An-Najah National University

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Polyacrylic Acid With Amide Crosslinks Decorated With Silver Nanoparticles: Synthesis And Application In Waste Water Treatment

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This Thesis was defended successfully on 5 /5/ 2019, and approved by:

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Dedication

I dedicate this thesis to my wonderful parents for their love, unfailing support and continuous encouragement throughout my life. Also to my lovely sister Saba and my brothers, whom I am truly grateful for having in my life.

Acknowledgments

I would like to express my gratitude for everyone who helped me in this research starting with endless thanks for my supervisor Prof. Shehdeh Jodeh and Dr.Othman Hamed their professional advice, guidance, and continued support throughout this project. I appreciate all his contributions of time, support and ideas. Many thanks to whom our thanks go as well to them for their follow up the project.

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Furthermore, I would like to thank my family for supporting me all the o way, and I wish that I made them proud of me and my hard work.

Finally, I won't also forget to present my special thanks for my friends who have been in my side during this research.

الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحت عنوان:

Polyacrylic Acid With Amide Crosslinks Decorated With Silver Nanoparticles: Synthesis And Application In Waste Water Treatment

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 قبل لنيل أية درجة علمية أو بحثية لدى أية مؤسسة تعليمية أو بحثية أخرى.

Declaration

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

Student's Name: **اسم الطالب:**

Signature: **التوقيع:**

Date: **التاريخ:**

List of contents

List of Tables

List of Figures

List of Abbreviations

Symbol	Abbreviation
AA	Acrylic Acid
PAA	Polyacrlic Acid
NPs	Nanoparticles
PhCs	Pharmaceutical compounds
WWTP	Waste water treatment plant
DW	Distilled Water
R^2	Correlation coefficient
UV	Ultra-Violet
IR	Infrared
C_e	The equilibrium concentration of the adsorbate (ppm).
C_o	The initial concentration of the adsorbate (ppm).
q_e	The amount of adsorbate per unit mass of adsorbent (mg/g).
b	The Langmuir affinity constant (L/mg).
Q_o	The adsorption capacity at equilibrium (mg/g).
V	The volume of the solution (L).
M	The mass of the adsorbent (g).
K_F	The Freundlich constant related to adsorption capacity (mg/g).
q_t	The mass of adsorbate per unit mass of adsorbent at time t (mg/g).

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Abstract

In this study, Polyacrylic Acid with amide crosslinked (PAA) was decorated with Silver Nanoparticles (NPs). The resulting polymers PAA and PAA with silver NPs (PAA-Ag) were characterized by IR spectrophotometer. Both were used as adsorbents for Lead(II) and 5-Fluorouracil from aqueous solutions. The adsorption efficiency of each adsorption process was investigated as a function of adsorbent dose, adsorbate concentration, contact time, temperature and pH value.

Tendency of prepared PAA-Ag for extracting Pb(II) from water was evaluated and compared to PAA. It was observed that adsorption of lead on PAA-Ag and PAA was affected by the amount of PAA-Ag until the equilibrium level. The optimum pH value for lead adsorption was *7.33* and *4.7* for PAA-Ag and PAA respectively and the equilibrium was established within the first 10 min adsorption was done at room temperature. It was found that Lead adsorption kinetics has followed pseudo-second-order. Experimental data were analyzed using two model equations: Langmuir and Freudlinch and it was found that the data fitted well with Freundlich isotherm model.

Meanwhile, PAA-Ag was used as adsorbents for the removal of 5-FU from aqueous solution. The concentration of 5-FU in the supernatant was

measured by UV-vis spectrophotometer. It was observed that adsorption of 5-FU was affected by the amount of PAA-Ag until the equilibrium level. The optimum pH value for 5-FU adsorption was 8.18 and the equilibrium was established in 5 min. It was also evident that the adsorbed 5-FU was decreasing as the concentration of 5- FU was increased in solution. It was found that 5-FU adsorption kinetics has followed pseudo-second-order. And it was found that the data fitted well with Langmuir isotherm model.

CHAPTER 1
Introduction

1.1 Background

Water is the most precious natural substance for all living organisms. The major drinking water sources including ground water, lakes, reservoirs and sea water struggle enormous challenges both old and new. The fast growing water demands due to population growth, modernization, global climate change and economic growth with poor water management which's severely limited the water supply.[1,3]

While reliable access to clean and affordable water is the most basic human need.[2] Various type of untreated pollutants including heavy metals, organic substances, petroleum refining, paper and textile[8] involve processes that produce a wide variety of effluents discharging into aquatic system and their adverse environmental and health effects are investigated over the years.[5,6] Wastewater from these types of effluents typically has high levels of colloidal suspension and dissolved organic pollutants.[4] Researchers have utilized on finding an efficient treatment of these water problems by using numerous advanced methods including reverse osmosis, ion-exchange and membrane separation processes[7] and adsorption onto different adsorbents. The later one is considered as the most effective technologies.[27]

Always, there is a continuing need for the development of efficient, cost effective, and environmentally friendly techniques for water treatment.[4] So, in this work we intend to develop new, simple, feasible and economical

polymeric material for removing metals and organic substances from wastewater in effective manner.

1.2 Sources of water pollution

Water pollution is the presence of excessive amount of pollutants in water bodies due to human or industrial activities. Emergent pollutants such as pesticides, synthetic fertilizers, chemical compounds like dyes, heavy metals, hormones, personal care products, detergents, pharmaceuticals product directly or indirectly enter into the ecosystems have adverse effects on human health and aquatic systems.[4,5]

The discharge of untreated pollutants, chemicals and hazardous waste from domestic, agricultural and industrial sources into freshwater sources such as rivers, lakes, oceans and groundwater aquifers cause change in the physical, chemical and biological properties of water.[4]

1.2.1 Heavy metals

Heavy metals defined as metallic elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0.[9]

They are naturally occurring elements that are found throughout the earth's crust, these elements play an essential role in biochemical and physiological functions in plants and animals, they are needed in various oxidation–reduction reactions and also they are important constituents of several key enzymes.[10]

Heavy metal pollution is a global problem, although severity and levels of pollution differ from one metal to another. The environment is continuously exposed to varied loads of heavy metals from anthropogenic activities[11] such as mining and smelting operations, industrial production and use, domestic and agricultural use of metals and metal-containing compounds and it can also occur through metal corrosion, atmospheric deposition and soil erosion of metal ions.[10]

Although crucial biological functions of heavy metals in the living organism, their chemical coordination and oxidation-reduction properties have given them an additional benefit, that they can escape control mechanisms such as transport and binding to required cell constituents. These metals bind with protein sites which are not made for them by displacing original metals from their natural binding sites causing DNA damage, protein modification and others.[11]

Heavy metals are also considered as trace elements, they are ubiquitous, non-biodegradable and tend to accumulate in living organisms. Their toxicity depends on several factors including the dose, route of exposure, and chemical species, as well as the age, gender, genetics, and nutritional status of exposed individuals.[10] Because of their high degree of toxicity, arsenic, cadmium, chromium, lead, and mercury rank among the priority metals that are of public health significance. They are considered as systemic toxicants since they are known to induce multiple organ damage even at low concentrations. These elements classified as human carcinogens

according to the US Environmental Protection Agency and the International Agency for Research on Cancer.

To protect human health from the adverse effects of heavy metals especially in drinking water, international organizations set standards using individual metals. These safety standards are set with the assumption that there is a minimal interaction between metal or chemical species and, even if there are interactions, the degree will not exceed safety factors applied.[10,11]

1.2.1.1 Lead

Lead is a naturally occurring bluish-gray metal present in small amounts in the earth's crust metals with the atomic number and the atomic weight equal 82 and 207.19 respectively.[13]

Lead is a persistent metal which is commonly used in various industrial processes. It is toxic to living systems and may stay in the environment for a prolonged period of time. The maximal lead level in tap water should not exceed 10 ppm. [11]

The major sources of lead entering an ecosystem are atmospheric lead that results primarily from automobile emissions, lead-acid batteries, paint chips, fertilizers, pesticides and many other industrial products.[12,30] It is known that lead accumulates in the soil especially that with a high organic content. Hence, displacing many other metals from the binding sites on the organic matter and hindering the chemical breakdown of inorganic soil fragments. As a result, lead in the soil may become more soluble, thus

more readily to be taken up by plants.[33]

This toxic metal can enter the human body through uptake of water, air and food containing lead. For example, lead can enter drinking water through corrosion of pipes. This is more likely to be happened when water is slightly acidic.[12,33] Lead can cause several adversely health effects like: disruption of nervous systems, causes damage to liver, kidney, reproductive system, basic cellular processes, brain functions.[9]

1.2.2 Pharmaceuticals

In recent years, Pharmaceutical Compounds (PhCs) have gained increasing attention, particularly as no legal requirements have been set for discharge into surface water bodies besides that the most of PhCs are biologically active and hydrophilic, in order that the human body can take them up easily and persistence against biological degradation, which is key properties of these pollutants.[13,32]

Pharmaceuticals are large and diverse group of medicinal compounds used for the diagnosis, cure, mitigation, treatment, or prevention of diseases and they are designed to have a physiological effect on humans and animals in trace concentrations, such as hormones, anticancer drugs and antimicrobials.[15]

Pharmaceutical pollution is considered as one of the most modern issues, although PhCs present at low concentrations in the environment, it can have adverse effects on human health and aquatic organisms.

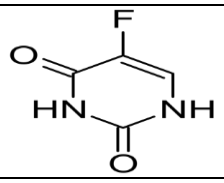
Trace amount of PhCs have been detected in surface waters, groundwater, drinking water resources.[16] There are multiple path ways by which PhCs enter aquatic system such as effluent from waste water treatment plants where most of them are not completely removed low concentrations of PhCs, Leakage from underground sewage infrastructure which are recognized as a main pathway, household disposal of unused medicines, manufacturing and hospital effluent also contribute to the occurrence of pharmaceuticals in the environment.[14]

1.2.2.1 5-Fluorouracil

Anticancer drugs are very harmful chemical which use for cancer patient. It has a lot of side effect to cancer patient or anyone who consume contaminated body intake. 5-Fluorouracil (5-Fu) has received particular attention because it is one of the most commonly used anticancer drugs in the world.[18]

5-FU was patented in 1956, came into medical use in 1962 and remains one of the most effective chemotherapeutic agents which still use widely today for systemic and local cancer treatment. The chemical structure and general physical properties of 5-FU are outlined in Table.[17]

Table 1.1: Structure and properties of 5-FU.

Name	5-FU
Chemical structure	
Synonym	5-fluoro-1H-pyrimidine-2,4-dione5-Fluorouracil
Molecular weight	130.08 g/mol
Chemical formula	$C_4H_3FN_2O_2$
Water solubility	1.11×10^4 ppm
Volume	95.34 $Å^3$
pKa	8.02
λ_{max}	265-266 nm

5-FU extensively used in chemotherapy for carcinomas of colon, breast, pancreas, head, neck, and ovary[20]. Its function is to inhibit the action of enzymes and to stop the growth of cancer cells through inhibition of thymidilate synthesise or by being incorporated into macromolecules, such as DNA and RNA, inhibiting their normal function.[21]

5-FU may be regarded as one of the pilot cytostatics for the assessment of environmental contamination originating from hospital effluents. 5-FU can be given by injection, by infusion, orally, or dermally. Metabolism of 5-FU is rapid, resulting in about 60% up to 90% of 5-FU being metabolized, whereas unmetabolised administered drug is excreted within 24h. consequently, 5-FU usually enter the hospital wastewater partially transformed or even unchanged via urine and faeces of patients under medical treatment while hospital effluents reach the municipal sewer network without any preliminary treatment, hospital effluents represent the primary source of 5-FU in the environment.[18] Regarding the high resistance of 5-FU towards biodegradation. Moreover, Its very low vapour

pressure and its low adsorption to suspended solids present in water matrices suggest that this drug will be extremely persistent in the aqueous environment and the inefficient, incomplete degradation and removal of such hazardous substance by conventional WWTPs. It is expected that 5-Fu can reach surface and ground waters.[19]

1.3 Adsorption

Adsorption is a phase transfer process that is widely used in practice to remove substances from fluid phases (gases or liquids). It can be observed as a natural process in different environmental compartments. The most general definition describes adsorption as an enrichment of chemical species from a fluid phase on the surface of a liquid or a solid via physical or chemical bonds.[40]

The solid material that provides the surface for adsorption is called adsorbent, the species that will be adsorbed are named adsorbate and it can be gas, liquid or dissolved solids. The efficiency of adsorption process depends on various factors; nature of adsorbate and adsorbent, surface area, porosity and chemical surface and moisture content. Also there are some external factors affecting adsorption process such as temperature, pH of solution, presence of competing compounds.[22,39]

In water treatment, adsorption has been proved to be an efficient removal process for a multiplicity of solutes. Here, the molecules are removed from the aqueous solution by adsorption onto solid surfaces. It is recognized as an efficient, promising and widely used approach for wastewater treatment;

simple, economically viable and technically feasible.

The adsorbents used for water treatment are either of natural origin (clay minerals, natural zeolites, oxides) or the result of an industrial production, such as carbonaceous adsorbents, polymeric adsorbents.[41]

Polymeric adsorbents constitute a new and unique class of adsorbents have large surface areas and fine pore structures inside the particle similar to bonded phase silica and activated carbon.[34] Because of this characteristic, these resins can effectively adsorb organic compounds from aqueous solutions. They are produced by copolymerization of nonpolar or weakly polar monomers such as styrene, or acrylic acid with specific cross-linking agents.[22]

1.3.1 Polyacrylic acid

Polyacrylic acid (PAA) belongs to the class of commercial polymers produced on a large scale and widely used in various industries, agriculture and medicine. PAA-based polymeric materials are used as emulsifiers and thickening agents for aqueous solutions, adsorbents and plastics, etc. Polymers and copolymers of acrylic acid are known as efficient flocculants.

Acrylic Acid (AA) is the key functional group for synthesis these polymers. AA is an organic compound with the IUPAC nomenclature propenoic acid and chemical formula CH_2=CHCOOH. It is the simplest unsaturated carboxylic acid. This colourless liquid has a characteristic acrid smell. Its chemical structure facilitates the combination

with large chain of compounds forming polymers.

PAA is a synthetic high-molecular weight polymer. In the solid state, PAA is obtained by polymerization of AA in the presence of photo-initiators or under the action γ-radiation. Hydrogen peroxide, alkali metal or ammonium persulfates initiate the polymerization of AA in aqueous solution. Only non-ionized AA molecules enter into the polymerization reaction.[24]

PAA is a weak polyelectrolyte, whose degree of ionisation is dependent on solution pH[36]. PPA is hard, durable, insoluble spheres of high surface area and porosity. Its ionizable carboxylic acid groups along its backbone make it soluble in aqueous media at neutral pH whereas its non-ionised form at low pH. [25,34]

Recent years, the use of the polymeric adsorbents for treatment of drinking water or wastewater has attracted great attention. There are various studies used PAA as adsorbent to remove different contaminants and pollutants from aqueous solutions. Magdy converted PAA into modified polymers and tested for their ability to adsorb heavy metal ions from aqueous solutions.[24] Małgorzata and Katarzyna have studied the possibilities of removal chromium(III) oxide from water using PAA.[35] PAA bound iron oxide magnetic nanoparticles were used to remove methylene[37] and bromelain[38] from aqueous solution. The development and employed of PAA adsorbents in adsorption process can be considered as the best choice to provide a very effective process for wastewater treatment. Herein, PAA with amide crosslinks decorated with silver nanoparticles were used as

polymeric adsorbent for removal of lead and 5-FU from aqueous solution.

1.4 Adsorption isotherm

Adsorption isotherm is an invaluable non-liner curve describing the adsorption phenomenon in which the amount of the adsorbate on the adsorbent as a function of its concentration (if liquid) or pressure (if gas) at constant temperature and pH.

Adsorption isotherm is an essential way for determining performance of an adsorbent and the efficiency, is done by Modeling the adsorption isotherm data which is obtained by batch experimental tests in labs. Several isotherm models were developed over the years. There are several models used in modelling the adsorption data such as Langmuir and Freundlich isotherms. In order to determine the best fit isotherm model, the correlation coefficient (R^2) for linearized isotherm model is usually used. In this study, the experimental data were analyzed by two well known methods Langmuir and Freundlich isotherms models.

1.4.1 Langmuir Adsorption Isotherm

It is the simplest and most common isotherm equation used. It was developed to represent chemisorptions. Langmuir Isotherm is based on the following assumptions; the surface of adsorbent is uniform that means all of the adsorption sites are energetic equivalent, also it's a monolayer adsorption so there is no interaction between the adsorbed molecules, even on adjacent sites.

The mathematical form for Langmuir Isotherm is given by the following equation:

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_e K_L C_e}$$

Where:

C_e = the equilibrium concentration of adsorbate (ppm).

q_o = maximum monolayer coverage capacity (mg/g).

K_L = Langmuir isotherm constant (L/mg).

q_e = the amount of adsorbate per unit mass of adsorbent at equilibrium (mg/g), and it can be calculated using the following relation:

$$q_e = (C_o - C_e)\frac{V}{m}$$

Where:

C_o =the initial concentration of the adsorbate (ppm)

V = the volume of the solution (L).

m = the mass of the adsorbent (g).

1.4.2 Freundlich Adsorption Isotherm:

It is an empirical model, which can be applied to multilayer adsorption with non-uniform distribution of adsorption heat over the heterogeneous surface**.** Freundlich isotherm supposes that stronger binding sites are occupied first,

so; the binding strength reduces with increasing degree of site occupation.

The Freundlich adsorption isotherm is expressed in following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Where:

K_F is the Freundlich constant which indicates the adsorption capacity of the sorbent (mg/g).

n is the heterogeneity coefficient that gives an indication of the Favourable way of the adsorption process (g/L).[26,27]

1.5 Objectives of the study

1.5.1 General Objectives

The main objective of this research is to develop a new polymeric based material with high affinity for both metals and non metals and for adsorption of organic emergent pollutants.

1.5.1 Specific objectives

1. Develop a method for preparing the target polymeric material.
2. Develop and extraction techniques for removal of organic pollutants and metal ions from water using the prepared polymer.
3. Characterization of decorating silver nanoparticles on the polymer surface.

The materials chosen for this purpose are acrylic acid and 1,4-pheneylene diamine. 1,4 -Phenylene diamine will be used as a crosslinking agent for polymer acrylic acid. In this case a polymer with a 3D structure is expected to form with binding sites for metals and organic substances. The prepared polymer will be evaluated as follows:

1. Its efficiency for heavy metal ions present in synthesized water.
2. Its efficiency for removing the drug 5-FU in synthesized water.
3. Determine the optimum adsorption conditions by evaluating the effect of various factors such as pH, temperature, amount of adsorbent, concentration of adsorbate and contact time.

CHAPTER 2
EXPERIMENTAL

2.1 Materials and methods:

All chemicals including acrylic acid, NaOH, HCl, 5-FU, 1,4-Phenylenediamine, Sodium borohydride, potassium persulfate, Sodium thiosulfate were purchased from Aldrich Chemical Company, and were used as received without further purifications. The required instruments for this research include the following: shaking water bath (DaihanLabtech, 20 to 250 rpm Digital Speed Control), pH meter (model: 3510, JENWAY), glassware, Atomic Absorption Spectrometer (ICE 3500 AA System, Thermo Scientific), UV spectrometry (model: UV-1601, SHIMADZU), IR Spectrometer (Nicolet iS5, iD3 ATR, Thermo Scientific).

2.2 Polymers Preparation

2.2.1 Preparation of Polyacrylic acid (PAA) with Amide crosslinks

PAA was synthesized by radical polymerization as follows: potassium persulfate and Sodium thiosulfate (0.05 g in 0.05 mL distilled water) as initiator was prepared and added to acrylic acid (20 mL) in a beaker (50 mL). The solution was stirred magnetically at 65 ^{o}C till heat-shock-induced polymerization occurred.

The produced PAA polymer was crosslinked by dissolving a sample of it (1.5 g) in a beaker (100 mL) in DW (30 mL). To the beaker content was added 0.5 g of 1,4 -Phenylenediamine with stirring. The solution was

heated till removing all distilled water. The solid product was place in an oven at 180^0 C°C for 10 min. Solid product was washed several times with distilled water and acetone then dried at room temperature.

2.2.2 Preparation of PAA decorated with nano Ag particles

A solution of $AgNO_3$ (300 ppm) was prepared in 500 mL volumetric flask. 50 mL DW containing 1.5 g of polymer was mixed with 25 mL of $AgNO_3$ solution. Then $NaBH_4$ (0.3 g) was carefully added to 20 mL DW and added to the polymer silver nitrate solution and stirred for 24 hours. The resulting solid was filtered, washed with distilled water and acetone then left to dry at room temperature.

2.3 Removal of Lead metal from polluted water using PAA and PAA-Ag

2.3.1 Preparation of lead solutions

A stock solution of lead with a concentration of 1000 ppm was prepared by dissolving 0.5 g of Lead nitrate in 500 mL water in a volumetric flask. A set of solutions of lead with various concentrations: 5 to 50 ppm were prepared by dilution.

2.3.2 Calibration curve

Calibration curve is a quality control method for determining the concentration of a substance in an unknown solution by comparing the unknown to a set of standard solutions with known concentrations.

Atomic Absorption Spectrophotometer (AAS) was used to construct the calibration curves of Pb (II) through measuring the concentration and absorbance for the prepared standard solutions. According to Beer-Lambert law, solution with low concentration absorbs less light than solution of higher concentration. Since the absorbance and concentration are directly proportional. This law can be used to determine an unknown concentration depending on using the calibration curve of standard solution of lead ion. Atomic adsorption measurements of prepared Standard solutions were investigated in order to have a calibration curve of lead as shown in figure 2.1:

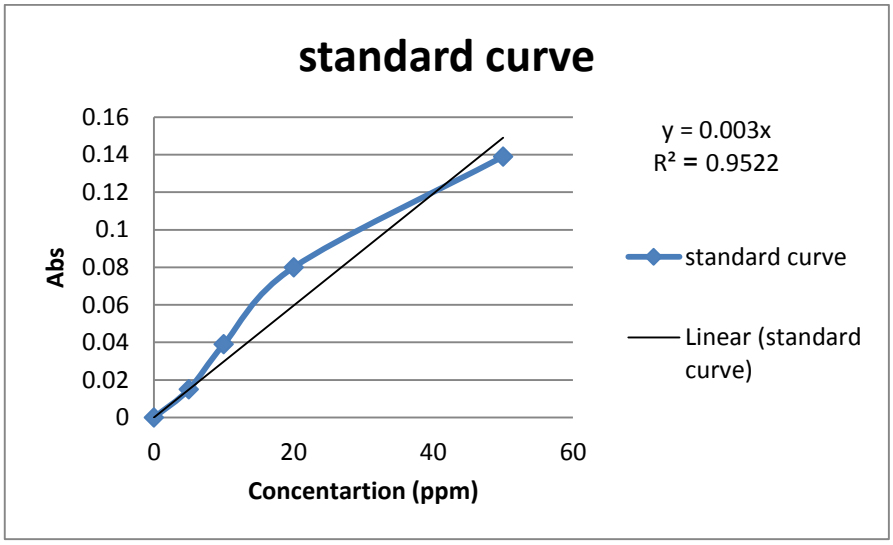


Figure 2.1: Calibration curve of Pb(II).

2.3.3 Batch experiments

A mixture of 0.15 mg adsorbent PPA or PPA/Ag-NPs in 10 mL of DW containing known concentration of Pb(II) was shaken.

The effect of several conditions including; contact time, pH value, temperature, amount of adsorbent and the concentration of lead ion were

evaluated. Atomic absorption measurements were used for the filtrate mixture of each sample to determine the remained amount of lead ion and investigate the adsorption efficiency of the extent.

2.3.3.1 Effect of adsorbent dose

To study the effect of dose of adsorbent on the removal of lead (II), various doses of adsorbent between 10–200 mg was tested. Lead (II) concentration used in this study was 50 ppm. The samples were placed in a water bath equipped with a shaker at constant temperature (25°C) for 30 min at PH= 6.33. The mixture was filtered to remove adsorbent and the Pb (II) concentration in the filtrate was measured using AAS.

2.3.3.2Effect of adsorbate concentration

To find the optimum concentration of lead metal. The resulting optimum mass of adsorbent determined from experiment above was added to a number of vials, each contains 10 mL of various concentrations of lead at pH equals 6.33 for 30 min at room temperature.

2.3.3.3Effect of contact time

The adsorption efficiency of the polymers were evaluated as a function of time at room temperature, pH value equals 6.33, optimum amount of adsorbent and optimum concentration of Pb(II). A sample of 50 ppm of standard solution was taken in a volumetric flask and shaken with 0.15 mg of an adsorbent at various contact times ranging from 5 to 30 min.

2.3.3.4Effect of pH value

Effect of pH value on the efficiency of lead adsorption was investigated at various pH values ranging from (2.0-9.0). The pH was adjusted using roughly concentrations of 0.1M NaOH and 0.1M HCl 0.15 g adsorbent samples were added to 10 mL of lead solution with concentration 50 ppm. The mixtures were placed in Shaking Water Bath for 10 min taking into consideration the optimum temperature for each adsorption process.

2.3.3.5 Effect of temperature

The effect of temperature on adsorption was also evaluated; 0.15 g adsorbent samples were added to 10 mL of lead solutions with concentration of 50 ppm. Each vial was shaked in a water bath at various temperatures ranging from 15 - 40°C for 10 min.

2.4 Adsorption of 5-FU using PAA/Ag-NPs

2.4.1 Preparation of 5-FU solutions

5-FU in 100 mL DW in volumetric flask. The stock solution was used to prepare standard solutions with different 5-FU concentrations (5, 15, 20, 25, 30 ppm). All solutions were preserved in refrigeration until their use.

2.4.2 Calibration Curve

The absorbance of the prepared solutions in section 2.4.1 were measured by UV-visible Spectrophotometer at 266 nm wavelength. The absorbance was plotted versus concentration. Linear calibration curve between absorbance

and concentration was obtained with 5-FU concentrations in the range 1-20 ppm as shown in Figure 2.2

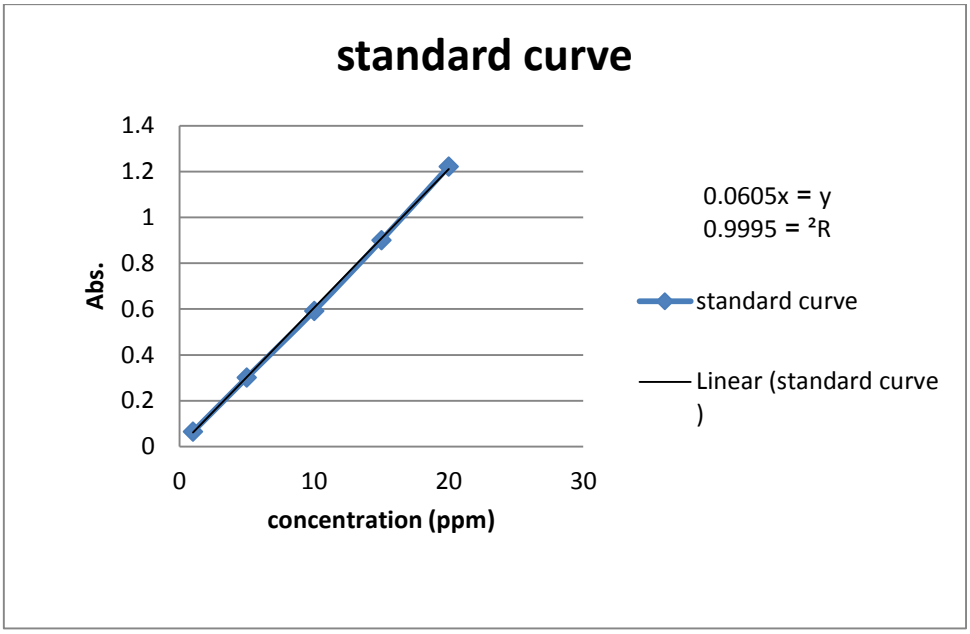


Figure 2.2: Calibration curve of 5-FU

2.4.3 Batch experiments

A mixture of 0.05mg sample of PPA with sliver NPs adsorbent was added to a 10 mL of DW containing known concentration of 5-FU than shaked. The effect of various parameters such as amount of adsorbent, contact time, pH value, effect of temperature and concentration of 5-FU on adsorption process was studied. The UV-Spectrophotometer was set at 266 nm (which is the characteristic wavelength for 5-FU molecule) for measurements of the absorbance for all trials.

2.4.3.1 Effect of adsorbent dose

To study the effect of dose of adsorbent on the removal of 5-FU on the polymer surfaces different experiment were done using different dose

ranging between 0.05-0.2 g. This experiment was studied using 5 ppm solution at room temperature. The samples were placed in Shaking Water Bath for 30 min. The absorbance of supernatant was measured by UV-visible for the residual concentration of solution

2.4.3.2 Effect of adsorbate concentration

To determine the optimum concentration of 5-FU drug. A known mass of adsorbent was added to a number of vials, each contains 10 mL of standard solution. After that, the solution was filtered and the absorbance of supernatant solution was measured using UV-spectrophotometer at λ_{max} equals 266 nm.

2.4.3.3 Effect of contact time

The adsorption of 5-FU onto PAA with silver NPs was studied at different contact time ranging from 5 to 35 min. The concentration of 5-FU was 5 ppm with 0.05 mg of polymer at room temperature.

2.4.3.4 Effect of pH

The effect of initial pH value on the adsorption behaviour was investigated at pH range 4.0-9.0. The pH was adjusted using roughly concentrations of 0.1M NaOH and 0.1M HCl. (0.05mg) of PAA with silver nanoparticles was added to 10 mL of 5-FU solution with concentration 5 ppm. The mixtures were placed in Shaking Water Bath at 25°C for 5 min.

2.4.3.5 Effect of temperature

The adsorption of 5-FU was studied at different temperatures ranging from 15 to 40°C. In each experiment, 0.05 g of PAA-Ag was added into 10 mL of 5 ppm 5-FU solution shaking for 5 min.

CHAPTER 3
RESULTS AND DISCUSSION

3.1 Polymer Synthesis

The target polymer was synthesized from reacting polyacrylic acid (PAA) with 1,4 -pheneylen diamine (1,4-PDA). Polyacrylic acid was prepared by polymerization of acrylic acid using an initiator. PAA is water soluble, so by reacting it 1,4 -PDA it was converted to across linked 3-D polymer that is water insoluble. Amine groups as shown in Figure 3.1 undergoes condensation reaction with carboxyl group at high temperature (180 °C) to lose a water molecule and form an amide bond. As shown in Figure 3.1, the crosslinked polymer has several binding sites for metal ions which makes excellent candidate as an adsorbent for metal ion present in water. Also, the presence of carboxyl and amide groups that form H-bonding acceptor and electron donor, makes the polymer a good trapping ageing for polar drugs and organic matters present in water.

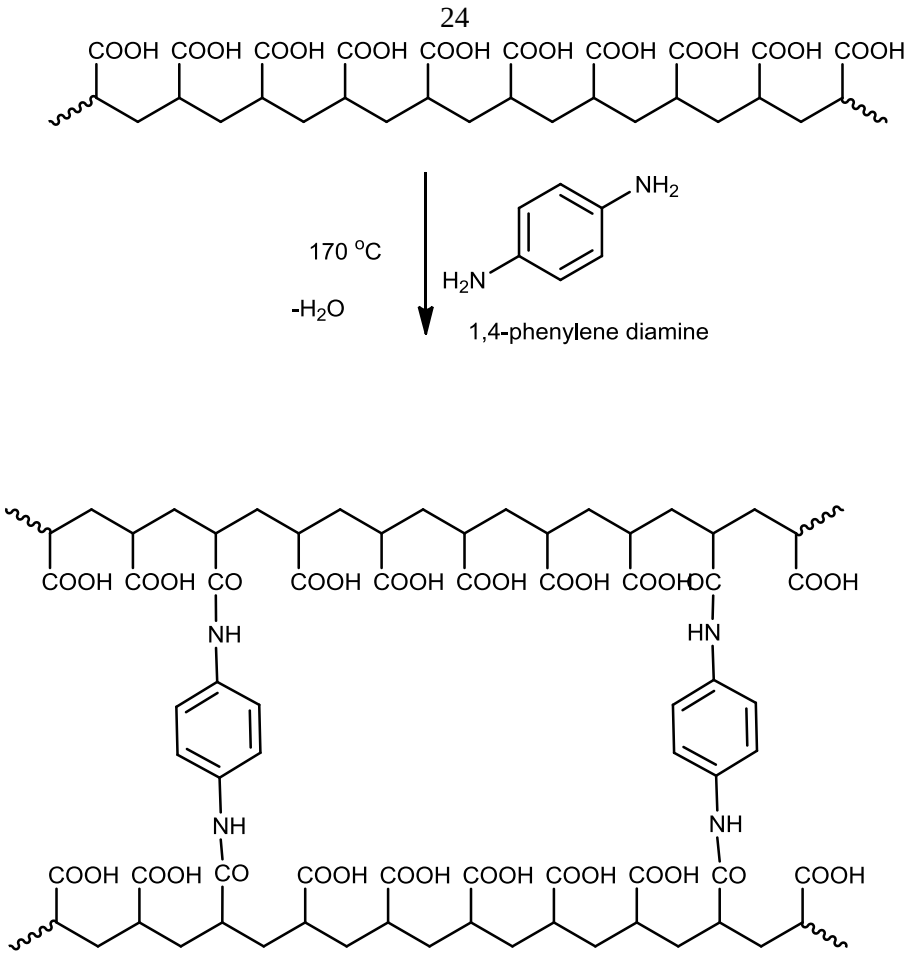


Figure 3.1: Cross-linking of PAA with 1,4-PDA

Suspending the polymer in aqueous solution with silver nitrate then adding sodium borohydride caused reduction of Ag (I) to Ag(0) and cause it to deposit as a nanoparticle on the polymer surface as shown in Figure 3.2.

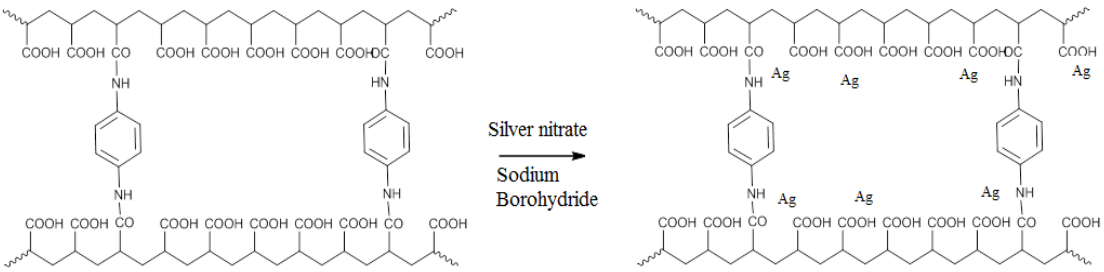


Figure 3.2: Crosslinked PAA decorated with silver nanoparticles.

3.2 FT-IR Characterization

FT-IR spectrum of PAA with amide crosslink is shown in Figure 3.3. The spectrum shows a peak at 1723.48 cm^{-1} corresponds to the C=O of acrylate unit and absorbance at 1178.36 cm^{-1} corresponds to the -CO-O- stretching of acrylate unit. The peak around 1680 cm^{-1} is assigned to tensional stretching of C=O amide (-CO and -CN). The C=O of carboxy groups in the crosslinked PAA decorated with Ag nanoparticles shows at 1716 cm^{-1}. However, in the parent PAA is shows at 1723 cm^{-1}. So the wave number shifted to a lower number. This blues indicates existence of silver NPs on the polymer surface as shown in Figure 3.4. The silver particles make an electrostatic interaction with the carboxyl group so, it lower the bond order of the carbonyl groups as a results of that, the C=O stretching appear at lower wavenumber.

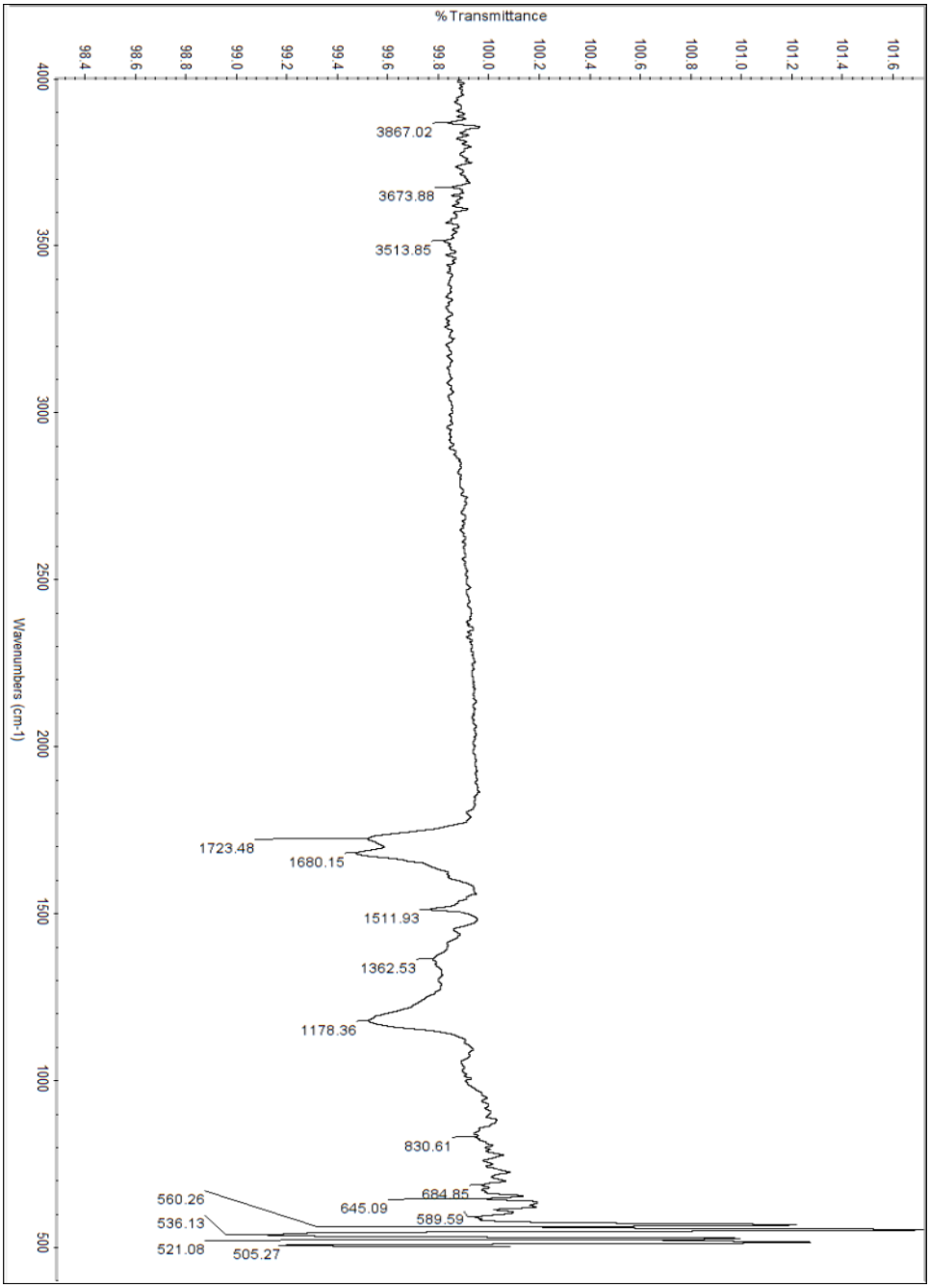


Figure 3.3: IR spectrum of PPA with amide crosslinks.

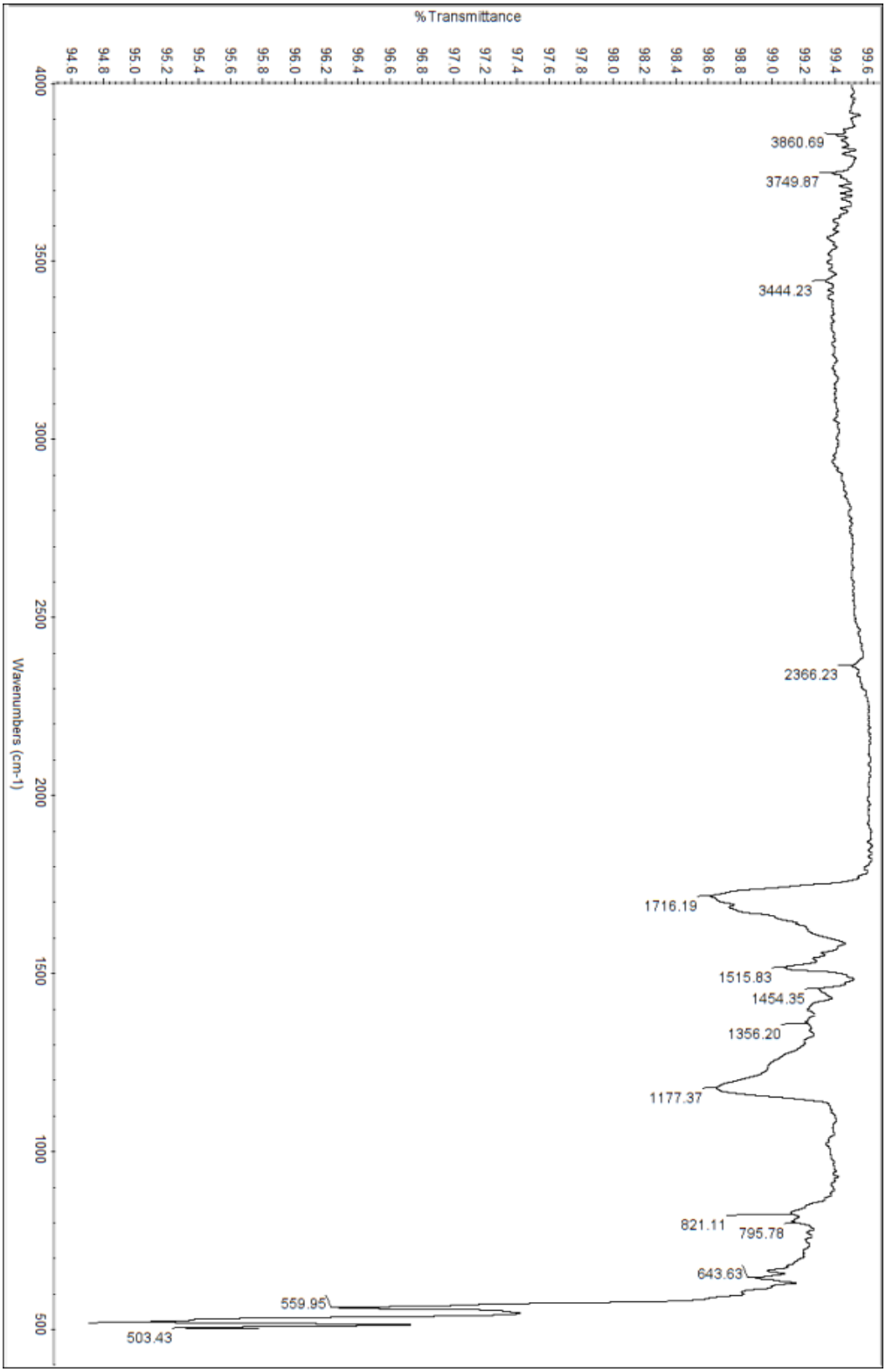


Figure 3.4: IR spectrum of PPA-Ag.

So, the FT-IR spectrum clear shows the formation of the crosslinked polymer and the deposition of the silver nanoparticles on the surface. The FT-IR shows that silver particles bond to the carboxyl group not to the amide bond, since wavenumber of C=O of the amide didn't make any shift.

3.3 Adsorption results

In this study, the synthesized modified PAA was used as an adsorbent for heavy metals and pharmaceutical compounds from water. This process was done by studying the adsorption capacities for PPA with silver nanoparticles towards lead and Fluorouracil (5-FU) adsorbates and PPA toward lead metal ion. The chemical structure of 5-FU in figure 3.5, as shown in figure 3.5, it is considered a H-bonding donor and electron acceptor and highly polar. It is expected to interact well with PAA-Ag.

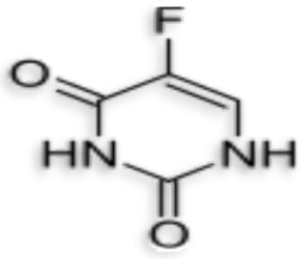


Figure 3.5: Chemical structure of 5-fluorouracil

The effect of various parameters such as amount of adsorbent, contact time, pH value, adsorbate concentration and temperature were discuss for each adsorption process.

After finding the remaining concentration, the percentage removal for each adsorption process was determined. This value is defined as the ratio of

difference in adsorbate before and after adsorption (C_0-C_f) to the initial concentration of adsorbate in the aqueous solution (C_0) and was calculated *using Eq. 3.1:*

$$E\ (\%) = \frac{C_0 - Cf}{C_0} * 100\% \quad (3.1)$$

Where C_0 is the initial concentration of adsorbate and C_f is the final concentration.

3.3.1 Adsorption of lead

The effect of solution conditions for the adsorption of lead on PAA and PAA-Ag adsorbents is determined. The extracted concentration of lead ions was determined using atomic absorption spectrophotomter. The adsorption processes are compared according to using lead with different adsorbents.

3.3.1.1 Effect of adsorbent dose

The experimental results for adsorptive removal of lead ions with respect to each dose of PAA and PAA-Ag adsorbents are shown in Figure 3.6 over the range 0.01 g to 0.2 g, at room temperature for 30 minutes and neutral pH value.

The maximum percent of lead removal was 97.97 % using 0.15 g of PAA-Ag. Such that, this polymer showed an increase in percentage removal with increasing the adsorbent dose. Also, the same relation between adsorption efficiency and dosage effect is observed for PAA with 0.15 g and 72.59% percentage of removal. The rapidly increased in the percent of removal for

lead ions with increase in the dose of PAA and PAA-Ag receptors is due to the greater availability of the adsorption sites on the adsorbent surface.

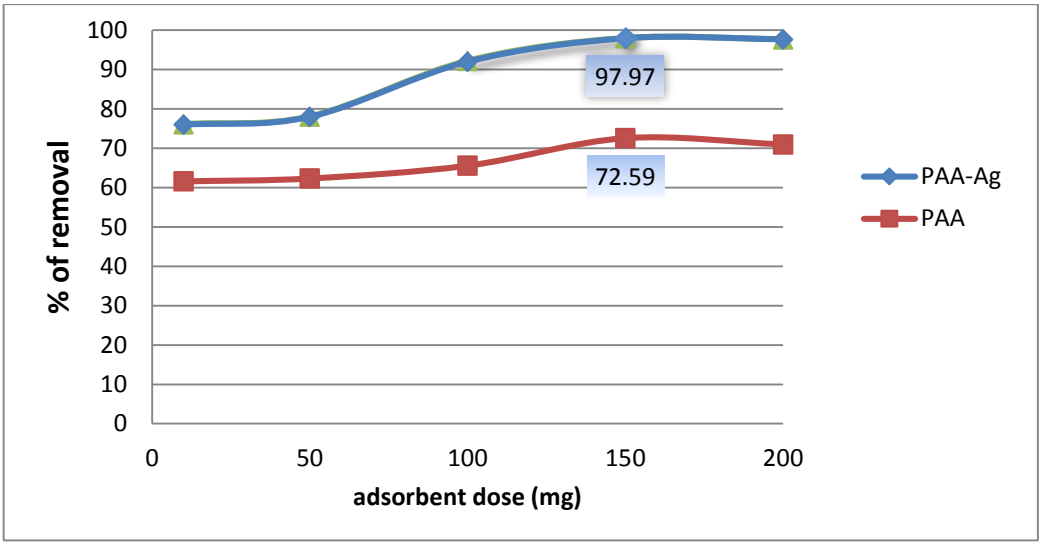


Figure 3.6: Effect of adsorbent dose on the removal of Pb(II).(time= 30 min, concentration of Pb(II) = 50 mg/L, solution Volume= 10 mL, at 25 ^{o}C ,pH=6.33) **.**

3.3.1.2 Effect of adsorbate concentration

The effect of initial concentration of lead ions on the percent of removal using PAA and PAA-Ag indicated that the adsorptive removal increases with the increase in the initial lead ions concentration. The maximum percentage removal was 97.97% for PAA-Ag using 50 ppm concentration of lead solution as shows in Figure 3.7, while the observed initial concentration for having maximum adsorption efficiency for PAA is 50 ppm with percentage removal equals 80.04%. When we increased the initial concentration, the mass transfer driving force will accelerate Pb(II) ions diffusion from the bulk solution to polymer surfaces and this will increase the adsorption capacity.

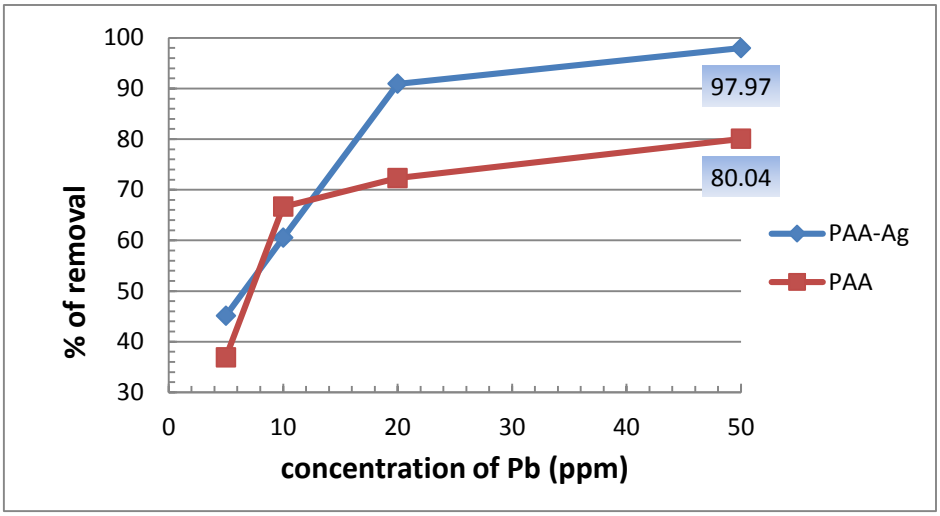


Figure 3.7: Effect of adsorbate concentration on the removal of Pb(II). (time= 30 min, adsorbent dose= 0.15g, solution Volume= 10 mL, at 25°C, pH=6.33) **.**

3.3.1.3 Effect of contact time

The effect of contact time on adsorption of lead ions on each adsorbent was studied at pH= 6.33 as shown in Figure 3.8.

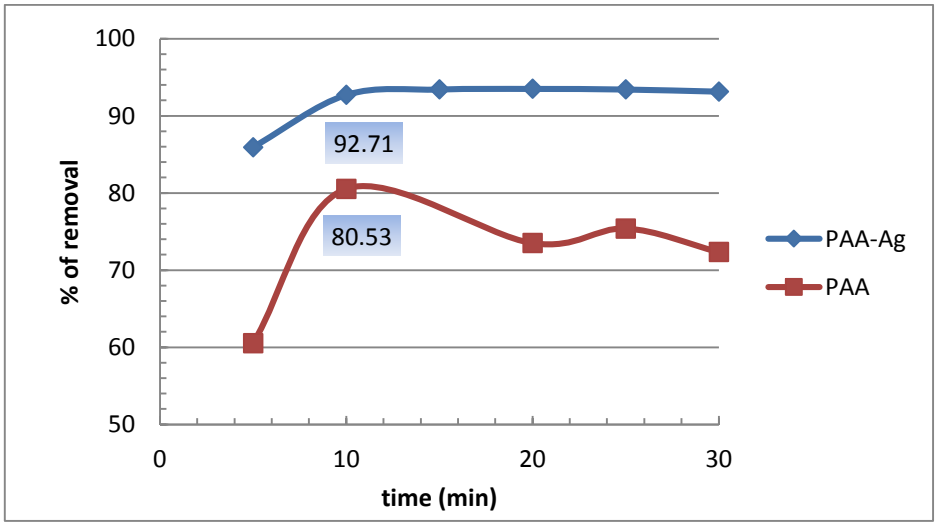


Figure 3.8: Effect of contact time on the adsorption of Lead on PAA and PAA-Ag.(C_0=50 ppm, volume = 10 mL, adsorbent dose =0.15 g, temperature=25°C, pH=6.33).

Herein, the highest percent of lead removal equals 92.71% for PAA-Ag after 10 min of shaking as optimum contact time. When lead ions were removed by PAA the optimum contact time is after 10 min and the percent

of removal is 80.53%. For both adsorbents, the remaining concentration of the lead ions after 10 min becomes approximately constant. The high percent of Pb(II) removal could be due to the availability of vacant sites on the adsorbent at the external surface. In general, the pore size becomes smaller and the surface area increases when silver NPs deposit in the polymer surface.

3.3.1.4 Effect of pH value

pH is considered one of the most important parameters that controlling the adsorption process. Several experiments were performed in this work for investigation the effect of pH in basic, acidic and medium. The effect of pH on Pb(II) removal efficiency on each polymers. These studies were carried out at room temperature with varying the pH value of the lead solution.

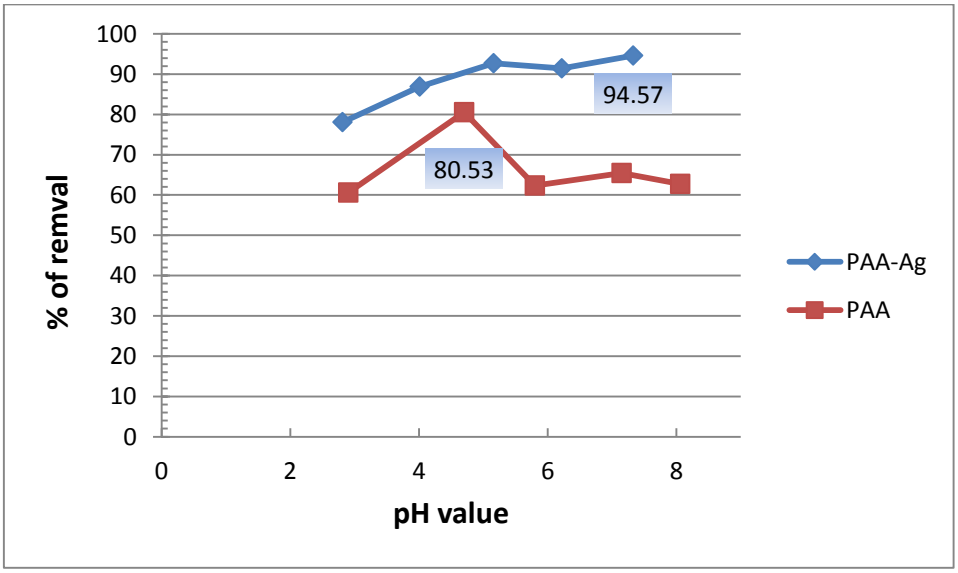


Figure 3.9: Effect of pH on removal efficiency of Pb(II). (10 mL of the Pb(II) solution(50ppm), shaking time= 10min, amount of adsorbent = 0.15g, at 25 ºC).

For PAA-Ag adsorbent, the percent of adsorption increases with increasing pH to reach a maximum at 7.33 (neutral). Which equals 94.57%, For PAA

adsorbent, 80.53% is the maximum percentage removal of lead ions at pH 4.7 as shown in figure 3.9, thereafter the percentage removal decreases and becomes approximately constant with increasing pH value of solution. The increase in lead removal as the pH increase could be due to decrease in competition between lead ions and the proton and by decrease the positive surface charge.

3.3.1.5 Effect of temperature

Studying the effect of temperature on the adsorption of lead ions using both adsorbent. As shown in Figure 3.10, the adsorption of Pb(II) using two different adsorbents including PAA and PAA-Ag has found to increase with an increase in temperature until reaching maximum at 25°C, and thereafter the percentage removal decreases with more heating using PAA and becomes roughly constant in PAA-Ag adsorbent.

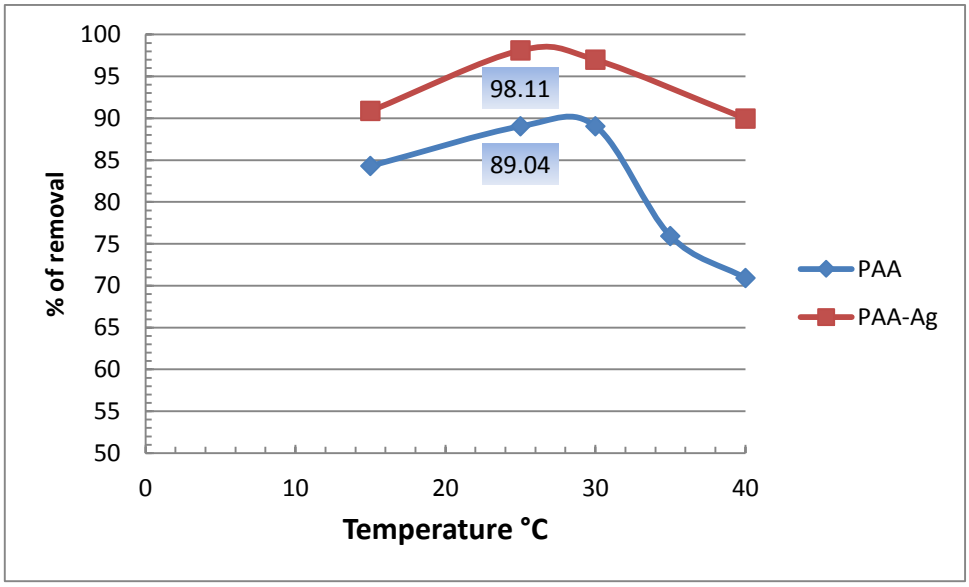


Figure 3.10: Effect of temperature on the adsorption of Pb(II). (C_o=50 ppm with volume = 10 mL, adsorbent dose=0.15g, for 10 min).

3.3.2 Adsorption isotherm models

This part was performed to determine the best adsorption isotherm for lead adsorption onto PAA and PAA-Ag.

The observed data were fitted to two adsorption models Langmuir and Freundlich. These models describe the relationship between the amounts of Pb(II) adsorbed and its equilibrium concentration in solution. Relationship between C_e and C_e/q_e describes Langmuir isotherm model; monolayer coverage of adsorption surface. Whereas, Freundlich isotherm model describes multilayer adsorption If the figure log $q_e$vs log c_e gives a straight line with high R^2 value.

3.3.2.1 Testing the two models for two adsorbents (PAA and PAA-Ag)

3.3.2.1.1 PAA Adsorbent

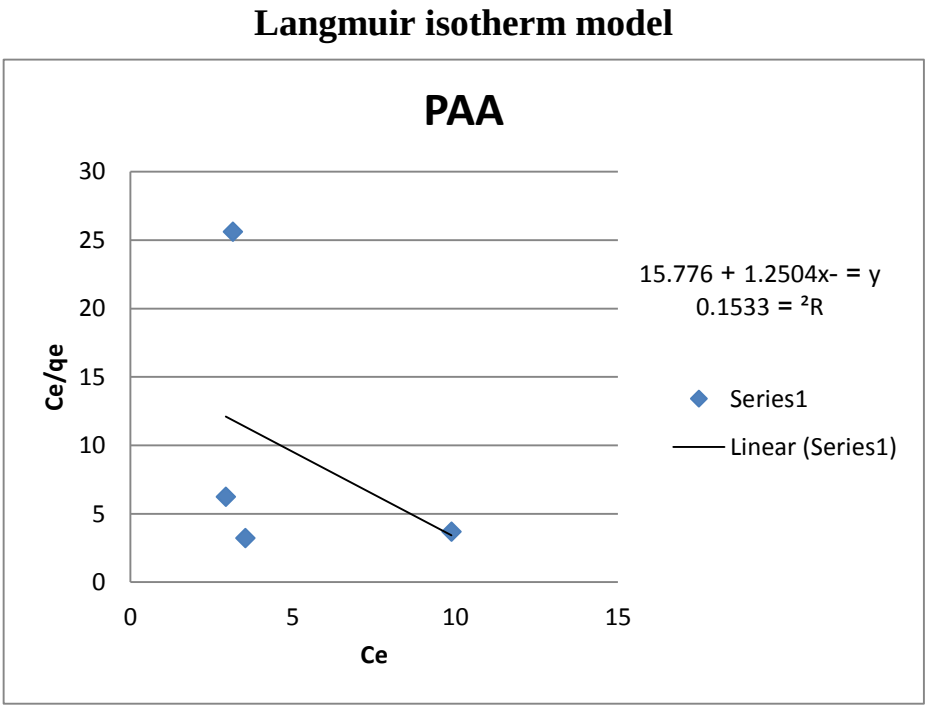


Figure 3.11: Langmuir isotherms of Pb(II) onto PAA. (adsorbent dose= 0,15 g, time= 30 min, temperature= 25 ^{o}C,volume= 10mL).

Freundlich isotherm model

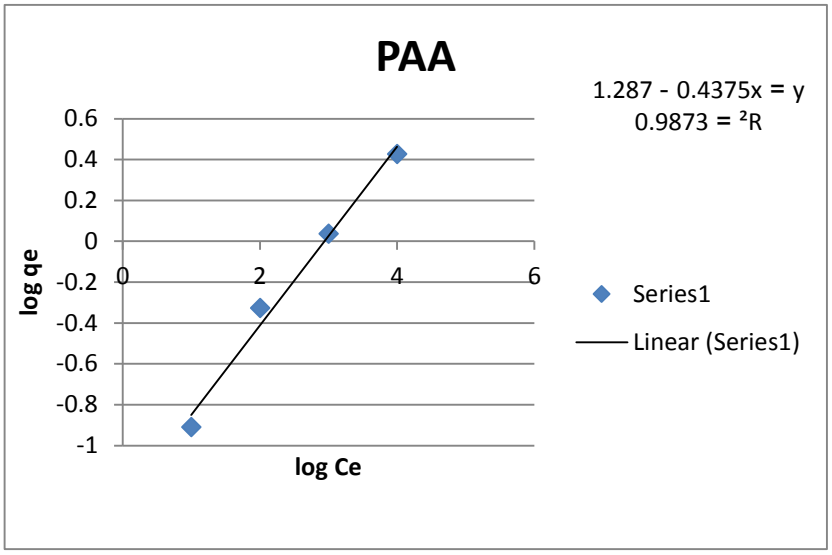


Figure 3.12: Freundlich isotherms of Pb (II) onto PAA.(adsorbent dose= 0,15g, time= 30 min, temperature= 25 ^{o}C, volume= 10mL).

As shown from the previous figures 3.11 and 3.12, the values of R^2 using freundlich adsorption isotherm are approximately 1. This means that the adsorption of Pb (II) onto PAA is physical adsorption and follows freundlich equation.

3.3.2.1.2 PAA-Ag adsorbent

Langmuir isotherm model

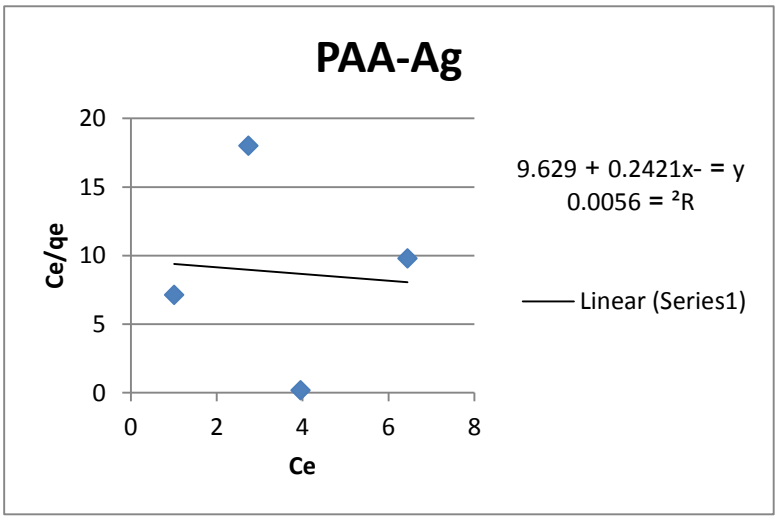


Figure 3.13: Langmuir isotherms of Pb(II) onto PAA-Ag. (adsorbent dose= 0,15 g, time= 30 min, temperature= 25 ^{o}C, volume= 10mL)**.**

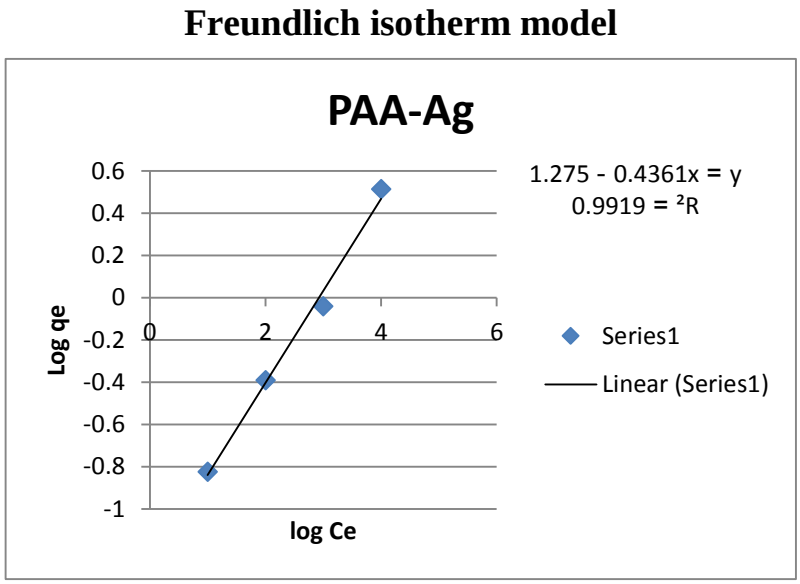


Figure 3.14: Freundlich isotherms of Pb (II) onto PAA-Ag. (adsorbent dose= 0,15g, time= 30 min, temperature= 25 ^{o}C,volume= 10mL).

According to R^2 values from two figures 3.13 and 3.14, adsorption of Pb(II) onto PAA-Ag follows freundlich isotherm model.

The following table represents the values of freundlich and Langmuir isotherm constants for the adsorption of Pb (II) on PAA and PAA-Ag.

Table 3.1: The constants of Langmuir and freundlich isotherm for the adsorption of Pb(II) on PAA and PAA-Ag.

Adsorbent	Langmuir constants			Freundlich constants		
	K_L	q_m	R^2	K_F	1/n	R^2
PAA	0.079	0.8	0.135	0.051	0.437	0.987
PAA-Ag	0.251	0.413	0.005	0.053	0.436	0.991

3.3.3 Adsorption kinetic models

The experimental kinetic data for Pb(II) adsorption on the adsorbents are fitted with pseudo- second order and pseudo-first order diffusion kinetic models to investigate the mechanism for each adsorption process.

3.3.3.1 Testing the two models on two adsorbents (PAA and PAA-A

3.3.3.1.1 PAA adsorbent

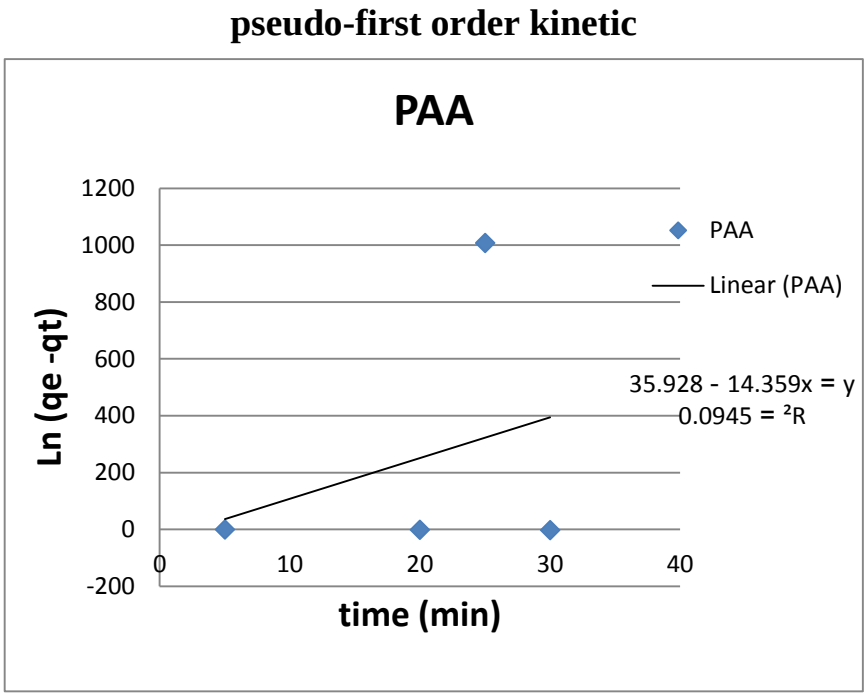


Figure 3.15: Pseudo-first order model for the adsorption of Pb (II) onto PAA. (adsorbent dose= 0,15g, C_0= 50ppm, temperature= 25 °C ,volume= 10mL)**.**

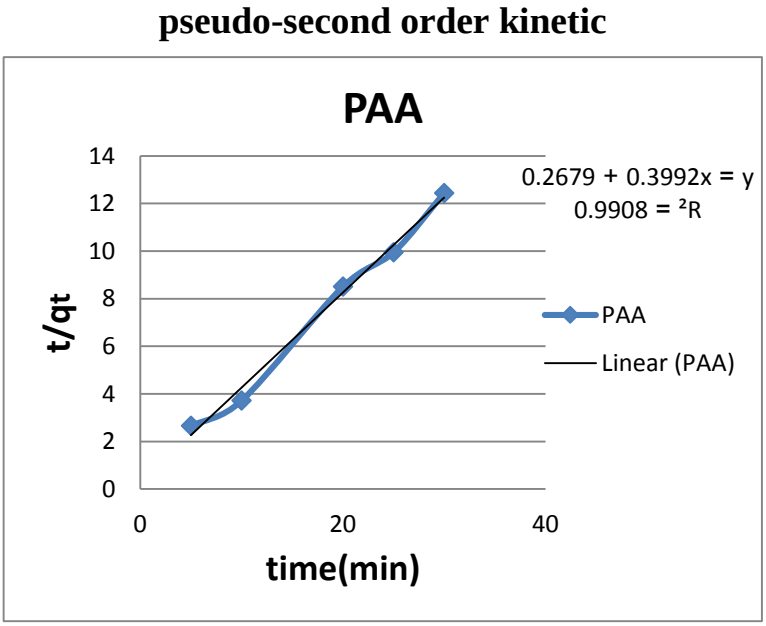


Figure 3.16: pseudo-second order model for the adsorption of Pb(II) onto PAA.(adsorbent dose= 0,15g, C_0= 50ppm,volume= 10mL, temperature= 25°C)**.**

According to R^2 values from two figures 3.15 and 3.16, adsorption of Pb(II) onto PAA follows pseudo- second order model.

3.3.3.1.2 PAA-Ag adsorbent

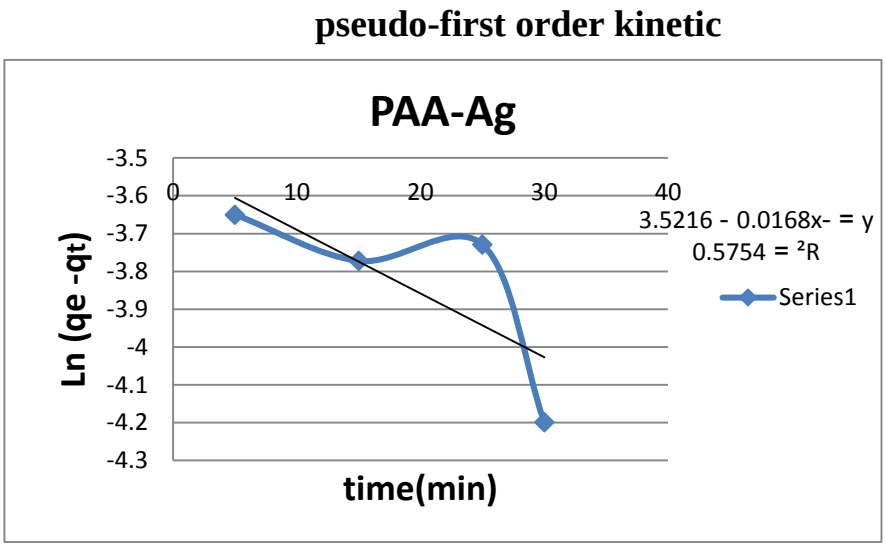


Figure 3.17: pseudo-first order model for the adsorption of Pb(II) onto PAA-Ag. (adsorbent dose= 0,15g, C_0= 50ppm,volume= 10mL, temperature= 25 ºC).

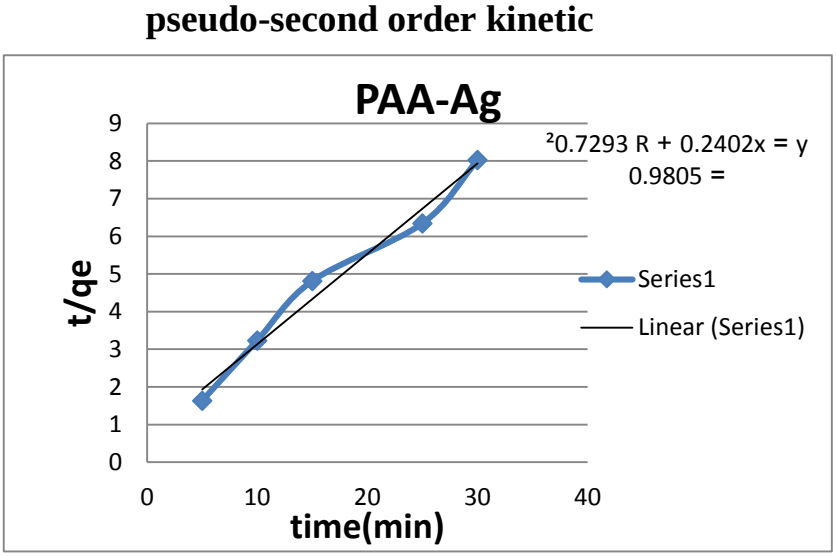


Figure 3.18: pseudo-second order model for the adsorption of Pb(II) onto PAA-Ag. (adsorbent dose= 0,15g, C_0= 50ppm,volume= 10mL, temperature= 25 ºC).

According to R^2 values from two figures 3.17 and 3.18, adsorption of Pb (II) onto PAA follows pseudo- second order model.

3.4.1 5-FU adsorption on PAA-Ag

The effect of solution conditions for the adsorption of 5-FU on PAA-Ag adsorbent is determined. The absorbance of the supernatant was measured using UV- Spectrophotometer at λ_{max}= 266 nm.

3.4.1.1 Effect of adsorbent dose

To study the effect of dose of adsorbent on the removal of 5-FU on the PAA-Ag surfaces different experiment were done using different dose of PAA-Ag substrates ranging between 0.01 – 0.2 g as shown in Figure 3.19. This experiment was studied using 10 mL solution of 5-FU (15 ppm) at 25 ºC. From the figure 3.19, It was observed that the percentage of adsorbed 5-FU increased from 15 to 38.9%. With increasing the PAA-Ag dosage from 0.01 to 0.05 g. Above 0.05 g of adsorbent, the adsorption of the 5-FU was in the equilibrium so extraction percentage remains constant 0.05 g PAA-Ag was used accordingly for subsequent experiments.

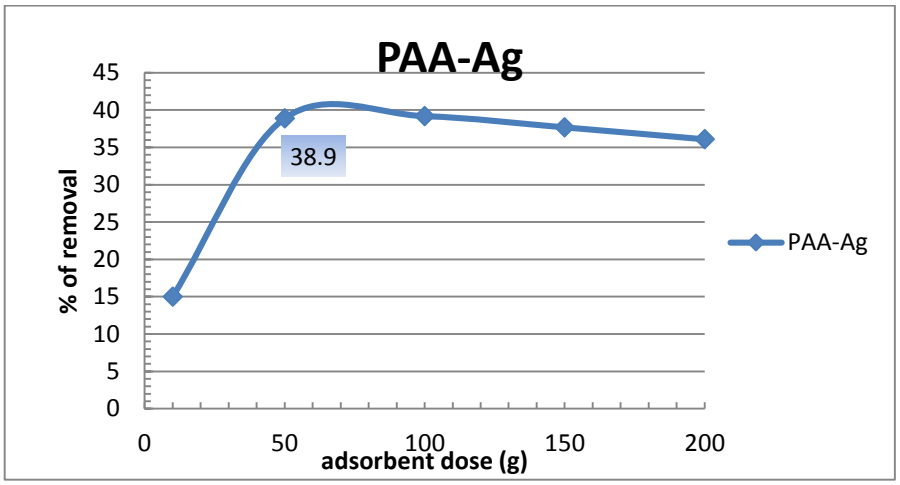


Figure 3.19: Effect of adsorbent dose on the removal of 5-FU. (temperature= 25 ºC, time=30 min, concentration Of 5-FU= 15 ppm, volume= 10 mL, pH=4.31).

3.4.1.2 Effect of adsorbate concentration

The effect of initial concentration of 5-FU on the percentage removal using optimum amount of PAA-Ag (0.05 g). As shown in Figure 3.20, the adsorptive removal decreases with increase in concentration of 5-FU. The maximum percentage removal is 46.5 by using 5ppm. Lower initial 5-FU concentration results in sufficient adsorption sites to be available for adsorption process.

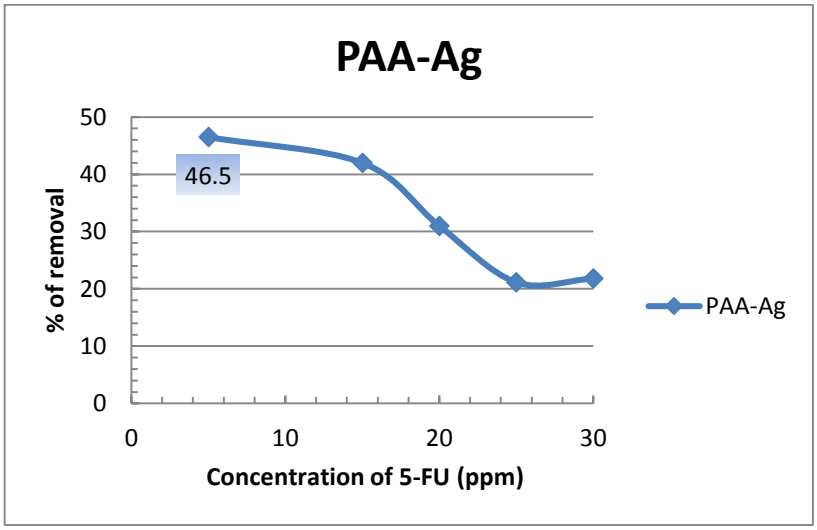


Figure 3.20: Effect of adsorbate concentration on the removal of 5-FU. (Temperature= 25 ^{o}C , time=30 min, concentration of 5-FU= 15 ppm, volume= 10 mL, pH=4.31)

3.4.1.3 Effect of contact time

The effect of contact time on the adsorption of 5-FU using PAA-Ag was studied. The optimum conditions of adsorbent dose and adsorbate concentration was used. Figure 3.21 illustrates the adsorption of 5-FU onto PAA-Ag at different contact time. As seen, the adsorption of 5-FU increases fast in the first 5 min reaching the highest percentage equals 86.96%, and then slowed down until the adsorption process achieves equilibrium.

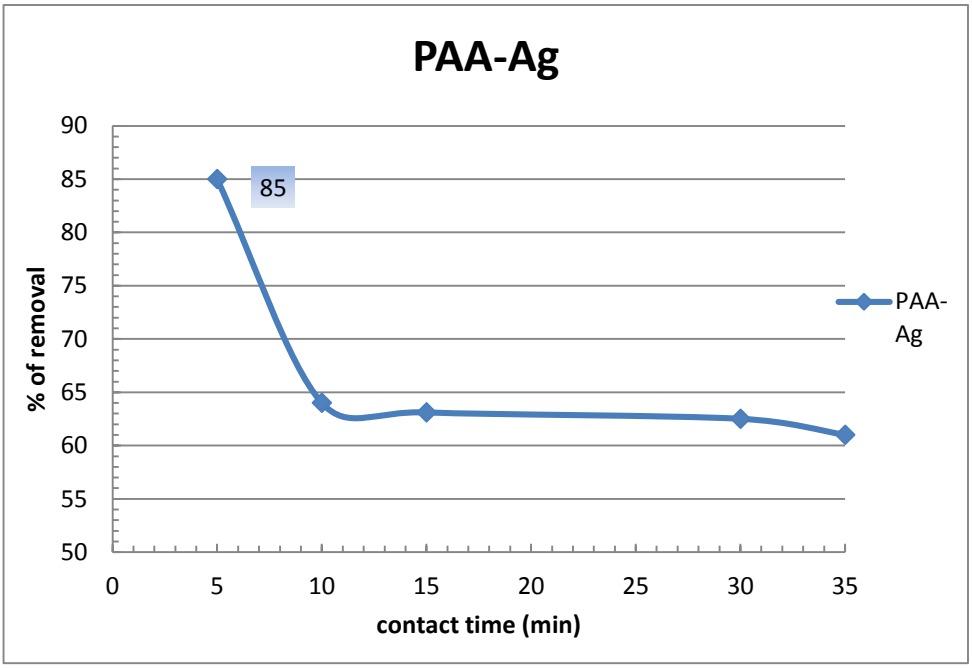


Figure 3.21: Effect of contact time (min) on removal efficiency. (10 mL of the 5-FUsolution (5 ppm), amount of adsorbent = 0.05 g, at 25 ^{o}C, pH=4.31)

Herein, it is worth noting that the fast removal rate during 5 min may be attributed to the rapid diffusion of 5-FU from the solution to the external surfaces of PAA-Ag.the rapid removal of 5-FU by PAA decorated with silver NPs is due to their small size which was favorable for the diffusion of adsorbate from bulk solution onto the active sites of the solid surface. Meanwhile, as the sites being gradually occupied, the adsorbed 5-FU tends to be transported slowly from the bulk solution to the actual occupied sorption sites. Such slow diffusion will decrease the adsorption rate of 5-FU later.

3.4.1.4 Effect of temperature

The effect of temperature on the uptake of 5-FU by PAA-Ag was studied at (15- 40^{o}C) as shown in Figure. The optimum conditions of adsorbate concentration, contact time and adsorbent dose were taken in consideration.

The adsorption of 5-FU using PAA-Ag has been found to increase with increasing the temperature until reaching a maximum at 25 ^{o}C, and thereafter the percent of removal decreases with further heating as shown in Figure 3.22. Such that; the percent of removal at 25 ^{o}C is 85.26%. Low temperatures of 5-FU solution enhance the complexation ability between PAA with silver NPs and 5-FU and hence increase the adsorption efficiency.

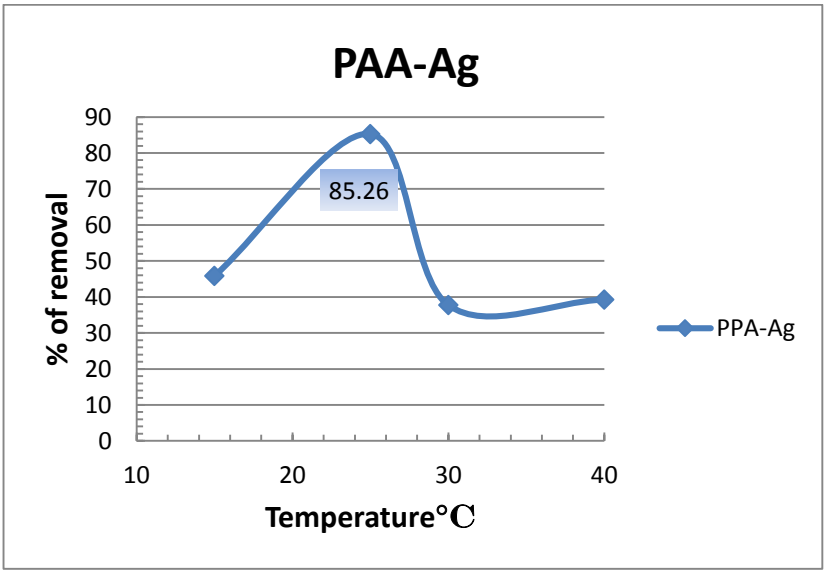


Figure 3.22: Effect of temperature on 5-FU adsorption. (C_0= 5ppm, time= 5 min, adsorbent dose= 0.05 g, solution volume= 10 mL, pH=4.31)

3.4.1.5 Effect of pH value

Figure 3.23 showed the effect of pH value on the efficiency of removing 5-FU onto PAA-Ag adsorbent. This study was conducted at the optimum amount of adsorbent, contact time concentration of adsorbate with varying the value of pH at room temperature.

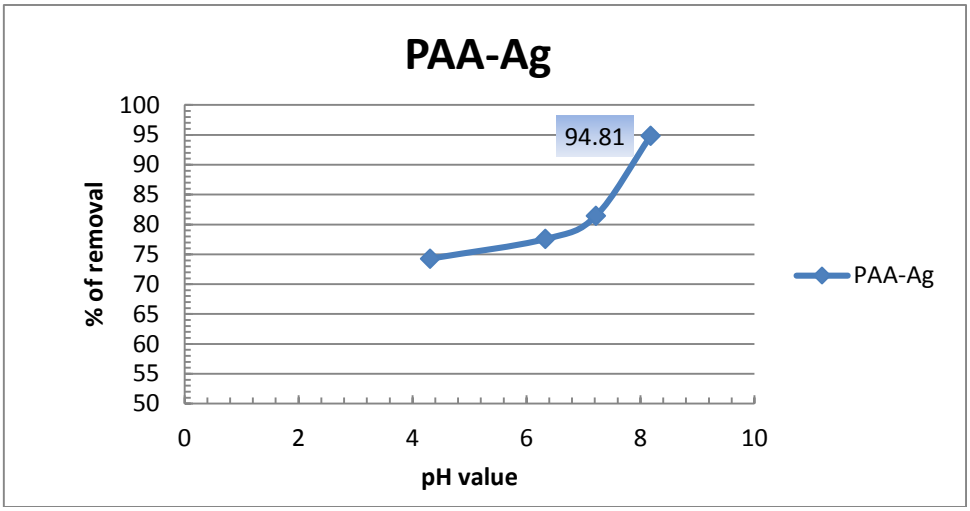


Figure 3.23: Effect of pH on 5-FU adsorption. (C_0= 5 ppm, temperature =25 ^oC, time= 5 min, adsorbent dose= 0.05 g, solution volume= 10 mL)

To evaluate the effect of pH on the adsorption capacity of the PAA-Ag the adsorption experiments were carried out in solutions having different pH values. As shown in Figure 3.23. The maximum percentage removal was 94.8% at pH 8.18 with using 0.05 g of adsorbent, shaking for 5 min at room temperature.

3.4.2 Adsorption isotherm models

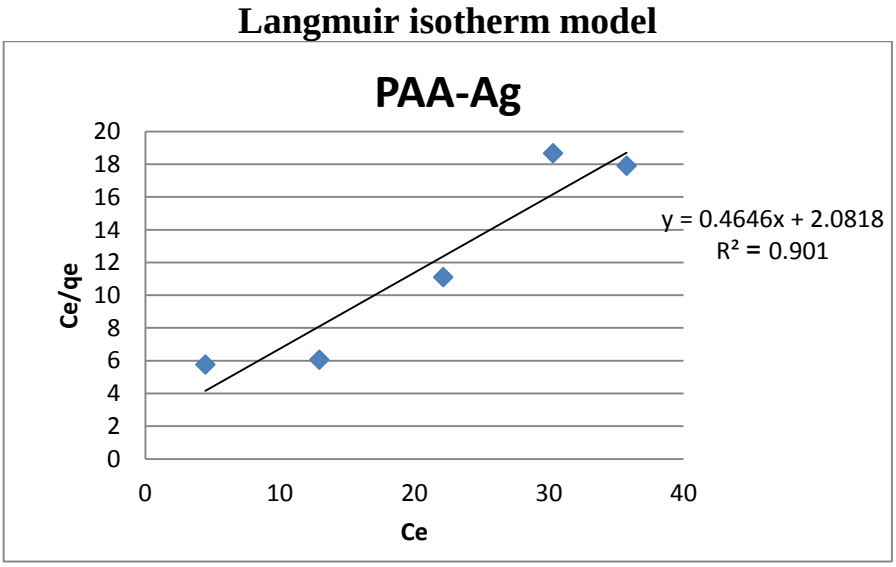


Figure 3.24: Langmuir isotherms model for the adsorption of 5-FU onto PAA-Ag. (adsorbent dose= 0,05 g, time= 30 min, temperature= 25 ^oC, volume= 10mL).

Freundlich isotherm model

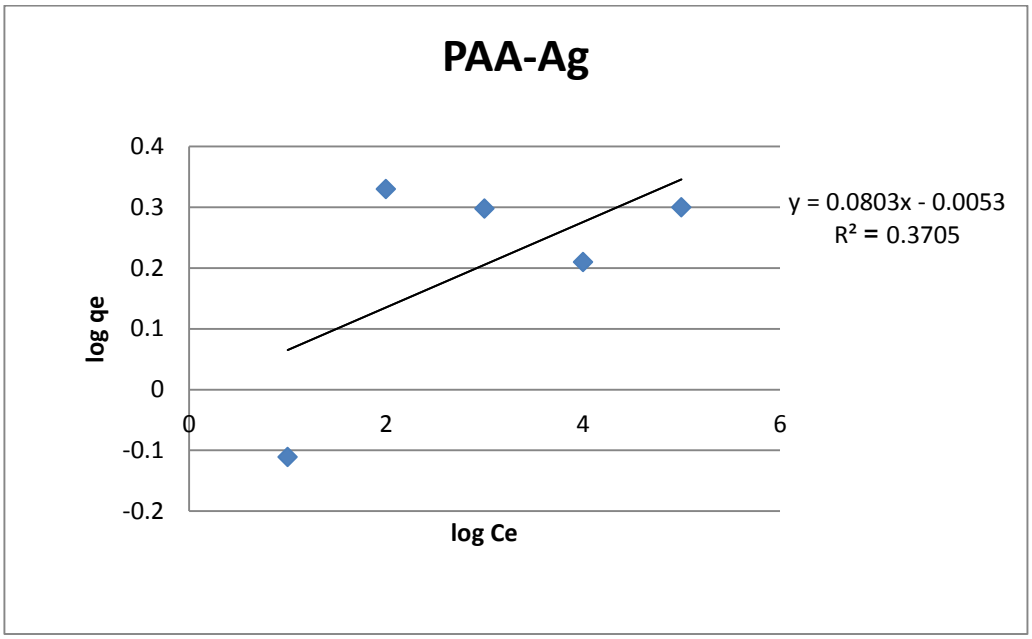


Figure 3.25: Freundlich isotherms model for the adsorption of 5-FU onto PAA-Ag. (adsorbent dose= 0,05 g, time= 30 min, temperature= 25 ^{o}C, volume= 10mL).

According to correlation coefficient values from two figures 3.24 and 3.25, adsorption of 5-FU onto PAA-Ag follows Langmuir isotherm model. The following table shows the Langmuir and Freundlich constants for the adsorption of 5-FU onto PAA-Ag.

Table 3.2: The constants of Langmuir and Freundlich for the adsorption of 5-FU on PAA-Ag

Adsorbent	Langmuir Constants			Freundlich constants		
	K_L	q_m	R^2	K_F	1/n	R^2
PAA-Ag	2.17	0.221	0.901	0.89	0.07	0.370

3.4.3 Adsorption kinetic models

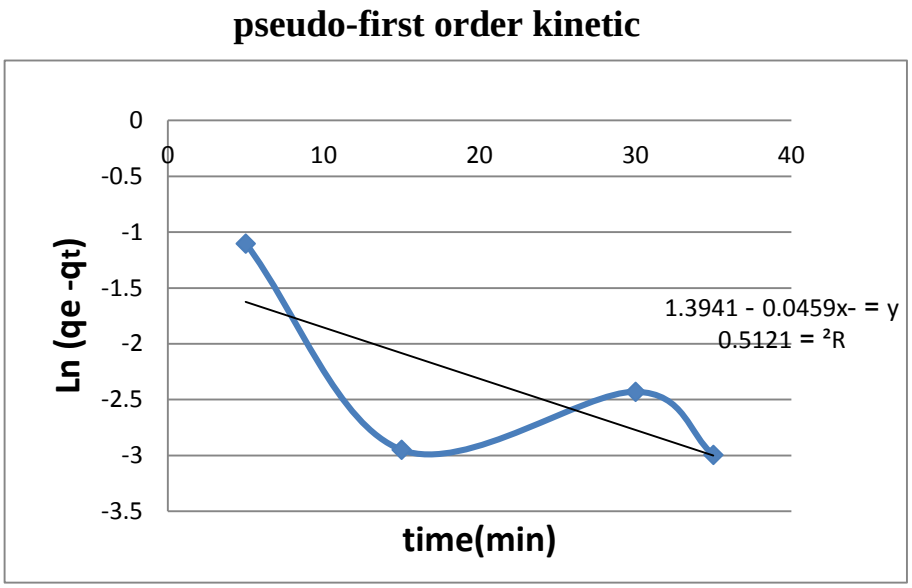


Figure 3.26: pseudo-first order model for the adsorption of 5-FU onto PAA-Ag. (adsorbent dose= 0,05 g, C_0= 5ppm, temperature= 25 ^oC ,volume= 10mL).

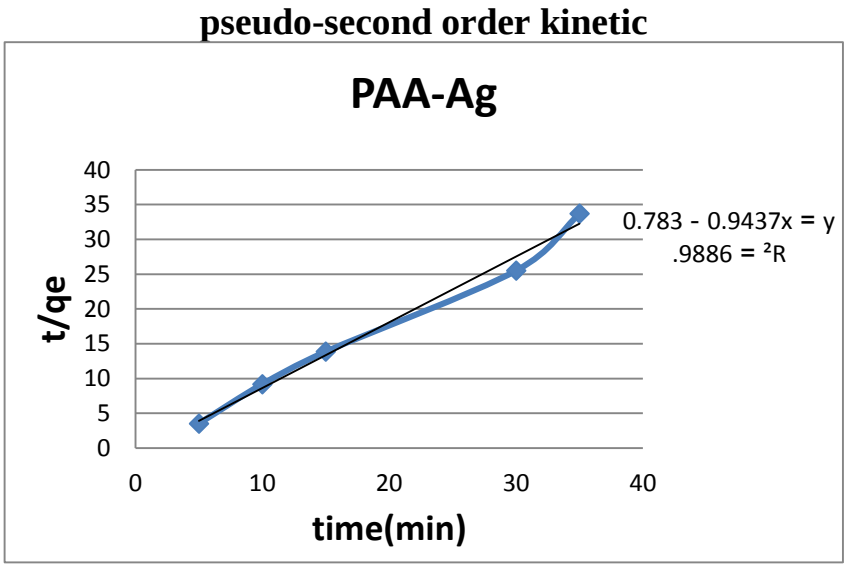


Figure 3.27: pseudo-second order model for the adsorption of 5-FU onto PAA-Ag. (adsorbent dose= 0,05g, C_0= 5ppm, temperature= 25 ^oC ,volume= 10mL)**.**

According to R^2 values from two figures 3.26 and 3.27, adsorption of 5-FU onto PAA follows pseudo- second order model.

Conclusion

The synthesis and characterization of the new Polyacrylic acid modified surfaces including PAA and PAA-Ag showed that these polymers have very good thermal and chemical stabilities, and hence they can be used as perfect adsorbents to uptake Pb (II) and 5-FU from aqueous solutions.

The observed results of this research include the following:

1. The maximum extent of adsorption was for PAA-Ag polymer in the presence of lead ions. This adsorption needed only 10 minute of shaking at 25ºC, 0.15g of polymer to have 98.19% as percent of Pb (II) removal. The maximum percent of lead removal onto PAA was 89.06% at the same condition.
2. Adsorption thermodynamics of lead ions onto the two materials PAA and PAA-Ag was studied, both followed Freundlich isotherm model and pseudo–second order kinetic model.
3. 5-FU was adsorbed onto PAA-Ag polymer, the maximum percent of 5-FU removal was 94.8% after 5 min of shaking, 0.05 g of PAA-Ag and 5 ppm of 5-FU solution at room temperature.
4. The results showed that the adsorption of 5-FU followed Langmuir isotherm and the mechanism of this reaction followed pseudo-second order kinetic adsorption model.

Recommendations for Future Works

1. Using the synthesized adsorbents to remove other toxic heavy metal ions rather than lead ion from water.

2. Using the synthesized adsorbents to remove other PhCs rather than 5-FU from water.

3. Up taking of toxic metal ions and PhCs from water using others modified polymer surfaces and compare between the adsorption efficiency between them and the synthesized polymers in this research.

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جامعة النجاح الوطنية

كلية الدراسات العليا

مُبلمر حمض الأكريلك المُعدل بالأميد ودقائق الفضة النانوية: تحضيره وتطبيقاته لمعالجة المياه العادمة

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

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الملخص

تهدف هذه الدراسة إلى تنقية المياه من أيونات الفلزات الثقيلة السامة والمركبات الدوائية. في البداية تم تحضير محاليل معيارية معروفة التراكيز لكل من الرصاص والفلورويوراسيل وبعدها تمت إزالة هذه الملوثات السامة بالأعتماد على طريقة الأمتزاز، حيث تم تحضير بولمر الأكريلك اسد المعدل مع دقائق الفضة المثبتة على سطح البولمر (PAA-Ag and PAA) .

حيث تمت دراسة العوامل المؤثرة على عملية التقنية ومنها : كمية المادة المازة، التركيز الابتدائي للمادة الممتزة، زمن التحريك، درجة الحرارة ودرجة الحموضة، وذلك من أجل معرفة الظروف المثالية التي تؤدي الى أكبر نسبة إزالة لعنصر الرصاص والفلورويورسيل بطريقة فعالة.

أشارت النتائج أن عملية الامتزازالرصاص باستخدام (PAA–Ag) كانت أفضل عند درجة حرارة الغرفة ودرجة حموضة 7.33 حيث كانت نسبة الامتزاز 98.19% وكانت النسبة الامتزاز لرصاص باستخدام (PAA) تساوي 89.06 % عند درجة حرارة الغرفة و درجة حموضة تساوي 4.7 .

وبعد ذلك تم تطبيق عمليات الامتزاز على نماذج الامتزاز ثابتة الحرارة (Langmuir and Freundlich isotherm) حيث تم ملاحظة أن كل عمليات الأمتزاز لأيون الرصاص كانت تابعة لمنوذج Freundlich.

أما عملية امتزاز الفلوروفورسيل لقد تمت باستخدامPAA–Agعلى درجة حرارة الغرفة ودرجة حموضة 8.18 حيث كانت اعلى نسبة امتزاز تساوي 94.8% والوقت اللازم للوصول الى حالة الاتزان خمس دقائق وكانت العملية تتبع نموذج Langmuir.

من أجل معرفة ميكانيكة كل من تفاعلات الامتزاز تم تطبيق هذه العمليات على نماذج الامتزاز الحركية وهي: (pseudo-second order kinetic وpseudo-first order kinetic) وبالاعتماد على قيمة معامل الارتباط لكل عملية امتزاز كانت النتائج تشير ان كل تفاعلات الامتزاز تابعة لمنوذج pseudo-second order kinetic.

وبشكل عام اشارات نتائج هذه البحث ان المادة المازة المحضرة في هذا البحث كانت فعالة جدا في امتزاز لكلا من المواد العضوية السامة وايونات الرصاص الثقيلة على درجة حرارة الغرفة ودرجة حموضة تتروح ما بين 7–9 وزمن تحريك ما بين 5 الى 10 دقائق باستخدام PAA–Ag.