An-Najah National University

Faculty of Graduate Studies

EXTRACTION AND MODIFICATION OF LIGNIN FROM OLIVE INDUSTRY LIQUID WASTE AND APPLICATION IN WASTE WATER PURIFICATION

By

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Dedication

To my lovely parents, my dear brothers, my family and my husband's family, thank you for your continuous support.

To my lovely husband, thank you from the bottom of my heart for your greatest support.

To my son Jawad, I thank God for being in my life.

To my colleagues, and my friends. Everyone who helped and supported me to complete this research.

To all of them I dedicate this work.

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Firstly, the greatest thanks to my Allah, who always guided me and facilitates my right ways of excellence and success.

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

Extraction and Modification of Lignin from Olive Industry Liquid Waste and Application in Waste Water Purification

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي من نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل أو أي جزء منها لم يقدم من قبلي 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 or qualification.

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List of Abbreviations

Symbol	Abbreviation
BOD	Biological Oxygen Demand.
C_e	Concentration of metal ions in the sample solution after treatment at equilibrium (ppm).
C_o	Initial concentration of metal ions in the sample solution (ppm).
COD	Chemical Oxygen Demand.
Conc.	Concentration .
DMF	Dimethyl form amide.
DMSO	Dimethyl sulfoxide.
FT-IR	Fourier Transform Infrared.
G	Guaiacyl unit.
H	Hydroxy phenyl unit.
ICP-MS	Inductively Coupled Plasma Mass Spectrometry.
IWW	Industrial wastewater.
K_1	The pseudo-first order rate constant.
K_2	The pseudo-second order rate constant.
Kd	Distribution coefficient.
K_F	Freundlich constant which is an approximate indicator of adsorption capacity of the sorbent (mg/g $(L/mg)^{1/n}$).
K_L	Langmuir isotherm constant (L/mg).
LBNT	Lignin-Based Nano-Trap.
LBPAA	Lignin based poly (Acrylic Acid).
L-CNTs	Lignin grafted with carbon nanotubes.
M	Mass (g).
min	Minute .
$\frac{1}{n}$	Dimensionless Freundlich constant giving an indication of how favourable the adsorption process.
OILW	Olive Industry Liquid Wastes
OISW	Olive Industry Solid Wastes .
OMLW	Olive Mill Liquid Waste.
OMW	Olive Mill Wastewater.
Org MMT	Organo montmorillonite.
PAA	Poly(Acrylic Acid).
PAA-Lignin-A	Cross-linked poly(Acrylic Acid) grafted with Lignin polymer A.
PAA-Lignin-B	Cross-linked poly(Acrylic Acid)grafted with Lignin polymer B.

PSt@p (NIPMAM-Aac)	Polystyrene- poly (N-isopropyl-meth acryl amide- Acrylic Acid.
q_e	The mass of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g).
q_{max}	Maximum monolayer adsorption capacity of the adsorbent (mg/g) theoretically.
q_t	Amount of adsorbate per unit mass of adsorbent at time t (min).
R_L	Dimensionless constant separation factor.
R^2	Correlation coefficient (regression coefficient).
S	Syringyl unit.
SEM	Scanning Electron Microscopy.
St-g-PAA/SH	Starch-grafted-poly(Acrylic Acid) /sodium humate.
T,t	Time.
Temp.	Temperature (^oC).
THF	Tetrahydrofuran.
Tg	Transition temperature.
V	Volume of solution.
w/v	The amount by weight (mass) of a solid substance dissolved in a measured quantity of liquid.
WHO	World Health Organization.
Wt	Weight of the adsorbent (g).

Extraction and Modification of Lignin From Olive Industry Liquid Waste and Application in Waste Water Purification

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Abstract

Contamination of water by toxic metal ions is of a great worry due to their high harmfulness and carcinogenicity. Scientists have been devoting a great time and effort searching for new cost-effective natural based adsorbents for these toxic metals. Lignin is a cheap waste polymer that is natural amorphous with a high potential for use in the production of bio-renewable materials. The polyphenolic structure of lignin in addition to its availability make it a unique starting material for preparing adsorbents for a wide variety of heavy metal ion.

In this study, two new copolymers from lignin, acrylic acid and a cross-linking agent, N,N-methylenebisacrylamide, were synthesized and evaluated as adsorbents for toxic metal ions from contaminated water. The lignin used in this work was extracted from liquid waste of olive industry (Zebar). The two synthesized polymers PAA-Lignin-A and B with different lignin content were characterized by Fourier Transform Infrared (FT-IR) and Scanning Electronic Microscopy (SEM).The SEM analysis results showed that, polymer A is more porous. The two polymers were used as adsorbents for Pb(II) from wastewater. The adsorption efficiencies of the prepared two polymers toward Pb(II) was investigated as a function of adsorbent dose, metal ion concentration, adsorption time, temperature, and pH value. The adsorption parameters that lead to an excellent adsorption efficiency were determined. In addition, the two polymers showed medium to excellent extraction efficiencies toward sixteen different metal ions present in a sewer sample collected from Hebron Palestine.

The high efficiency of the prepared polymers toward various metal ions could be attributed to the several coordination sites present in the polymers including aromatic, hydroxyl, carboxyl and amine. The adsorption efficiency reached about 90% for polymer PAA-lignin-A and 85.5% for PAA-lignin-B. The grater efficiency of PAA-lignin-A could be attributed to the higher porosity.

The isotherm models that best fits the results were investigated according to the value of the correlation coefficient of Langmuir and Freundlich isotherm adsorption models. The kinetics of adsorption were also investigated using pseudo first-order and pseudo second- order models.

The results showed that, the adsorption follows the Langmuir isotherm and the mechanism of the reaction is consistent with pseudo second-order kinetic adsorption model.

CHAPTER ONE

INTRODUCTION

1.1 Background

Water is considered a fundamental natural resources and covers about 70% of the Earth. Out of the 90% more than 97.0% is salt water (distributes in oceans and seas). The fresh water represents less than 3.0% that is distributed in ice and snow 1.9%, underground 0.4%, lakes 0.009%, atmosphere 0.0013%, rivers and streams 0.0002%). Water is important for all forms of life, for drinking, cleaning, as habitat for aquatic organisms and as a reproductive medium and for irrigation purposes. It comprises up to 90% of the creature's body weights. It is also crucial for metabolic processes and as a transport mechanism of most living organism [1].

Water pollution is a major issue that is affecting the people all around the world. It reduces the efficacy of water and it brings diseases to human health and other aquatic forms of life. Human is considered one of the main causes of water contamination through dumping waste in rivers, seas and oceans. In addition to the agricultural, industrial and mining wastes [2]. Unfortunately, natural water resources have been contaminated with inorganic and organic pollutants due to intensive industrialization and urbanization [3].

Toxic metal ions are main pollutant nowadays, which are defined as elements having atomic weights of up to 200.0, and a specific gravity higher than 5.0 [4]. The majority of the metals ions are toxic to mankind.

On the other hand, people in developing countries dependent on these heavy metals in producing daily requirements such as electroplates, pigments, tannery, battery and pesticides, results in the heavy metal exposure to the environment increasingly, especially to the water directly or indirectly, which in turn reduces the amount of drinkable water [5]. Organic contaminants are biodegradable, so over the years they could decompose into carbon dioxide and water, however the metal ion are not and tend to pile up in living organisms. The high solubility of the metals ion aqueous medium and it ability to migrate makes them severe toxic and carcinogenic [6].

Some of the toxic metal ions that raise a serious concern are Zinc (II), Copper (II), Nickel(II), Mercury (I) and (II), Cadmium(II), Lead(II) and Chromium with various oxidation states [7]. These metal ions cause physiologic and genetic problems in organisms even when they present at ppb concentrations. For instance, Zinc is an element that is crucial to human health. But the excessive ingestion of it can lead to severe health issues, such as stomach spasms, vomiting, skin redness, nausea and anemia[8]. Copper also considered an essential metal in animal digestion. However, too much copper can cause serious medical problems, such as vomiting, convulsions, spasms, or even death [9]. In addition, Nickel(II) is known to be a carcinogenic. Exceeding the amount of Nickel allowed by U.S. Environmental Protection Agency can also causes serious kidney and lung problems beside pulmonary fibrosis distress, gastrointestinal and skin issues [10]. Mercury is neurotoxin element; it damages the central nervous system. Moreover, it can cause impairment of kidney and pulmonary function, dyspnoea and chest pain [11]. Cadmium has been classified by U.S. Environmental Protection Agency as a possible cancer agent. Frequent exposure to high levels of Cadmium results in kidney dysfunction which can lead to death. Lead is another toxic element attacks the central nervous system and causes damage to it. Lead could also damage the reproductive system, brain, liver, and kidney. Some of the toxic symptoms of Lead ion are headache, insomnia, irritability, dizziness, anemia and muscles weakness [12]. Chromium, Cr(VI) tend to pile up in the food chain and affects human physiology, and causes severe health issues ranging from skin irritation to cancer in the lung cancer [13].

Extraction of heavy metal ions from wastewater before they reach water sources became mandatory for preventing pollution. Several methods for heavy metal ions removal from wastewaters are reported in the literature. Among these are chemical precipitation, evaporation and concentration, ion-exchange, reverse osmosis, electrodialysis, and adsorption[14]. The adsorption method is the most favorable and widely used methods for extraction of heavy metal ions form water. This could be attributed to the low cost, ease of handling, could be recyclable and the availability of many adsorbents that are naturally based [15]. The adsorbents include zeolites, clay minerals, activated carbons, industrial by-products, agricultural byproducts and polymeric adsorbents [16]. Additionally, natural-based materials, such as clay, zeolites, and peat, are among the most evaluated materials as adsorbents for toxic heavy metal ions from wastewater. They are the most attractive because they are renewable and available at a relatively low cost .In addition, other natural products, such as cellulosic materials, Lignin, chitosan, and hemicelluloses, received a lot of attention [17].

1.2 Olive Oil Waste Water

Olive oil production is considered as a major industry in different Mediterranean countries (e.g. Spain, Italy, Morocco, Tunisia, Turkey, Greece) and one of the fastest growing agro-food sectors in EU with >4% of average annual growth rate [18]. However, the olive industry produces large quantities of black wastewaters: olive Mill Wastewater (OMW), which is also known locally as “Zebar” [19]. The amount of Olive Mill Liquid Waste (OMLW) produced yearly during the olive season almost match the municipal sewage produced by 22 million people [20].

The olive also generates a solid waste equivalent to about 40% of Olive Industry Solid waste ,(OISW) which is known locally as “Jeft”, usually used for generating heat during the winter time [21]. These wastes are acidic with pH values between 3.0 and 5.9, have high Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) values, in addition it contains high concentration of Potassium compounds, and antibacterial phenolic compounds which resist biological degradation [22]. If untreated OMW is discharged into streams or rivers, it will consume the dissolved oxygen, and therefore causing fish death and other harmful effects, such as malodorous gases produced due to the decomposition of organic materials.

Other compounds (for instance, lipids and humic-like substances) also contribute to the toxicity of OMW. Untreated OMW also contains numerous microorganisms, pathogenic and toxic compounds (especially phenolic compounds), which affects human health negatively [23].

The OMLW also contains high concentrations of macromolecules such as Lignin and Tannic Acid , which give it the black color. The analysis showed that the raw OMLW is highly toxic to microorganisms, plants, and animals. It is considered toxic even at low concentrations. One way of reducing its toxicity and the impact of this liquid on the environmental is by dilution which could be done prior to the disposal. Another way of reducing the toxicity effect is by the establishment of guidelines to manage the disposal of OMLW. The proper way of handling the OMLW issue is converting it to useful materials with commercial value [20].

On the other hand, OMLW could add value to the planting soil. It contains Potassium, which could enhance the plant growth and acts as a conditioner, compost [24].

1.3 Lignin

Lignin is one of the major by-product of olive industry. It is the second in abundance after cellulose , and also the most abundant natural phenolic polymers in the world [25].

1.3.1 Lignin definition and structure

Lignin[$C_9H_{10}O_2(OCH_3)_n$] is an amorphous and a 3D biopolymer .Unprocessed Lignin is insoluble in many solvents including water, however Lignin extracted from plants and other industrial waste is very soluble in polar solvents such as Dioxane, acetone, Tetrahydrofuran (THF), Dimethylformamide (DMF) and Dimethylsulfoxide (DMSO) [26].

The exact structure of Lignin is not determined yet, Essington[27] suggested the structure that is shown in Figure 1.1.

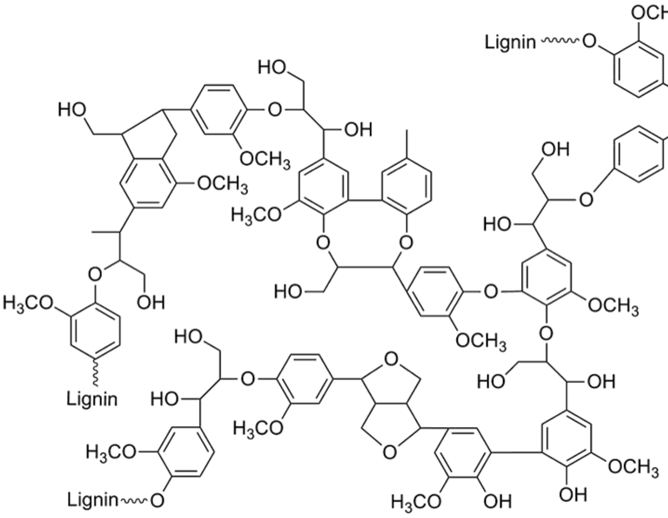

Figure 1.1: Possible chemical structure of Lignin

Several techniques have been employed to characterize the structure and functional groups of the extracted Lignin. These techniques include chemical oxidation and reduction, thermo gravimetric analysis, IR and UV spectroscopy, pyrolytic degradation followed by chromatographic detection and nuclear magnetic resonance [28].

1.3.2 Synthesis of Lignin

The main structure of a Lignin molecule is biosynthesized using three cinnamyl alcohol derivatives [29], with varying percentage and combinations, that polymerize into a three-dimensional huge polymer that is bond together randomLy with C-O-C and C-C bonding. The monomers are almost identical in structures with various bonding combinations, a result of these combinations is a heterogeneous and random structure of Lignin. The Lignin structure varies based on source. These three monomers that are known as monolignols are p-Coumaryl alcohol, Coniferyl alcohol and Sinapyl alcohol [30]. The three monolignols become the constituents of a Lignin molecule to p-hydroxy phenyl (H), guaiacyl (G) and syringyl (S) units, respectively [29]. The chemical structures of the three major monolignols and their respective forms in a polymer are shown in Figure 1.2.

As shown below, it should be noted that the double bond in the precursors is saturated after polymerization. Besides the three main monolignol precursors, other monomeric phenolic compounds such as hydroxyl cinnamyl acetate and phenyl aldehyde may also be observed in different Lignins. The content of each Lignin unit is depending on the species. Softwood Lignin consists of majorly G unit and little of H unit, while hardwood Lignin consists of both S unit and G unit with a trace amount of H unit. In monocotyledons, Lignin is composed of S, G and H units while the content of H unit is relatively higher than that in higher plants [31]. Lignin extracted from hardwood contains a higher content of methoxyl due to the presence of equal amount of guaiacyl and syringyl units. However Lignin extracted from softwood, guaiacyl units accounting for around 90 % of the total molar mass [32].

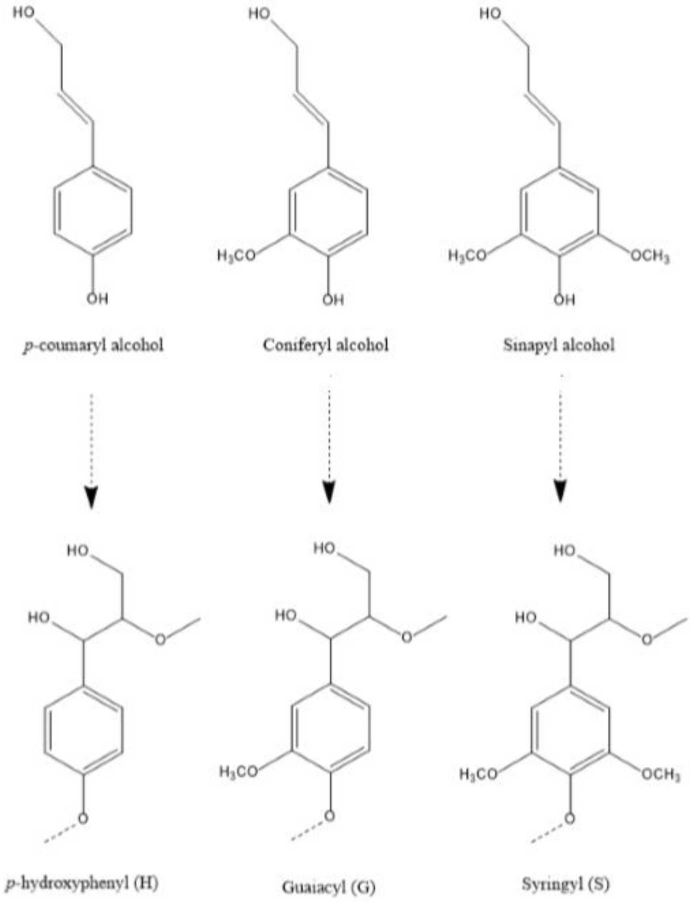

Figure 1.2: The chemical structure of three monolignol precursors and their polymerized forms in Lignin [33].

The biosynthesis of Lignin begins with the oxidation of the hydroxyl groups of the phenolics that occurs enzymatically by electron transfer reaction. That generates a free radical which is delocalized as shown in Figure 1.3 below [34]. A Lignin macromolecule is formed through the connection and random polymerization between the dehydrogenated oxidized phenolics, as a result of this a Lignin with irregular chemical structure [33]. The common linkages and their percentages in extracted Lignin were determined and documented as shown in Table 1.1 [34].

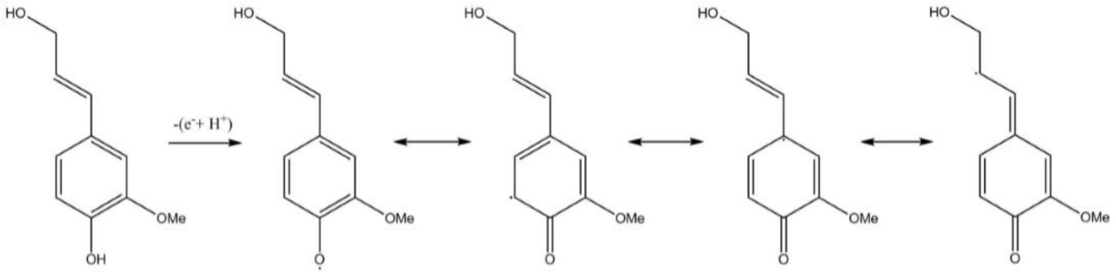

Figure 1.3: Radical formation of coniferyl alcohol.

Table 1.1: Relative abundance of different Lignin bonds connecting.

Linkage Type	**Dimer Structure**	**Approximate Abundance (%)**
β-*O*-4	Phenylpropane β-aryl ether	45 – 50
α-*O*-4	Phenylpropane α-aryl ether	6 – 8
β-5	Phenylcoumaran	9 – 12
5-5	Biphenyl and dibenzodioxocin	18 – 25
4-*O*-5	Diaryl ether	4 – 8
β-1	1,2-Diaryl propane	7 – 10
β-β	β-β-Linked structures	3

Carbon-carbon bonding represent about 30% of connecting linkages and ether bonds represents about 70%. The β-O-4 is the most common, making up 45-50% of the overall linkages in wood biomass [35]. Other major linkages include β-5-, 5-5-, 4-O-5-, β -1-, α-O-4- and β-β-linkages, as shown in Figure 1.4 [36].

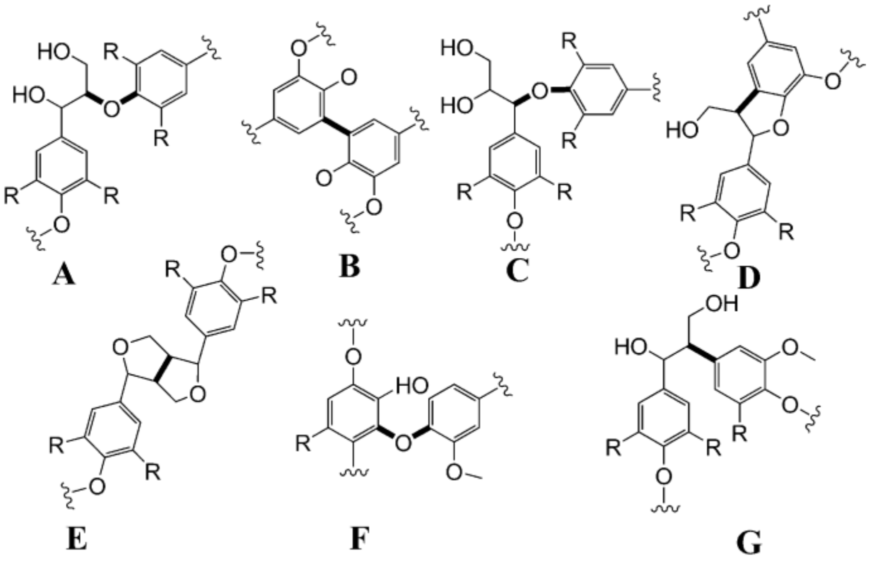

Figure 1.4: Main linkages present in Lignin macromolecule: (A) β-O-4, (B) 5-5, (C) α-O-4, (D) β-5, (E) β-β, (F) 4-O-5, and (G) β-1.

1.3.3 Lignin sources

Lignin name comes from the Latin noun “lignum” meaning “wood”. Lignin is the stuff that makes plants “woody” [37]. It is referred to as the glue that offers the overall rigidity to the structure of trees and plants [30]. The native state of Lignin known as proto-Lignin. In trees, for example, proto-Lignin makes up 35%. It is found in plant cell walls connecting cellulose to hemicelluloses, these combination (the ligno-cellulosic biomass) which allows for fighting the biological and mechanical degradation [34]. It is hydrophobic but facilitates the transport of water up the length of a tree [38]. Deferent sources of lingo-cellulose contain different ratios of these constructive polymers. In softwood stem, the xylem usually contains 45–50% of cellulose, 25–35% of hemicellulose and 25–35% of Lignin while the hardwood stem contains 40–55% of cellulose, 24–40% of hemicellulose and 18–25% of Lignin [39].The pulp and paper industry generates every year about 50 million tons of Lignin as a by-product, only 2 % of which is commercially used [34].

1.3.4 Extraction of Lignin

Chemical structure of Ligninactually depends on the method of isolation. Several methods for extracting of Lignin from feedstock are available which include various mechanical and chemical processes. These methods can classified into two main groups. In the first group, cellulose and hemicelluloses are removed by solubilisation, leaving Lignin as insoluble residue. The second group present methods for dissolution of Lignin from the stock leaving cellulose and hemicelluloses as insoluble polymers, then Lignin is recovered by precipitation [40].

Kraft process is one of the main processes for separating cellulose from Lignin. The second major method is sulfite pulping (generating lignosulfonate). Both methods belong to the second category where Lignin is solubilised the recovered. A third method known as the organo-solv process, where water/ethanol mixture used as solvent, that produces pure Lignin with unaltered structure since it is a mild process [41]. Milled wood Lignin resulted by the Björkman process is considered to be most similar to the native form. With variation in the methods of isolation, different other types of Lignin, such as cellulolytic enzyme Lignin [36], steam explosion Lignin, Klason Lignin [42], soda Lignin and acid hydrolysis Lignin are obtained [28].

The isolation method has an effective role in determining the nature and structure of Lignin. Kraft Lignin is relatively free from sulfur pollution, while considerable amounts of sulfonate groups are incorporated into Lignin during sulfite pulping; thus, the Lignin sulfonate has higher average molecular weights [41]. Cleavage of ether linkages and loss of methoxyl groups may occur, this reduces the hydroxyl phenol content, while condensation reactions may lead to new carbon-carbon bonds. For instance, the Klason Lignin process uses 72 % sulfuric acid and the Lignin structure is widely changed during this procedure [43]. Similar is the case with kraft Lignin whereas other mild methods like cellulolytic enzyme and MWL produce structures relatively identical to that of native Lignin [40].During the extraction process, the β-O-4 bond breaks, as a result if that phenolic hydroxyl group, methoxyl groups and some aldehyde groups are generated [35]. The structure and properties of extracted Lignin depend on the extraction and isolation processes. Various extraction processes will generate different abundances of methoxyl, phenolic hydroxyl and aldehyde groups. Moreover, new functional groups might be generated into Lignin structure [44].

1.3.5 Applications of Lignin

Lignin is not a desired component in the pulp and paper industry because Lignin generates dark colour during the pulping process and Lignin interferes the hydrogen bonding between fibbers which substantially reduces the strength of the product. On the other hand, modern bio-refinery technologies are using Lignin in different materials such as antioxidants, adhesives, antibiotics, and adsorbents [29].

1.3.5.1 Lignin as adsorbent

Lignin can be potentially used as adsorbent for treating heavy metal cations in wastewater. This is because of the complicated cross-linking structure which involving several heavy metal adsorption functional groups within the molecule, including aliphatic hydroxyl, phenolic hydroxyl, carboxyl and methoxyl groups and electrophilic groups [45]. The functional groups Lignin possess affect its reactivity and chemical properties. The he hydroxyl and aromatic groups are the most useful functional groups that determine the application of the polymers [28].

The use of Lignin as a heavy metal adsorbent has been checked on various heavy metal species including Pb(II), Cr(VI), Cu(II), Zn(II), Ni(II), Cd(II), Cr(III), and Ca(II). Basically, all the studied Lignin were obtained from pulp mills by precipitation from the black liquor [46]. Many studies were isolated Lignin directly from wood species. The Lignin used by Demirbas (2004) was isolated from beech and polar through alkali glycerol delignication [47]. Parajuli et al. (2005) separated Lignin from the Japanese cedar trees powder [48].

Celik and Demirbas (2005) reported the adsorption capacity of their Kraft Lignin sample following the order of Pb(II)> Zn(II)> Cd(II) [49].

The different arrangement of adsorption capacities indicates that the absorption capacity of Lignin may vary depending on its source. Guo et al. (2008) studied the adsorption capacity of Kraft Lignin isolated from black liquor. Their results showed that the Lignin affinity to heavy metal ions in the order of Pb(II)>Cu(II)>Cd(II)>Zn(II)>Ni(II). They recorded the adsorption capacities with an initial metal concentration of 0.8 mM, which are 0.3 mmol/g, 0.27 mmol/g, 0.16 mmol/g, 0.13 mmol/g and 0.10 mmol/g respectively [50]. On the other hand, Šćiban and Klasnja (2011) studied the adsorption of Cr(VI), Cd(II), Cu(II) and Zn(II) on Kraft Lignin. The results showed that Cr(VI) has the highest affinity to the Lignin. The stronger interaction between Lignin and chromium ion is potentially because of the higher electrical charge of Cr(VI) than other metal ions [46].

1.3.5.2 Chemically modified Lignin for removing heavy metals

Lignin modification has been studied in order to improve its heavy metal removal efficiency. Modifications of the Lignin structure provides better solubility and add various properties that allow better performance of Lignin polymer composites structures [51]. Several chemically modified Lignin polymers were prepared and used in water purification, and there is some of these studies:

Quintana et al. (2008) prepared oxidized Lignin and evaluated its adsorption performance. It showed higher adsorption capacities than original Lignin, which was attributed to the larger quantity of carboxyl groups present in Lignin [52]. Ge et al. (2014) developed a Lignin derivative by converting it to dithiocarbamate, which showed a high adsorption efficiency of 103.4 mg/g for Pb(II) and 175.9 mg/g for Cu(II) at pH 6.0 and 25 ℃ [53]. Qin et al. (2017) also produced a composite from Lignin grafted with poly(ethyleneimine). The adsorption efficiency of the composite toward Cu(II), Zn(II) and Ni(II) was evaluated. Systemically studied. The results showed an adsorption capacity for Cu(II), Zn(II) and Ni(II) were 98.0 mg/g, 78.0 mg/g and 67.0 mg/g, respectively, at pH 6.0 and 25 ℃ [54].

Li et al. (2017) reported a Lignin grafted with carbon nanotubes. This generated composite has a three-dimensional structure, plenty functional groups with good binding for metal ions, high surface area and mechanical stability. The composite exhibited an adsorption capacity of 235.0 mg/g for lead ions at pH 5.8 and 25 ℃, furthermore, the distribution coefficient for Pb(II) was very high (Kd =3.6 x 10^5 mL/g) [55]. Y. Zhang et al. (2019) generated a novel hybrid nano-particle form cross-linking between amino functionalized magnetic nano-particles and carboxy-methylated Lignin using epichlorohydrin . The synthesized nano-particles showed high adsorption capacities of 150.33 and 70.69 mg/g for Pb(II) and Cu(II), respectively. The adsorption equilibriums of Pb(II) and Cu(II) onto hybrid nano-particles was reached within 30 seconds [56]. Duo Xiao et al. (2019) prepared a Lignin-based nano-particles through functionalized Lignin, with both soft and borderline hard bases. The nano-particles showed a removal efficiencies of > 99% toward both soft (Ag (I), Hg(II), Cd(II)) and borderline (Pb(II), Cu(II), Zn(II)) ions, of which the concentrations were diminished from 5 mg/L to 3–9 μg/L below which is below the permitted values in drinking [57].

1.4 Poly Acrylic Acid

1.4.1 PAA definition and structure

Poly(Acrylic Acid) (PAA) is a synthetic Poly(Carboxylic Acid) that is a water soluble polymer [58]. Its trade name is Carbomer and the IUPAC name is poly (1-carboxyethylene) with chemical formula $(C_3H_4O_2)_n$, and its structural formula shown in Figure 1.5.

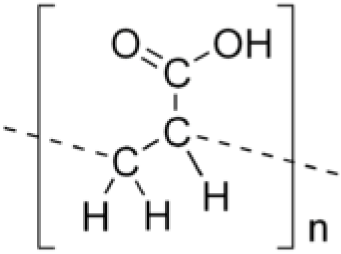

Figure 1.5: Molecular structure of PAA.

They may be homo-polymers of Acrylic Acid, or cross-linked with an allyl ether of sucrose, allyl ether of pentaerythritol, or allyl ether of propylene .

PAA is hydrophilic, hygroscopic, brittle and colourless in nature, its average molecular weight is 1800 g/mol, with Transition Temperature (Tg) at nearly 106°C. At temperatures higher than 200 up to 250°C, the acid loses water and becomes a water insoluble polymer anhydride. Solubility of PAA in water increases as temperature increases. Solutions of PAA in water usually exhibits a thixotropic behaviour [59].

1.4.2 Synthesis of PAA

PAA is a polymer that can be prepared in water from polymerizing Acrylic Acid with a free radical initiator usually Sodium Persulfate. This polymerization reaction is an exothermic, requires a good control of the temperature [60].

1.4.3 Applications of PAA

PAA and the derivatives of PAA are widely used as thickening agent and emulsifying agents in mainly in paints, cosmetics and pharmaceutical [58]. They are cross-linked and used as superabsorbent polymer in also baby diapers and adult incontinent. It also it can be copolymerized zeolites and phosphates and used as washing powder [61]. Dry PAAs are sold as soft white powders, often used in the form of gels in cosmetics and personal care [59]. Neutralized PAA gels are suitable for obtaining biocompatible matrices for medical applications such as skin care gels or dermatological products. PAA films can be deposited on bone implants to protect them from corrosion. The intertwined hydrogels of Acrylic Acid and gelatine were also used as a medical glue, which has a high binding strength.

Moreover they used as super absorbent polymers [62]. They have electrostatic affinity to cationic pollutants, which is expected to enhance the adsorption performance [63].

PAA is an anionic polyelectrolyte, its degree of ionization is pH dependent. Degree of ionization affects greatly the chain mobility and conformation in water. At low pH value it stays in the acid form. It may interact with various non-ionic polar polymers such as polyethylene oxide, poly-N-vinyl pyrrolidone, polyacrylamide, and cellulose ethers through hydrogen-bonded inter-polymer complexes [64]. In water, PAA tend to complexes with positively charged polymers such as chitosan, surfactants, and drug molecules like for instance streptomycin [65]. As the pH value of PAA solution increases, the ionization increases and becomes in the carboxylate from(COO^-)which interact strongly with metal ions [66].Recently, it was shown that PAA could be used to modifying the inorganic adsorbent to add more binding sites and enhances adsorption efficiency [67].

1.4.4 Chemically modified PAA for removing toxic metals

Chemically modified PAAs were synthesized and used in water purification, several are reported in the literature, among these are:

Wang et al. (2010) prepared A series of starch-g- (PAA)/sodium humate (St-g-PAA/SH) copolymers and used it for adsorption of Cu(II) from an aqueous solution within a pH range of 2.7–5.0. The copolymer exhibited a high adsorption capacity within the studied pH range. FTIR spectra study showed that complexation of Cu(II) was the main adsorption mechanism. The adsorption isotherm followed Langmuir model. The adsorption capacity for Cu(II) ion reached about 177.9 mg/g [68].

Naim Sezgin& Nilgun Balkaya (2015) used PAA hydrogel to purify waste water from heavy metals such as Cu(II), Ni(II), Zn(II), and total Cr. The wastewater used was a real sample collected from Galvano Technique Industry. The adsorption capacities of PAA hydrogel for the mentioned above metal ions were 2.74, 1.91, 6.83, and 6.61 mg/g, respectively. The adsorption mechanism follows Freundlich isotherm and pseudo-second-order kinetic models. Thermodynamic analysis showed the process was exothermic and spontaneous [69].

On the other hand, a novel polymer polystyrene-poly-N-isopropyl-methacrylamide -Acrylic Acid was prepared by Khalida Naseem et.al. (2018). It was produced in the shape of core/shell gel particles by two step precipitation polymerizations method. The particle used for removal of some heavy metal ions from contaminated water. The adsorption capacity of the gel particles for Pb(II), Cu(II), Cd(II) and Cr(III) ions reached about 555.6, 526.3, 476.2 and 434.8 mg/g, respectively [70].

1.5 Lignin based Poly(Acrylic Acid)

Ma. Y.et.al. (2017) prepared A copolymer of Lignin grafted with N,N'-methylene-bisacrylamide and Acrylic Acid the organomontmorillonite was uniformly dispersed in the co-polymer matrix. The used in adsorption of Pb(II). The study demonstrated that, the adsorption is a pH dependent and obeyed Freundlich multilayer adsorption and a pseudo second-order kinetic model. The removal capacity for Pb(II) was 1.0803 mmol/g [71].

Recently, a biodegradable Lignin based PAA composite was prepared by Zhao T et.al. (2019) and used as a chelating agent to clean soil contaminated with Cu(II), Zn(II), Cd(II) and Pb(II) ions. The removal of the ion by the Lignin-PAA composite improved the remediation of soil during the soil. After soil treatment for five times, the Lignin-PAA assisted reduced the amount of Cu(II), Zn(II), Cd(II) and Pb(II) ions in contaminated soil to 22.57%, 52.60%, 13.63% and 17.95%, respectively [72].

1.6 Scope of the study

This research will achieve the following Objectives :

1.6.1 General Objectives

1. Purify the wastewater from toxic metal ions by using of our preparation metal adsorbent, whose prepared from natural based, low cost waste material.
2. To study the several factors that affect the efficiency and the extent of adsorption technique.

1.6.2 Specific Objectives

1. Extraction of Lignin from Zebar (olive industry liquid waste).
2. Synthesis and characterization of two new hybrid co-polymers containing Lignin, Acrylic Acid and a cross-linking agent (N,N-methylenebisacrylamide).
3. Comparison of the efficiency of the two co-polymers PAA-Lignin-A and B for the adsorption of lead from contaminated.
4. Evaluate the possibility of using the prepared polymer for sewage treatment from toxic metal ions.

CHAPTER TWO

EXPERIMENTAL

2.1 General experimental

2.1.1 Instrumentation

The following instruments were used to accomplish the present research: Water bath equipped with a thermostat and a shaker with a digital Speed control, pH meter, FT-IR Spectrometer, SEM , FT-IR and ICP-MS.

The functional groups of the produced polymers were checked by Fourier Transform Infrared Spectrometer (FT-IR), which were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) and equipped with the Smart Split Peam Hemi Micro ATR accessory (International Crystal Laboratories, Garfield, NJ, USA). The following parameters were used: resolution was 4 cm^{-1}, spectral range was 600 cm^{-1} to 4000 cm^{-1} and number of scans was 128.

The surface morphology of the Lignin-Poly(Acrylic Acid) polymers were examined using Scanning Electron Microscopy (SEM) (S-4800; Hitachi, Tokyo, Japan) , at an acceleration voltage of 3.0 kV. The contaminated water samples were shacked with the polymers using a Water Bath equipped with a shaker (Daihan Lab tech, 20 to 250 rpm Digital Speed Control).

The Pb(II) solution concentrations studied in this work were measured by Flame Atomic Absorption Spectrometer at 217 nm (ICE 3xxx C113500021 v1.30) to determine residual Lead ions concentration. All analysis studies were accomplished three times and the mean of the three runs was reported. The error range in the experimental data were analyzed using Microsoft Excel, a certainty interval of 95% was used. The metal ions concentrations the sewer samples before and after treatment were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (ELAN9000, Parkin Elmer, USA).

2.1.2 Materials

Reagents, solvents and chemicals used in this work were of analytical grade and used as received. They were purchased form Aldrich chemical company (Jerusalem). The reagents are Acrylic Acid, Potassium Persulfate, Sodium thiosulfate, lead nitrate, HCl, NaOH and N, N-methylene bisacrylamide. Demonized water was used to prepare the polymers and stock solutions. Lignin used in this study was extracted from olive industry liquid waste (Zebar) which was brought from the Olive Mill factory located in Ta’anek village, Jenin, Palestine.

2.2 Extraction of Lignin from Zebar

A 500 mL sample of Zebar was added to a 1000 mL beaker. The sample was heated with stirring under the hood at 90℃ for 10 hours until the water almost completely evaporated to produce residue with thick structure.

2.3 Synthesis of cross-linked Lignin based Poly(Acrylic Acid)

The Acrylic Acid was polymerized and cross-linked within Lignin that extracted from Zebar . Two copolymers were prepared PAA-Lignin-A and PAA-Lignin-A ,they were different in the Lignin to Acrylic Acid ratios.

2.3.1 Preparation of Polymer (PAA-Lignin-A)

The preparation of PAA-Lignin-A polymer was carried out in a Pyrex reaction flask (1.0 L). The reaction flask was equipped with a thermocouple inserted through a rubber septum, a Teflon bladed agitator on a glass shaft attached to a mechanical mixer, gas inlet Teflon tubing inserted through a rubber septum, and a gas outlet adapter connected to a gas trap filled with some oil. To the reaction kettle was added the Acrylic Acid 100 g and condensed Zebar (50.0 g). An aqueous solution of Sodium Hydroxide (45.0 g, 50 wt.%) was added in portions to neutralize the reaction mixture to a pH 4.5. The reaction mixture was diluted with water (35.0 mL). Then the cross-linking agent N,N-methylene bisacrylamide was added (5.0 g) to the reaction mixture followed with the initiator solution that is an aqueous solution of Potassium Persulfate (0.05 g) and Sodium Thiosulfate (0.05 g) in 5.0 mL water was added at once. An exothermic reaction accompanied with gelation started almost immediately after the addition of the initiator. The reaction temperature reached about $100^{o}C$, and a mass of porous gel formed in less than 10 min for the addition of the initiator. After the exothermic reaction has subsided (50 min), the reaction mixture was left under these reconditions for another 1 hr. The produced solid mass was dried for 24 hours at about 85°C. Then it was ground in a Wiley mill to pass through a 20-mesh screen and retained on a 30-mesh screen.

2.3.2 Preparation of Polymer (PAA-Lignin-B)

The preparation of PAA-Lignin-B was carried out in a Pyrex reaction flask (1.0 L). The reaction flask was equipped with a thermocouple inserted through a rubber septum, a Teflon bladed agitator on a glass shaft attached to a mechanical mixer, gas inlet Teflon tubing inserted through a rubber septum, and a gas outlet adapter connected to a gas trap partially filled with oil. To the reaction kettle was added the Acrylic Acid 60 g and condensed Zebar (5.0 g). An aqueous solution of Sodium Hydroxide (45.0 g, 50 wt. %) was added in portions to neutralize the reaction mixture to a pH 4.5. The reaction mixture was diluted with water (35.0 mL). Then the cross-linking agent N,N-methylene bisacrylamide was added (5.0 g) to the reaction mixture followed with the initiator solution that is an aqueous solution of Potassium Persulfate (0.05 g) and Sodium Thiosulfate (0.05 g) in 5.0 mL water was added at once. An exothermic reaction accompanied with gelation started immediately after the addition of the initiator. The reaction temperature reached about 100°C, and a mass of porous gel formed in less than 10 min for the addition of the initiator. After the exothermic reaction has subsided (50 min), the reaction mixture was left under these reconditions for another 1 hr. The produced solid mass was dried for 24 hours at about 85^oC. Then it was ground in a Wiley mill to pass through a 20-mesh screen and retained on a 30-mesh screen.

2.4 Polymers solubility in water

A small sample of each polymer with known weight (1.00 g) was suspended in a 100 mL water and stirred all the neight. Then collected by suction filtration, dried in an oven at 100^oC, and weighed again. No change in the weight was noticed

2.5 Preparation of lead solutions

Stock solution of Pb(II) with (1000 ppm) concentration was prepared by dissolving 0.404 g of lead nitrate in 100.0 mL distilled water. Then various concentrations of 5.0, 10.0, 20.0,40.0 and 50.0 ppm were prepared form the stock solution by dilution.

2.6 Adsorption of Pb(II) ions

A batch extraction process was used, a known amount of the adsorbent polymer (Lignin based Poly (Acrylic Acid)) was added to the lead ions solution with known concentration in a plastic bottle, then the plastic bottle was closed and shocked in at constant temperature and at a specific speed for certain period of time according to the factor which is under study. A sample from the studied mixture was withdrawn with a syringe, filtered through a 0.45 µm syringe filter and subjected to analysis to determine residual metal ion concentrations by atomic absorption spectroscopy.

The proportion of metal adsorption (% Adsorption) was calculated as shown in the equation below, the final metal ions concentration was substrated from the initial concentration of the metal ions in the aqueous solution and divided by the initial concentration of Pb(II) [73]:

$$Removal\ efficiency\ (\%) = \left[\frac{(C_o - C_e)}{C_o}\right] \times 100 \qquad (2.1)$$

As shown in Equation (2.1) , C_o is the initial metal ions concentration (mg/L) in the sample and C_e is the final metal ions concentration in the sample solution after treatment.

Under the experimental conditions, the adsorption capacity for each concentration of metal ions at equilibrium (q_e) was determined as shown in (2.2) equation [74].

$$q_e\left(\frac{mg}{g}\right) = \left[\frac{C_i - C_e}{m}\right] V \qquad (2.2)$$

Where V is the volume of solution (in Litters) and M is the mass of adsorbent used (in grams).

2.6.1 Effect of polymer dose on Pb(II) removal efficiency

The effect of polymer dose on the removal of Pb(II) was studied, in order to determine the optimum dose. Doses of 0.005 g, 0.01 g, 0.05 g, 0.1 g, 0.15 g of the polymer were added to each of five vials each contains10.0 mL of 50.0 ppm Pb(II) solution at pH 4.5. The mixtures were placed in a shaking water bath at 25°C for 30 min. Then, a sample from every solution was withdrawn via a syringe, filtered through a syringe equipped with a

0.45 µm filter and subjected to analysis for residual metal ions concentrations. The concentration of lead metal was determined by atomic absorption spectroscopy. Similar procedure was repeated using polymer B but at pH 6.5.

2.6.2 Effect of initial concentration on Pb(II) removal efficiency

To determine the optimum initial concentration of ions, a 0.05 g of polymer (A) was added to a number of vials each contains a 10.0 mL with different concentrations of lead ions solution (5-50 mg/L), each vial was shaken at 25°C and the pH was adjusted to 4.5 during a 30 min period. The concentration of residual metal ions was determined by atomic absorption spectroscopy. The previous steps were repeated using 0.1 of polymer B at pH 6.5.

2.6.3 Effect of Contact Time

The removal of metal ions by the prepared polymers was studied as a function of contact time at 25°C. Five samples a 10.0 each of the metal ion solution with concentration of 50 mg/L adjusted to pH value of 4.5 were taken in five bottles and shaken with a 0.05 g of polymer A that was added to each one. The solutions were shaken for various periods (5, 10, 15, 20, and 30 minutes). A portion of each solution was withdrawn with a syringe, filtered through a syringe equipped with a 0.45 µm filterand subjected to analysis for residual metal ions concentrations. The concentration of metal ions was determined by atomic absorption spectroscopy. The same procedures were repeated using 0.1 of polymer B at pH 6.5.

2.6.4 Optimization of Temperature

Effect of the temperature on adsorption was performed by adding a 0.10 g sample of polymer A to several samples 10 mL each of metal ions solutions with concentration of 50 mg/L at pH around 4.5. The mixtures were placed in Shaking water bath at a desired temperature (the range was 15-40 °C) for 30 min. At the end of each time interval of the specified temperature, a sample of each mixture was extracted with a syringe, filtered through a syringe equipped with a 0.45 µm filterand subjected to analysis to determine residual metal ion concentrations. The concentration of residual metal ions was determined by atomic absorption spectroscopy. The previous steps were repeated using 0.1 g of polymer B at pH 6.5.

2.6.5 Optimization of pH value

Effect of solution pH on adsorption capacity was investigated in the range of 2.0-12. The pH was adjusted using roughly concentrations of 0.1M HCl and 0.1M NaOH. Samples of 0.05 g polymer PAA-Lignin-A were added to a 10.0 mL of metal ions solutions with concentration 50.0 mg/L. The mixtures were placed in a thermostated water bath at 30 °C for 30 min. At the end of each time interval, an aliquot of each mixture was withdrawn with a syringe, filtered through a 0.45 µm syringe filter and subjected to analysis to determine PAA-Lignin-A mine residual metal ion concentrations by atomic absorption spectroscopy. The previous steps were repeated using0.1 of polymer B, but the temperature was 40°C.

2.7 Adsorption Kinetics

The removal of toxic lead ions kinetics by polymers PAA-Lignin-A and B was studied. The kinetic was studied under the optimized condition of polymer dose, concentration of metal ions, contact time, temperature and pH. Using atomic absorption spectroscopy, the concentration of metal ions was determined before and after adsorption. The data were subjected to Langmuir and Freundlich adsorption isotherm equations.

Amount of 0.1 g of polymer was added to a 10.0 mL of 50 mg/L solution of Pb(II) at pH 4.5. The mixture was placed in a water bath equipped with a shaker at a constant temperature of 25°C. The rate of adsorption was observed by studying the contact time up to 2 hours and matched to theoretical models. Pseudo first-order and second-order kinetic models were examined in this study using experimental data obtained for various periods of contact time. Pseudo first and second order kinetic models parameters (K, q_e and R^2) for lead ions adsorption on polymers A and B were determined. The values of the calculated and experimental q_e were compared.

2.8 Wastewater purification

A sample of sewer collected from the sewage system in one of the Palestinian cities was used in this work. The sample was subject to analysis by ICP-MS which was performed by the Water Centre at An-Najah National University (Nablus, Palestine) to determine the types and concentrations of metals ions present. The optimized parameters determined above were used in this experiment. Two samples (10.0 mL each) of sewage water was withdrawn with a syringe, filtered through syringe equipped with a 0.45 µm filter and placed in two bottles. Then optimized conditions for each polymer were applied on each bottle individually, (for polymer PAA-Lignin-A: 0.05 g, shacked for 30 minutes at 30℃, at pH of 8.5 and for polymer PAA-Lignin-B: 0.1 g, shacked for 30 minutes at 40℃, at pH 8.5).

A sample of each mixture was withdrawn with a syringe and filtered through a 0.45 µm syringe filter and subjected to analysis by ICP-MS for residual metal ions concentrations.

CHAPTER THREE
RESULTS AND DISSCUSION

3.1 Synthesis of Poly (Acrylic Acid)-Lignin copolymer

A new copolymer was synthesized from Lignin, Acrylic Acid and a cross-linking agent, N, N-methylene bis acrylamide. Lignin used in this work was extracted from olive industry liquid waste (Zebar). A sample of Zebar was evaporated to dryness, a part of the residue was used as it without any further purification, since the major components of Zebar are mixtures of phenols and Lignin. The sample was mixed with Acrylic Acid, a cross-linking agent and treated with a free radical initiator. A reaction scheme shows the starting materials and expected product shown in Figure 3.1.

As shown in Figure 3.1, a cross-linked poly (Acrylic Acid) grafted with Lignin was produced, and there were several sites of association, which had been marked by the small arrows before and after the polymerization. The polymer shows various and large number of metal binding sites, including carboxyl, aryl and hydroxyl. Two polymers were prepared with various amount of Lignin polymers **PAA-Lignin-A** and **PAA-Lignin-B**. **PAA-Lignin-A** has much higher content of Lignin. The polymers were analyzed by FT-IR and Scanning Electronic Microscope (SEM).

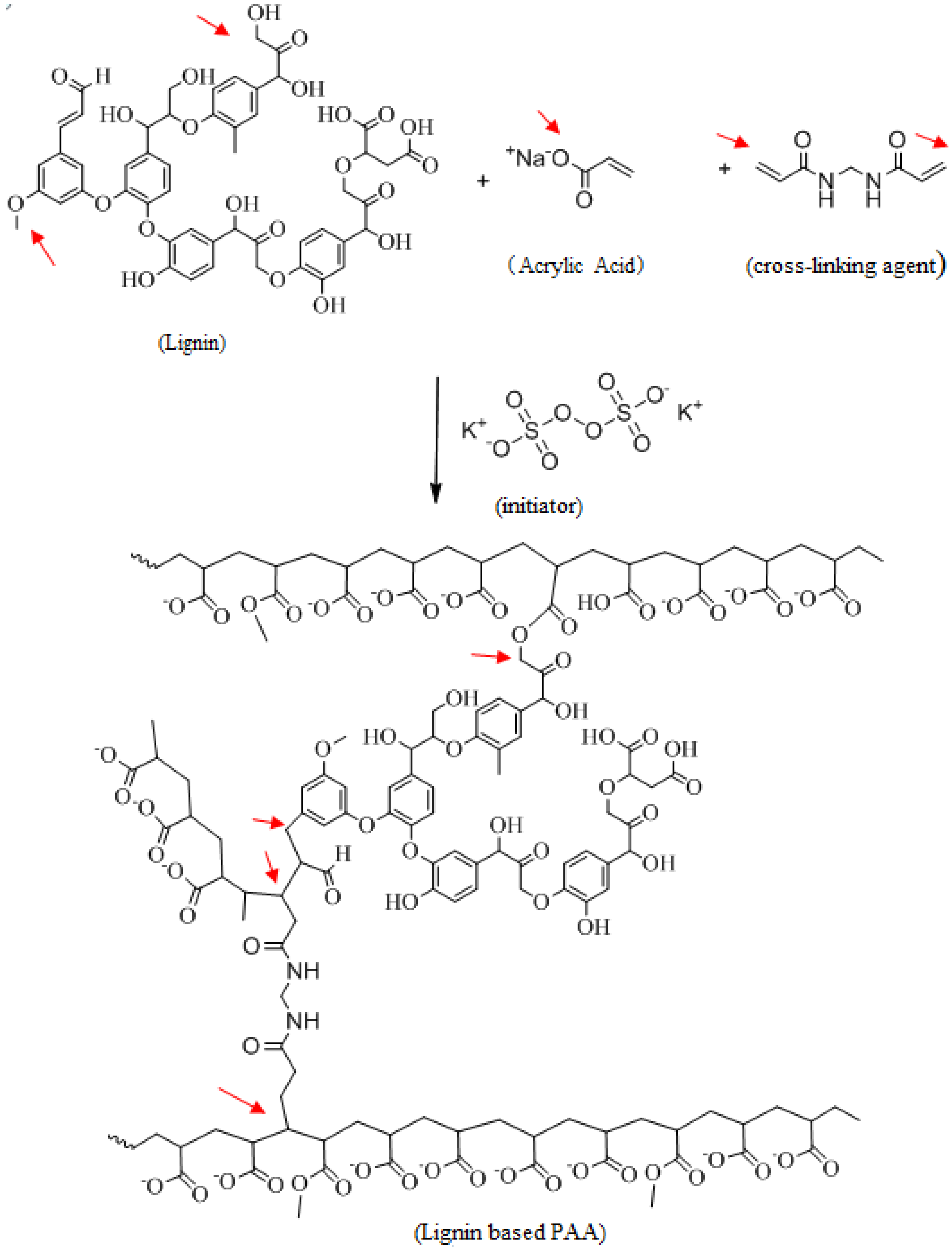

Figure 3.1: Reaction scheme shows the formation of poly(Acrylic Acid)-Lignin copolymer.

3.2 FT-IR Characterization of PAA-Lignin-A and B

The FT-IR spectrum of polymer **PAA-Lignin-A** is shown in Figure 3.2. The FT-IR spectrum shows a broad band that extends from 3600 cm^{-1} to 2700 cm^{-1} corresponding to O-H stretching of carboxylic and moisture.

Aromatic and aliphatic C-H starching appears at 3050 and 2950-2990 cm^{-1}, respectively. A strong starching band of C=O of carboxyl groups appears at 1722 cm^{-1}. Two weak bands appear at 1636 and 1600 cm^{-1} could be attributed to C=O of amid linkage and C=C of aromatic, respectively. The IR also shows strong peak at 1558 cm^{-1} corresponding to asymmetric starching of COO (carboxylate), and symmetric starching band at 1408 cm^{-1} corresponding to COO carboxylate. A strong peak appears at about 1185 cm^{-1} could be related to C-O-C (ether) stretching of Lignin side groups.

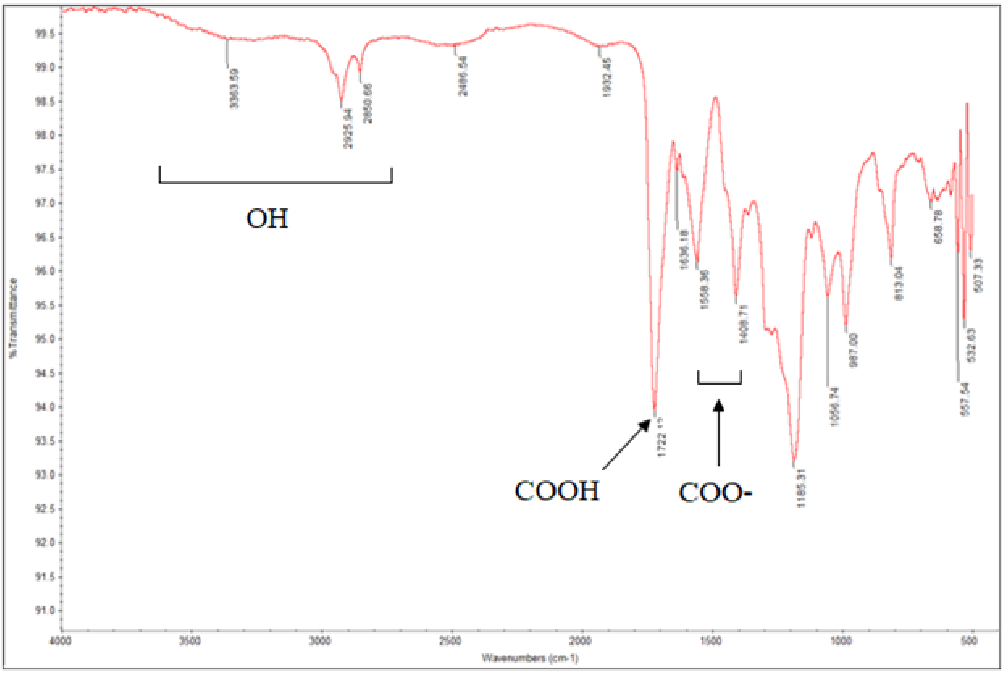

Figure 3.2: IR spectrum for polymer PAA-Lignin-A**.**

The FT-IR spectrum of polymer **PAA-Lignin-B** is shown in Figure 3.3. The FT-IR spectrum shows a broad band that extends from 3600 cm^{-1} to 2720 cm^{-1} corresponding to O-H stretching of carboxylic acid. Aromatic and aliphatic C-H starching appears at 3050 and 2950-2990 cm^{-1}, respectively. A weak starching band of C=O of carboxyl groups appears at 1710 cm^{-1}. A weak band appear at 1636 could be attributed to C=O of amid linkage, the C=C of aromatic band didn't show up in this case because low amount of Lignin was used. The IR also shows strong peak at 1556 cm^{-1} corresponding to asymmetric starching of COO (carboxylate), and symmetric starching band at 1453 cm^{-1} corresponding to COO (carboxylate). The strong band in polymer appears at about 1185 cm^{-1} related to C-O-C (ether) stretching of Lignin side groups didn't show up in this spectrum. The FT-R spectrum of polymer B is almost similar to that shown in Figure 3.4 for cross-linked poly(Acrylic Acid).

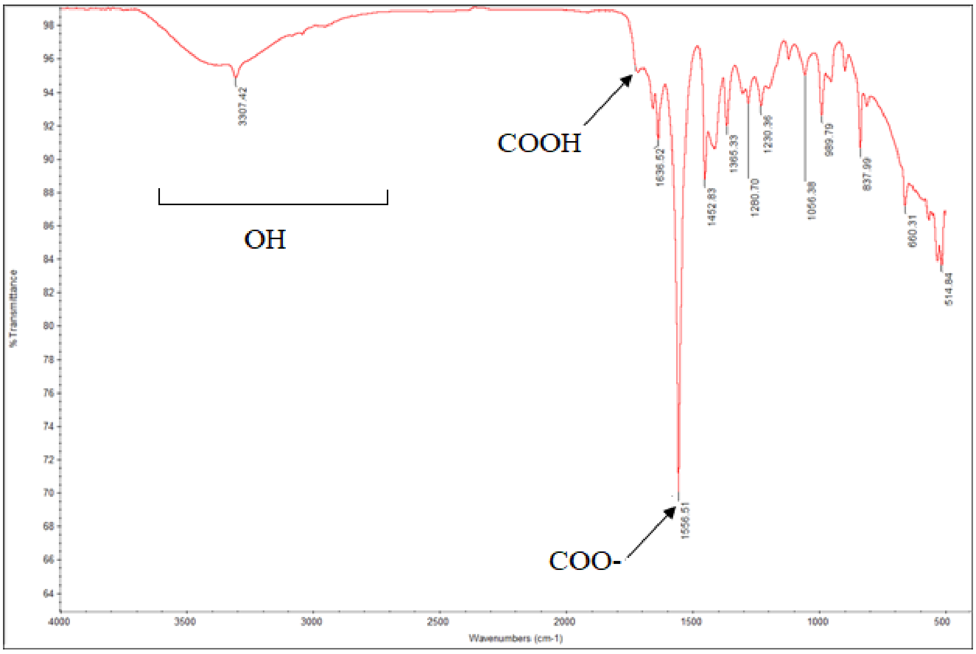

Figure 3.3:IR spectrum for polymer **PAA-Lignin-B**.

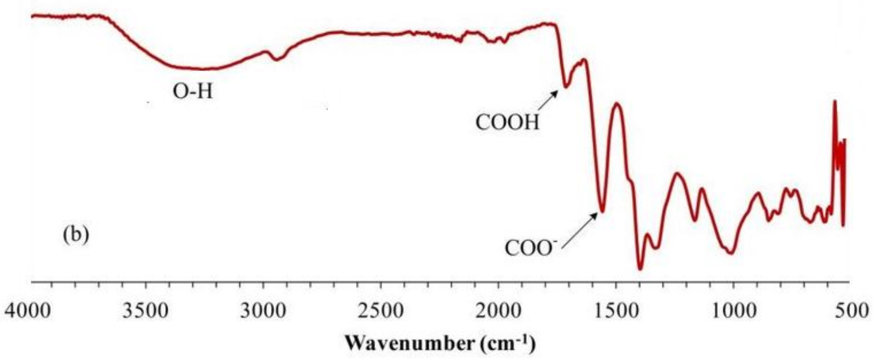

Figure 3.4: IR spectrum for PAA neat.

3.3 Morphological Analysis of polymers A and B

SEM micrographs of polymers PAA-Lignin-A and B are shown in Figures 3.5 and 3.6, respectively. The differences between the two polymers morphologies are noticeable. Polymer PAA-Lignin-A that contains large quantity of Lignin shows surface covered with high number of micro cavities which could be attributed to porous polymeric network. While polymer PAA-Lignin-A has more of a solid smooth surface.

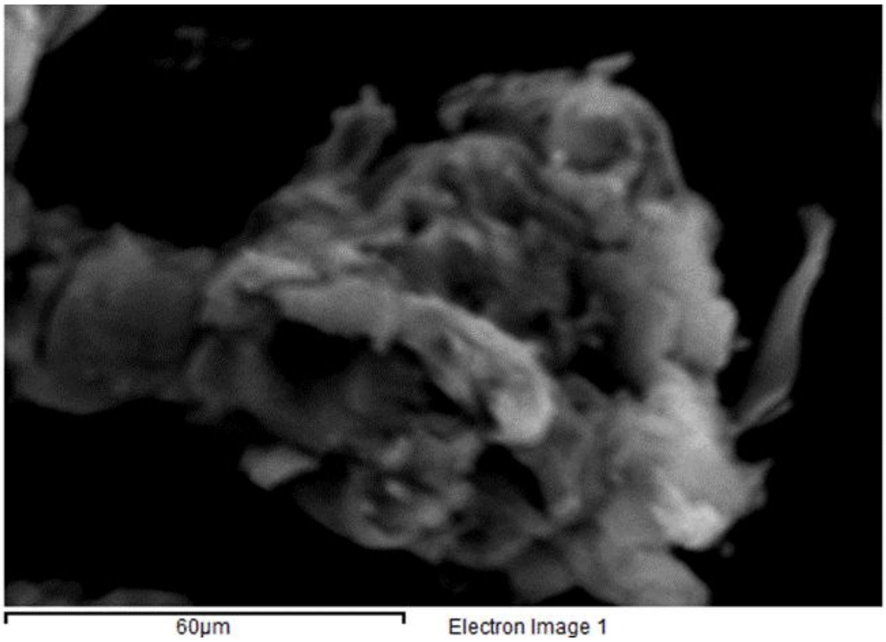

Figure 3.5: SEM image of polymer PAA-Lignin-A at 250x magnification.

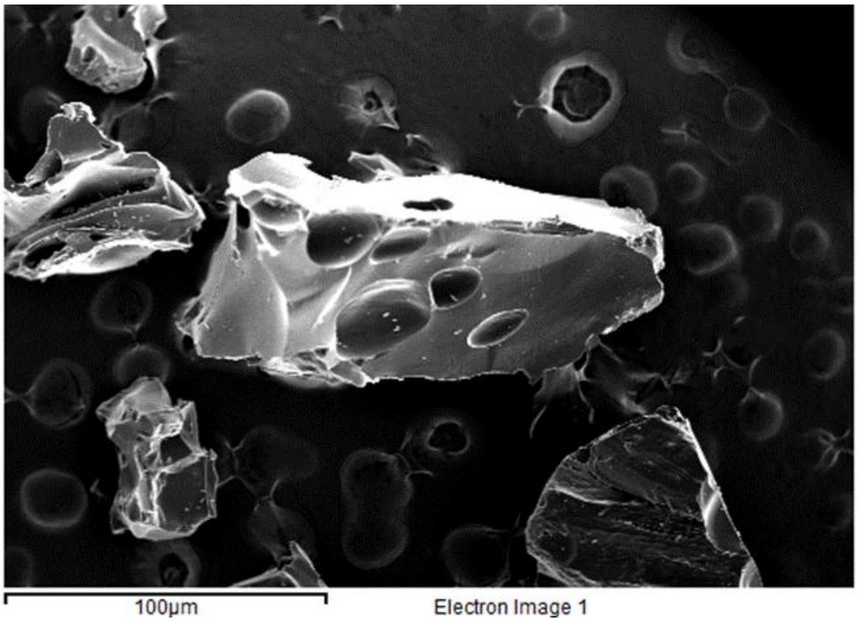

Figure 3.6: SEM image of polymer PAA-Lignin-B at 500x magnification.

3.4 Effect of various parameters on adsorption efficiency of Pb(II)

The second objective of this study is to examine the efficiency of Lignin based polymers as adsorbents for toxic metal ions from wastewater. The effect of various factors such as amount of adsorbent, the metal concentration, contact time, temperature and pH value on the adsorption of metals ions were studied. The equilibrium isotherm was studied by varying the parameters of initial concentration of metal ions and adsorbent dose.

3.4.1 Effect of polymer dose

The effect of PAA-Lignin-A and B dose on the removal of Pb(II) from an aqueous solution was investigated. The initial concentration of lead ions solution was fixed at 50.0 mg/L, solution volume was 10.0 mL and extraction time was 30 min. The pH of the studied solutions was adjusted to 4.5 for PAA-Lignin-A and 6.5 for PAA-Lignin-B. The temperature was maintained at 25°C. The obtained results for PAA-Lignin-A are shown in Table 3.1and were depicted in Figure 3.7 A, for polymer PAA-Lignin-B are shown Table 3.2 and Figure 3.7 B.

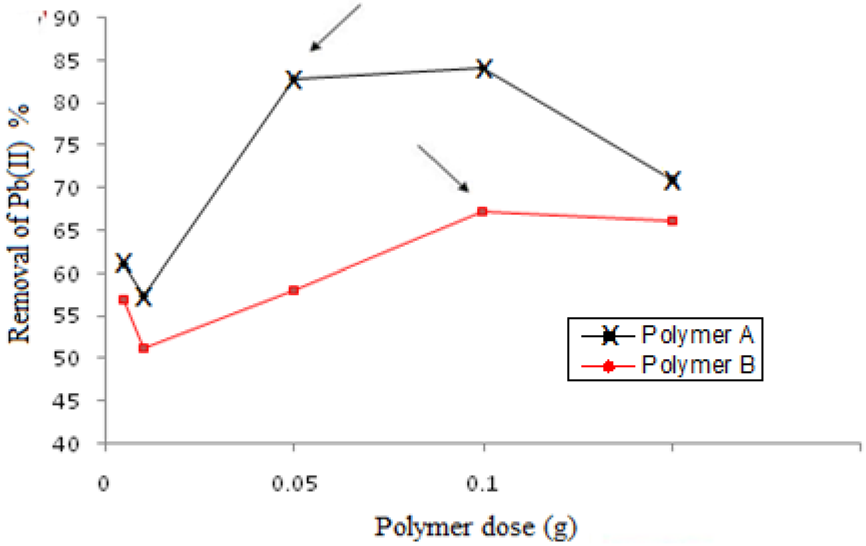

Figure 3.7: Effect of polymer dose on the adsorption efficiency of lead ions by A. PAA-Lignin-A and B. PAA-Lignin-B.

Table 3.1: Effect of polymer dose on the adsorption efficiency of lead ions by PAA-Lignin-A.

sample	wt. of dose (g)	% of removal
1	0.005	61.17
2	0.01	57.38
3	0.05	82.78
4	0.1	84.05
5	0.15	70.96

As shown in Figure 3.7 B, the removal efficiency increased as the polymer dosage increased, then the removal efficiency leveled off at a dose of 0.05 g for polymer PAA-Lignin-A. At a dose higher than 0.1 g it started to decrease. The optimum does could be 0.05 g (82.0%) since increasing it to 0.1 g (84.05%) increased the efficiency by two points only.

Table 2.2: Effect of polymer dose on the adsorption efficiency of lead ions by PAA-Lignin-B.

sample	wt. of dose (g)	% of removal
1	0.005	56.80
2	0.01	51.28
3	0.05	58.00
4	0.10	67.18
5	0.15	66.05

As shown in Figure 3.7 B, the removal efficiency increased for polymer PAA-Lignin-B as the polymer dosage increased, then the removal efficiency leveled off at a dose of 0.1 g. At a dose higher than 0.1 g it became almost constant. The optimum does could be 0.1 g (67.2%). Polymer PAA-Lignin-A showed higher efficiency than polymer PAA-Lignin-B, this could be because PAA-Lignin-A is more porous.

The dependence of adsorption efficiency on adsorbent dose could be because the adsorption process is controlled by diffusion and surface coordination mechanisms. As the dose increases the number of available active sites increases, and that cause an increase the ion adsorption. When all coordination sites are occupied, the diffusion process starts, which mainly controlled by osmosis, so as the concentration of the lead ions adsorbed by the polymer is equal to that in the solution, the adsorption equilibrium is attained [75].

3.4.2 The effect of initial concentration of lead ions

In order to determine the optimum concentration of lead at a dose of 0.05 g of polymer PAA-Lignin-A and 0.1 g for PAA-Lignin-B. The extraction experiment was performed using 10.0 mL solutions with various concentrations of lead ions ranging from 5.0 to 50.0 mg/L at room temperature of 25^{o}C, for 30 min at pH of 4.5 for PAA-Lignin-A and 6.5 for PAA-Lignin-B. The results are shown in Figure 3.8 A for PAA-Lignin-A,and in Figure 3.8 B for PAA-Lignin-B.

As shown in Figures 3.8 A and 3.8 B, the highest removal was attained a concentration of 50 ppm for both polymers. At 50 ppm concentration, the percent of lead ions reached 89.3% and 79.2%, respectively. At concentrations higher than 50 ppm, the removal started to become steady. So, at low concentrations of Pb(II) ions, the driving force for adsorption was controlled by the ion diffusion [76]. At high concentrations, the adsorption was controlled by the availability of the binding sites and this controlled by the adsorbent dosage.

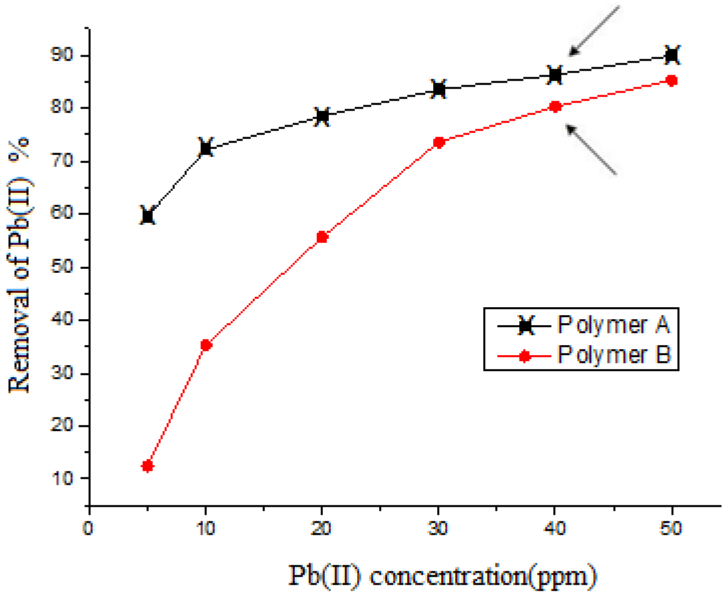

Figure 3.8: Effect of Pb(II) concentration on the removal efficiency by polymer A: PAA-Lignin-A.and B : PAA-Lignin-B

3.4.3 Effect of contact time

The contact time suitable to achieve a maximum removal of lead ions from an aqueous solution by polymers PAA-Lignin-A and PAA-Lignin-B was determined. The results are shown in Figure 3.9 A for PAA-Lignin-A. The results related to polymer PAA-Lignin-B are shown in Figure 3.9 B.

As shown in Figs. 3.9 A and 3.9 B, the adsorption increased rapidly in the first 10 min for polymer PAA-Lignin-A and stayed constant for PAA-Lignin-B after 25 min. The results show that, the coordination sites are occupied become occupied in the first 10 min. [77]. So contact time of 10 min was chosen as the optimal contact time for PAA-Lignin-A but contact time of 25 min was chosen as the optimal contact time for PAA-Lignin-B.

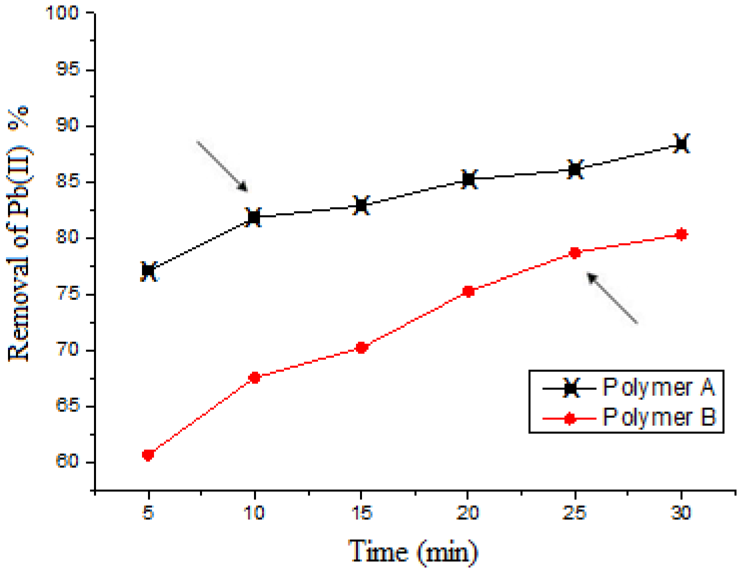

Figure 3.9: Effect of contact time on the removal efficiency of lead ions for polymer A.PAA-Lignin-A and B.

3.4.4 Effect of Temperature

The effect of temperature on the adsorption of Pb(II) by the two polymers A and B was also studied. The temperature range chosen for this study was from 20°C to 40°C. The highest removal of lead ion was achieved at 30°C for PAA-Lignin-A and 40°C for PAA-Lignin-B. The results are summarized in Figures 3.10 A and 3.10 B

The adsorption efficiency showed some dependence on the temperature for both polymers. The adsorption could be slightly endothermic.

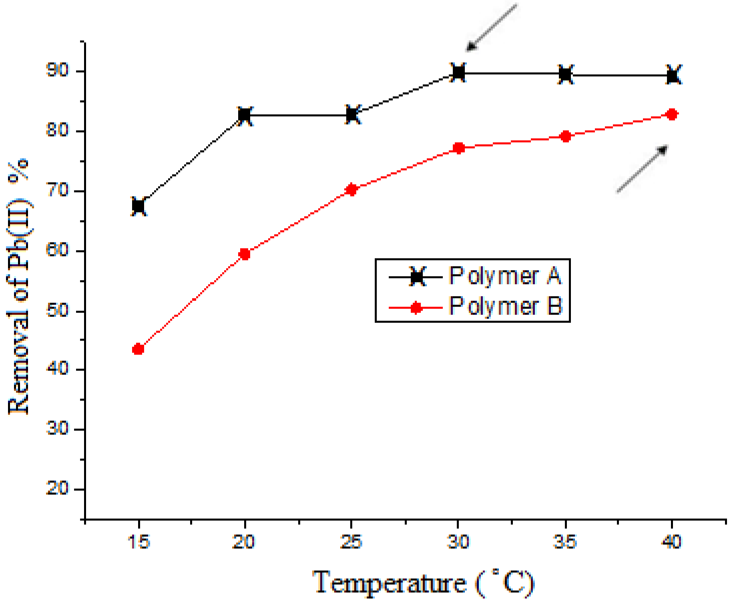

Figure 3.10: Temperature effect on the removal efficiency of lead ions A. PAA-Lignin-A and B. PAA-Lignin-B.

3.4.5 Effect of pH

The effect of the pH on the adsorption efficiency was evaluated while maintaining the other factors mentioned previously constant. The effect of pH is important since the pH value could affect the surface charge of polar polymers.

For instance, at low pH values (≤ 3.0), the polymer is in acid form (R-CO_2H). However, at pH values higher than 4.5, the proton is removed from the carboxyl groups and it becomes R-CO_2^-. The highest adsorption efficiency was achieved at pH between 8.0 and 9.0 for polymer PAA-Lignin-A and B. At the pH higher than 9, the increased in the efficiency could be due at metal oxide precipitation.

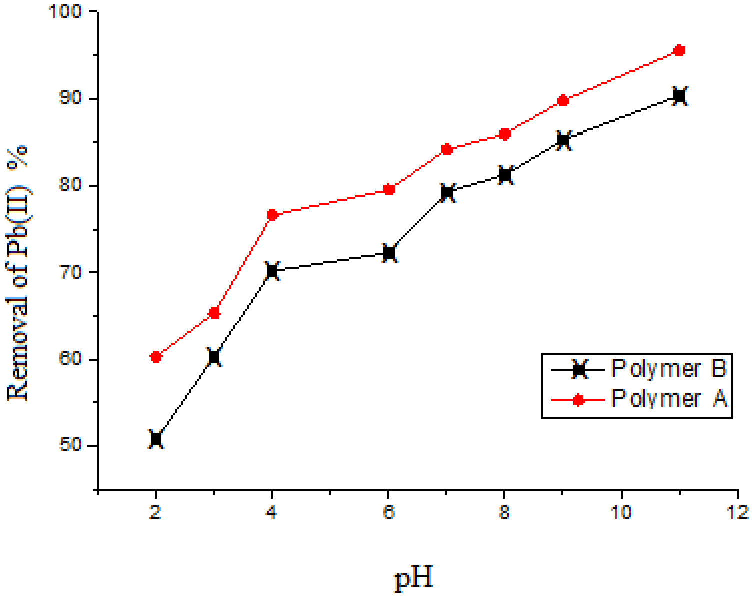

Figure 3.11: pH effect on lead ions removal by polymers A. PAA-Lignin-A and B. PAA-Lignin-B.

3.5 Adsorption kinetics(pseudo-first and second –order)

To understand the adsorption mechanism, it is important that a kinetic study is performed. Two models are available for describing the adsorption kinetics: pseudo-first-order (Eq. 1) and pseudo-second-order (Eq. 2).

$$\ln(q_\mathrm{e} - q_\mathrm{t}) = \ln q_e - K_1 t \tag{1}$$

$$\frac{t}{q_\mathrm{t}} = \frac{1}{k_{2q_e^2}} + \frac{t}{q_e} \tag{2}$$

where q_e and q_t are the adsorption capacities at equilibrium (mg/g) and with time, K_1 is the first-rate constant (1/min), K_2 is the second-order rate constant (g mg^{-1} min^{-1}).

3.5.1 Testing the two models on PAA-Lignin-A

The pseudo-first-order and pseudo-second-order models were tested on PAA-Lignin-A ,the results were summarized in Tables 3.3and 3.4, and shown in Figures 3.12 A and 3.13A .

Table 3.3: pseudo-first order model for PAA-Lignin-A.

Time (min)	Conc. of Pb^{2+} after extraction	q_t (mg/g)	$\ln(q_e-q_t)$
5	11.49	0.39	3.90
10	9.12	0.41	4.17
15	9.59	0.40	4.21
20	9.42	0.41	4.30
25	7.97	0.42	4.33
30	10.75	0.39	4.33

Table 3.4: Pseudo-second order model for PAA-Lignin-A

Time (min)	Conc. of Pb(II) after extraction	q_t (mg/g)	t/q_t
5	11.49	0.39	1.40
10	9.12	0.41	2.04
15	9.59	0.40	2.18
20	9.42	0.41	2.55
25	7.97	0.42	2.88
30	10.75	0.39	3.39

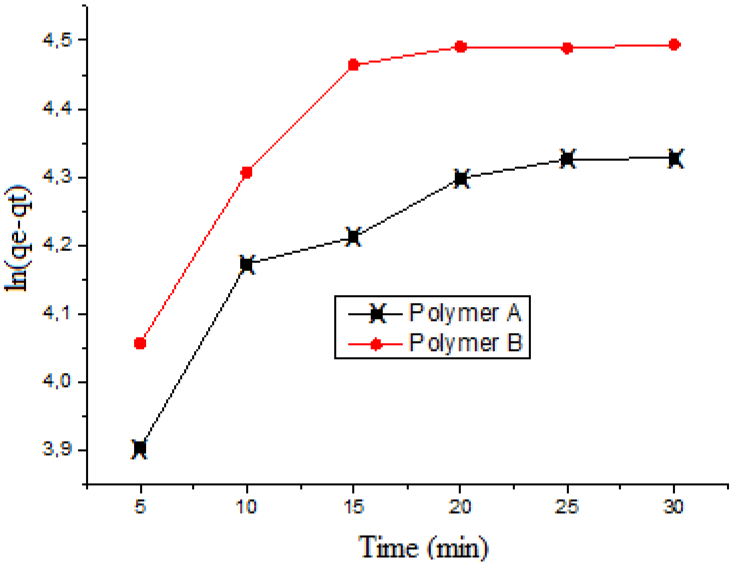

Figure 3.12: Pseudo-first order model for polymers PAA-Lignin-A & B.

3.5.2 Testing the two models on PAA-Lignin-B

The previous work was applied on PAA-Lignin-B ,the results were summarized in Tables 3.5 and 3.6, and shown in Figures 3.12 B and 3.13B

Table 3.5: Pseudo-first order model for PAA-Lignin-B

Time (min)	Conc. of Pb(II) after extraction (ppm)	q_t (mg/g)	$\ln(q_e-q_t)$
5	19.67	3.03	4.06
10	12.33	3.77	4.31
15	16.88	3.31	4.46
20	17.25	3.28	4.49
25	10.67	3.93	4.49
30	9.87	4.01	4.49

Table 3.6: pseudo-second order model for PAA-Lignin-B.

Time (min)	Conc. of Pb(II) after extraction (ppm)	q_t (mg/g)	t/q_t
5	19.67	3.03	1.19
10	12.33	3.77	1.95
1	16.88	3.31	2.06
20	17.25	3.28	2.22
25	10.67	3.93	2.48
30	9.87	4.01	2.74

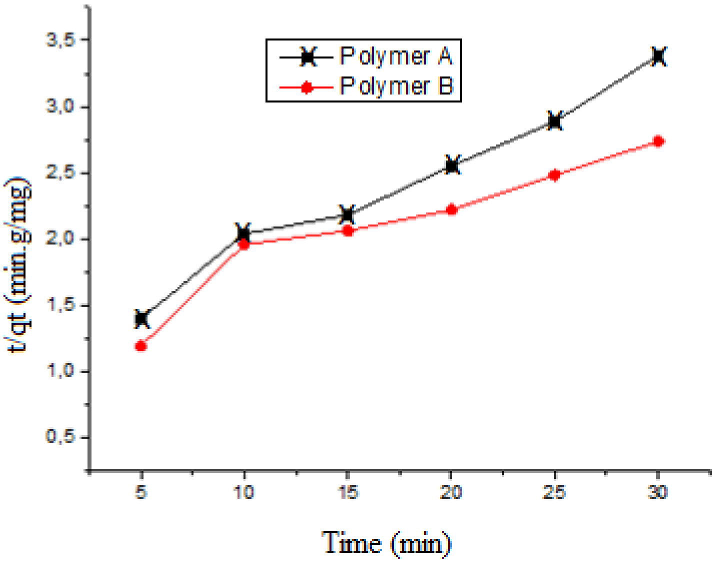

Figure 3.13: Pseudo-second order model for polymer PAA-Lignin-A& B.

The values of obtained parameters shown equations 1 and 2 are summarized in Table 3.5 and Figure 3.4 K_1 vale was obtained by plotting $\ln(q_e - q_t)$ vs. t (Figure 3.12) , while the K_2 and q_e were calculated from the slope and the intercept form the graph produced form plotting t/q_t vs. t

(Figure 3.13). K_{id} and Z values were calculated from the graph of plotting q_t vs. $t^{1/2}$ (Figure 3.13).

The obtained correlation coefficients (R^2) for the pseudo-second-order was (0.92 to 0.96) which is higher than the pseudo-first-order (0.88). The calculated q_e values was 2.67 mg/g, 15.14 mg/g, and 20.73 mg/g for the pseudo-second-order (Table 3.6 and Figure 3.13). While the experimental values of q_e values were 2.13 mg/g, 13.91 mg/g, and 18.79 mg/g. The experimental and the theoretical are almost equal, indicating that the adsorption process of Pb(II) ions on the surfaces of polymer PAA-Lignin-A follows the pseudo-second-order.

3.6 Adsorption isotherms(Freundlich vs. Langmuir)models

The Langmuir (equation 3) and Freundlich isotherm (equation 4) models were used to evaluate the distribution of lead ions on the surface of PAA-Lignin-A and B polymers after attaining the equilibrium at a constant temperature [78]. The Langmuir model describes the formation of a single layer of ions on a adsorbent surface. The Freundlich model describes the adsorption between the ions and the adsorbent with a heterogeneous surface.

Langmuir isotherm model: $\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max} K_L}$ (3)

where C_e is the equilibrium concentration of lead ion (ppm), q_e is the mass of adsorbate adsorbed per unit mass of PAA-Lignin-A at equilibrium (mg/g), q_{max} is the monolayer adsorption capacity of the adsorbent (mg/g) theoretically, and K_L is the Langmuir isotherm constant related to the adsorption energy (L/mg).

Freundlich isotherm model: $ln(q_e) = \; ln\, k_f + \frac{1}{n} ln\, C_e$ (4)

Where k_f and $\frac{1}{n}$ are empirical constants that indicate the adsorption capacity and intensity related to the affinity of the metal toward the polymers, respectively.

The Langmuir isotherm model could predict if the adsorption was favourable or not using the dimensionless constant separation factor shown in Eq. 5,

$$R_L = \frac{1}{1+ K_L C_0} \tag{5}$$

where K_L is the Langmuir constant and C_0 is the initial adsorbate concentration. The adsorption is unfavourable if the R_L value is greater than 1. However, if the value of R_L is between 1 and 0, then the adsorption is favourable. The adsorption is linear if R_L= 1.

3.6.1 Testing the two models on PAA-Lignin-A

The Adsorption isotherms models were tested on PAA-Lignin-A ,the results were summarized in Tables 3.7 and 3.8, and shown in Figures 3.14 A and 3.15A .

Table 3.7: Langmuir model for polymer A.

Initial conc. of Pb(II) (ppm)	Conc. of Pb(II) after extraction (ppm)	q	1/c	1/q
5	2.03	0.30	0.20	3.36
10	2.78	0.72	0.10	1.39
20	5.90	1.41	0.05	0.71
30	4.95	2.51	0.03	0.40
50	5.00	4.50	0.02	0.22

Table 3.8: Freundlich model for polymer A.

Initial conc. of Pb(II) (ppm)	Conc. of Pb(II) after extraction (ppm)	q	ln c	ln q
5	2.025	0.30	1.61	-1.21
10	2.78	0.72	2.30	-0.33
20	5.90	1.41	3.00	0.34
30	4.95	2.51	3.40	0.92
50	5.00	4.50	3.91	1.50

3.6.2 Testing the two models on PAA-Lignin-B

The previous work was repeated for PAA-Lignin-B ,the results were summarized in Tables 3.9 and 3.10, and shown in Figures 3.14 B and 3.15B .

Table 3.9:Langmuir model for polymer B.

Initial conc. of Pb(II) (ppm)	Conc. of Pb(II) after extraction (ppm)	q	1/c	1/q
5	4.37	0.13	0.20	7.99
10	6.47	0.71	0.10	1.42
20	16.27	0.75	0.05	1.34
30	10.91	3.82	0.03	0.26
40	21.72	3.66	0.03	0.27
50	16.41	6.72	0.02	0.15

Table 3.10: Freundlich model for polymer B.

Initial conc. of Pb(II) (ppm)	Conc. of Pb(II) after extraction (ppm)	q	ln c	ln q
5	4.37	0.13	1.61	-2.08
10	6.47	0.71	2.30	-0.35
20	16.27	0.75	3.00	-0.29
30	10.91	3.82	3.40	1.34
40	21.72	3.66	3.69	1.30
50	16.41	6.72	3.91	1.90

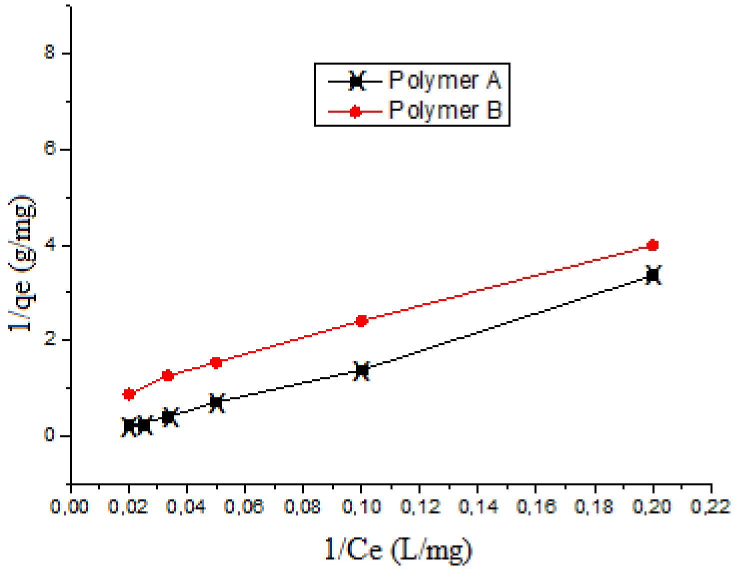

Figure 3.14: Langmuir model for polymers A&B.

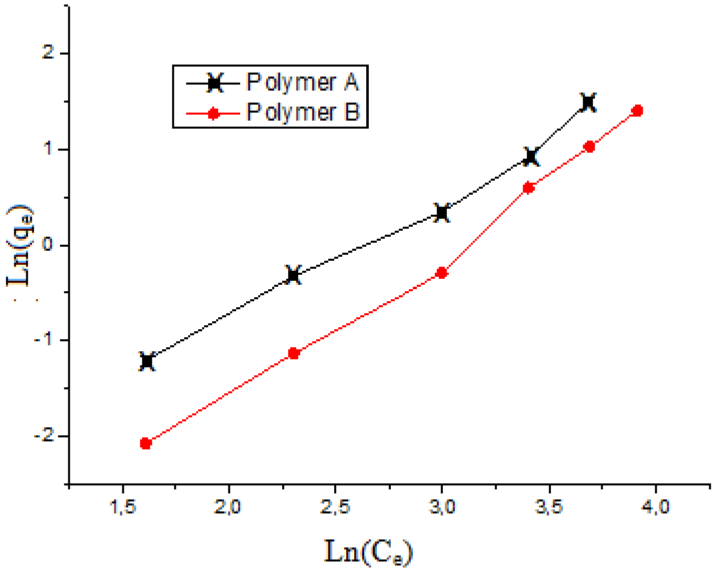

Figure 3.15: Freundlich model for polymers A & B.

All obtained parameters from Figure 3.14 are summarized in Table 3.9.The correlation coefficients for the Langmuir isotherm model were higher than those obtained from the Freundlich isotherm model. The results indicate that, the adsorption of Pb(II) followed the Langmuir isotherm model shown in Figure 3.15, Table 3.7. Where Pb(II) ions were equally and homogeneously distributed the polymer surface. The R_L value which was calculated for various amounts of adsorbents was $0<R_L<1$ (Table 3.7). The R values were smaller than 1 means a high affinity of PAA-Lignin-A for lead ions.

3.7 Wastewater purification from metals

The prepared polymers PAA-Lignin-A and B were evaluated as absorbents for metals present in real sewage water at pH 8.5.

Samples of sewer water were collected from different cities in the West Bank then mixed. Then two samples of them were collected and treated with polymers PAA-Lignin-A and B individually. The metal content of each sample present in the sewer water samples before and after purification are summarized in Table 3.11 and Table 3.12, respectively.

The metal concentration was determined using ICP-MS. Excellent efficiency toward some metals present in the swage samples was obtained for the two polymers.

Table 3.11: Metal concentration (ppm) of the wastewater before and after treatment at pH 8.5 using polymer PAA-Lignin-A

Metal ion	**Ag**	**Al**	**Bi**	**Cr**	**Co**	**Cs**	**Cu**	**Fe**
Before	38.2	4680	1.7	523	12.5	0.31	103	8156
After	3.28	344	.14	41	1.58	0.17	18.9	488
Removal	91.4	92.6	91.8	92.2	87.4	45.2	81.7	94.02
Metal ion	**Ga**	**Li**	**Mn**	**Mo**	**Ni**	**Sr**	**V**	**Zn**
Before	2.4	6.8	167	9.7	43	609	17	696
After	0.54	3.85	8.87	3.48	8.19	113	4.32	163
Removal	77.5	43.4	94.7	64.1	81	81.4	74.6	76.6

Table 3.12: Metal concentration (ppm) of the wastewater before and after treatment at pH 8.5 using PAA-Lignin-B

Metal ion	**Ag**	**Al**	**Bi**	**Cr**	**Co**	**Cs**	**Cu**	**Fe**
Before	38.2	4680	1.7	523	12.5	0.31	103	8156
After	2.5	295	0.10	55.6	2.04	0.26	20.4	591
Removal	93.5	93.7	94.1	89.4	83.7	16.1	80.2	92.8
Metal ion	**Ga**	**Li**	**Mn**	**Mo**	**Ni**	**Sr**	**V**	**Zn**
Before	2.4	6.8	167	9.7	43	609	17	696
After	0.54	4.50	76.60	2.80	10.70	359	7.89	93.2
Removal	77.5	33.8	54.1	71.1	75.1	41.1	53.6	86.6

4. Conclusion

Lignin is a valuable natural polymer ,it can be extracted from Zebar (olive industry liquid waste) ,which is low cost waste material. Here ,two polymers PAA-Lignin-A and B were prepared from Lignin and Acrylic acid and cross linking agent . These polymers have high chemical stability and hence they can be used as ideal adsorbents to uptake metal ions from wastewater.

The observed results of this research include the following:

1. Over 90% removal efficiency of Pb (II) was achieved using 0.05 g PAA-Lignin-A , after a contact time of 10 min, at pH 8.5 and temp of 30 °C, using Pb (II) solution with initial concentration of 50 ppm.90% for polymer PAA-Lignin-A .
2. Above 85.5% removal efficiency of Pb (II) was achieved using 0.1 g PAA-Lignin-B , after a contact time of 25 min, at pH 8.5 and temp of 40 °C, using Pb (II) solution with initial concentration of 50 ppm.
3. The grater efficiency of PAA-lignin-A could be attributed to the higher porosity.
4. All two polymers obey pseudo-second order model for adsorption kinetics, and obey Langmuir isotherm model.
5. They have been successful in being as perfect adsorbents to uptake various type of metal ions from real sewer samples with removal efficiency ranges from medium to excellent.

5. Recommendations

a. Studying the preparation of Lignin co-polymers using substances other than Acrylic Acid, or other cross-linking agents.

b. Studying the polymer regeneration ability.

c. The adsorption thermodynamic studies should be done.

d. Application of compounds in groundwater purification.

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كلية الدراسات العليا

استخلاص الليجنين من النفايات السائلة لعصر الزيتون وتحسينه واستخدامه في تنقية المياه العادمة

إعداد

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د.عثمان حامد

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

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الملخص

يشكل تلوث الماء بأيونات المعادن السامة مصدر قلق كبير، وذلك بسبب ضررها الشديد وتسببها بالسرطانات. كان العلماء يكرسون وقتًا وجهدًا كبيرًا في البحث عن مواد امتصاص طبيعية جديدة وفعالة من حيث التكلفة لهذه المعادن السامة. الليجنين هو بوليمر طبيعي رخيص الثمن وغير متبلور، يعتبر كنفايات عضوية، مع إمكانية عالية لاستخدامه في إنتاج المواد المتجددة الحيوية. صيغته البنائية المميزة حيث يملك هيكل متعدد الفينول، بالإضافة إلى وفرته بكثرة هما سببان كافيان لجعل اللجنين مادة فريدة نبدأ بها لإعداد الممتزات لمجموعة متنوعة من أيونات المعادن الثقيلة.

في هذه الدراسة تم استخلاص اللجنين من النفايات السائلة لصناعة الزيتون (الزيبار)، ثم استخدم الليجنين المستخلص بالإضافة إلى حمض الأكريليك وعامل الربط المتقاطع (N,N-methylenebisacrylamide) لتحضير اثنين من البوليمرات المشتركة الجديدة، بحيث يحوي كل بوليمر على نسبة مختلفة من الليجنين، وقد أطلق عليهما: (PAA-Lignin-A) و(PAA-Lignin-B). ثم تم اختبارهما كمواد ممتزة لأيونات المعادن السامة من المياه الملوثة ، كما أجريت عليهما جميع الفحوصات اللازمة لتشخيصهما والتعرف على خصائص سطحهما مثل فحصي: (FT-IR) و (SEM)، وقد أظهرت نتائج تحليل SEM أن البوليمر A أكثر مسامية من B. ثم استخدم البوليمرين كممتزات لأيونات الرصاص(II) من مياه الصرف الصحي، حيث فحصت كفاءة الامتزاز للبوليمرات المحضرة تجاه Pb (II) كدالة كمية المادة المازة وتركيز أيونات المعادن وزمن الامتزاز ودرجة الحرارة وقيمة الرقم الهيدروجيني، ثم تم تحديد الظروف المثلى

لأفضل نسبة امتزاز لأيونات Pb (II) على كل بوليمر . بالإضافة إلى ذلك ، أظهر البوليمران كفاءة استخراج متوسطة إلى ممتازة نحو ستة عشر أيونًا معدنيًا مختلفًا موجودًا في عينة الصرف الصحي التي تم جمعها من مدينة الخليل في فلسطين.

ويمكن أن تعزى الكفاءة العالية للبوليمرات المحضرة تجاه أيونات المعادن المختلفة إلى المجموعات الوظيفية المتعددة و الموجودة في البوليمرات بما في ذلك : المجموعات الأروماتية ، الهيدروكسيل، الكربوكسيل والأمين. وبلغت كفاءة الامتزاز حوالي 90٪ للبوليمر PAA–lignin–A و 85.5٪ لـ PAA–lignin–B ، ويمكن أن تعزى الكفاءة المبشرة لـ PAA–lignin–A إلى المسامية العالية.

تم تطبيق عمليات الإمتزاز المختلفة على نماذج الإمتزاز ثابتة الحرارة (Langmuir and Freundlich) ، وتحديد النموذج الأكثر ملاءمة للنتائج وفقًا لقيمة معامل الارتباط ، حيث تم ملاحظة أنّ كل عمليات الإمتزاز كانت تابعة لنموذج (Langmuir) و بالتالي فهي إمتزازات كيميائية، مما يدل على وجود روابط كيميائية حقيقية بين كل من المادة المازة و المُمتزة.

ولتحديد ميكانيكية تفاعلات الامتزاز تم تطبيق هذه العمليات على نماذج الإمتزاز الحركية و هي:

(pseudo first-order, pseudo second-order). وقد أظهرت النتائج أن آلية التفاعل تتوافق مع نموذج الامتزاز الحركي من الدرجة الثانية (pseudo second-order).