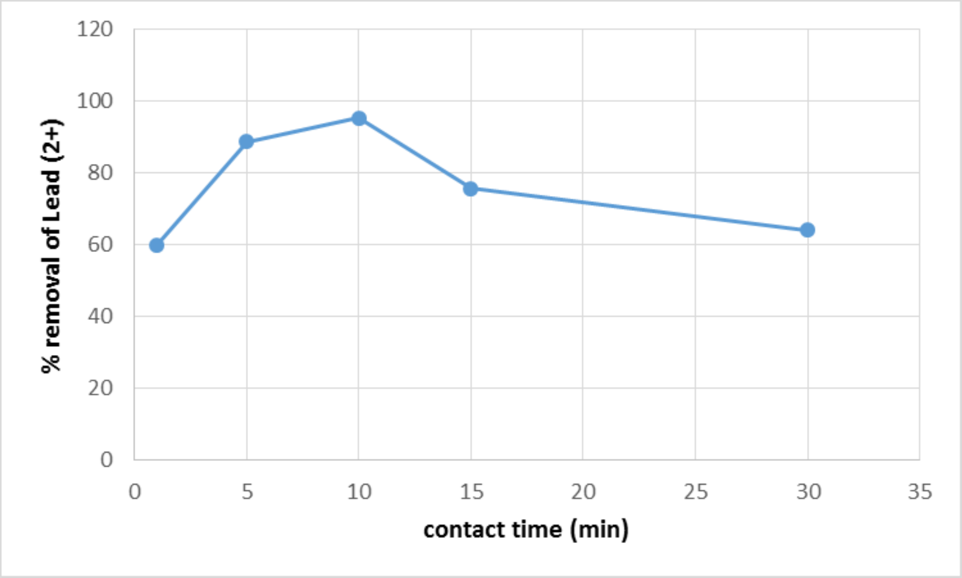


Figure 3.3.5: The effect of contact time on the removal efficiency for polymer **B**.

Polymer C

The effect of the contact time on the removal of Pb(II) ion by polymer C is shown in figure 3.3.6. Polymer C shows similar behavior as polymer A. As shown in the figure, the adsorbed metal ions increased rapidly for the first 10 min due to the availability of the coordination sites. Followed by a slower adsorption rate for the next 10 min, it reached to the equilibrium after 10 min, so at this period almost all coordination sites are occupied. A contact time of 10 min was chosen as the optimum contact time. It reached the equilibrium at lower time than polymer A due to the availability of more carboxyl groups.

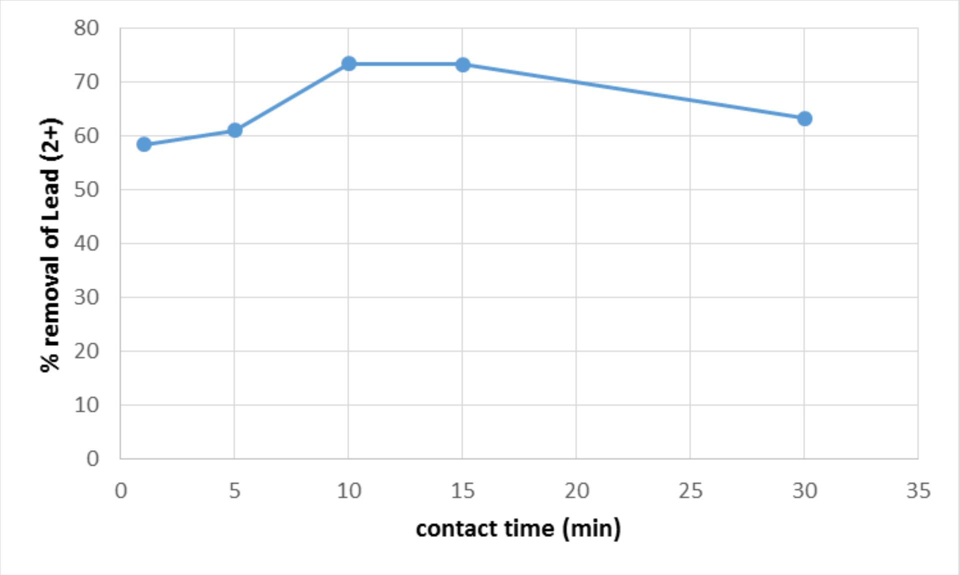


Figure 3.3.6: The effect of contact time on the removal efficiency for polymer **C**.

3.3.1.3 Optimum temperature

The temperature that provided the lowest residual concentration of metal ion was chosen as an optimum temperature. This was achieved by performing the experiment on 10 mL of each Pb^{2+} with a concentration of 50.0 ppm, pH value of 6.3 for 30 min and at different temperatures.

Polymer A

The effect of the temperature on the removal of Pb(II) ion by polymer A is shown in figure 3.3.7. Maximum adsorption efficiency was observed at room temperature. At higher temperature, over 30 ^{o}C, the percentage of metal started to decrease. The results could be an indication that the adsorption is spontaneous at room temperature.

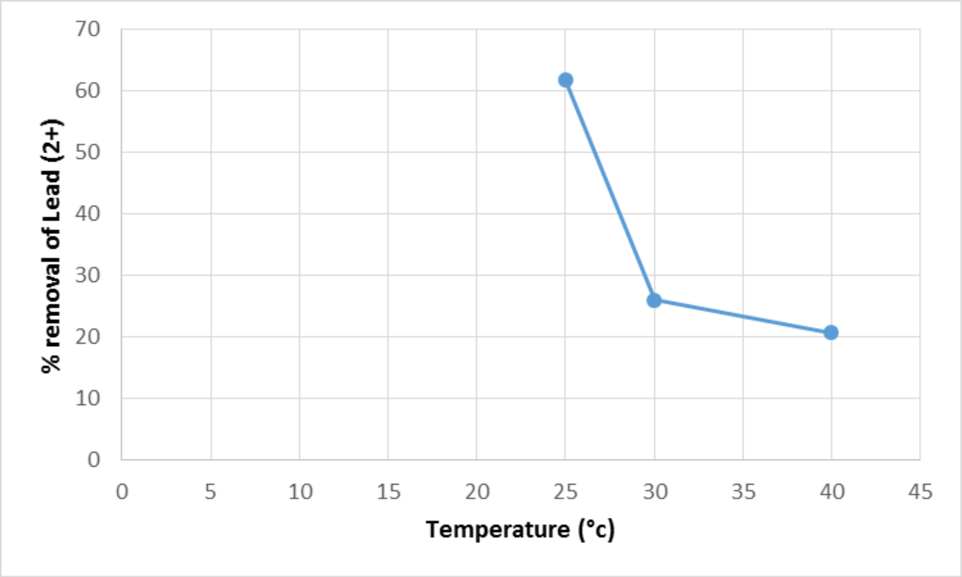


Figure 3.3.7: The effect of temperature on the removal efficiency for polymer **A**.

Polymer B

The effect of the temperature on the removal of Pb(II) ion by polymer B is shown in figure 3.3.8. Maximum adsorption efficiency was observed at room temperature. At higher temperature, over 30 ^{o}C, the percentage of metal started to decrease. The results could be an indication that the adsorption is spontaneous at room temperature.

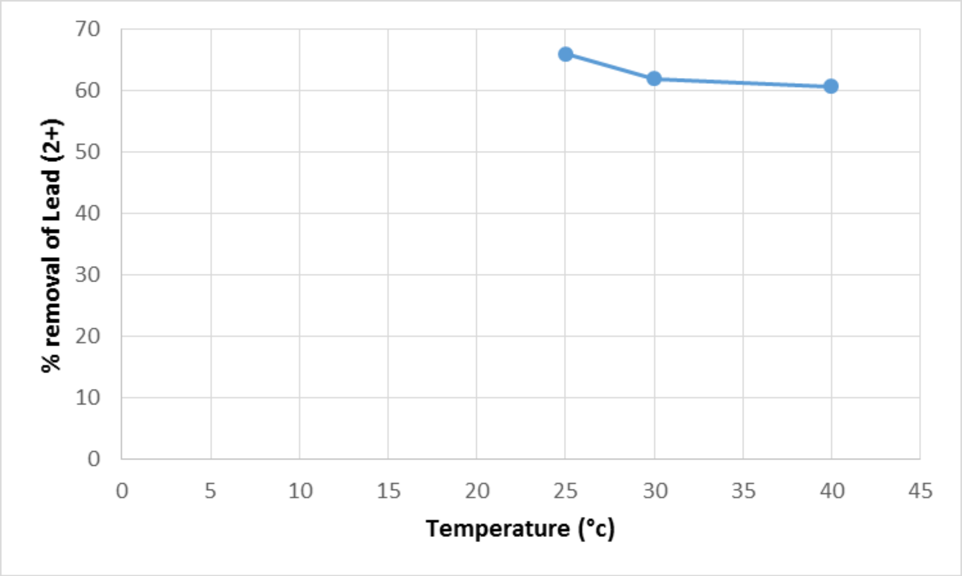


Figure 3.3.8: The effect of temperature on the removal efficiency for polymer **B**.

Polymer C

The effect of the temperature on the removal of Pb(II) ion by polymer C is shown in figure 3.3.9. Maximum adsorption efficiency was observed at room temperature. At higher temperature, over 30 ^{o}C, the percentage of metal started to decrease. The results could be an indication that the adsorption is spontaneous at room temperature.

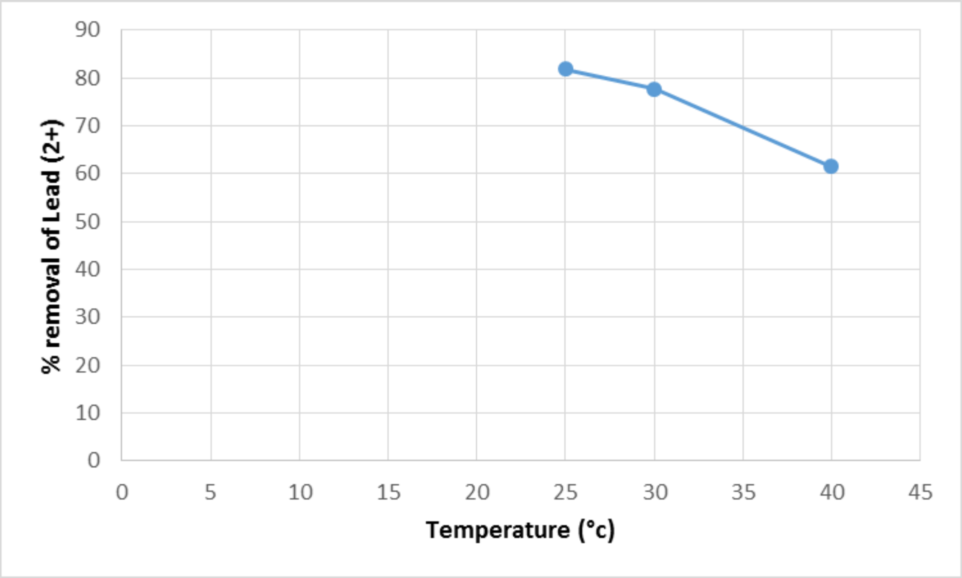


Figure 3.3.9: The effect of temperature on the removal efficiency for polymer **C**.

3.3.1.4 Optimum Lead solution concentration

This variable is relative variable, the highest percent of extraction is not important, but a comparison between the concentration and the percent of extraction is important, if this comparison is performed, the following result is reached: as the concentration of lead solution increased, the removal efficiency became better and more noticeable.

Polymer A

The effect of the lead (II) initial concentration on the removal of Pb(II) ion by polymer A is shown in figure 3.3.10. As shown in Figure3.3.10, the % of ion removal became constant when the initial concertation reached 10 ppm. According to the obtained results, the polymer efficiency is not affected by metal ion concentration. the main mechanism in this case is ion diffusion.

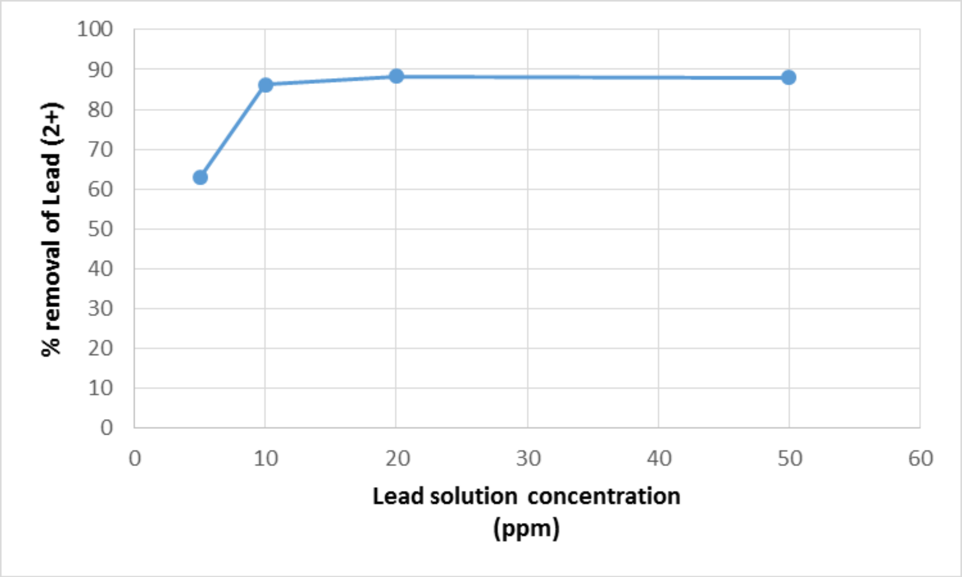


Figure 3.3.10: The effect of lead solution concentration on the removal efficiency for polymer **A**.

Polymer B

The effect of the lead solution concentration on the removal of Pb(II) ion by polymer B is shown in figure 3.3.11. Polymer B shows similar behavior to polymer A, regarding initial ion concertation.

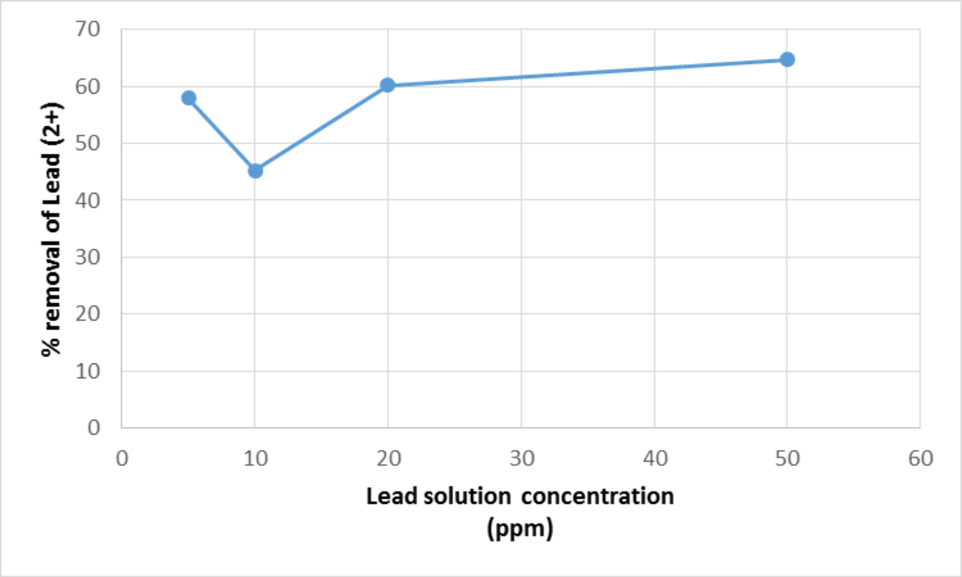


Figure 3.3.11: The effect of lead solution concentration on the removal efficiency for polymer **B**.

Polymer C

The effect of the lead solution concentration on the removal of Pb(II) ion by polymer C is shown in figure 3.3.12. Polymer C shows almost similar behavior to polymer B, regarding initial ion concertation.

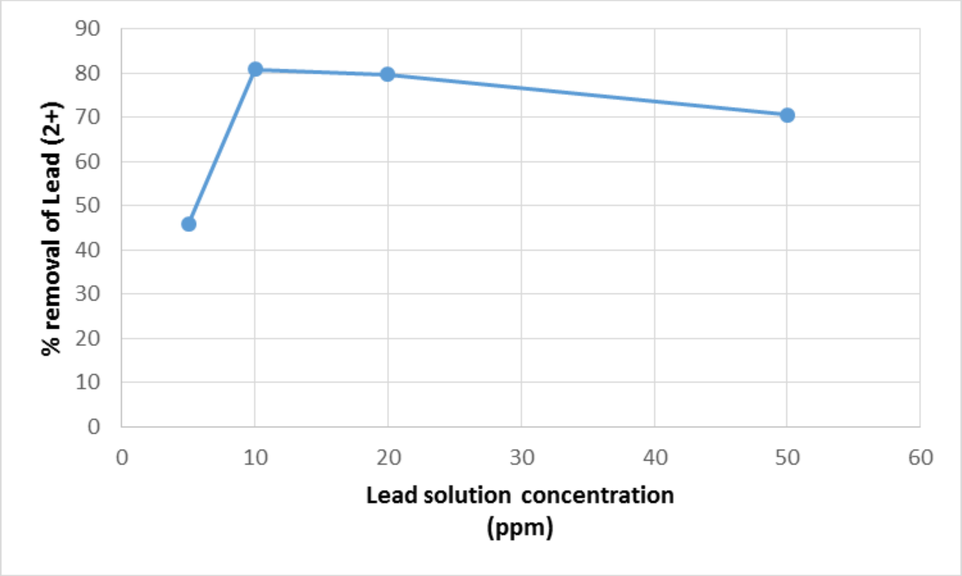


Figure 3.3.12: The effect of lead solution concentration on the removal efficiency for polymer **C**.

3.3.1.5 Optimum pH

The pH that provided the lowest residual concentration of metal ion was chosen as an optimum pH. This was achieved by performing the experiment on 10 mL of each Pb^{2+} with a concentration of 50.0 ppm, different pH for 30 min and at room temperature.

Polymer A

The effect of the pH on the removal of Pb(II) ion by polymer A is shown in figure 3.3.13. The pH value is critical in adsorption, since it could be used to control polymer surface charge. At low pH value (3.0 or lower) the carboxyl groups and the hydroxyl are in acid form (COOH and -OH). Due to this reason, the adsorption efficiency was the lowest (about 20%). However, at pH value higher than 8.0, the H becomes partially bonded to O, so lone pair of electrons are more available, causing the hydroxyl group to behave as much stronger chelating agent. So, the highest efficiency was noticed at pH 8.0. At a pH value higher than 9.0, the adsorption increased, it could be not due to the absorbency, it could be because it is precipitating out of solution as lead hydroxide and is remove by filtration. So the optimum pH value is about 8.0.

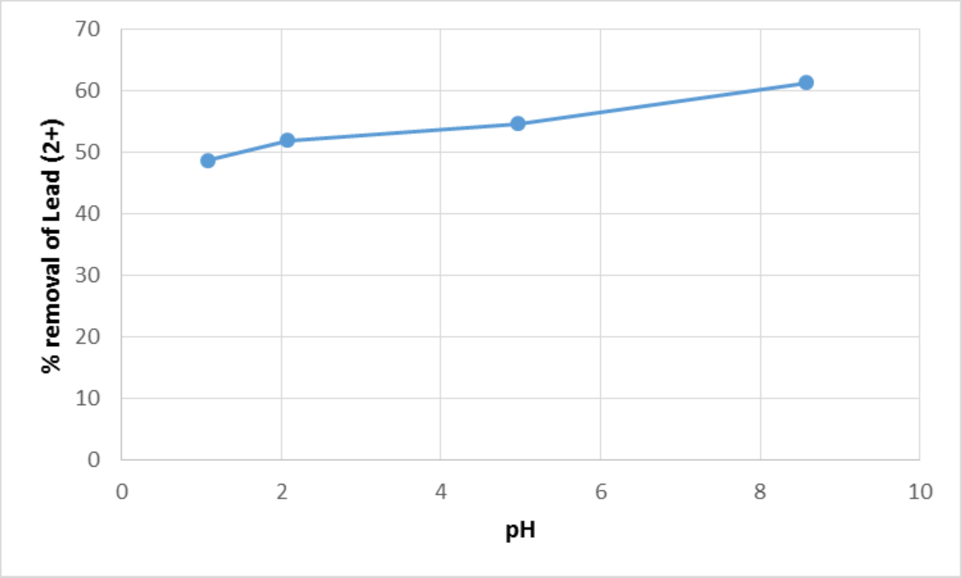


Figure 3.3.13: The effect of pH on the removal efficiency for polymer **A**.

Polymer B

The effect of the pH on the removal of Pb (II) ion by polymer B is shown in figure 3.3.14. As mentioned above polymer B has more carboxyl groups than Polymer A. Due to this reason, the adsorption efficiency was the highest at pH value of about 8.0. At this pH value, most of the carboxyl groups are in the carboxylate form. However, At a pH value higher than 9.0, the adsorption increased, it could be not due to the absorbency, it could be because it is precipitating out of solution as lead hydroxide and is remove by filtration. So the optimum pH value is about 8.0.

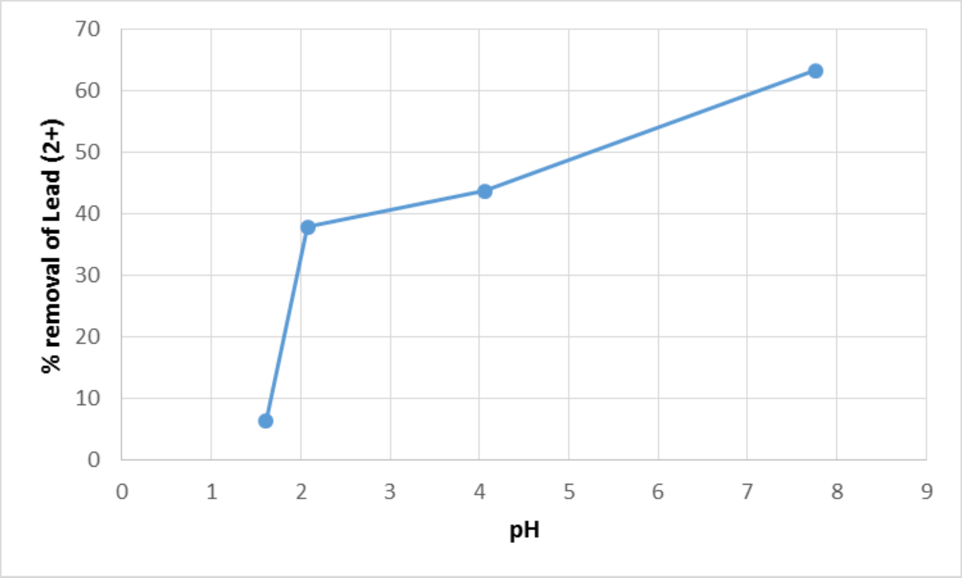


Figure 3.3.14: The effect of pH on the removal efficiency for polymer **B**.

Polymer C

The effect of the pH on the removal of Pb (II) ion by polymer C is shown in figure 3.3.15.

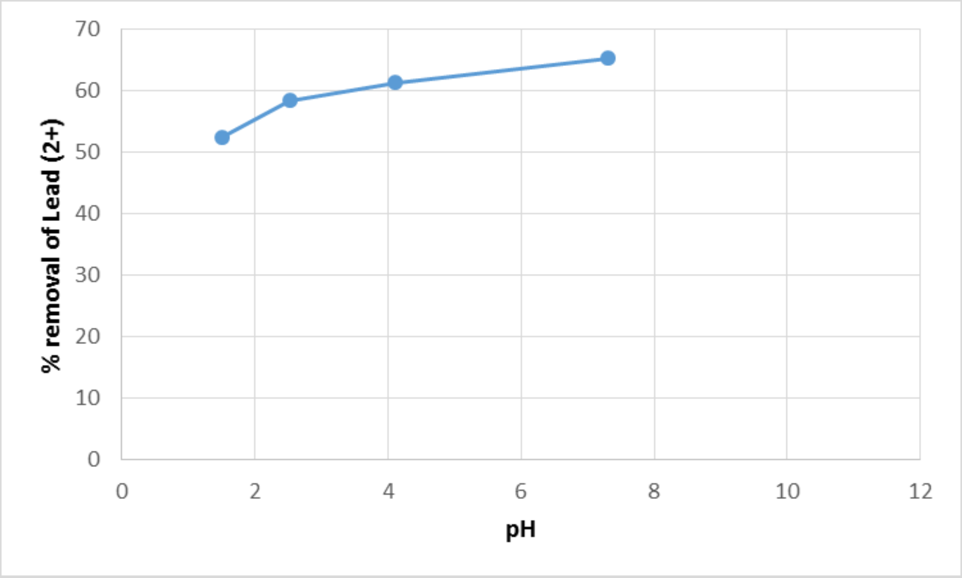


Figure 3.3.15: The effect of pH on the removal efficiency for polymer **C**.

Polymer C showed a behavior almost similar to that showed by polymer B.

3.4 Adsorption kinetics

It is important to study the adsorption kinetically in order to understand the mechanism. By monitoring if the mentioned conditions affect on the adsorption speed or not. So there are two models used:

1. Pseudo-first order model: if the figure $\ln(q_e-q_t)$ vs time gives straight line with high R^2 value, then the adsorption will be obeying this model.

Where $q_{e:}$ is the amount adsorbed per unit mass at equilibrium.

2. Pseudo-second order model: if the figure t/q_e vs time gives straight line with high R^2 value, then the adsorption will obey this model.

3.4.1 Testing the two models on three polymers (A, B and C):

3.4.1.1 Polymer A:

Table 3.4.1: pseudo-first order model for polymer A.

Time (min)	**Conc. Of Pb^{2+} after extraction**	**q_e (mg/g)**	**$\ln(q_e-q_t)$ q_t= 7.37554**
1	13.0180	7.3964	-3.8699
5	9.7913	8.04174	-0.40617
10	8.4254	8.31492	-0.062535
15	6.5672	8.68656	0.27081
30	13.2266	7.35468	-3.8699

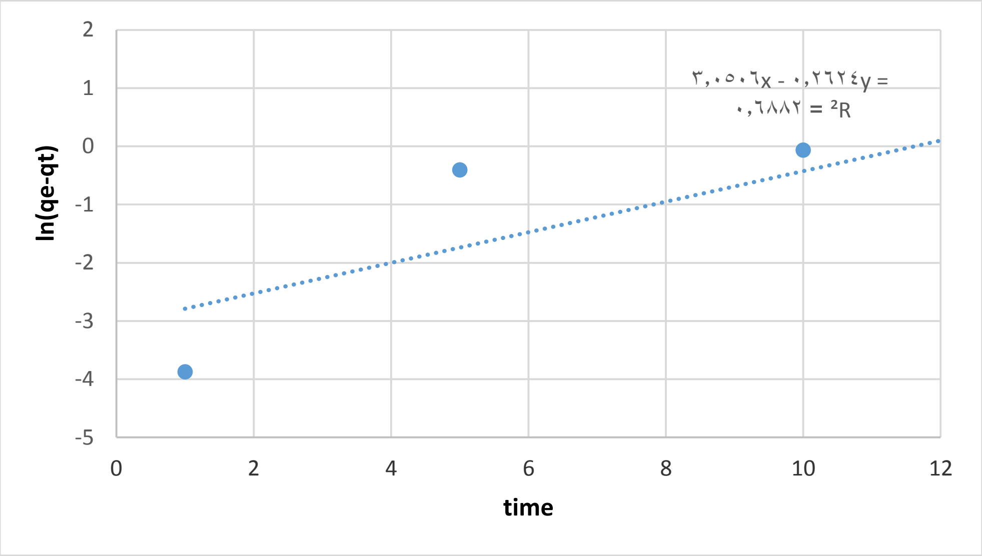


Figure 3.4.1: pseudo-first order model for polymer **A**.

Table 3.4.2: pseudo-second order model for polymer A.

Time (min)	**Conc. Of Pb^{2+} after extraction**	**q_e (mg/g)**	**t/q_e**
1	13.0180	7.3964	0.1352
5	9.7913	8.04174	0.6218
10	8.4254	8.31492	1.203
15	6.5672	8.68656	1.727
30	13.2266	7.35468	4.079

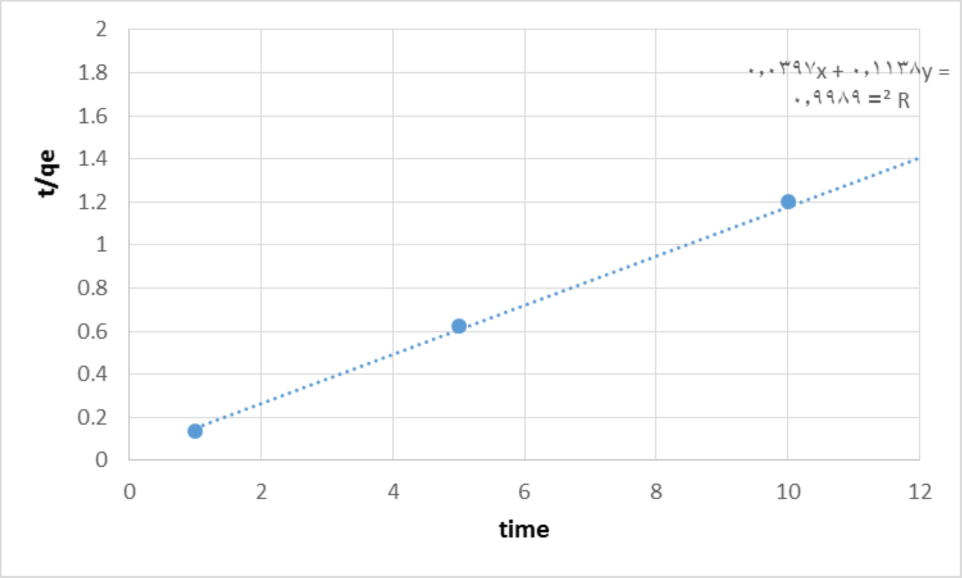


Figure 3.4.2: pseudo-second order model for polymer **A**.

So from the two figures, and from the values of R^2, polymer A follows pseudo-second order model for the adsorption.

3.4.1.2 Polymer B:

Table 3.4.3: pseudo-first order model for polymer B.

Time (min)	**Conc. Of Pb^{2+} after extraction**	**q_e (mg/g)**	**$\ln(q_e\text{-}q_t)$ q_t= 2.3015**
1	19.9442	1.5027	-0.22464
5	5.6077	2.2196	-2.5023
10	2.3320	2.3834	-2.5023
15	12.0984	1.8951	-0.90042
30	17.8804	1.6059	-0.36298

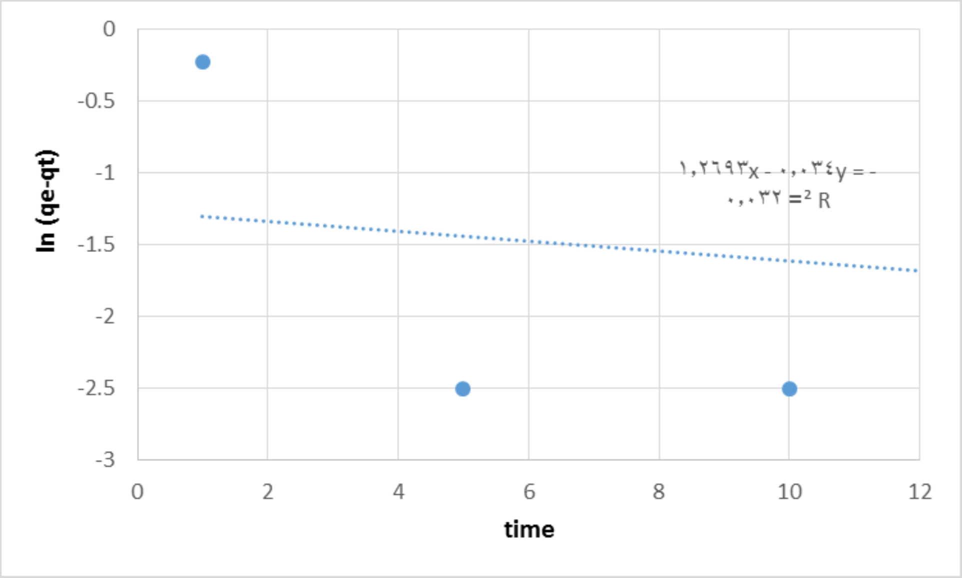


Figure 3.4.3: pseudo-first order model for polymer **B**.

Table 3.4.4: pseudo-second order model for polymer B.

Time (min)	**Conc. Of Pb^{2+} after extraction**	**q_e (mg/g)**	**t/q_e**
1	19.9442	1.5027	0.6654
5	5.6077	2.2196	2.2527
10	2.3320	2.3834	4.1957
15	12.0984	1.8951	7.9151
30	17.8804	1.6059	18.6811

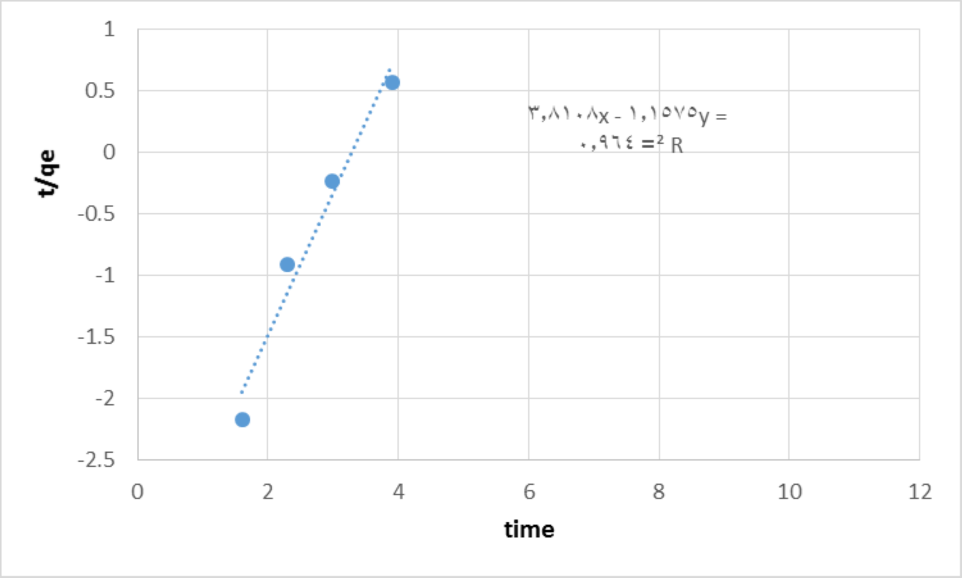


Figure 3.4.4: pseudo-second order model for polymer **B**.

From the two figures, and from the values of R^2, polymer B follows pseudo- second order model for the adsorption.

3.4.1.3 Polymer C:

Table 3.4.5: pseudo-first order model for polymer C.

Time (min)	**Conc. Of Pb^{2+} after extraction**	**q_e (mg/g)**	**$\ln(q_e\text{-}q_t)$ qt= 1.8351**
1	20.7364	1.4632	--0.98913
5	19.4599	1.5270	-1.1773
10	13.2814	1.8359	-7.1309
15	13.3134	1.8343	-7.1309
30	18.2929	1.5854	-1.3875

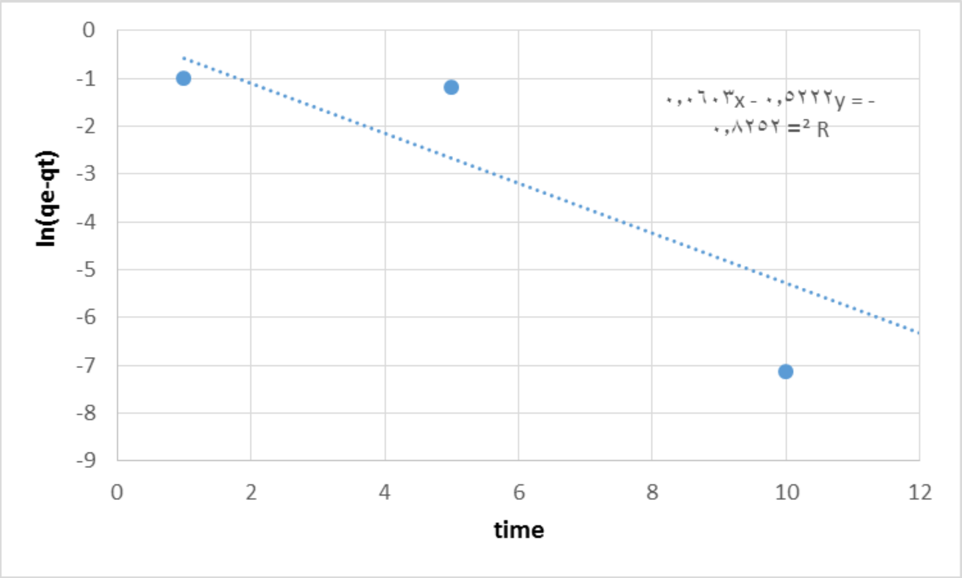


Figure 3.4.5: pseudo-first order model for polymer **C**.

Table 3.4.6: pseudo-second order model for polymer **C**.

Time (min)	**Conc. Of Pb^{2+} after extraction**	**q_e (mg/g)**	**t/q_e**
1	20.7364	1.4632	0.6834
5	19.4599	1.5270	3.2744
10	13.2814	1.8359	5.4469
15	13.3134	1.8343	8.1775
30	18.2929	1.5854	18.923

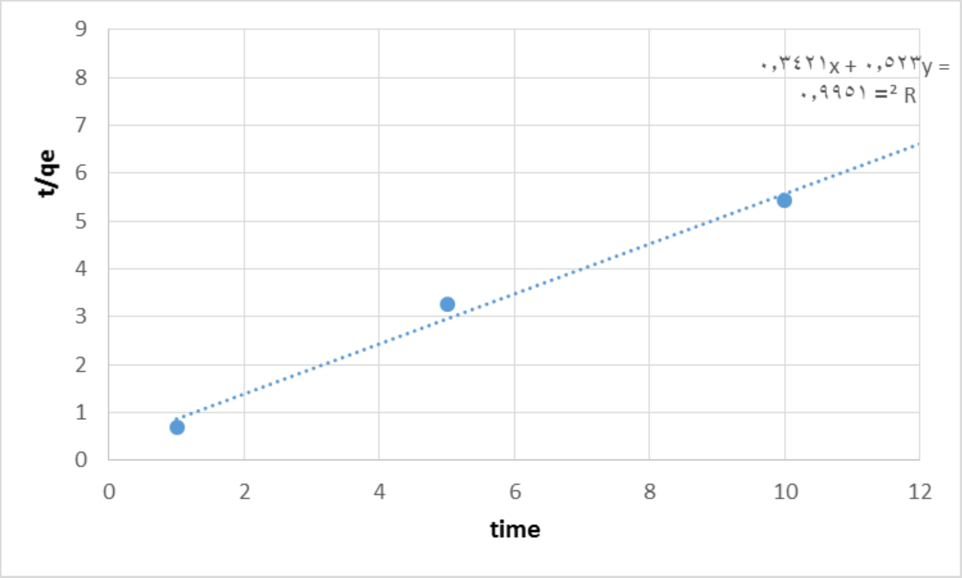


Figure 3.4.6: pseudo-second order model for polymer **C**.

From the two figures, and R^2 values, we find polymer C also obeys pseudo-second order model for adsorption.

3.5 Adsorption Isotherms

This part was performed to decide the adsorption type proceeds. There are two models to describe the adsorption:

1. Langmuir isotherm model: describes monolayer coverage of adsorption surface.

If the figure plot between 1/q vs 1/c gives a straight line with high R^2 value so the adsorption obey this model.

2. Freundlich isotherm model: It describes multilayer adsorption.

If the figure lnq vs lnc gives a straight line with high R^2 value, then the adsorption obey this model.

3.5.1 Testing the two models for the polymers (A, B and C):

3.5.1.1 Polymer A:

Table 3.5.1: Langmuir model for polymer A.

Concentration of lead nitrate solution (ppm)	Concentration of lead (Pb^{2+}) after extraction	q	1/c	1/q
5	1.8595	0.6281	0.2	1.5921
10	1.3836	1.7233	0.1	0.5803
20	2.3460	3.5308	0.05	0.2832
50	6.0288	8.7942	0.02	0.1137

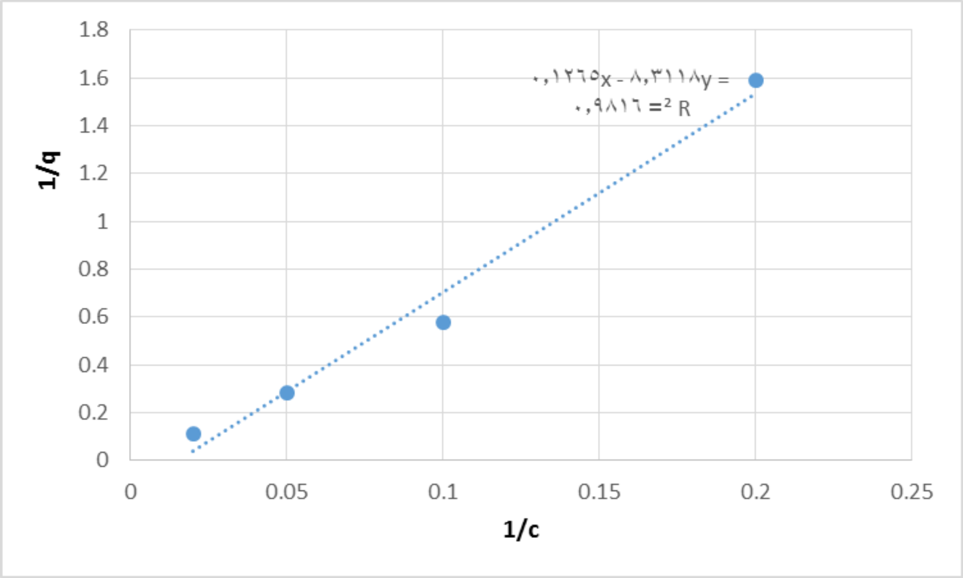


Figure 3.5.1: Langmuir model for polymer **A**.

Table 3.5.2: Freundlich model for polymer A.

Concentration of lead nitrate solution (ppm)	Concentration of lead (Pb^{2+}) after extraction	q	lnc	lnq
5	1.8595	0.6281	1.61	-0.4651
10	1.3836	1.7233	2.30	0.5442
20	2.3460	3.5308	2.99	1.2615
50	6.0288	8.7942	3.91	2.1741

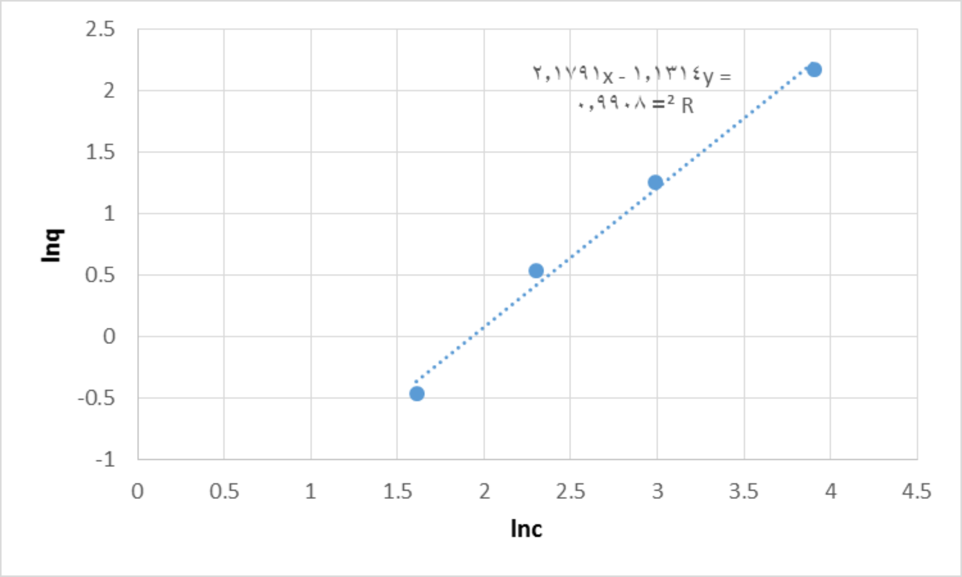


Figure 3.5.2: Freundlich model for polymer **A**.

From two figures, and R^2 values, polymer A follows freundlich model in the adsorption.

3.5.1.2 Polymer B:

Table 3.5.3: Langmuir model for polymer B.

Concentration of lead nitrate solution (ppm)	Concentration of lead (Pb^{2+}) after extraction	q	1/c	1/q
5	2.1004	0.1449	0.2	6.9013
10	5.4810	0.2259	0.1	4.4267
20	7.9474	0.6026	0.05	1.6595
50	17.6463	1.6177	0.02	0.6182

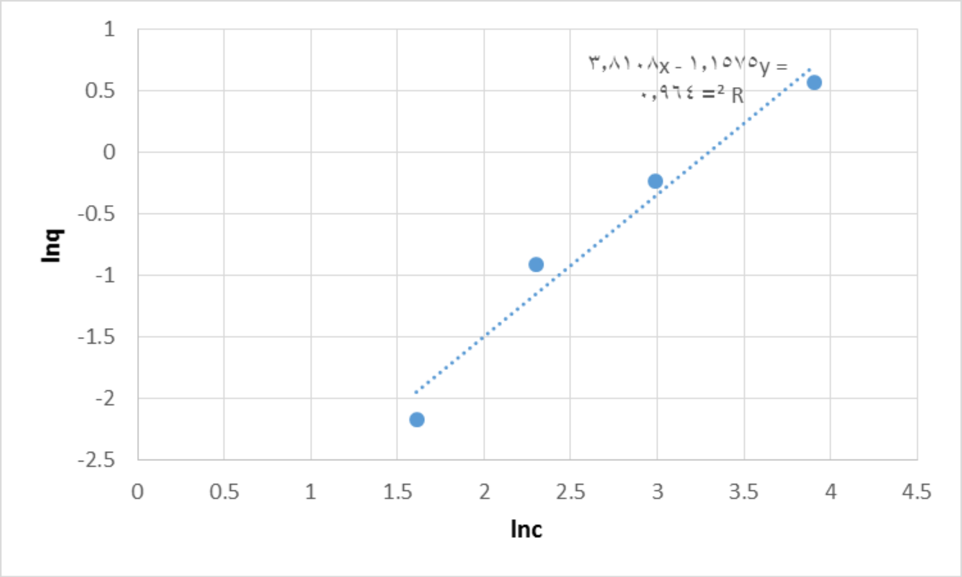


Figure 3.5.3: Langmuir model for polymer **B**.

Table 3.5.4: Freundlich model for polymer B.

Concentration of lead nitrate solution (ppm)	Concentration of lead (Pb^{2+}) after extraction	q	lnc	lnq
5	2.1004	0.1449	1.61	-1.9317
10	5.4810	0.2259	2.30	-1.4877
20	7.9474	0.6026	2.99	-0.5065
50	17.6463	1.6177	3.91	0.4810

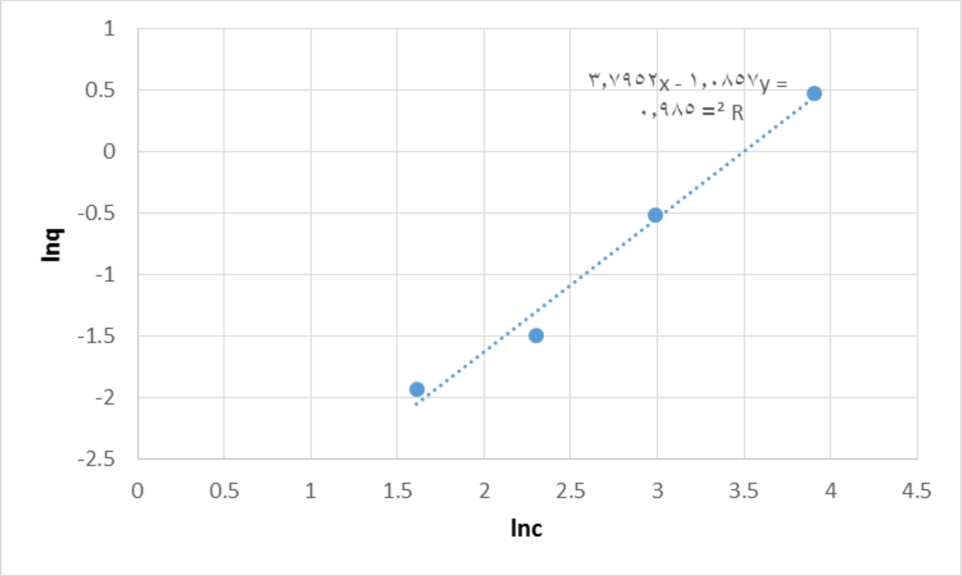


Figure 3.5.4: Freundlich model for polymer **B**.

From the two figures, and R^2 values, polymer B follows freundlich model in the adsorption.

3.5.1.3 Polymer C:

Table 3.5.5: Langmuir model for polymer C.

Concentration of lead nitrate solution (ppm)	Concentration of lead (Pb^{2+}) after extraction	q	1/c	1/q
5	2.7100	0.1145	0.2	8.7336
10	1.9054	0.4047	0.1	2.4709
20	4.0509	0.7975	0.05	1.2539
50	14.7049	1.7648	0.02	0.5666

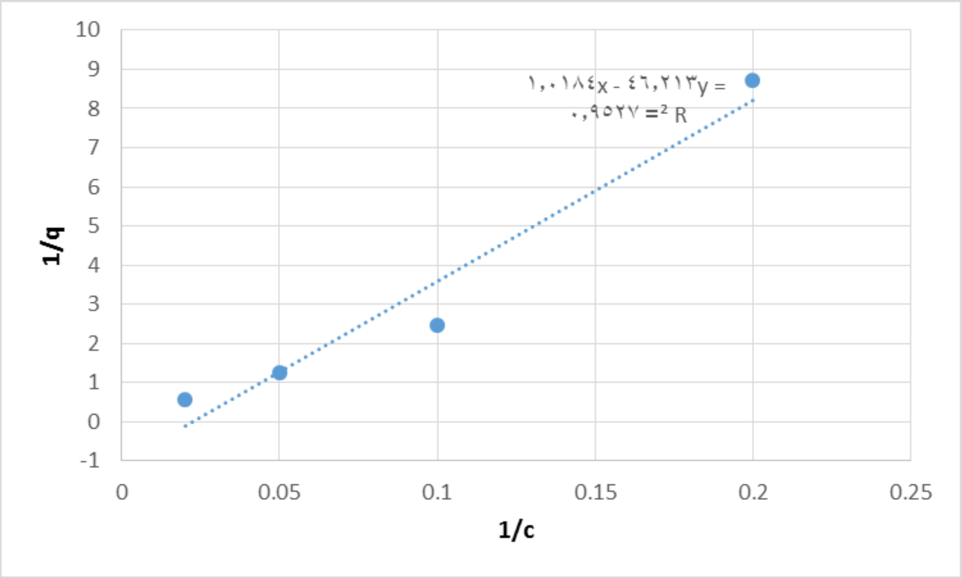


Figure 3.5.5: Langmuir model for polymer **C**.

Table 3.5.6: Freundlich model for polymer C.

Concentration of lead nitrate solution (ppm)	Concentration of lead (Pb^{2+}) after extraction	q	lnc	lnq
5	2.7100	0.1145	1.61	-2.1672
10	1.9054	0.4047	2.30	-0.9046
20	4.0509	0.7975	2.99	-0.2263
50	14.7049	1.7648	3.91	0.5680

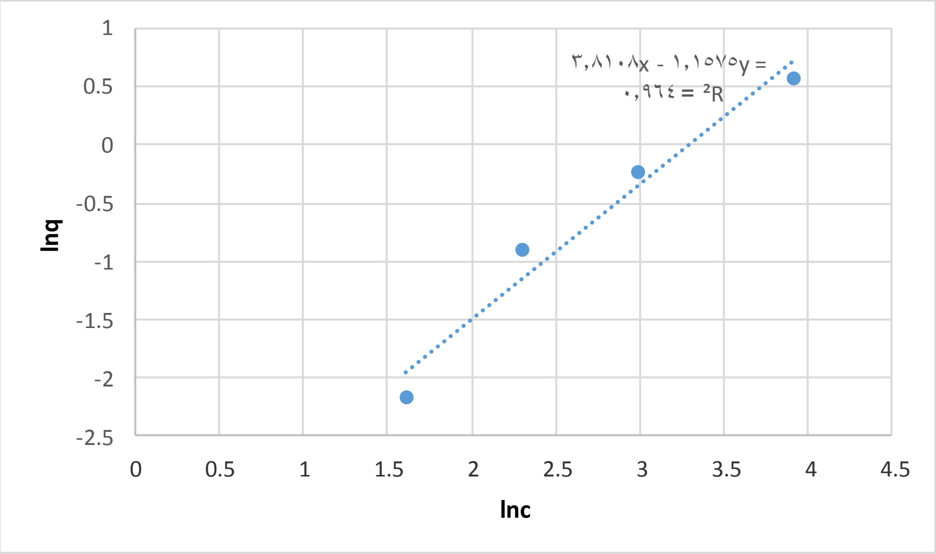


Figure 3.5.6: Freundlich model for polymer **C**.

From the two figures, and R^2 values, polymer C follows freundlich model in the adsorption.

Conclusion

In this work, three polymers **(A, B and C)** were prepared by mixing various amounts of cellulose, β-cyclodextrin and citric acid.

The polymers were used in water purification from lead (II), the three polymers showed high adsorption efficiency toward lead (II). The optimized adsorption conditions for polymers were determined.

The optimum adsorption conditions for polymer **A** were polymer dosage 0.05 g, 15 minutes of extraction time at room temperature (25°C) and a pH value of 8.0.

For polymer **B,** the polymer dosage was 0.2 g, 10 minutes of extraction time at room temperature (25°C) and a pH value of 8.0.

And for polymer **C,** the polymer dosage was 0.2 g, 10 minutes of extraction time, room temperature (25 °C) and pH value of 8.0.

All three polymers obey pseudo-second order model for adsorption kinetics, and freundlich model for the adsorption isotherm.

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جامعة النجاح الوطنية

كلية الدراسات العليا

السليولوز المعدل بالبيتاسايكلوديكسترين الحلقي في تنقية المياه الملوثة من أيونات المعادن السامة

إعداد

هديل يوسف محمد أبو دهماز

إشراف

د. عثمان حامد

أ.د. شحدة جودة

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

2019

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الملخص

مصادر المياه الصالحة للشرب على كوكب الأرض قليلة، وهذه المصادر معرضة للتلوث باستمرار نظرا لتطور الحياة وانتشار الصناعات المختلفة، والتي تلوث المياه بالمواد العضوية والمعادن الثقيلة السامة، والتي تؤثر على صحة الانسان بشكل مباشر.

فنظرا لقلة مصادر المياه الصالحة للشرب على كوكب الأرض، وتعرضها المستمر للتلوث، ظهرت الحاجة الملحة لأن يتم تنقية المياه قبل وصولها للإنسان.

يعد تلوث المياه بالمعادن الثقيلة ظاهرة خطيرة، حيث تؤثر هذه المعادن الثقيلة على صحة الإنسان بشكل تراكمي، بحيث أن الجسم لا يتخلص من التراكيز القليلة من هذه المعادن إذا دخلته من المصادر المختلفة.

يستطيع جسم الإنسان استيعاب كمية قليلة من هذه المعادن دون أن يتعرض للخطر، ولكن اذا زادت كمية هذه المعادن في الجسم عن الكمية المسموح بها، فإن ذلك يؤثر سلبا على صحة الإنسان، ومن المخاطر التي تسببها هذه المعادن على سبيل المثال: يؤدي الزئبق الى تدمير الأعصاب ويقود في النهاية الى الموت، قد يؤدي عنصر الزرنيخ للتسبب في السرطان، كما أن التعرض الطويل لعنصر النحاس قد يؤدي إلى تدمير الكبد، كما يؤثر على النباتات، وأيضا عنصر الرصاص والذي قد يؤدي إلى تدمير الدماغ، ويسبب التشنجات، كما يسبب اضطراب سلوكي، ويقود في النهاية إلى الموت.

يصل عنصر الرصاص إلى مياه الشرب عن طريق أنابيب المياه المستخدمة في أنظمة توزيع المياه والتي يكون عنصر الرصاص مكون أساسي فيها، ويصل أيضا عن طريق عوادم السيارات والدهانات وغيرها.

ظلت الجهود ولا زالت مركزة نحو تنقية المياه من هذه المعادن السامة، فقد استخدمت العديد من الطرق الكيمائية لتخليص المياه من هذه الملوثات، ولكن الجهود ركزت في الآونة الأخيرة على استخدام طرق سهلة وبسيطة ومصاحبة للبيئة للتخلص من مثل هذه الملوثات.

وعلى اعتبار أن السليولوز من أكثر البوليمرات الطبيعية تواجدا في الطبيعة، ويمتلك العديد من الميزات تجعله مرشحا لأن يستخدم في عمليات التنقية تلك، كرخص ثمنه، وسهولة الحصول عليه، وامكانية تفككه في الطبيعة ما يجعله غير ضار للبيئة، فقد تم استخدامه كماص لتلك الملوثات.

في بحثي هذا كان الهدف الرئيسي ايجاد طريقة سهلة لتنقية المياه من عنصر الرصاص باستخدام مواد طبيعية منخفضة التكلفة.

ولتحقيق ذلك الهدف تم استخدام السليولوز كمادة أساسية في تشكيل بوليمر، ليتم استخدامه في تنقية المياه من عنصر الرصاص.

في هذه الدراسة أولا تم مفاعلة السليولوز مع كلا من البيتاسايكلوديكسترين والسيترك أسد كعامل ربط بين هاتين المادتين، ومن ثم وضع هذا المزيج في الفرن على درجة حرارة 180 درجة سيلسيوس لمدة ساعتين، بعد هذه المدة نتوقع تكون روابط ايسترية، تم الكشف عنها باستخدام أطياف الأشعة تحت الحمراء.

تم تحضير ثلاثة بوليمرات من تلك المواد باستخدام نسب مختلفة، ولكل بوليمر تم فحص فعاليته في تنقية المياه من عنصر الرصاص، وتم دراسة أثر العديد من العوامل على فعالية إزالة عنصر الرصاص من المياه، وهذه العوامل هي: كمية البوليمر، والوقت الذي تعرضت له المياه الملوثة

بالرصاص للبوليمر، ودرجة الحرارة، وتركيز محلول الرصاص ودرجة الحموضة، وذلك للتوصل للظروف المثالية التي تؤدي الى أقصى فعالية في إزالة عنصر الرصاص من المياه.

تم التوصل الى الظروف المثالية للحصول على أقصى فعالية لإزالة عنصر الرصاص من المياه لكل بوليمر والتي قادت إلى نسب إزالة عالية نوعا ما.

فتشير النتائج في هذه الأطروحة الى أننا نجحنا في تكوين بوليمرات بطريقة سهلة، ومن مواد متوافرة (السليولوز الذي تم استخلاصه من مخلفات الزيتون الصلبة والمتعارف عليها باسم الجفت، البيتاسايكلوديكسترين والسيترك أسد)، واستخدامها في تنقية المياه الملوثة من عنصر الرصاص.