An-Najah National University

Faculty of Graduate Studies

POLYACRYLATE BASED FILM MODIFIED WITH PHENYL BIGANIDE: SYNTHESIS AND APPLICATION IN WASTEWATER PURIFICATION FORM TOXIC METALS

By

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This Thesis is Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Chemistry, Faculty of Graduate Studies, An-Najah National University, Nablus - Palestine.

2022

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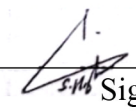
Dr. Hisham Qararia	
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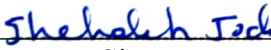
Prof. Shehdeh Jodeh	
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Dedication

I dedicate my thesis to my beloved family, my lovely children (Maryam and Mahmoud), and my supportive husband all the time.

I also dedicate it to my loving mother and great father, wishing them both long lives and good health, as well as my brothers and sisters, and also my second family, my husband's family.

I also dedicate it to all of my teachers who never failed to supply me with vital information and served as a light for me on my road to attaining my goals during my studies. Finally, I would like to thank everyone who has helped and supported me throughout my studies.

Acknowledgment

Praise and thanks to Allah, the Most Merciful, for guiding and leading me in the correct direction.

My heartfelt gratitude goes to Prof. Othman Hamed, my amazing professor and supervisor, who assisted me with my master's thesis and did not spare me any knowledge, as well as being a continuous motivator at work and encouraging me to bring out my strengths and work with great energy. All of my gratitude goes to him for enabling me to work with him and benefit from his wonderful knowledge and experience.

I would also like to thank all of my instructors and doctors who helped me earn my master's degree, especially Dr. Nawaf and many others who have exceeded me in every class I have taken.

I would also want to thank Mr. Nafeth Dwaikat for his assistance in the research laboratories. I also appreciate my colleagues and friends especially, Angham, Raneem, Jomana, Haneen and I am thankful for the days that brought us together. Many thanks to my children and husband for their love and assistance in obtaining my master's degree.

Declaration

I, the undersigned, declare that I submitted the thesis entitled:

POLYACRYLATE BASED FILM MODIFIED WITH PHENYL BIGANIDE: SYNTHESIS AND APPLICATION IN WASTEWATER PURIFICATION FORM TOXIC METALS

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

Student's Name: Reem Bassam Tallouzi

Signature:

Date: 22.5.2022

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POLYACRYLATE BASED FILM MODIFIED WITH PHENYL BIGANIDE: SYNTHESIS AND APPLICATION IN WASTE WATER PURIFICATION FORM TOXIC METALS

By
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Abstract

Background: Pollution in the water supply has become a major source of concern for society as well as an environmental issue. Contaminants enter the water in a variety of ways, including industrial, altering the water's quality and containing hazardous substances that threaten the health of humans and animals. To remove dangerous heavy metals contaminants and improve water quality, researchers used several methods. Modifying existing polymers could be the simplest and most effective way to create a low-cost adsorbent with excellent efficiency against metals and hazardous organic compounds.

Objectives: The purpose of this research was to establish a low-cost technique to make a novel adsorbent for hazardous metal ions. Surface modified polyacrylic acid with multidentate chelating functionalities was selected for this purpose. Polyacrylic acid (PAA) was covalently bonded via amide linkages to phenyl biguanide in a polymer modification process. Because of its unusual structure and the huge number of metal ion coordination sites, this adsorbent could be ideal for wastewater purification.

Methodology: Three modified polymers were prepared, in which the polyacrylic acid (PAA) was mixed with phenyl biguanide in different ratios, so that the addition of phenyl biguanide reduces the solubility of PAA and adds functionality with high affinity for metal ions. The enhanced PAA was evaluated as a Pb (II) water adsorbent. FT-IR and TGA were used to examine the polymers structures and thermal stability, respectively.

Results: The polymers were evaluated as an adsorbent for Pb (II) ions. Adsorbent dosage, metal ion concentration, temperature, pH, contact time and shaking speed were all

evaluated as parameters influencing the adsorption process. The percentage removal of Pb (II) by PAA/PBG-50 was 40.36 percent rate, PAA/PBG-25 was removed at a 75.93 percent rate, and by PAA/PBG-75 reached about 93.19 percent rate. Adsorption isotherm, kinetics, and thermodynamics were also studied to acquire a better knowledge of adsorption spontaneity and mechanism. As determined by the adsorption parameters, these adsorptions were matched with the Langmuir isotherm of adsorption, and all adsorption processes follow the second order adsorption kinetics model.

Conclusion: Adsorption efficiency of the three polymers were evaluated on a real-world wastewater sample as well. The three polymers showed quantitative removal for most of the toxic metal ions present in wastewater like, lead, and mercury.

Keywords: Water pollution, water treatment, polymers, heavy metal, Lead, phenyl biguanide, poly acrylic acid,

Chapter One

Introduction

1. Background

1.1 Public Health and the Quality of Drinking Water

Water and human health are deeply connected. Water is not only vital for living, but also for excellent health. Given that water accounts for more than 60% of the human body, having enough quantities and of good quality is critical to our health and well-being. Furthermore, water is the most essential natural resource, and it is required for the continued existence of all living organism, including humans, as well as food production and economic development [1]. Today, many cities throughout the world experience severe water shortages, and irrigation is used to raise over 40% of the world's food supply, as well as a variety of industrial operations. And due to increased development and manufacturing, previously considered safe groundwater has become contaminated with toxic heavy metals and organic matters. These heavy metals are non-biodegradable and causes several disease to human and other creatures such as cancer, so they are of great concern. While some metals are necessary for human and animal biological health, excessive amounts can be dangerous. Because metal collection occurs gradually in body systems over time, it can reach dangerous levels far above assigned limits. And as a result of that the effect of metal ions on human health related to water intake has been a major attention of environmental researchers all over the world [1, 2].

Understanding the aspects that drive drinking water quality is also essential for making decisions about drinking water protection and management, such as the quality of source water, treatment in treated water before distribution, the water distribution system, and the containers used for water storage and domestic filters all have an impact on the drinking water quality [3].

1.2 Water Pollution

The availability of pure water, clean air, and a healthy environment is shrinking rapidly. Water is a fundamental resource for life, and having access to safe drinking water is critical for both living organism and the environment. The increasing population, rapid industrialization, and irresponsible use of natural resources affect negatively on water

quality in recent decades. Also Organic matter, nutrition, pharmaceutical and personal care products, heavy metals, pigments, and plastics are only a few examples on the key pollutants to concern about [4, 5].

Due to its toxicity to aquatic life, humans, and the environment, heavy metal contamination, such as those caused by cadmium, lead, mercury, chromium, and arsenic, has recently received an attention [6].

Because of heavy metals bioaccumulation, they are dangerous, which described as an increase in chemicals concentrations in a biological organism over time in comparison to the chemicals concentrations in the environment. Heavy metal ions, as mentioned above are not biodegradable. They are also stable, and because of biomagnification, they can affect a variety of organisms directly or indirectly. Even though in very little amounts, they can damage in many organs, including the lungs, kidneys, liver, esophagus, stomach, and skin [7-9].

1.3 Waste Water Treatment

Water contamination not only limits accessible freshwater, but also has an impact on human health and the environment, therefore having access to healthy drinking water was vital [10].

Water, which is made up of two hydrogen atoms linked by an oxygen atom, is the most important source of survival. It could be contaminated by a range of contaminants, such as harmful chemicals used in human operations, naturally occurring minerals and chemicals, and contaminants that modify flavor, smell, and color, among others. Water must be treated to remove and reduce the number of impurities in order to be suitable for its intended application. Water treatment is the process of making water appropriate and acceptable [11].

For society, government, and industry, water quality is a major issue. The majority of residential and industrial operations were produce wastewater that contains dangerous contaminants. Current wastewater treatment systems use a variety of approaches, as well as procedures for removing insoluble particles and soluble impurities. Chemical precipitation, membrane separation, ion exchange, biological techniques, coagulation, reverse osmosis, and flocculation, catalysis, photodegradation, and adsorption were

among the procedures employed for the treatment and purification of waste-contaminated water. Adsorption is one of these wastewater treatment solutions since it is cheap, quick, and ecologically friendly and have proven to be particularly effective at removing colors, odors, organic and inorganic pollution [12-14].

1.3.1 Adsorption technique

The negative effects of heavy metals on living creatures and the environment, particularly their bioaccumulation tendency and persistence in nature, have made heavy metal-polluted water a severe problem. Several approaches, such as adsorption technologies, have been developed in recent years for cleaning natural water form heavy metals and industrial waste. Conventional adsorbents, such as activated carbon, are sometimes less effective while also producing toxic sludge that requires post-treatment. Although nanotechnology adsorbents have been used recently in water purification, their practical applications in toxic heavy metals removal are limited due to the complicated synthesis procedure and high cost [15]. An appropriate adsorbent in the removal of heavy metals should have a low cost, stability, simplicity of design, high absorptivity, high adsorption capacity, ease of separation, and acceptable reusability [16-19].

Adsorption is a separation process in which liquid, or gas molecules bond to the outer and interior surfaces of a solid object known the adsorbent. The separation is based on the selective adsorption (kinetic and/or thermodynamic selectivity) of pollutants by an adsorbent as a result of specific interactions between the adsorbent material's surface and the adsorbed contaminants. This surface phenomenon depicts the numerous interactions between the three components involved, namely the adsorbent, adsorbate, and wastewater. The affinity between the adsorbent and metal ion is the most important interaction factor controlling adsorption. The affinities between the adsorbate and the solution, the adsorbent and the solution, and the contaminant molecules can all influence adsorption. Adsorbent classification: conventional and non-conventional adsorbents. Commercial ion-exchange resins (polymeric organic resins), commercial activated carbons (CAC), and inorganic materials such as activated aluminas (CAA), zeolites, silica gel, and molecular sieves are examples of conventional adsorbents. Non-conventional adsorbents include activated carbons (AC) generated from agricultural solid waste and industrial byproducts, natural materials such as clays, industrial byproducts, and biosorbents such as chitosan. [20-24].

1.3.2 Heavy Metals

The term "heavy transition metals" refers to metals that are "bad" for the environment. It can mean a variety of things based on the atomic weight, atomic number, density, or other properties of the elements or their compounds [25].

Heavy metals are metals that exist naturally and have an atomic number (Z) more than 20 and an elemental density larger than 5.0 g/cm3. Based on this classification, scientists classify periodic table 51 elements as heavy metals. Heavy metals also have atomic weights ranging between (63.5to200.6). Heavy metals are divided into three categories: toxic, precious, and radionuclides [26, 27].

Unlike organic based pollutants, heavy metals cannot be biodegraded once they reach the environment. They will continue to damage the air, water, and soil for the rest of their lives. The basic pollution reduction approaches are reduced metal bioavailability, mobility, and toxicity. While some transition heavy metals are essential trace elements, the vast majority are toxic to all living creatures [28]. Heavy metals are released into the environment through human activities such as industrial production, mining, agriculture, and transportation. Metal contamination is caused by the combustion of fossil fuels, municipal garbage, fertilizers, pesticides, and sewage [29]. The heavy metals that cause the most harm to human health include lead, cadmium, mercury, and arsenic. These metals have been carefully researched, and international organizations such as the World Health Organization (WHO) monitor their impact on human health on a regular basis. Heavy metals have been used by humanity for thousands of years. Even though heavy metal pollution has decreased in most affluent countries over the last 100 years [30], exposure to heavy metals remains and is even growing in some regions of the world, mainly in developing countries.

1.3.2.1 Lead

Lead is a naturally occurring element with a density higher than the bulk of other materials. Lead is silvery with a trace of blue when freshly cut, but it oxidizes to a dark gray tint when exposed to air. Lead has the greatest atomic number of any stable element. It has a low reactivity and its oxides generate covalent bonds when they react with acids and bases. Lead compounds are usually found in the +2 oxidation state, rather than the +4 oxidation state found in lighter carbon group members.

It was used in electroplating, metallurgy, chemicals, and a variety of other industries. Lead is a hazardous heavy metal that can cause damage to your bones, brain, blood, kidneys, and thyroid glands. Lead in the discharge, as well as its poisonous character, has other negative consequences. Even at very low levels. Lead metal concentrations in water can be harmful [31, 32].

Lead (II) that is discharged into the nature eventually enters the human organs through the food chain or drinking water. Humans' neurological, hematopoietic, and reproductive systems may be harmed as a result, putting their health at danger. Lead is a poisonous substance that accumulates in soft tissues and bones, causing harm to the nervous system. Neurological illnesses, such as brain damage, can occur even if blood levels are quickly restored with treatment [33, 34].

Finally, Lead poisoning can be caused by a variety of lead sources, including lead paint, lead-contaminated house dust, soil, drinking water, and food. Because lead accumulates in the body, all sources of lead should be managed or eliminated.

1.4 Acrylic acid (AA)

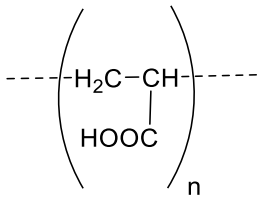
Acrylic acid is an organic chemical that is the simplest of the unsaturated acids. Acrylic acid is a liquid with a pronounced acid odor that is liquid at ambient temperature. Acrylic acid, as well as its amide and ester derivatives, are commonly used in the manufacture of polymeric materials. Acrylic acid is a popular polymer that is utilized in a number of industrial and consumer products as a raw material. Among the applications are textiles, adhesives, surface coatings, paper treatment, feminine hygiene products, baby diapers detergents, and super absorbent [35, 36].

1.5 Polyacrylic acid (PAA)

Because of its strong selective filling qualities, polyacrylic acid (PAA) is a common post-tanning chemical that is widely used in the leather industry. Functional groups in polyacrylic acid (PAA)-based polymer hydrogel adsorbents trap metal ions. At low concentrations, soluble PAA could bind with lanthanide ions, but no precipitates were formed, whereas sufficient lanthanide ions stimulated the production of insoluble Ln-PAA precipitates [37, 38].

Polyacrylic acid is a one-of-a-kind polymer with a high water absorption capability. Because it is biologically inert, this chemical is widely used in the manufacture of cleaning and cosmetic products, as well as a medical supplementary substance. Polyacrylates (acid salts) with improved physicomechanical properties have a broader variety of uses. The crosslinked polyacrylic acid (PAA) hydrogel can adsorb and retain huge quantities of water without dissolving, and it can also provide many active sites to absorb adsorbate, such as COO^-, which has a lot of potential in wastewater treatment. Radical polymerization is used to create polymeric hydrogels. Acrylic acid-rich wastewater was used as both the monomer and the solvent in the synthesis of a new polycarboxylate, which is constituted of both adsorption groups and long side chains [39, 40].

This polymer distinguishes by its lack of toxicity, high water solubility, and resistance to high alkalinity. The chemical structure of polyacrylic acid is shown in Figure 1.1.



The first application of polyacrylic acid in water purification was to remove methylene blue (MB) dye using a polymeric hydrogel absorbent consisting of poly (acrylic acid) (PAA)/poly (acrylamide) (PAM)/calcium hydroxide nanoparticles (CHN).This type of PAA/PAM/CHN hydrogel adsorbent is created using free-radical polymerization with CHN as a cross-linker and is utilized to purify MB dye from wastewater [40].

Polyacrylic acid was also employed in water purification in the form of poly (acrylic acid)/nanocrystalline cellulose nanocomposite hydrogels. In this study, in situ free radical polymerization in an aqueous environment produces crosslinked PAA/NCC nanocomposite hydrogels with varying quantities of NCC, which are then employed to remove MB [41]. The phase separation generated by the polarity difference between lignin and polyacrylic acid expansion properties is employed to create a porous hydrogel in PAA-g-lignin. When utilized as a selective adsorbent for Pb^{+2}, Cu^{+2}, and Cd^{+2} ions in wastewater, it displayed a good selective removal coefficient. This study indicates a highly promising candidate for heavy metal-contaminated wastewater treatment [42].

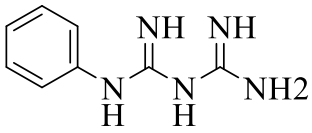
PAA/CTS/BC is a novel poly acrylic acid grafted chitosan and biochar composite designed for very efficient and selective removal of heavy metals. PAA/CTS/BC showed efficient and quick removal of Ni^{+2}, Pb^{+2}, Cu^{+2}, Zn^{+2}, , Co^{+2}, Cd^{+2}, $Mn^{+2}$and Cr^{+3} [43].

1.6 1 Phenylbiguanide (PBG)

A phenyl biguanide is a biguanide in which a phenyl group has replaced one of the terminal hydrogen atoms. It is used to treat the central nervous system. It is made up of a biguanide. Antibacterial medicines have made extensive use of biguanide compounds in particular. Furthermore, the strong basicity and electrondonating properties of the guanidine family can result in a diverse range of charge-transfer (CT) complexes. [44]**.** Because PBG is amphiphilic, it will be soluble in both water and more hydrophobic conditions[45]. Figure 1.2 shows the chemical structure of phenyl biguanide.

Figure 1.2

1-Phenyl biguanide



In this study, phenyl biguanide creates an amide bond with PAA in a water solvent to remove hazardous compounds from the water.

The general aim of this work

To prepare polymers with functional groups that have a high affinity for metal ions and utilize them to remove water from harmful metals and organic particles.

The sub-objectives are as follows:

1. Synthesized PAA with a metal ion-binding substituent. The substituent selected for this purpose is phenyl biguanide, it reacts with acrylic acid to form amide bond. The presence of such group makes the polymer water insoluble.
2. Develop a method for derivatizing PAA with phenyl biguanide.
3. Develop a method to produce a porous film form the target polymer and characterize the new adsorbent by various spectroscopic techniques.
4. Evaluate the efficiency of prepared polymer as a metal adsorbent and in wastewater purification and prepare several PAA-PG polymers with various ratios of PAA to PG and

determine the optimum ratio that produces polymer with lowest water solubility and highest efficiency for metals.

5. Determine the optimum adsorption efficiency by studying the effect of various factors such as, solution pH, solution temperature, metal ion concentration and mixing time on adsorption.
6. Develop a process for recycling the polymer.

Chapter Two

Experimental

2.1 Materials

All the chemicals used in this study were purchased from Sigma Aldrich Chemical Company (Jerusalem) and used as they were without additional purification except for anything else. For this study, the chemicals used were: Acrylic acid, potassium persulfate ($K_2S_2O_8$), methanol, nitrogen gas, and phenyl biguanide. Distilled water was used in all experiments.

2.2 Instrumentation

The following instruments were used in this study: a water shaking bath (Daihan Labtech, 20.0 to 250.0 rpm Digital Speed Control), pH meter (JENWAY, model: 3510), Fourier-Transform Infrared Spectrophotometer (FT-IR) (Nicolet iS5, iD3 ATR, Thermo-scientific), Thermo Gravimetric Analysis (TGA) (rate of increasing temperature =10 °C/min, N_2 is used as gaseous atmosphere), Flame Atomic Absorption Spectrometer at 217 nm (ICE 3000 series AA System, Thermo Scientific), and an Inductively Coupled Plasma Mass Spectrometer ICP-MS (ICE 3xxx C113500021 v1.30).

2.3 Polymer synthesis

2.3.1 Preparation of polyacrylic acid

To produce the polymer, first polyacrylic acid was prepared by adding 25.0 mL acrylic acid to a two-necked round-bottomed flask and was stirred for 1 minute under nitrogen (N_2). The flask was connected to a condenser and a magnetic stirrer. A solution of potassium persulfate ($K_2S_2O_8$) (1.0 ml water and 0.1 g $K_2S_2O_8$) was added to the reaction flask, then was heated to 60 °C. A vigorous exothermic reaction was started. The reaction was kept stirring for around 2 hours. The obtained solid mass was crushed, washed with methanol and dried at 80 °C for 2.0 hrs. Finally, it was analyzed by FT-IR spectroscopy[46, 47] .

2.3.2 Preparation of polyacrylic acid/phenyl biguanide (PAA-PBG) polymer

The PAA/PBG-75 polymer was prepared by mixing (three moles) of polyacrylic acid and (one moles) of phenyl biguanide in deionized water. The mixture was stirred until a clear solution was obtained. The solution was heated at 110 °C until the water evaporated, then the temperature was raised to 160 ºC for 30 minutes to induce curing[48]. The produced polymer was ground and analyzed by FT-IR spectroscopy.

Another two more polymer samples were prepared in the same way using the weight ratio of polyacrylic acid to phenyl biguanide 1:1(PAA/PBG-50) and 1:3 (PAA/PBG-25).

2.3.3 Water Solubility

Weighing polymers of known weight in water was used to determine their solubility in water. This test was used to determine the polymer's water solubility. In this experiment, 0.1 g of polymer was suspended in 100 mL of water for around 1 hour, then gravity filtered, dried at 110°C, and weighed.

Table 2.1

Solubility result for the polymers.

Adsorbent	**Weight of polymer before**	**Weight of polymer after**
PAA-PBG-50	0.1 g	0.07 g
PAA-PBG-25	0.1 g	0.08 g
PAA-PBG-75	0.1 g	0.08 g

2.4 Adsorption by batch method

2.4.1 Calibration Curves

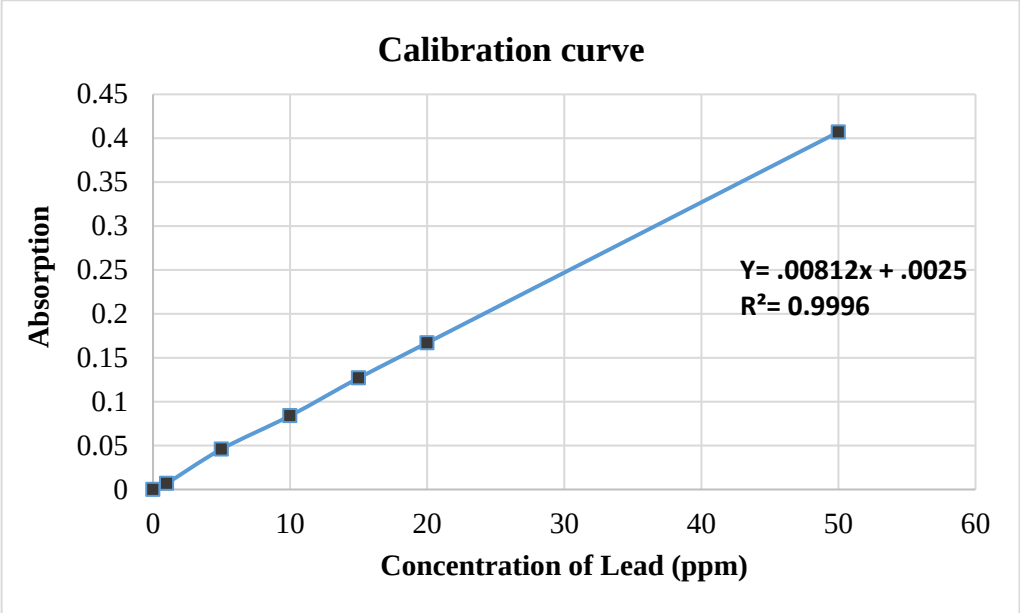
A stock solution of Pb (II) was prepared by dissolving a 0.15985 g of lead nitrate Pb $(NO_3)_2$ (MM= 331.21 g/mol) in a 100.0 mL water in a volumetric flask. A lead (II) stock solution with a 1000.0 ppm concentration was generated. Several standard solutions of Pb (II) with concentrations ranging from 1.0 ppm to 50 ppm were prepared by diluting the stock solution. The standard solutions were used in batch experiments to investigate the effects of several parameters on the efficiency of the adsorption process, including adsorbent dosage, initial metal ion concentration, temperature, pH, and contact time.

2.4.3 Calibration curve for lead

The lead ion concentrations in the samples were measured, and a calibration curve for Pb (II) ions was produced using flame atomic adsorption spectroscopy (FAAS). Calibration curves were obtained by measuring the absorbency of the prepared standard solutions.

Figure 2.1

Calibration curve between absorbance vs. concentration for lead Pb (II)



The impacts of solution conditions refer to the investigation of solution parameters such as the amount of synthesized polymer, time, temperature, pH value, and initial concentration of metal ions. Such for each filtered sample, flame atomic adsorption was utilized to determine the remaining concentration of the metal ion and consequently the adsorption efficiency.

2.4.4 Effect of adsorbate (Pb^{+2}) concentration

To determine the ideal lead concentration, 20.0 mg of adsorbent was mixed with 10.0 ml of each standard concentration (5.0 ppm, 10.0 ppm, 15.0 ppm, 20.0 ppm, 50.0 ppm) while other parameters were held constant for the five samples (Temp = 25 °C, pH = 5.09, time = 30 min), and the filtrate of the solution was analyzed by FAAS to determine the remaining lead concentration in each solution. Table 2.2 represents the result obtained for lead concentration and removal adsorption by PAA/PBG-50, PAA/PBG-25, and PAA/PBG-75.

Table 2.2

Effect of the adsorbate concentrations for the adsorption of lead (II) ions.

Adsorbent	Initial concentration of Pb(II) (ppm)	Final concentration of Pb(II) (ppm)	Removal (%)
PAA/PBG-50	5.0	1.0957	78.09
	10.0	1.9936	80.06
	15.0	3.0367	79.76
	20.0	3.8451	80.77
	50.0	27.7778	44.44
PAA/PBG-25	5.0	3.3802	32.40
	10.0	6.2368	37.63
	15.0	8.725	41.83
	20.0	10.4111	47.94
	50.0	33.9561	32.09
PAA/PBG-75	5.0	2.489	50.22
	10.0	4.7104	52.90
	15.0	7.0002	53.33
	20.0	8.87266	55.64
	50.0	29.6829	40.63

Six solutions were prepared for each polymer, each solution contains 10.0 ml of 20.0 ppm of lead, 20 mg of adsorbent, 25ºC and a pH of 5.09. Therefore, all variables were kept constant except the shaking time 5, 10, 15, 20, 25, 30 min were used. The solutions were filtered, and the filtrate were used to measure the remaining lead in each solution by FAAS. Table 2.3 shows the results of the influence of shaking time on the adsorption of lead (II) ions by PAA/PBG-50, PAA/PBG-25, and PAA/PBG-75.

Table 2.3

Effect of the shaking time for PAA/PBG for the adsorption of lead (II) ions.

Adsorbent	Time (min)	Final concentration of Pb (II) (ppm)	Removal (%)
PAA/PBG-50	5.0	5.9692	70.15
	10.0	4.2071	78.96
	15.0	1.9599	90.20
	20.0	1.8014	90.99
	25.0	1.0026	94.99
	30.0	1.5179	92.41
PAA/PBG-25	5.0	11.2275	43.86
	10.0	9.6581	51.71
	15.0	7.0156	64.92
	20.0	2.9118	85.44
	25.0	1.7361	91.32
	30.0	1.9854	90.07
PAA/PBG-75	5.0	3.7851	81.07
	10.0	2.982	85.09
	15.0	1.6172	91.91
	20.0	1.2112	93.94
	25.0	0.2172	98.91
	30.0	1.047	94.77

2.4.6 Effect of pH

To study the effect of pH, appropriate parameters (contact time, adsorbent dosage, temperature, and standard concentration) were applied. The pH of each solution was adjusted from 3 to 13. At 25°C, 20 mg of each polymer was added to 10 ml of 20 ppm lead standard before filtering the samples and quantifying the remaining lead in each solution with FAAS.

Table 2.4 shows the results for the influence of pH value on the adsorption of lead (II) ions by PAA/PBG-50, PAA/PBG-25, and PAA/PBG-75.

Table 2.4

Effect of the pH value for PAA/PBG for the adsorption of lead (II) ions.

adsorbent	pH	Final concentration of Pb (II) (ppm)	Removal (%)
PAA/PBG-50	3.34	3.3502	83.25
	5.84	1.8097	90.95
	7.74	2.7141	86.43
	9.68	5.6544	71.73
	12.19	6.8213	65.89
PAA/PBG-25	3.50	11.709	41.46
	4.47	8.1721	59.14
	6.32	5.5415	72.29
	8.49	4.0109	79.95
	11.32	6.7245	66.38
PAA/PBG-75	3.00	9.3658	53.17
	5.17	4.892	75.54
	6.63	2.0996	89.50
	9.35	2.1636	89.18
	11.31	5.7431	71.28

2.4.7 Effect of Temperature

To test the effect of temperature on adsorption, 10 ml of a 20 ppm lead standard solution was mixed with 20 mg of each polymer, all other parameters (pH, time, concentration, adsorbent dosage) were kept constant except for the temperature, which varied from 15 to 45°C; after the process was completed, each solution was filtered off and FAAS was used to measure the remaining lead in each solution. Table 2.5 shows the temperature effect on the adsorption of lead (II) ions by PAA/PBG-50, PAA/PBG-25, and PAA/PBG-75.

Table 2.5

Effect of the temperature value for PAA/PBG for the adsorption of lead (II) ions.

Adsorbent	Temperature (°C)	Final concentration of Pb(II) (ppm)	Removal (%)
PAA/PBG-50	15.0	0.7898	96.05
	20.0	1.7307	91.35
	25.0	3.8451	80.77
	45.0	3.5059	82.47
PAA/PBG-25	15.0	7.763	61.19
	20.0	9.6283	51.86
	25.0	13.411	32.95
	45.0	13.1544	34.23
PAA/PBG-75	15.0	12.312	38.44
	20.0	14.0886	29.56
	25.0	16.0806	19.60
	45.0	15.2608	23.70

Table 2.6

Effect of the adsorbent dosage for PAA/PBG for the adsorption of lead (II) ions.

adsorbent	Wt. of dose (mg)	Final concentration of Pb (II) (ppm)	Removal (%)
PAA/PBG-50	10.00	4.3442	78.28
	15.00	2.7043	86.48
	20.00	3.8451	80.77
	25.00	4.1486	79.26
PAA/PBG-25	10.00	13.574	32.13
	15.00	12.6491	36.75
	20.00	13.1648	34.18
	25.00	13.5796	32.10
PAA/PBG-75	10.00	16.8652	15.67
	15.00	15.0947	24.53
	20.00	15.7757	21.12
	25.00	15.9715	20.14

2.5 Adsorption kinetics

Kinetic studies must be performed in order to understand the method by which metal ions are adsorbed and the process pathway. The adsorption process was explained using numerous kinetic models[49]. One model was pseudo-first order:

$$\ln (q_e - q_t) = \ln q_e - K_1 t \qquad \text{Eq .1}$$

While the other was pseudo-second order:

$$t/q_t = 1/(K_2 q^2) + (t/q_e) \quad \text{Eq .2}$$

q_e: equilibrium mass of adsorbate/unit mass of adsorbent (mg/g)

q_t: the mass adsorbate/adsorbent unit mass at time t (mg/g).

K_1 denotes the first-rate constant (min^{-1})

K_2 denotes the second-order rate constant (g mg^{-1} min^{-1})

2.6 Adsorption Thermodynamic

The thermodynamics of adsorption process which involves change in enthalpy (ΔH°), change in entropy (ΔS°) and change in Gibb's free energy (ΔG°). The ΔG° are necessary to decide the process is spontaneous or non-spontaneous, such the free Gibb's energy when be negative value indicated that the reaction was spontaneous reaction at a certain temperature[50, 51]. In addition, if ΔH° is positive, the process is endothermic; if ΔH° is negative, the process is exothermic. The relationship between them was described as follows:

$$\Delta G° = \Delta H° - T\Delta S° \quad \text{Eq .3}$$

Where ΔG° denotes the change in Gibbs free energy (J/mol).

ΔH° denotes the change in enthalpy (J/mol)

ΔS° denotes the change in entropy (KJ/mol.K).

T equal the absolute temperature (K).

$$\ln K_d = \Delta S°/R - \Delta H°/R \quad \text{Eq .4}$$

In addition, the Gibbs free energy of adsorption is also linked to the equilibrium constant in the following way:

$$\Delta G° = -RT \ln K_d \quad \text{Eq .5}$$

Where R denotes the ideal gas constant (8.314 $J.mol^{-1}. K^{-1}$).

K_d: the thermodynamic equilibrium constant equal to (q_e/C_e) in (L/g).

The equation will be as follows if equation 4 is applied to equation 3.

2.7 Polymer adsorption cycles

Polymer recycling is an essential aspect of developing an ecologically friendly and cost-effective method. The polymer's efficiency after use was evaluated by reusing the polymer under ideal conditions for another adsorption process. The efficiency of the polymer after use was tested by reusing the polymer under optimal conditions for another adsorption process. This was accomplished by loading 100.0 g of adsorbents with 10 mL of 10.0 ppm lead nitrate solutions, adjusting the pH to 9.0, and shaking for 30 minutes at room temperature. The supernatant was centrifuged off the adsorbent, and residual lead ion concentrations were determined using FAAS. A 100 mg of adsorbent was suspended in a 10 ml water, the pH was reduced to 3.0 with 0.1 M solution of hydrochloric acid, and the solutions were shaken for 20 minutes to remove adsorbed metal ions before being decanted. These procedures were carried out five times to see whether the polymer used was still effective at removing lead ion from contaminated water.

The results for the polymers used are summarized in the following table:

Table 2.7

Recycling of polymer PAA/PBG-25

Number of reusing	**Concentration of lead (Pb^{2+}) after extraction**	**% adsorption**
1	0.5405	94.60
2	0.5759	94.24
3	0.6049	93.95
4	0.9920	90.08
5	2.491	75.09

Table 2.8

Recycling of polymer PAA/PBG-50

Number of reusing	**Concentration of lead (Pb^{2+}) after extraction**	**% adsorption**
1	0.5559	94.44
2	0.5593	94.41
3	0.6062	93.94
4	0.9088	90.91
5	1.6154	83.85

Table 2.9

Recycling of polymer PAA/PBG-75

Number of reusing	Concentration of lead (Pb^{2+}) after extraction	% adsorption
1	0.3819	96.18
2	0.4143	95.86
3	0.89	91.10
4	0.9521	90.48
5	1.6867	83.13

2.8 Real-world wastewater sample

A sewage sample was taken from a Jerico water source to test the efficiency of the polymer produced during the process of purifying water from hazardous metals. Three samples were generated, each containing 10 mL of sewage and three different polymer ratios. In each sample, one polymer type was mixed with sewage, and the best parameters (temperature, dosage, duration, and pH) were chosen. The ICP-MS technique was used to determine the types and amounts of metal ions present in the sample, which compared with the original sewerage water.

Chapter Three

Results and Discussion

3.1 Polymer Synthesis

As illustrated in Figure 3.1, the target polymers were produced by reacting PAA with phenyl biguanide in water as the solvent. Both reactants were dissolved in water at a specific ratio, the water was evaporated at 100°C, and the produced mixture of the two reactants was heated at 160°C for about 30 min. At 160 °C, lose a water molecule and generate an anhydride, which then reacts with phenylguinide to form the desired polymer., the reaction involves a loss of water molecule and the production of an amide bond. As can be observed from the structure, the polymer comprises functional groups amine, imine, and carboxyl, all of which have a high affinity for metals (Figure 3.2), meaning that the PAA-PBG should be able to remove metal ions quantitatively[52].

Figure. 3.1

Functionalization of PAA with phenyl biguanide (PAA-PBG)

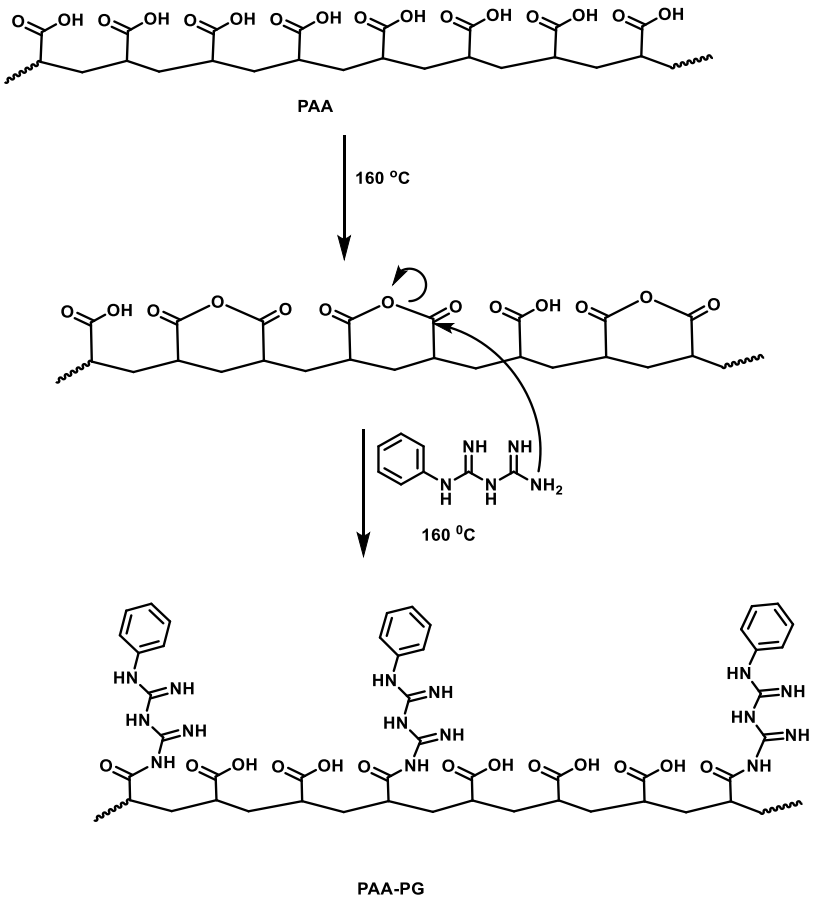
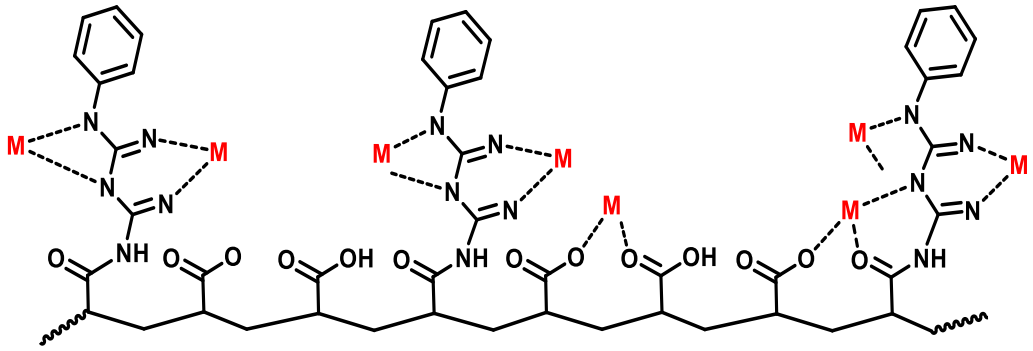


Figure. 3.2

Active site for metal bonding



3.2 Characterization of Materials

3.2.1 FT-IR Characterization

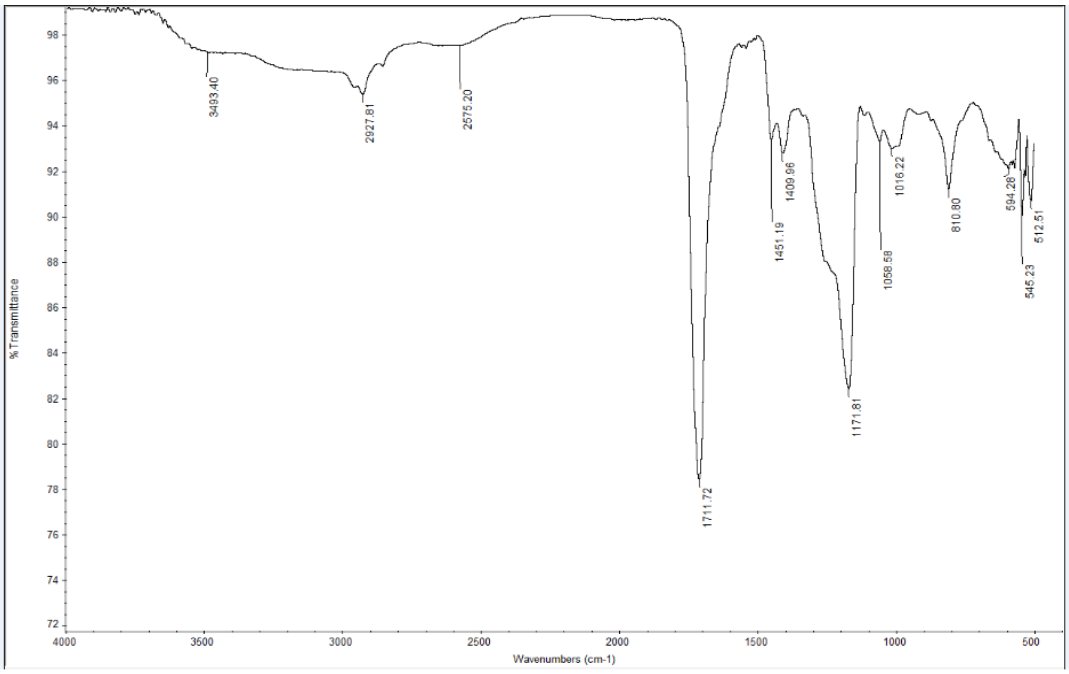
FT-IR was utilized to demonstrate the existence of various functional groups; in this case, it was used to detect the functional group for the polymer PAA-PBG, which was produced in various ratios.

3.2.1.1 FT-IR spectra for polyacrylic acid (PAA)

The FT-IR spectra of the synthesized polyacrylic acid is shown in Figure 3.3, reveals the presence of a band at 1711.72 cm^{-1} that corresponds to C=O stretching, a broad band at 3493 cm^{-1} that corresponds to O-H stretching, bands at 2927 cm^{-1} that correspond to C-H stretching, other bands at 1451.91 cm^{-1} and 1409.96 cm^{-1} that relate to C-O-H bending, and the bands at 1171.81 and 810.80 cm^{-1} belongs to C-O medium stretching and O-H bending respectively [53].

Figure 3.3

IR spectrum for the PAA

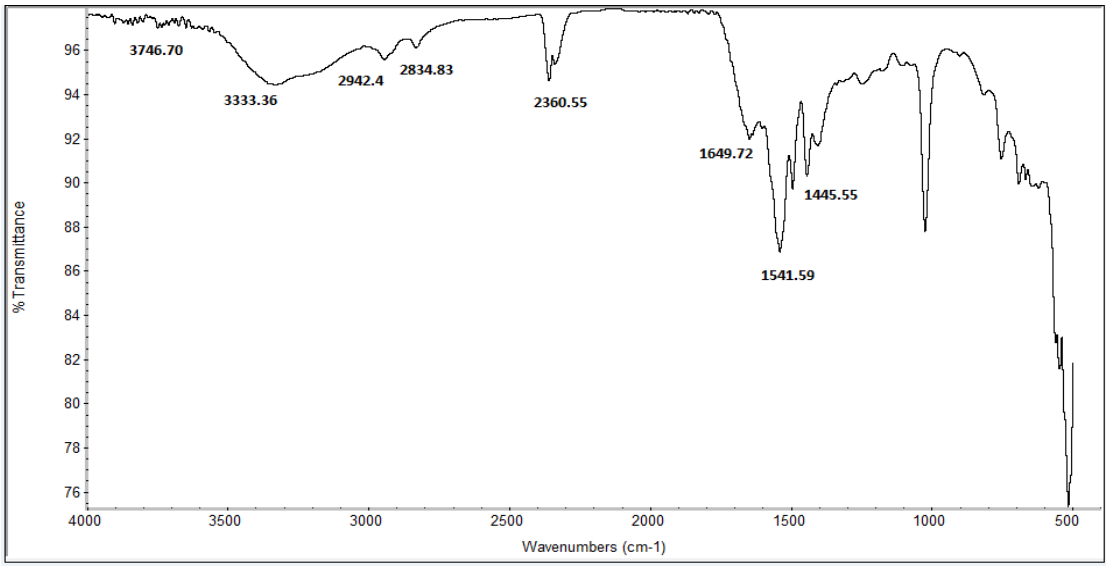


3.2.1.2 FT-IR spectra for the polymer (PAA/PBG-50)

The polymer (PAA-PBG) formed by binding PAA with phenyl biguanide in a 1:1 ratio comprises several groups that may be detected via FT-IR. The bands at 3746.70, 3333.36 cm^{-1} are related to O-H and N-H of amines and carboxyl groups. Bands at 2942.48 and 2834.83 cm^{-1} are related to C-H stretching, 1649.72 cm^{-1} is related to C=N, 1541.59 cm^{-1} is related to C=O amide and carboxyl bond, and 1445.55 cm^{-1} could be related to the C-N stretching[54].

Figure 3.4

IR spectrum for the polymer PAA/PBG-50

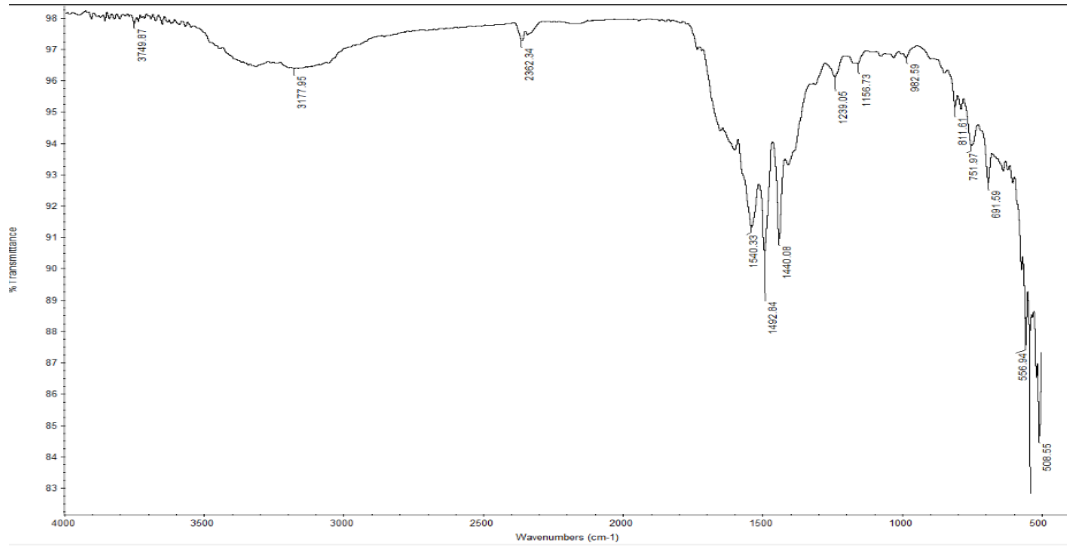


3.2.1.3 FT-IR spectra for the polymer PAA/PBG-25

The second polymer ratio was 1:3, which made combining 1.0 mole of PAA with 3.0 mole of phenyl biguanide. The produced polymer was also analyzed by FT-IR, the produced spectrum is shown in Figure 3.5, and the spectrum shows almost the same peaks of PAA/PBG-50, with small change in intensity of the peaks.

Figure 3.5

IR spectrum for the polymer PAA/PBG-25

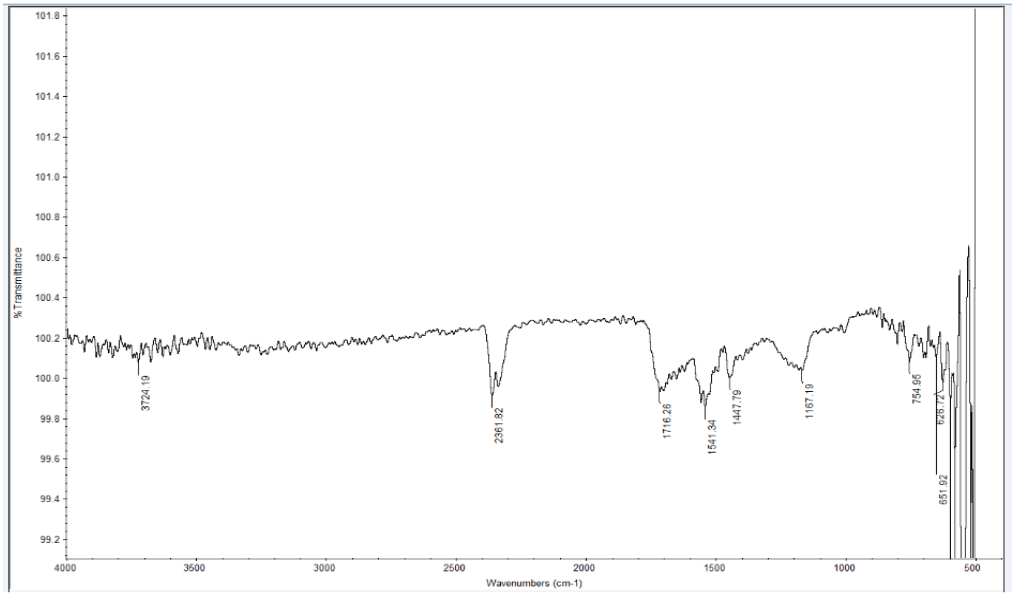


3.2.1.4 FT-IR spectrum for the polymer PAA/PBG-75

The third polymer ratio was 3:1, which made combining 3.0 mole of PAA with 1.0 mole of phenyl biguanide. The produced spectrum is shown in Figure 3.6. The peak is comparable in some readings, with a minor displacement and a change in chemical shift related to the reason for the change in polymer concentration. The principal peaks in the three various PAA/PBG proportions are the same, but the intensity of the peak varies, as the chemical shift. Does

Figure 3.6

IR spectra for the polymer PAA/PBG-75

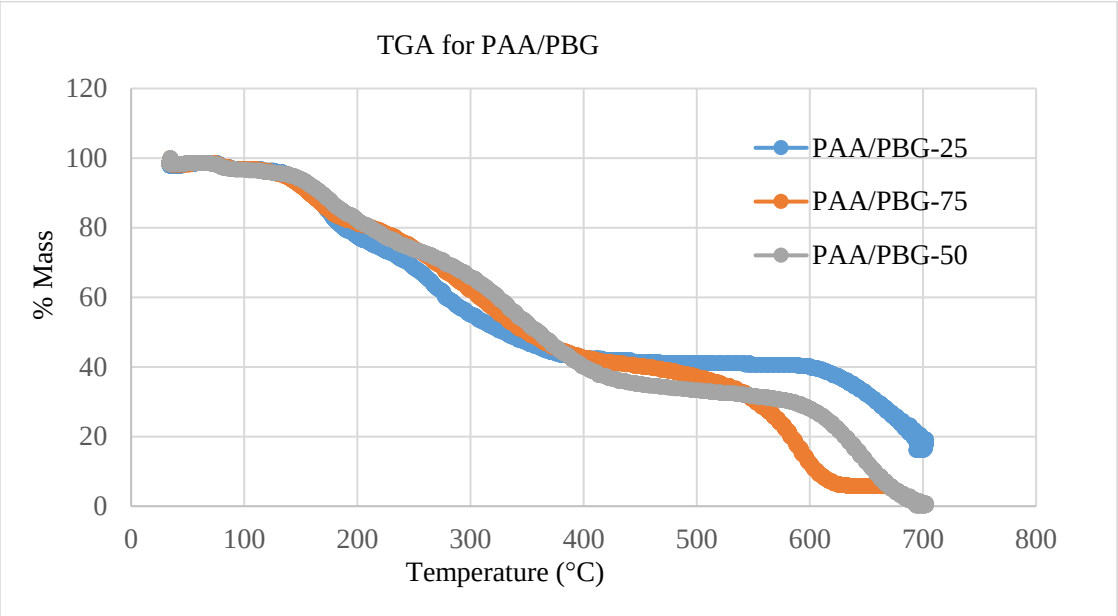


3.2.2 Thermal Gravimetric Analysis (TGA)

Thermal stability was determined via TGA analysis, which involved measuring the mass of each sample over time as a function of temperature and declaring the material thermal stability at high temperatures. The three polymers were subjected to TGA, and the results are shown in figures 3.7. The graph shows the mass losses for each polymer as the temperature rises, and the results show that the polymers are relatively stable. The first loss occurred at 155 ^{o}C, that could be related to decarboxylation. The second loss started at 300 ^{o}C, that could be relate to amid bond breaking and decomposition of biguanide. The polymer decomposed completely at about 580 ^{0}C.

Figure 3.7

Thermal Gravimetric Analysis for the polymer PAA/PBG-50, PAA/PBG-75 and PAA/PBG-25



3.3 Investigation of adsorption parameters

This study produced the PAA/PBG polymer to measure the extent at which the hazardous pollutants eliminated_from wastewater and to measure its efficiency in removing heavy elements. Metal residual analysis was performed using Atomic Absorption Spectrometer at 217 cm^{-1} (ICE 3000 series AA System, Thermo Scientific), and the percent of removal was calculated using the following equation:

$$\% \text{ adsorption} = (C_i - C_f/C_i) \times 100\% \qquad \text{Eq. 6}$$

Where: C_i = the heavy metal ion's initial concentration in solution (ppm).

C_f = Finial concentrations of heavy metal ion in solution (ppm).

The adsorption capacity q_e (mg/g) was evaluated under optimized reaction conditions at equilibrium for various ion concentrations, as stated in the equation:

$$q_e = (C_i - C_f/m) * V \qquad \text{Eq. 7}$$

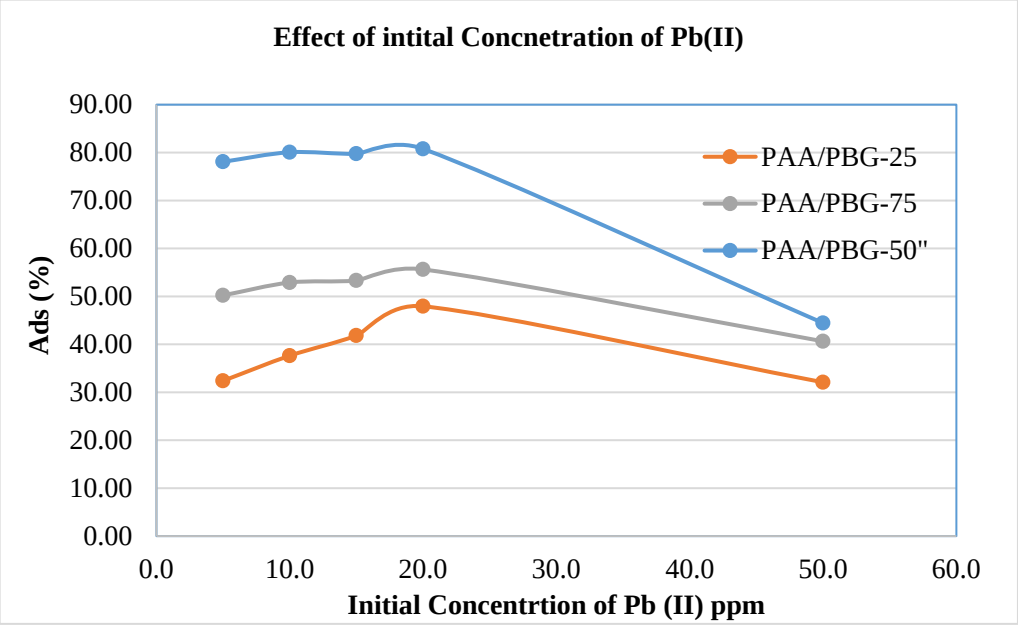
Where; V is the volume of the solution (L), and m is the mass of the adsorbent (g),

3.3.1 Lead initial concentration effect

While keeping other parameters constant such as pH, temperature, dosage, and contact time at (5.09, 25 °C, 20 mg , 30 min), the effect of initial lead concentration on percentage removal by PAA-PBG was investigated, with the percent adsorption increasing with increasing the initial concentration and reaching a maximum percentage when the initial concentration reached 20.0 ppm for the three polymer ratios, then declining, such as for PAA/PBG-50 the maximum percent of removal was 80.77 %, and for PAA/PBG-25 the maximum percent of removal was 80.77 percent and for PAA/PBG-75 the maximum percent of removal was 55.64 percent. The increase in the adsorption percent is explained by the fact that as lead ion concentrations have increased, more binding sites have become available. At low lead concentrations, most of lead ions were adsorbed into the polymer mass and bonded to the active sites, where they remain until all active sites are occupied. The absorption process reaches a peak at 20 ppm. Following this concentration, the adsorption process is slowed by coating the surface layer, preventing the absorption of further lead ions[55].

Figure 3.8

Effect of Lead concentration on the adsorption of Pb^{+2} by PAA/PBG



3.3.2 Contact Time Effect

All parameters constant such as pH, temperature, dosage, and initial ion concentration at (5.09, 25 °C, 20 mg, 20 ppm) were kept constant and the effect of contact time on lead (II) adsorption removal was studied, results are depicted in Figure 3.9 (in appendix B). The percent removal was steadily increased from 5 to 20 minutes, then after, the removal became almost constant for the three polymers. The results show that the highest adsorption performance was at 25 minutes since all active sites were occupied. Almost three polymer ratios followed the same pattern, with PAA/PBG-50 and PAA/PBG-75 readings nearly identical. However, the polymer PAA/PBG-25 at 5 min, the absorption ratio was less than the other ratio, which was 43.86%, and it increased to a reading close to other polymers at 20 min, after that time it began to stabilize like other polymers. As a result, when the contact time was short, the energy required to drive lead ions to the pores of the polymer was not produced, resulting in minimal adsorption. Because the lead ions were easily diffused to the pores and surface, they adsorbed faster when the contact duration was increased, resulting in better adsorption efficiency[56].

3.3.3 Effect of pH

The pH of the solution was a critical parameter that influenced the adsorption effectiveness and removal rate of lead ions from waste water because it influenced the binding site for heavy metals. PAA/PBG adsorbent contains -COOH and -NHR groups, which are the heavy metal's binding sites, changes in the pH of the solution altered the removal of lead ions and the % adsorption. The % removal was evaluated as a function of pH while other parameters constant such as temperature, dosage, and contact time at (25 °C, 20 mg, and 25 min) were kept constant. The results in Figure 3.10 (in appendix B) shows that under low pH ($pH \leq 5$, acidic conditions), since predominate form was the protonated form (-COOH and $-NH_2R^+$), which cannot bond to the lead ions. The % adsorption increased and improved as the pH climbed from 6 to 9, which was attributed to the alteration in the form of -COOH and -NHR groups in basic conditions to deprotonation form-COO^- and $-NR^-$, which had the ability to adsorb the lead ions due to the availability of binding sites. At a pH higher than 9 and further increases in pH value, the adsorption declined, Such an excessive amount of Na^{+1} has a negative effect on the interaction of Pb^{+2} with $-COO^-$ and $-NR^-$ [57].

3.3.4 Temperature Effect

Temperature influences the adsorption process depending on the chemical structure of the adsorbent and the physiochemical state of the solution. As a result, the optimal adsorption temperature for the three adsorbents was discovered, while other parameters such as initial concentration, dosage, and contact time (20ppm, 20 mg, and 25 min) were held constant, as well as the optimal pH for PAA/PBG-25 (8.5), PAA/PBG-50 (6), and PAA/PBG-75 (7) for all polymers. The percent adsorption from 15°C to 25°C is nearly identical, but when the temperature is increased from 25°C to 45°C, the percent adsorption decreases, indicating that there is no need to cool or heat the solution to adsorb the metal ion. That is, the adsorption occurred spontaneously at ambient temperature. The PAA/PBG-50 ratio had a higher percent adsorption value than the other polymer ratios, according to the figure 3.11 (in appendix B), Because of the nature of the polymer, which contains polyacrylic acid and phenyl biguanide in the same quantity [58].

3.3.5 Adsorbent Dosage Effect

The effect of dosage was crucial to investigate because it is related to the amount of active state available. Temperature, initial ion concentration, and contact time (15 °C, 20 ppm, and 25 min) remained constant, as well as the ideal pH for PAA/PBG-25 was (8.5), PAA/PBG-50 was (6.0), and PAA/PBG-75 was (7.0) in order to investigate the effect of Adsorbent Dosage on adsorption process. The figure 3.12 (in appendix B) shows that as the adsorbent dosage was increased, the absorption process increased until it reached maximum adsorption, after that it became constant, which is due to the fact that when the dosage was low, the active site at the surface was available and was occupied by the lead ions, and when the dosage was high, all active site at the surface was occupied by the lead ion and the access for interchangeable site for metal ions decreased. The % adsorption was higher at 15 mg, so 15 mg was the ideal adsorbent dosage. Due to the occupation of all active sites, the % removal of lead ions was reduced after this quantity of dosage and then stayed constant[59].

3.4 Optimum adsorption parameters

The Optimum adsorption parameters was shown in table 3.1 (in appendix A).

3.5 Adsorption isotherm

Two isotherm equations were utilized to examine the efficiency of the polymer to investigate the surface's ability to adsorb lead ions Langmuir and Freundlich [60].

3.5.1 Langmuir adsorption isotherm

The equilibrium between the adsorbate and adsorbent system is described by the Langmuir adsorption isotherm. Where adsorption of the adsorbate is restricted to a single molecular layer As a result, there is no contact between adsorbed molecules in Langmuir.

$$1/q_e = 1/(Q_{max}\, K_l\, C_e) + 1/Q_{max} \qquad \text{Eq .8}$$

Where;

C_e: the ion equilibrium concentration (ppm).

At equilibrium, q_e is the mass of adsorbate adsorbed per unit mass of polymer (mg/g).

Q_{max} is the adsorbent's monolayer adsorption capacity (mg/g).

K_l is the Langmuir affinity constant (L/mg) that is related to the adsorption energy.

Using the $\mathbf{R}_l$ constant, Langmuir's equation can be utilized to determine whether the adsorption process is attractive.

$$R_1 = 1/(1+K_1C_i) = 1 + 1/K_1C_i \qquad \text{Eq .9}$$

If $0<R<1$, adsorption is favorable, whereas if $R=1$, means the linear equation, also if R is greater than 1, this means that the adsorption is unfavorable.

Figure3.13 (in appendix B) represents Langmuir model for adsorption of Pb^{+2}on PAA/PBG.

Table 3.2 (in appendix A) represents Langmuir isotherms parameters for PAA/PBG.

3.5.2 Freundlich adsorption isotherm

The Freundlich isotherm can be used to describe adsorption processes on heterogonous surfaces.

The Freundlich isotherm has the following linear form:

$$\ln q_e = \ln K_f + 1/n \ln C_e \qquad \text{Eq .10}$$

Where;

K_f is the Freundlich constant, which is related to the adsorption capacity (mg/g).

The heterogeneity coefficient (g/L) is denoted by the letter n.

Figure3.14 (in appendix B) represents Freundlich model for adsorption of Pb^{+2}on PAA/PBG.

Table 3.3 (in appendix A) represents Freundlich isotherms parameters for PAA/PBG.

In all cases, R^2 values with the Langmuir isotherm are very near to 1. This suggests that the Langmuir isotherm regulates the adsorption of Lead (II) ions on the surfaces of polymers (PAA/PBG).

3.6 Adsorption Kinetics

To investigate the mechanism of adsorption, kinetic models such as pseudo-first order and pseudo-second order were employed as models to characterize the mechanism.

3.6.1 Pseudo-first order model

$$\ln(q_e - q_t) = \ln q_e - K_1 t \qquad \text{Eq .11}$$

K_1: the first-order rate constant (min^{-1})

q_e: the equilibrium amount of solute adsorbed per unit weight of adsorbent (mg/g).

q_t: the amount of solute adsorbed per unit weight of adsorbent at any given time (mg/g).

Figure3.15 (in appendix B) represents Pseudo-first order model for the adsorption of Pb^{+2} on PAA/PBG.

Table 3.4 (in appendix A) represents Adsorption kinetic parameters (pseudo-first order model) for the adsorption of Pb (II) on PAA/PBG.

3.6.2 Pseudo-second order model

$$t/q_t = 1/k_2 q^2_e + t/q_e \qquad \text{Eq .12}$$

K_2: the second-order rate constant (g mg^{-1} min^{-1})

q_e: the equilibrium amount of solute adsorbed per unit weight of adsorbent.

q_t: the amount of solute adsorbed per unit weight of adsorbent at any given time.

In every case, the obtained correlation coefficients (R^2) for the pseudo-second order were higher than the correlation coefficients (R^2) for the pseudo-first order. The pseudo second order kinetic adsorption model matches the adsorption process effectively.

Figure3.16 (in appendix B) represents Pseudo- second order model for the adsorption of Pb^{+2} on PAA/PBG.

Table 3.5 (in appendix A) represents Adsorption kinetic parameters (pseudo- second order model) for the adsorption of Pb (II) on PAA/PBG.

3.7 Adsorption Thermodynamics

Adsorption experiments involve thermodynamic considerations to determine the spontaneity and feasibility of such processes. Measurable thermodynamic parameters like temperature equilibrium constant, as well as their non-measurable equivalents like Gibbs free energy change, enthalpy, entropy, and so on, are critical design factors. Using the Van't Hoff plot's thermodynamic equation. The slope and y-intercept of the graph of In ($K_{d)}$ versus (1/T) can be used to compute the thermodynamic parameters ($\Delta H°$ and $\Delta S°$) of lead (II) ion absorption on PAA/PBG, figure 3.17 (in appendix B) represents Van't Hoff plot for the adsorption of Pb (II) on PAA/PBG.

The table 3.6 (in appendix A) shows that because $\Delta G°$ is negative, Pb (II) adsorption on PAA/PBG adsorbent is spontaneous. Exothermic ($\Delta H°<0$) and non-spontaneous ($\Delta S°<0$) processes are also involved. The negative value of $\Delta S°$ also indicates that the adsorbent's internal structure does not change much during the adsorption process.

3.8 Adsorption on a Real samples of sewage

Sample of sewage water was collected from various cities in Palestine, and a mixture was constructed to test the polymers efficiency in adsorbing of harmful metals. Table 3.7, 3.8 and 3.9 (in appendix A) summarizes the metal ion concentrations in each of the sewage samples before and after employing the polymers. ICP-MS was used to determine the amounts of metal ions.

As shown in the tables, the polymers showed excellent efficiency for toxic metals ion such Pb (II), V (IV), Zinc (II), Mn (II), Cr (VI), Cd (II) and others.

3.9 Polymer adsorption cycle

The purpose of the regeneration experiment was to determine the number of times the polymers may be employed and their efficiency. The experiment was carried out five times with the identical adsorbent, with the results displayed in fig 3.18 (in appendix B). As the number of regeneration cycles rises, the adsorption efficiency falls [61].

3.10 Conclusion

In this work, polyacrylic acid (PAA) was synthesized to make the target polymers, which were made by reacting PAA with phenyl biguanide in a condensation process that results in the loss of a water molecule and the production of an amide bond. The polymer is manufactured in three ratios, The structure of the three generated polymers was identified using FT-IR, and their thermal stability was also investigated. Adsorption settings such as time, temperature, adsorption dosage, metal ion start concertation, and pH values have been determined to provide the greatest adsorption efficiency for the polymers. The PAA/PBG developed in this study exhibited excellent results in adsorbing heavy metals from wastewater, with the maximum adsorption result for lead being 93.1927% for PAA/PBG-75 at pH = 7, weight of dose = 15 mg, and temperature 15°C. The thermodynamic parameters of lead (II) adsorption are spontaneous $\Delta G°<0$ and exothermic process ($\Delta H°<0$). The adsorption process was well-fit by the pseudo second order kinetic adsorption model.

3.11 Recommendations

- Other components can be added to the polymer to improve its absorption effectiveness.
- Development can also be accomplished by preparing alternative ratios and testing their efficiency in the process of harmful chemical absorption.
- Polymer applicability can be investigated in other sectors, including as medicine and the purification of materials used in industry.

List of Abbreviations

Abbreviation	Meaning
PAA	Polyacrylic acid
PBG	Phenyl biguanide
WHO	World Health Organization
R^2	Correlation coefficient (regression coefficient, fitting coefficient)
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
FAAS	Flame Atomic Adsorption Spectrometer
% Ads.	Percent Adsorption
Soln.	Solution
PAA/PBG	Polymer of polyacrylic acid/phenyl biguanide
Conc.	Concentration
Fig.	Figure
Wt.	Weight
Temp.	The temperature (^oC)
C_e	Concentration of metal ions in the sample solution after treatment at equilibrium(mg/L)
C_i	Initial concentration of metal ions in the sample solution (mg/L)
q_e	The mass of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g)
q_t	Amount of adsorbate per unit mass of adsorbent at time t (min)
K_1	The pseudo-first order rate constant
K_2	The pseudo-second order rate constant
K_f	Freundlich constant
K_l	Langmuir isotherm constant (L/mg)
K_d	The thermodynamic gas constant
1/n	Dimensionless Freundlich constant giving an indication of how favorable the adsorption process
R_l	Dimensionless constant separation factor
$\Delta H°$	The change in enthalpy
$\Delta S°$	The change in entropy
$\Delta G°$	The change in Gibbs free energy
R	The universal gas constant
T	The Absolut temperature

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Appendices

Appendix A

Tables

Table 3.1

Optimum Adsorption Parameters

Optimum condition/ Adsorbent	**Initial lead concentration (ppm)**	**Parameters pH, Temp (°C), Contact time (min), and Adsorbent dosage (mg)**
PAA/PBG-50	20	6 , 15, 25, and 15
PAA/PBG-75	20	7, 15, 25, and 15,
PAA/PBG-25	20	8.5, 15, 25 and 15

Table 3.2

Langmuir Adsorption isotherms parameters for PAA/PBG.

Adsorbent	**Langmuir R^2**	**Q_{max}**	**K_1**	**R_1**
PAA/PBG-25	0.9603	30.769	0.029	0.632
PAA/PBG-50	0.9538	157.438	0.050	0.50
PAA/PBG-75	0.9859	294.117	0.0069	0.878

Table 3.3

Freundlich Adsorption Isotherms parameters for PAA/PBG.

Adsorbent	**Freundlich R^2**	**n**	**K_f**
PAA/PBG-25	0.8973	1.0159	1.2808
PAA/PBG-50	0.7617	2.0768	1.2741
PAA/PBG-75	0.9464	1.1977	2.8402

Table 3.4

Adsorption kinetic parameters (pseudo-first order model) for the adsorption of Pb (II) on PAA/PBG.

Adsorbent	Adsorption kinetic pseudo-first order model			
	R^2	Theo. q_e	Exp. q_e	K_1
PAA/PBG-25	0.9208	19.1778	16.15	0.0174
PAA/PBG-50	0.7922	32.3098	25.29	0.0038
PAA/PBG-75	0.813	22.25468	14.30	0.0048

Table 3.5

Adsorption kinetic parameters (pseudo-second order model) for the adsorption of Pb (II) on PAA/PBG.

Adsorbent	Adsorption kinetic pseudo-second order model			
	R^2	Theo. q_e	Exp. q_e	K_2
PAA/PBG-25	0.9371	19.1778	13.072	0.002104
PAA/PBG-50	0.9972	32.3098	10.111	0.003028
PAA/PBG-75	0.9969	22.25468	10.121	0.037139

Table 3.6

The thermodynamic parameters for the adsorption of Pb (II) on PAA/PBG.

Adsorbent	Temp.(K)	Adsorption Thermodynamics		
		ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol.K)
PAA/PBG-25	288	-1.82132	-12.16089	-0.355897*10^-3
	293	-1.78188		
	298	-1.63543		
	318	-0.80301		
PAA/PBG-50	288	-7.21146	-34.55215	-0.938817*10^-3
	293	-7.1298		
	298	-6.95017		
	318	-4.53816		
PAA/PBG-75	288	-1.15958	-4.459962	-0.113644*10^-3
	293	-1.13106		
	298	-1.11659		
	318	-0.82963		

Table 3.7

The Center of Analyses for the Conc. of Toxic Metals' Results for PAA/PBG-50.

Metal Ions	Conc. Before (ppm)	Conc. Mean (PAA/PG-50) (ppm)	% adsorption (PAA/PG-50)
Al	3478	83.5	97.59
Ba	96.69	68.73	28.91
Be	0.17	0	100
B	267.91	237.28	11.43
Cd	0.66	0.02	96.96
Cr	28.9	8.06	72.11
Co	2.03	0.51	74.87
Cu	91.55	22.56	75.35
Fe	4574.97	308.63	93.25
Pb	10.43	6.22	40.36
Mn	100.96	20.82	79.37
Ni	19.51	8.06	58.68
Tl	0.1	0.002	98
V	20.03	5.06	74.73

Table 3.8

The Center of Analyses for the Conc. of Toxic Metals' Results for PAA/PBG -25.

Metal Ions	Conc. Before (ppm)	Conc. Mean (PAA/PG-25) (ppm)	% adsorption (PAA/PG-25)
Al	3478	85.24	97.55
Ba	96.69	66.73	30.98
Be	0.17	0.01	94.12
B	267.91	170.77	36.26
Cd	0.66	0.02	96.97
Cr	28.9	6.5	77.51
Co	2.03	0.35	82.76
Cu	91.55	20.67	77.42
Fe	4574.97	249.42	94.55
Pb	10.43	2.51	75.93
Mn	100.96	17.26	82.90
Ni	19.51	6.78	65.25
Tl	0.1	0.02	80.00
V	20.03	2.09	89.57

Table 3.9

The Center of Analyses for the Conc. of Toxic Metals' Results for PAA/PBG-75.

Metal Ions	**Conc. Before (ppm)**	**Conc. Mean (PAA/PG-75) (ppm)**	**% adsorption (PAA/PG-75)**
Al	3478	103.69	97.02
Ba	96.69	58.85	39.14
Be	0.17	0.02	88.24
B	267.91	135.87	49.29
Cd	0.66	0.02	96.97
Cr	28.9	6.19	78.58
Co	2.03	0.36	82.27
Cu	91.55	20.84	77.24
Fe	4574.97	164.22	96.41
Pb	10.43	0.71	93.19
Mn	100.96	14.32	85.82
Ni	19.51	4.49	76.99
Tl	0.1	0.01	90.00
V	20.03	0.66	96.70

Appendix B

Figures

Figure 3.9

Effect of Contact Time on the adsorption of Pb^{+2} by PAA/PBG

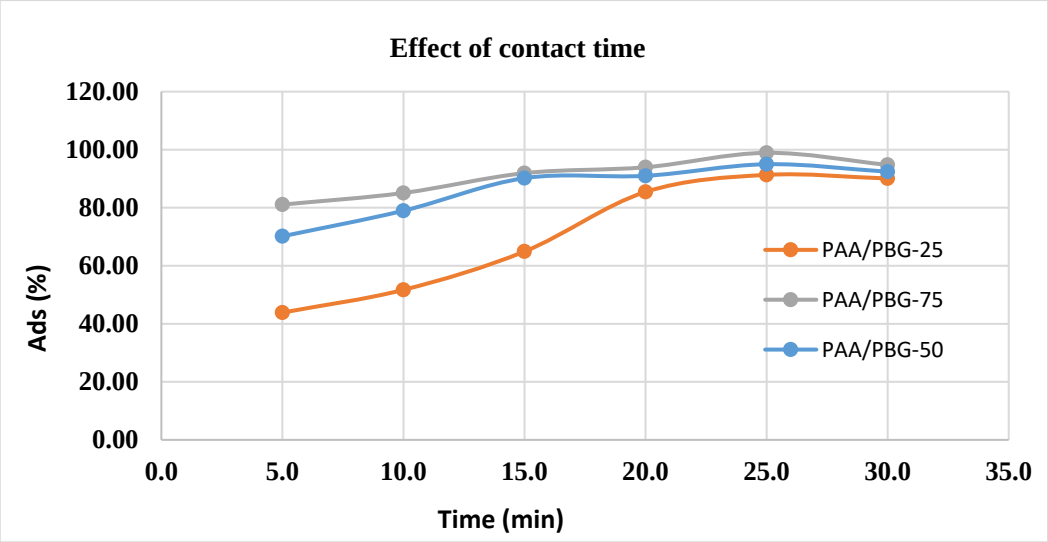


Figure 3.10

Effect of pH value on the adsorption of Pb^{+2} by PAA/PBG

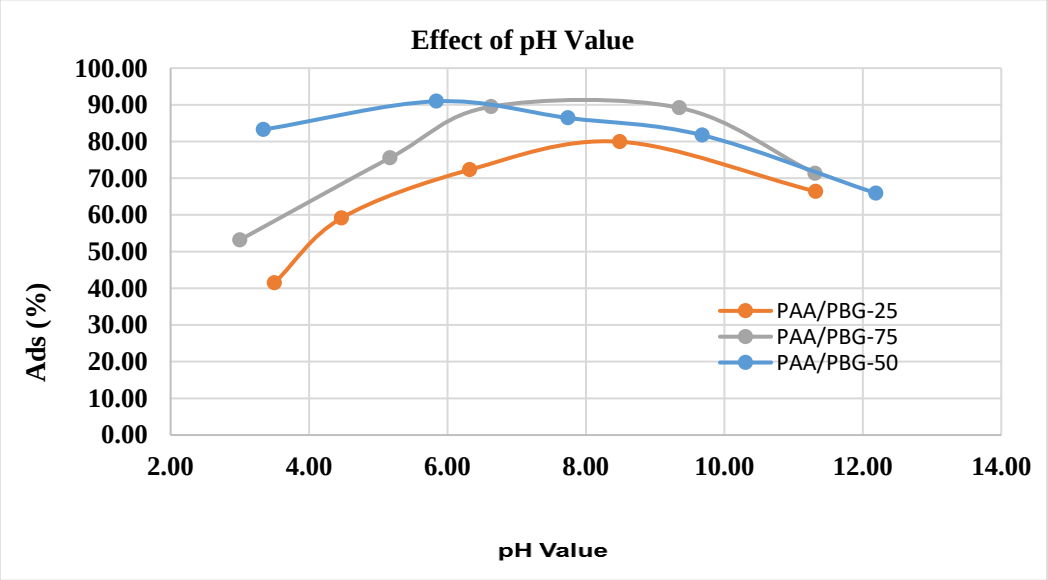


Figure 3.11

Effect of Temperature on the adsorption of Pb^{+2} by PAA/PBG

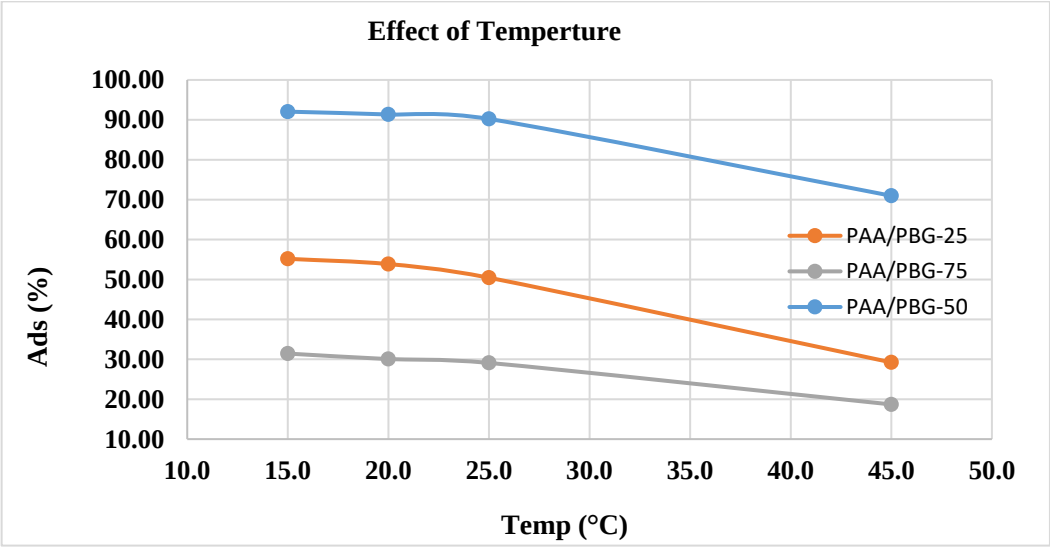


Figure 3.12

Effect of Adsorbent Dosage on the adsorption of Pb^{+2} by PAA/PBG

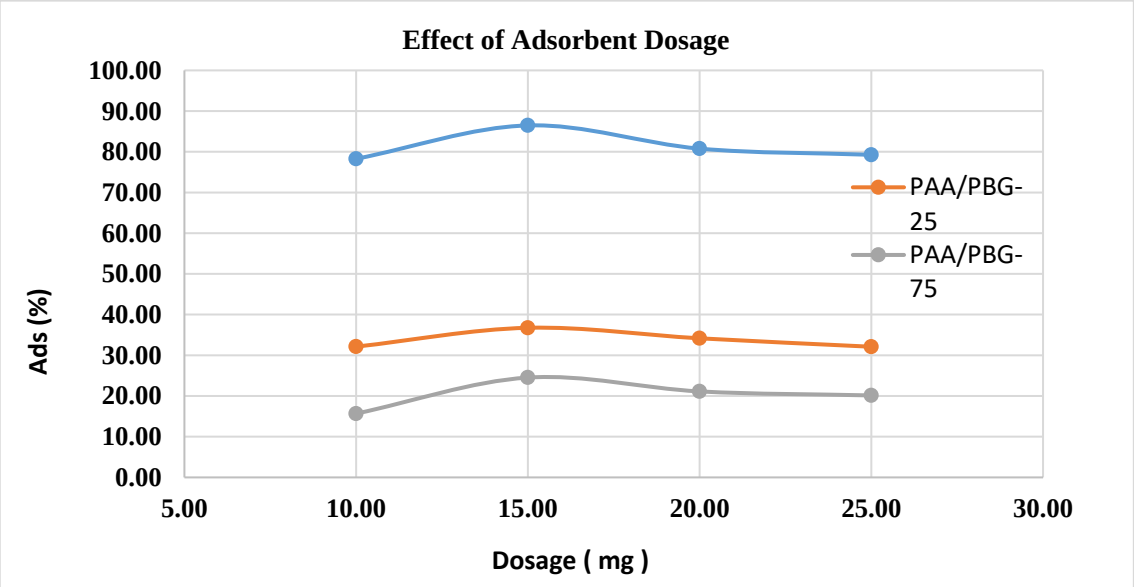


Figure 3.13

Langmuir model for adsorption of Pb^{+2} on PAA/PBG

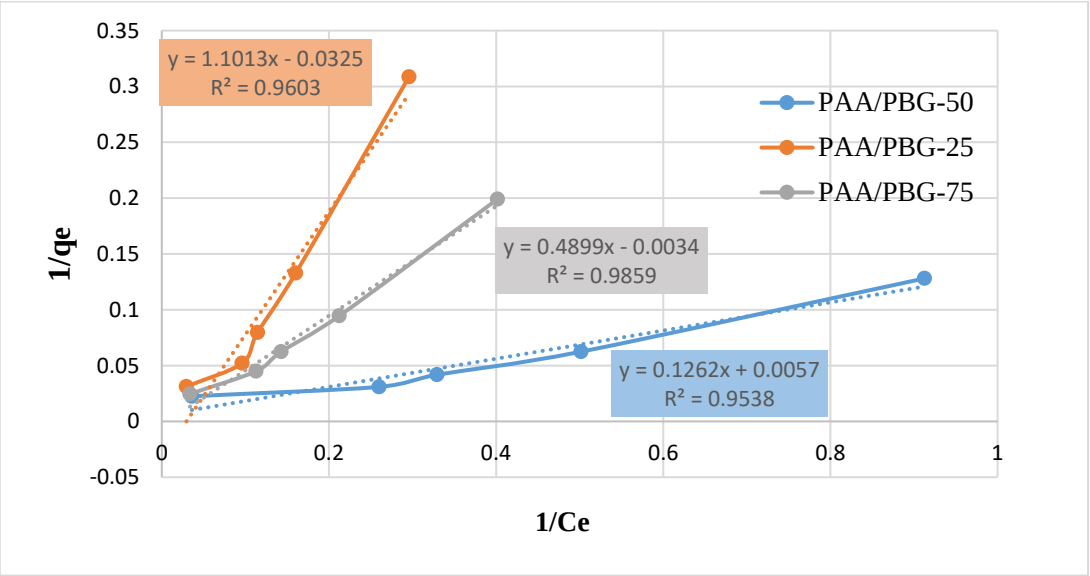


Figure 3.14

Freundlich model for adsorption of Pb^{+2} on PAA/PBG

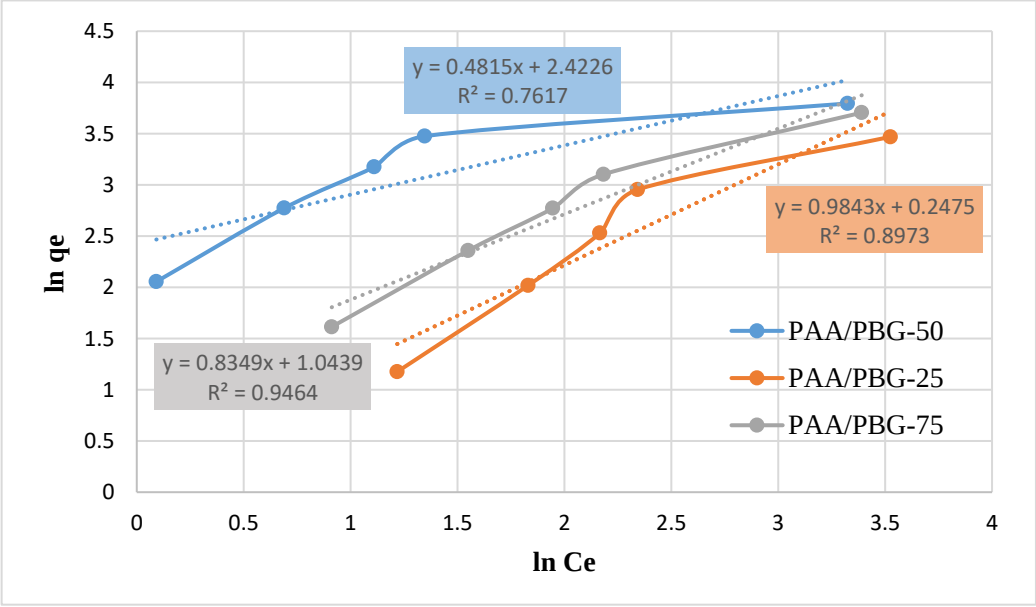


Figure 3.15

Pseudo-first order model for the adsorption of Pb^{+2} on PAA/PBG.

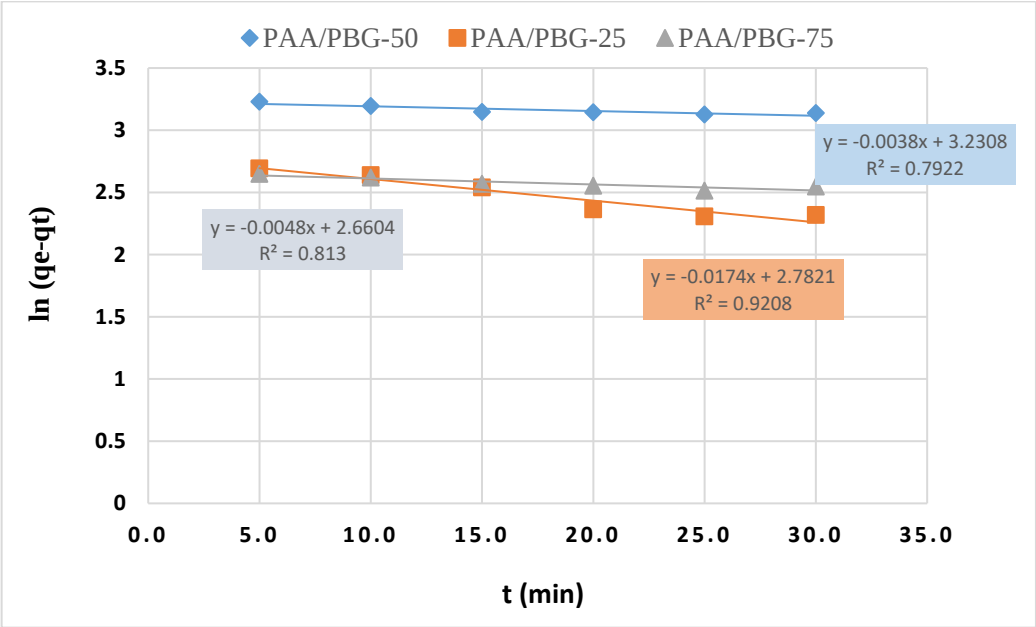


Figure 3.16

Pseudo-second order model for the adsorption of Pb^{+2} on PAA/PBG

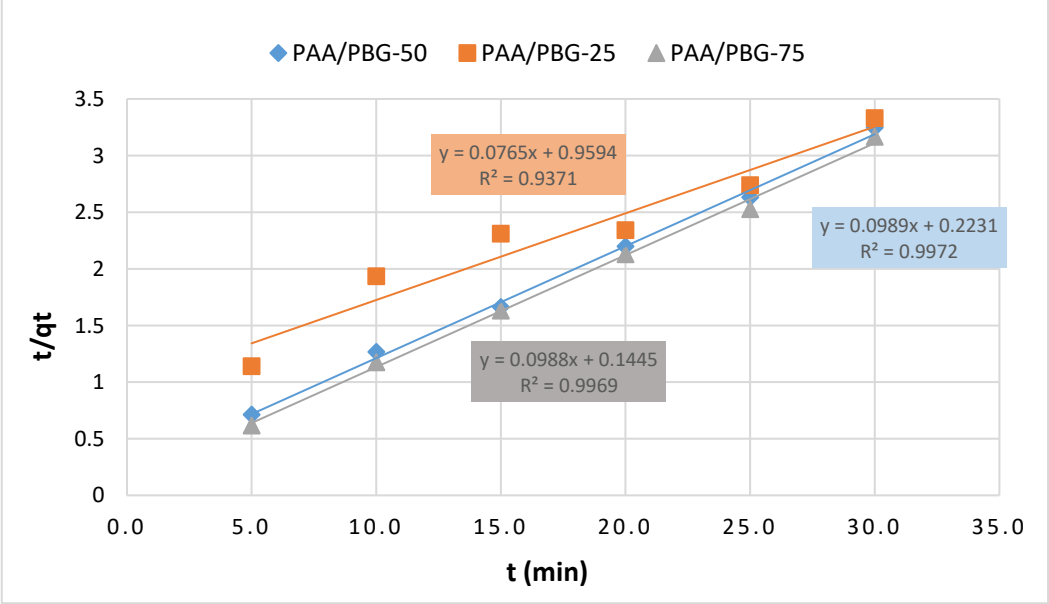


Figure 3.17

Van't Hoff plot for the adsorption of Pb (II) on PAA/PBG

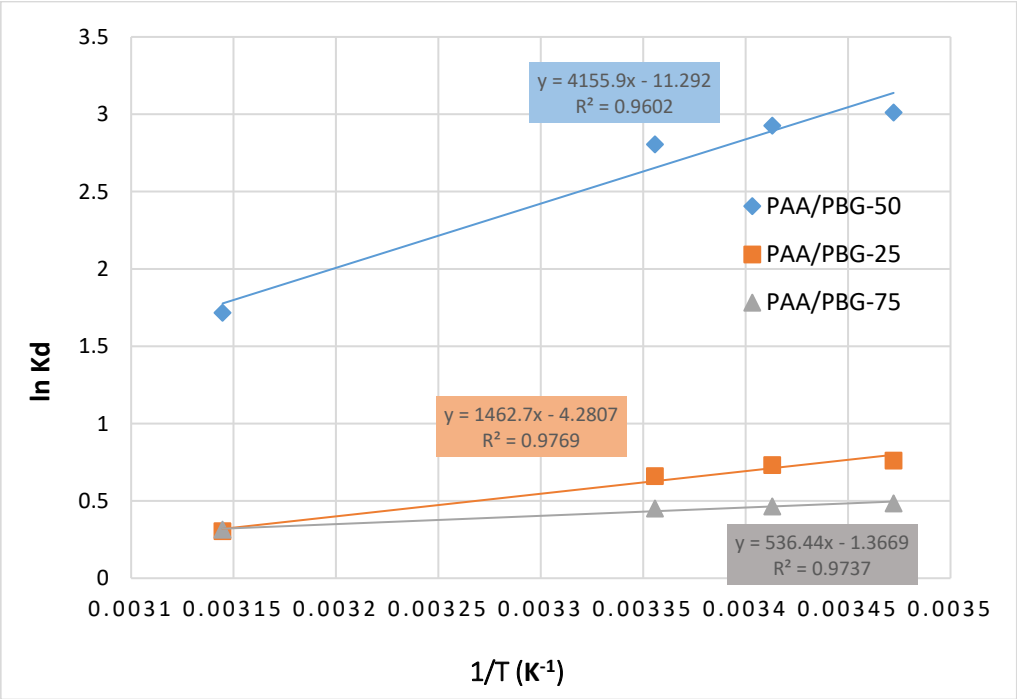
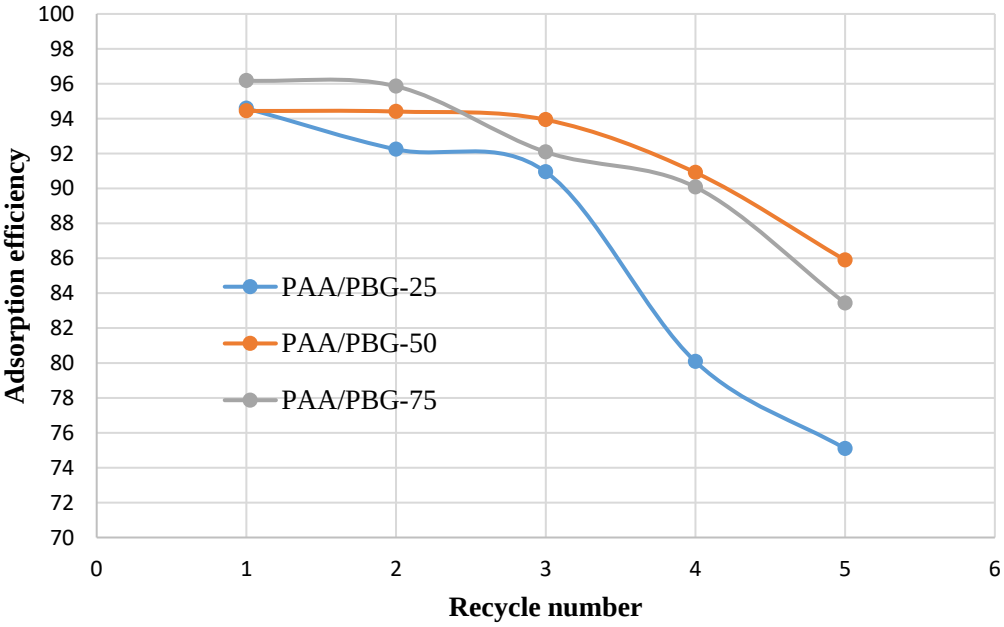


Figure 3.18

The three polymers' regeneration and adsorption efficiency



جـامعـــة النجاح الوطنية

كليـــة الدراســـات العليـــا

مبلمرات البولي اكريلات المعدلة باستخدام الفينيل بيجوانيد وتحضير وتطبيق في تنقية المياه من المعادن السامة

إعداد

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إشراف

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

2022

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الملخص

الخلفية: تلوث المياه هو تغيير في نوعية المياه بطريقة مباشرة او غير مباشرة وهذا التغيير يؤثر بشكل سلبي على الكائنات الحية ويلحق الضرر فيها. وأصبح التلوث في إمدادات المياه مصدرا رئيسيا للقلق. وقد حظي تلوث المعادن الثقيلة، مثل الكادميوم والرصاص والزئبق والزرنيخ، باهتمام كبير في الآونة الأخيرة بسبب سميته للحياة المائية والبشر. المعادن الثقيلة خطرة لأنها تتراكم أحيائياً. ويعرف التراكم الأحيائي بأنه زيادة في تركيز مادة كيميائية في كائن بيولوجي مع مرور الوقت. تميل العديد من الدراسات الحديثة إلى تطوير طرق مناسبة لإزالة هذه المواد السامة من المياه الملوَّثة.

الهدف: الهدف من هذه الدراسة هو تحضير بوليمر مع مجموعات وظيفية ذات صلة عالية بأيونات المعادن وتطبيقها في تنقية المياه من المعادن السامة وأن تكون طريقة التحضير فعالة وبسيطة من حيث التكلفة.

المنهجية: تم تحضير البوليمر عن طريق خلط حمض البولي اكريلات مع بيجوانيد الفينيل في الماء بثلاث نسب مختلفة. تم تحليل البوليمرات عن طريق TGA and FT-IR وتم فحص نشاط البوليمرات وقدرتها على امتصاص أيونات الرصاص (Pb^{2+}) وتم فحص العوامل التي تؤثر على عملية الامتزاز مثل كتلة المواد الماصَّة وتركيز أيونات المعادن في المحلول المائي ودرجة الحرارة ودرجة الحموضة والوقت. حيث أنه من خلال تجارب مختلفة تم اختيار أفضل الظروف وانسبها لتكون عملية الامتزاز وكفاءة البوليمر في اعلى مستوى.

النتائج: أظهر بوليمر PAA/PBG الذي تم تحضيره في هذه الدراسة نتائج ممتازة في امتصاص المعادن الثقيلة من المياه المستعملة، وكانت النتيجة القصوى للامتصاص بالنسبة للرصاص 93.19% بالنسبة PAA/PBG–75 عند pH = 7، ووزن الجرعة = 15 ملغم، ودرجة الحرارة 15 درجة مئوية. كما أظهرت الديناميكا الحرارية والدراسات الحركية أن إزالة الرصاص (Pb^{+2}) باستخدام هذه البوليمرات مناسبة وتتبع نموذج الامتزاز من الدرجة الثانية. وتم تصنيف عملية الامتزاز على انها عملية تلقائية على درجات الحرارة المحددة وطاردة للحرارة وإنها عملية ترابطية ولا يوجد تغيير في هيكل البوليمر اثناء عملية الامتزاز.

الخلاصة: تم تقييم كفاءة الامتزاز للبوليمرات الثلاثة على عينة مياه الصرف الصحي. أظهرت البوليمرات الثلاثة إزالة كمية لمعظم أيونات المعادن السامة الموجودة في مياه الصرف الصحي مثل الرصاص والزئبق. تم تحضير البوليمرات في هذه الدراسة وكانت طريقة التحضير بسيطة وفعالة لإنشاء مادة ماصة منخفضة التكلفة ذات كفاءة ممتازة ضد المعادن.

الكلمات المفتاحية: تلوث المياه، بوليمر، تنقية المياه، بيجوانيد الفينيل، حمض البولي اكريلات، الرصاص، المعادن الثقيلة، عملية الامتزاز.