# Deanship of Graduate Studies Al-Quds University



# Removal of lead (II) from water using polystyrene trisamine dithiocarbamate

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M.Sc. Thesis

**Jerusalem – Palestine** 

1435 - 2014

## Removal of lead (II) from water using polystyrene trisamine dithiocarbamate

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A thesis Submitted in partial fulfillment of requirements for the degree of Master of Pharmaceutical Industry in Applied and Industrial Technology Program. Al-Quds University

Jerusalem – Palestine

1435 - 2014

## **Al- Quds University Deanship of Graduate Studies Applied and Industrial Technology** Faculty of Science and Technology



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1435/2014

### **Dedication**

### TO MY PARENTS, SISTERS AND BROTHERS

TO MY HUSBAND

KHALIL

&

MY SON

**QASEM** 

<b>Declaration:</b>
I certify that this thesis submitted for the degree of master is the result of my own research, except where otherwise acknowledges, and that this thesis (or any part of the same) has not been submitted for the higher degree to any other university or institute.
Signed
Iman Yousef Atalah Makharzeh
Date

#### **Acknowledgements:**

I am very pleased to express my gratitude to all people who assisted me to go forward in my studies, and to all people who offered me help and support.

I would like to thank my supervisors Dr. Fuad Al-Rimawi and Dr. Imad Odeh for their continuous help and supervision during my research. Also I would like to thank the staff of the chemistry lab and Dr. Mutaz Qutub and Hussam Malasah for their assistance in doing the ICP-MS analysis.

Finally, I am glad to thank my family: my father, my mother, my sisters, my brothers and my husband for their help and encouragement.

#### **Abstract**

In this research, the Removal of lead (II) from water using the polymeric material polystyrene trisamine dithiocarbamate was studied. The influence of pH of solution, contact time, adsorbent dosage, and initial metal ion concentration on the adsorption process was investigated by using batch experiments. The optimal pH for the removal of lead (II) was determined to be 3, and the adsorption time was 120 minutes. The percentage removal decreased from 62.5% to 8.08% when the initial concentration of lead (II) was increased from 100 to 1000 ppb at pH=3 and 28°C as determined by ICP-MS instrument. The Langmiur and Freundlich isotherm models were used to evaluate the adsorption of lead (II) on polystyrene trisamine dithiocarbamate. The results demonstrated that the Langmiur isotherm method fitted the experimental data with maximum adsorption capacity of 319.49 mg/g. Desorption test indicated that 85% of the polymeric adsorbent was regenerated.

	List of contents	Page
1.	Introduction	1
2.	Experimental	9
	2.1.Proposed work	10
	2.2.Reagents	10
	2.3.Instruments	10
	2.4.Procedure	11
	2.4.1. Synthesis of polystyrene trisamine	11
	dithiocarbamate	
	2.4.2. Preparation of lead (II) solutions	11
	2.4.3. Determination of lead (II)	11
	2.4.4. Sample preparation for ICP-MS analysis	11
	2.5. Adsorption isotherms	12
	2.5.1. Effect of contact time	12
	2.5.2. Effect of pH	12
	2.5.3. Effect of adsorbent dosage	12
	2.5.4. Effect of initial lead (II) concentration	12
	2.6.Regeneration of the adsorbent	13
	2.7. Testing the removal of lead (II) by the regenerated	13
	adsorbent	
<b>3.</b>	Results and discussion	14
	3.1. Synthesis of polystyrene trisamine dithiocarbamate	15
	3.2. Determination of lead (II)	16
	3.3. Effect of contact time	17
	3.4. Effect of pH	18
	3.5. Effect of adsorbent dosage	19
	3.6. Effect of initial lead (II) concentration	20
	3.7. Regeneration of the adsorbent	21
	3.8. Testing the removal of lead (II) by the regenerated	22
	adsorbent	
	3.9. Adsorption isotherms	22
	3.9.1. Langmiur isotherm	22
	3.9.2. Freundlich isotherm	23
	3.10. Proposed mechanism for adsorption	25
	3.11. Comparison of adsorption capacity of various	25
	adsorbents	
	Conclusion	27
	References	29
	Appendices	34

## List of figures

Figure 1: Synthesis of polystyrene trisamine dithiocarbamate polymer8
Figure 2: FT-IR spectrum of polystyrene trisamine dithiocarbamate
Figure 3: Calibration curve for the determination of lead (II)
Figure 4: Percentage removal of lead(II) on polystyrene trisamine dithiocarbamate as a function of contact time by ICP-MS spectroscopy
Figure 5: Percentage removal of lead(II) on polystyrene trisamine dithiocarbamate as a function of pH by ICP-MS spectroscopy
Figure 6: Structures of dithiocarbamate group in acidic and basic medium19
Figure 7: Percentage removal of lead (II) on polystyrene trisamine dithiocarbamate as a function of adsorbent dosage by ICP-MS spectroscopy
Figure 8: Percentage removal of lead (II) on polystyrene trisamine dithiocarbamate as a function of initial lead (II) concentration by ICP-MS spectroscopy

Figure	9:Langmiur	isotherm	for t	the	adsorption	of	lead	(II)	on	polystyrene
trisami	ne dithiocarb	amate usin	g ICP	P-M	S spectrosc	opy	• • • • • •	• • • • • •	••••	23
Figure	10: Freundli	ch isother	m foi	r th	e adsorptio	on of	lead	l (II)	on	polystyrene
	ne dithiocarb				•			, ,		
Figure	11: Proposed	l mechanis	sm of	ads	sorption of	lead	by p	olys	tyre	ne trisamine
dithioc	earhamate									25

## List of tables

Table 1: Regeneration of the adsorbent	.21
Table 2: Testing the removal of lead(II) by the regenerated adsorbent	22
Table 3: Adsorption capacity of various adsorbents	26

## Chapter One

Introduction

#### 1. Introduction

Contamination of water by heavy metal ions is becoming more and a more serious ecological and health problem due to its toxic effects such as the blocking essential functional groups of biomolecules and disrupting the integrity of biomembranes. [1]

Heavy metals such as Mercury, Cadmium, Arsenic, lead, Iron, Nickel, Copper, Zinc, Manganese and Chromium, are defined as metals with a density higher than 5g/cm<sup>3</sup>.[2]

Lead is considered one of the most dangerous heavy metals, the presence of its ions in water and industrial wastewaters must be reduced to a minimum within the ppb level. [3]

The Guidelines for Canadian Drinking Water Quality, has determined the maximum acceptable concentration for lead in drinking water to protect public health is 10 micrograms per liter, while the Environmental Protection Agency has determined the maximum allowable concentration of lead in drinking water should be no more than 15 micrograms per liter. [4]

Lead is a metallic element, It tastes sweet and can enter the human body in different ways. Often, lead poisoning shows no symptoms. However, signs such as irritability, weight loss, vomiting, constipation, or stomach pain could occur. The human body can be damaged by ingested lead and the most acute cases of lead poisoning can cause death. Damage to the brain, kidneys, and bone marrow can occur with lower exposures. Coma and convulsions can also be associated with lower exposures of lead. Lead can also damage a person's nervous system and red blood cells.[5]

In children, lead causes a decrease in intelligent quotient (IQ) score, retardation of physical growth, hearing impairment, impaired learning, as well as decreased attention and classroom performance. In individuals of all ages, lead can cause anaemia, kidney malfunction, brain diseases and impaired function of peripheral nervous system, high blood pressure, reproduction abnormality, developmental defects, abnormal vitamin D metabolism, colic-like abnormal pains, dementia, madness and, in some situations, death. [6]

Children are more at risk than adults when it comes to the dangers of ingesting lead. Children will absorb 30-75% of the lead they ingest while adults will absorb only 11%. Individuals with the greatest risk, even with short-term exposure, are young children and pregnant women. lead in drinking water contributes between 10 and 20 percent of total lead exposure in young children. Reduced intelligence, impaired hearing and decreased growth, are associated with blood levels as low as 10 micrograms of lead per deciliter of blood ( $\mu$ g/dL). A 10  $\mu$ g/dL increase in blood levels correlates to a loss of 2 IQ points. Individuals will adsorb more lead if they have poor nutrition than those that have better diets. [7]

In the United States the EPA, under the authority of the Safe Drinking Water Act (SDWA), has set the Maximum Contaminant Level Goal (MCLG) for lead at zero. This is the health-based goal at which no known or anticipated adverse effects on human health occur and for which an adequate margin of safety exists. It means that it would be desirable to have totally lead free water for consumption. But due to economic considerations USEPA has set an action level for lead in drinking water at 15 ppb (15 micrograms per liter). This means that utilities must ensure that water from the customer's tap does not exceed this level in at least 90 percent of the homes sampled. The utility must take certain steps to correct the problem if the tap water exceeds the limit and they must notify citizens of all violations of the standard. Amendments to the SDWA require the use of "lead-free" pipe, solder, and flux in the installation or repair of any public water system, or any plumbing in a residential or non-residential facility connected to a public water system. Solders and flux are considered "lead-free" when they contain not more than 0.2 percent lead. [8]

Lead as Pb<sup>+2</sup> ion has a large affinity for the thio (-SH) and phosphate ion (PO<sub>4</sub><sup>-3</sup>) containing enzymes, ligands and biomolecules, thereby, inhibiting the biosynthesis of haeme units, affecting membrane permeability of kidney, liver and brain cells. These result in either reduced functions or complete breakdown of these organs.[9]

The main sources of lead in water are printed circuit board factories, electronics assembly plants, battery recycling plants and landfill leachate. In the printed circuit factory, solder plating and etching operations is the lead source. In the electronics assembly operations, the source is solder flux cleaning. In battery breaking, the lead is found in the sulfuric acid from the battery. In landfill leachate, it can be found as an organo metallic like tetra ethyl lead. [10]

Lead has a tendency to be complexed and precipitated by a large number of substances. When released to land, lead binds to soils and does not migrate to ground water. In water, it binds to sediments. It does not accumulate in fish. This is why it is seldom found in ground waters or natural waters in more than trace quantities, under 10 micrograms per liter. However, source waters that contain lead are an indication that intrusions from industrial, mine, or smelter wastes may have occurred. Typically, the source water contains less lead than the water at the "point-of-use". Studies indicate that nearly all the lead in users' tap water does not come from the primary water source or from the municipal treatment plant, but is a result of corrosion of lead containing materials that contact water after leaving the treatment plant. Lead can enter the home drinking water by leaching from lead service connections, from lead solder used in copper piping, and from brass fixtures. [11]

Lead has three oxidation states that should be considered when looking at aqueous reactions, IV, II and 0. Lead (IV) is so insoluble that the species it forms do not need to be considered in the aqueous phase. Lead (II) dissolves in the aqueous phase to form compounds such as Pb(OH)<sub>2</sub>, PbCO<sub>3</sub> and Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>. Finally, lead (0) as lead (IV) has a negligibly small dissolved concentration. [12]

Traditional technologies have been used in order to solve heavy metal pollution. These include precipitation, filtration, adsorption, chemical reduction, solvent extraction, membrane separation, biological treatment and solid phase extraction. High operational costs is considered as one of many disadvantages that make the removal process more complicated. [13]

Recently, adsorption was reported to be a promising technique for lead removal. Specific polymer sorbents consist of a metal chelate forming agent which interacts specifically with the heavy metal ions, and a carrier matrix which may be an inorganic material, or polymeric microspheres that contains functional groups that can bind to the heavy metal ions.[14]

A lot of works have been published in international journals about the removal of lead (II). [15-25]

M. Mahmoud et. al. studied the removal of lead by chemically and biologically treated carbonaceous materials. Hybrid sorbents and biosorbents synthesized via chemical and biological treatment of active carbon by simple and direct redox reaction followed by surface loading of baker's yeast. Surface functionality and morphology of chemically and biologically modified sorbents and biosorbents were studied by Fourier Transform Infrared analysis and scanning electron microscope imaging.

Hybrid carbonaceous sorbents and biosorbents were characterized by excellent efficiency and superiority toward lead (II) sorption compared to blank active carbon providing a maximum sorption capacity of lead (II) ion as 500  $\mu mol~g^{-1}$ . Sorption processes of lead (II) by these hybrid materials were investigated under the influence of several controlling parameters such as pH, contact time, mass of sorbent and biosorbent, lead (II) concentration, and foreign ions. Lead (II) sorption mechanisms were found to obey the Langmuir and BET isotherm models. The potential applications of chemically and biologically modified-active carbonaceous materials for removal and extraction of lead from real water matrices were also studied via a double-stage microcolumn technique. The results of this study were found to denote to superior recovery values of lead (95.0–9 9 . 0 ± 3 . 0–5.0%) by various carbonaceous-modified-bakers yeast biosorbents. [15]

- S. Akar et. al. studied the ammonium pyrrolidine dithiocarbamate anchored symphoricarpus albus biomass for lead (II) removal. The biosorption properties of APDC modified S. albus were tested in batch and column conditions. Effective experimental parameters such as pH, biosorbent dosage, contact time, temperature, initial lead (II) ion concentration and flow rate were investigated. The biosorption capacity of modified biosorbent was at maximum when lead (II) solution pH and biosorbent dosage were 5.5 and 2.0 g L<sup>-1</sup>, respectively. The biosorption equilibrium was established in 20 minute. Langmuir isotherm fitted well to the equilibrium data and kinetics was found to fit pseudo-second-order model. Increase in ionic strength of lead(II) solutions caused a slight decrease in the biosorption yield of APDC-modified biosorbent. Column biosorption of lead (II) showed higher biosorption yields at lower flow rates. Required time of breakthrough point was found to be 200 minutes. The recommended mechanism was found to depend mainly on electrostatic interaction, ion-exchange and complex formation. The ion-exchange mechanism for lead (II) biosorption onto the modified biosorbent was verified from the ionic strength effect and EDX analysis. Carbonyl, phosphate and CN groups on the modified surface of S. albus were found to be responsible for complexation with lead (II) ions. [16]
- P. Teekayuttasakul et. al. studied the Lead removal and toxicity reduction from industrial wastewater through biological sulfate reduction process. The practicability of lead removal from sulfate-rich wastewater through biological sulfate reduction process with hydrogen as electron donor was investigated. Sulfide, which was converted from sulfate by a sulfate-reducing bacteria (SRB) in a gas-lift reactor, was used to remove lead as lead sulfide precipitate. Furthermore, the toxicity of wastewater in terms of whole effluent toxicity (WET) before and after treatment was analyzed by using Microtox analyzer. In stage I, the volumetric sulfate-sulfur loading rate was gradually increased from 1.0 g/L.day until no improvement of sulfide-sulfur production efficiency was evident at 2.58 g/L.day and maximum sulfide-sulfur concentration was set to 340 mg/L. In stage II, the results showed that the laboratory scale reactor could treat a real wastewater without inhibition or any remarkable problem. The produced sulfide-sulfur, 200 mg/L, was a little less in comparison with that of the previous stage. It could be due to the higher concentration of total dissolved solid (TDS). However, the sulfate concentration was still reduced by approximately 30%. The WET test by Microtox showed that toxicity was reduced more than 13 times. In stage III, the effluent from the reactor containing sulfide-sulfur of about 200 mg/L and lead-containing solution of 20 mg/L were fed with sulfide to lead ratio 3 moles: 1 mole into the precipitation chamber in which the optimum pH for lead sulfide precipitation of 8.0 was maintained. It was found that lead removal of 99% was attained. [17]
- Z. Hubicki et. al. studied the removal of the heavy metal ions (lead, mercury, cadmium, nickel, vanadium, chromium, copper and zinc) using ion exchange method from water and industrial wastewaters, they showed that this technology is simple and enables efficient removal of even traces of impurities from solutions. [18]

- P. Ejikeme et. al. studied the removal of lead from wastewater using fluted pumpkin seed shell activated carbon. Adsorption tests were carried out in series of batch adsorption experiments. The Langmuir and Freundlich adsorption models were also used to test the data. The amount of lead (II) ion adsorbed at equilibrium from a 200 mg/L solute concentration was 14.286 mg/g. The adsorption isotherm obeyed the Langmuir model better than the Freundlich model. [19]
- I. Peric et. al. used a new adsorbents [poly(N-(3 dimethyl amino) propyl methacrylamide-co-acrylicacid),poly(N-(3-dimethylamino)propylmethacrylamide-co-4-acryloylmorpholine)],and poly (N-(3-dimethylamino) propylmethacrylamide-co-2-acrylamidoglycolicacid], to remove metal ions (cadimium (II), Zinc (II), lead (II), Mercury (II), and chromium (III)) which were examined by batch-equilibrium technique with respect to initial pH, temperature, and initial metal ion concentration. Maximum adsorption capacity was determined. Also, resins P(NDAPA-AA) and P(NDAPA-AMO) showed a great ability to retain Cr (III), whereas P(NDAPA-co-AAg) to retain Hg (II). [20]
- R. Brooks et. al. studied the removal of lead from contaminated water by alkali ash material permeable reactive barrier (AAM-PRB) which was made with fly ash alkali activating solution and filler material (sand and coarse aggregates). AAMPRB was used to remove lead from contaminated water. Analyses were performed by Atomic absorption techniques. [21]
- M. Singanan et. al. studied the effective removal of heavy metals (lead (II) and cadmium (II)) from industrial wastewater using activated biocarbon. Batch adsorption experiments were performed as a function of pH, contact time, solute concentration and adsorbent dose. The optimum pH required for maximum adsorption was found to be 4.5 and 4.8 for lead and cadmium, respectively. The maximum contact time for the equilibrium condition was 180 minutes at the sorbent dose rate of 2.5g. The maximum efficiencies of lead and cadmium removal by biocarbon were 95% and 98%, respectively. The results were well fitted by both Langmuir and Freundlich isotherm models. [22]
- L. Bingjie et. al. prepared a novel, bio-based dithiocarbamate modified chitosan beads using Pb (II) as imprinted ions (Pb–IDMCB), characterized and applied for selective removal of Pb (II) from aqueous solutions. Batch adsorption experiments were performed to evaluate the adsorption conditions, selectivity and reusability. The results showed that the maximum adsorption capacity of Pb–IDMCB for Pb (II) was 359.68 mg/g, observed at pH 6, 30 °C. Equilibrium adsorption was achieved within 180 min. The kinetic data, obtained at the optimum pH 6, could be fitted with a pseudo-second order equation. Adsorption process could be well described by Langmuir adsorption isotherms and the maximum adsorption capacity was calculated as 500 mg/g. The selectivity coefficient of Pb(II) ions and other metal cations onto Pb–IDMCB indicated an overall preference for Pb (II) ions, which was higher than that of non-imprinted dithiocarbamate modified chitosan beads (NIDMCBs). Furthermore, Pb–IDMCB represented high stability and good repeatability. It indicated that Pb–IDMCB is a very promising biosorbent for selective removal of Pb (II) from aqueous solutions. [23]

P. Roy et. al. studied the removal of heavy metal ions (Cu, Ni, Pb, Fe, As and Mn) using poly dithiocarbamate resin supported on poly styrene which was synthysized by emulsion polymerization of styrene and its subsequent reaction with carbon disulphide in alkaline medium. The sorbent was synthesized and characterized by elemental analysis, thermal and IR studies. The sorbent was also evaluated for its analytical characteristics and the optimum sorption conditions for metals was determined in order to assess the efficiency of the resin. The sorption capacity was higher when compared to other conventional polymers (dithizone and ovanillinthiosemicarbazone). [24]

R. Sublet et. al. studied the removal of lead from drinking water to develop a point-of-use water filter that could meet the regulation imposed by the new European Directive 98-83 lowering lead concentration in drinking water below 10 micrograms per liter. The objective of this research was to assess the potential of different adsorbents (zeolites, resins, activated carbon, manganese oxides, cellulose powder) to remove lead from tap water with a very short contact time. To begin, the repartition of the lead species in a tap water and a mineral water was computed with the computer model CHESS. It showed that in bicarbonated waters lead is mainly under lead carbonate form, either in the aqueous or in the mineral phase. Batch experiments were then conducted to measure the equilibrium adsorption isotherms of the adsorbents. Then, for five of them, dynamic experiments in micro-columns were carried out to assess the outlet lead concentration level. Three adsorbents gave rise to a leakage concentration lower than 10 micrograms per liter and were then selected for prototypes experiments: chabasite, an activated carbon coated with a synthetic zeolite and a natural manganese oxide. The proposed method clearly showed that the measurement of equilibrium isotherms is not sufficient to predict the effectiveness of an adsorbent, and must be coupled with dynamic experiments. [25]

In my work, I studied the removal of lead (II) from aqueous solutions by using polystyrene tris (2aminoethyl) amine dithiocarbamate. The effect of pH, contact time, adsorbent dosage and initial lead(II) concentration on the removal process was studied and the adsorption behavior was modeled by applying two adsorption isotherm models on our experimental data.

The choice of dithiocarbamate as adsorbents depends on its structure and behavior in the removal of heavy metals, in which in a previous work, L. Odeh et. al. synthesized polyvinylbenzyl tris (2-aminoethyl) amine dithiocarbamate and evaluated the microspheres for their capacity to detect and remove heavy metal ions particularly Hg (II), Pb (II) and Cd (II). The removal of heavy metal ions by the dithiocarbamate polymer microspheres was monitored by using atomic force microscopy (AFM), which showed that the dithiocarbamate polymer microspheres were selective towards Hg (II) ions since significant change in surface roughness was observed upon interaction of the Hg (II) ions with the dithiocarbamate polymer microspheres.[14]

So, my work is a continuation of the previous works and aims to explore the possibility of eliminating or reducing the toxicity posed by lead (II) ions discharged into the environment and water bodies, which has been on the increase due to rapid growth of cities in the world. Generally, water bodies are major sites of heavy metal deposits due to the fact that streams and rivers flow through agricultural areas where pesticides and fungicides may have been used, through industrial districts where there may have been many metal waste deposits or direct discharge of effluents into these water bodies. These metal pollutants are conservative contaminants that are not easily biodegradable chemically or biologically. When these metals are present in significant quantities in the environment, they constitute source of pollution and pose threat to the environment, human, animal and aquatic lives. Removal of trace amounts of heavy metal ions from wastewater and drinking water is of great importance due to their high toxicity. [26]

The dithiocarbamate functionalized polymer microspheres were synthesized from poly styrene trisamine and carbon disulfide as shown in (figure 1) and used to study the removal of lead (II) ions from water. FT-IR was used as an analytical technique to follow the reaction. [14]

Figure 1: Synthesis of polystyrene trisamine dithiocarbamate

## **Chapter Two**

Experimental

#### 2. Experimental

#### 2.1. Proposed work

Polystyrene trisamine dithiocarbamate was synthesized from polystyrene tris (2-aminoethyl)amine and carbon disulfide and used to remove lead (II) ions from water.

The removal of lead (II) from water was performed by batch experiments. The study investigated the effect of variable parameters such as pH, contact time, adsorbent dosage and initial ion concentration on the efficiency of the removal process. Langmiur and Freundlich isotherms were used to realize the linear correlation coefficient. Regeneration of the adsorbent was also achieved, and the removal of lead (II) ions by the regenerated microspheres was also studied.

#### 2.2. Reagents

Analytical grade of Polystyrene tris (2-aminoethyl) amine, carbon disulfide, 2-propanol, dimethylformamide, sodium hydroxide, sulfuric acid, nitric acid, Multi-element standard solution fluka (51844) and lead standard solution (1000 ppm) fluka (24239) as lead nitrate were purchased from Sigma-Aldrich company and potassium chloride.

All solutions were prepared in deionized distilled water.

#### 2.3. Instruments

- Inductively Coupled Plasma-Mass Spectrometry ICP-MS (Aglient Technologies 7500 series).
- Jenway pH meter (3310) with a combination glass electrode and a tolerance of ±0.01 pH units.
- Fourier transform infrared spectrophotometer FT-IR (Testscan Shimadzu FT-IR 8000 series).

#### 2.4. Procedure

#### 2.4.1. Synthesis of polystyrene trisamine dithiocarbamate

The aminated polymer microspheres (2g) were stirred with a mixture of 30 ml of 2-propanol, 10 ml carbon disulfide and 40 ml dimethyl formamide for one hour. This was followed by addition of 10ml of 10% aqueous NaOH and the resulting solution was stirred for five days. The dithiocarbamate polymer microsphere were then filtered and washed several times with distilled water and dried under reduced pressure.

#### 2.4.2. Preparation of lead (II) solutions

Stock solution of lead (II) with 1000 ppb concentration was prepared from lead standard solution (1000 ppm) by dissolving the appropriate amount of lead (as lead nitrate) in deionized distilled water. Solutions with different concentrations (100, 200, 400, 600, and 800 ppb) were prepared from the stock solution in deionized distilled water.

#### 2.4.3. Determination of lead (II)

Multi-element standard solution Fluka (51844, Multielement standard solution IV for ICP (in 10 % HNO<sub>3</sub>))

(Cr, Cu, Ni: 20 mg/L each Al, As, Ba, Pb, V: 40 mg/L each B, Fe, Se, Tl, Zn: 100 mg/L each Be, Cd, Co, Mn: 10mg/L each) was used to prepare 10, 25, 50 and 100 ppb standard solutions. Standards were analyzed by ICP-MS spectroscopy and a calibration curve was constructed.

#### 2.4.4. Sample preparation for ICP-MS analysis

 $200 \,\mu\text{L}$  of each sample was transferred to a 25 ml volumetric flask and 75  $\mu\text{L}$  of 10% Nitric acid were added, the volume was made up to 25 ml using Milli-Q water.

#### 2.5. Adsorption isotherms

#### 2.5.1. Effect of contact time

50 mg of adsorbent was transferred to 50 ml Erlenmeyer flask and 10 ml of 100 ppb lead (II) solution was added. The Solution was allowed to stir for 2 hours at pH=3 by  $0.2N~H_2SO_4$  and  $28^{\circ}C$ . Samples were taken at different time intervals 30, 60, 90, 120, 150 and 180 minutes. Each sample was filtered using a Millipore filter and concentration of lead (II) was determined by using ICP-MS.

#### 2.5.2. Effect of pH

50 mg of adsorbent was transferred to 50 ml Erlenmeyer flask consecutively and 10 ml of 100 ppb of lead (II) was added to the flask and the pH was adjusted to 3, 4, 5, 6 and 7 by  $0.2N\ H_2SO_4$  and 1M NaOH. The solutions were allowed to stir for 2 hours at  $28^{\circ}C$ . then the solutions were filtered and the concentration of lead (II) was determined by using ICP-MS.

#### 2.5.3. Effect of adsorbent dosage

0.01, 0.03, 0.05, 0.1, 0.3 and 0.5g of adsorbent were transferred to separate six 50ml Erlenmeyer flasks and 10 ml of 100 ppb lead (II) solutions were added to each flask. Solutions were left to stir for 2 hours and pH was adjusted to 3 using 0.2N H<sub>2</sub>SO<sub>4</sub> at  $28^{\circ}$ C, then solutions were filtered and concentration of lead (II) was determined by using ICP-MS.

#### 2.5.4. Effect of initial lead (II) concentration

100, 200, 400, 600, 800 and 1000 ppb of lead (II) solutions were used. 10 ml of each solution together with 0.05g of adsorbent were transferred to a 50 ml Erlenmeyer flask. The solutions were allowed to stir for 2 hours at pH 3 and 28°C. Then the solutions were filtered and the concentration of lead (II) was determined

#### 2.6. Regeneration of the adsorbent

50 mg of polystyrene trisamine dithiocarbamate was agitated with 10 ml of 100 ppb lead (II) solution for 2 hours at  $28^{\circ}$ C, then the solution was filtered with 0.45  $\mu$ m filter and the solid phase (polymer-metal complex) was left to dry for 48 hours. Then 50 mg of the polymer –metal complex was agitated with 10 ml of 1M potassium chloride for 2 hours at  $28^{\circ}$ C. A sample was taken from the solution filtered and tested for the presence of lead (II) using ICP-MS.

### 2.7. Testing the removal of lead (II) by the regenerated adsorbent

50 mg of the regenerated adsorbent was transferred to 50 ml Erlenmeyer flask and 10 ml of 100 ppb lead (II) solution was added. The Solution was allowed to stir for 2 hours at pH=3 and 28°C. Sample was filtered using a Millipore filter and concentration of lead (II) was determined by using ICP-MS.

## **Chapter Three**

## Results and discussion

#### 3. Results and discussion

#### 3.1. Synthesis of polystyrene trisamine dithiocarbamate

The dithiocarbamate polymer was prepared from polystyrene tris (2-aminoethyl) amine and carbondisulfide. The polymer was analyzed by FT-IR spectroscopy. The dithiocarbamate polymer showed sharp peak around 1700 cm<sup>-1</sup> which is related to the C-N vibration of  $CS_2$  NR<sub>2</sub> bond. Apparently, the C-N bond is a double bond one. So the chelation occurs between sulfur and lead most probably in a monodentate fashion as the sulfur is acting as a  $\sigma$ -donor as indicated in section 3.4 figure 6(a). The peaks between (1200-1050) cm<sup>-1</sup> are related to the C=S vibration of the CSS bond [figure 2].

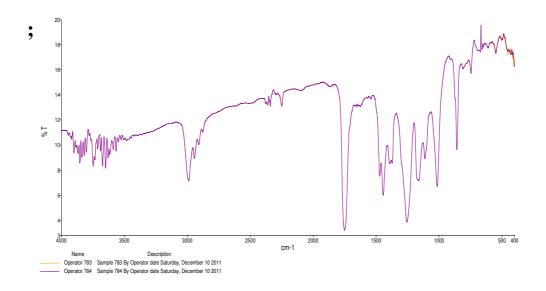


Figure 2: FT-IR spectrum of polystyrene trisamine dithiocarbamate

#### 3.2. Determination of lead (II)

Standard solutions were prepared from multi-element standard solution obtained from fluka (51844) were analyzed by ICP-MS. The calibration curve was constructed as shown in [figure 3]. The curve was linear through the selected concentrations; the correlation coefficient (R<sup>2</sup>) was high(0.9998) which indicated a strong positive linear relationship between the parameters.

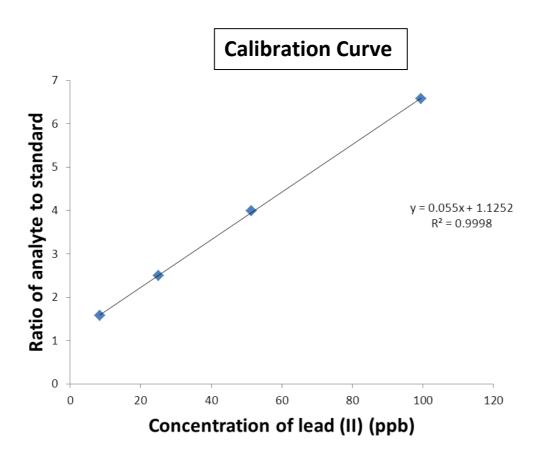


Figure 3: Calibration curve of lead (II) obtained by ICP-MS

#### 3.3. Effect of contact time

The percentage removal of lead (II) by polystyrene trisamine dithiocarbamate as a function of contact time was determined by using different times intervals (30-180 minutes) as shown in [figure 4].

The results obtained from ICP-MS showed that as the adsorption time increases the removal rate of lead (II) will increase and attained equilibrium at 120 minutes. However, it remains constant after an equilibrium time of 120 minutes, which indicated that the adsorption reached saturation. Therefore, the adsorption time was set at 120 minutes. The rate of adsorption was higher in the beginning due to a large available surface area of the adsorbent and high electrostatic attraction.

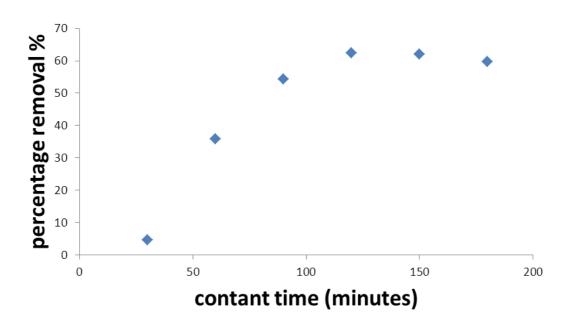


Figure 4: percentage removal of lead (II) on polystyrene trisamine dithiocarbamate as a function of contact time by ICP-MS spectroscopy (T= 28°C, pH= 3, initial conc.=100 ppb, adsorbent dosage=0.05 g).

#### 3.4. Effect of pH

The adsorption was performed at different pH values in the range of 3-7. From [figure 5] as the pH increases the percent removal of lead (II) decreases. The optimum pH is 3 and the percentage of adsorption was higher at low pH values in which due to a large amount of available protons which decreases as pH increases.

From [figure 6] we did not attempt to study below pH=3 because of possible decomposition of the dithiocarbamate functional group and we also did not study the effect of pH above 7 due to the precipitation of lead ions. At pH=3, the sulfur atom of dithiocarbamate functional group readily chelates to Pb <sup>2+</sup> ions.

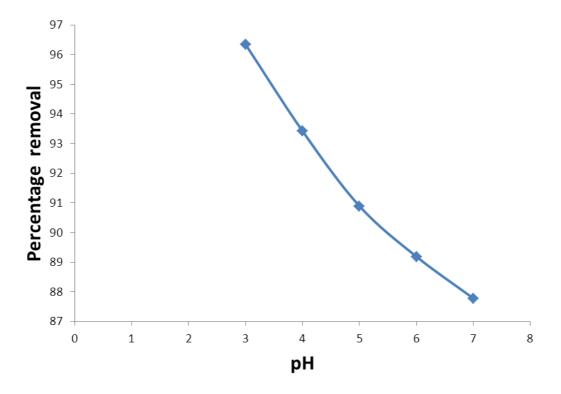


Figure 5: percentage removal of lead (II) on polystyrene trisamine dithiocarbamate as a function of pH by ICP-MS spectroscopy. T= 28°C, contact time= 120 min., initial conc.=100 ppb, adsorbent dosage= 0.05 g.

In acidic media the dithiocarbamate group takes the form (a) shown in [figure 6],the nitrogen (hard base) at low pH is protonated and the sulfur (soft base) is free. The form with the carbon nitrogen double bond is supported by the infra-red spectrum that showed a strong band around  $1700 \text{ cm}^{-1}$  so the chelation occurs between sulfur and lead [figure 6 (a)] most probably in a monodentate fashion as the sulfur is acting as a  $\sigma$ -donor.

As pH is raised, the dithiocarbamate group transforms from (a) to (b), leaving a delocalized negative charge over the two sulfur atoms. This delocalized system is expected to form a bidentate ligand with the heavy metal ion, apparently not so stable with Pb<sup>2+</sup> ions as demonstrated by the low removal of this ion as the pH increases from 3 to 7.

Cationic form Anionic form

(predominant in strongly acidic solutions) (predominant in strongly basic solutions)

Figure 6: Structures of dithiocarbamate group in (a) acidic and (b) basic medium

#### 3.5. Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of lead (II) is shown in [figure 7]. The initial lead (II) concentration used is 100 ppb for 120 minutes and adsorbent dosage from 0.01-0.5 g. The percentage removal of lead (II) increased with increase of adsorbent dosage. From (0.01 - 0.05 g) the percentage removal increasing dramatically (second order) with the increasing in the adsorbent dosage, while from (0.1 - 0.5 g) the increasing in the percentage removal is weaker (first order) increasing as the adsorbent dosage increases. This increase in removal is due to the availability of more adsorbent and so effectively a large surface area for lead (II) to be attached.

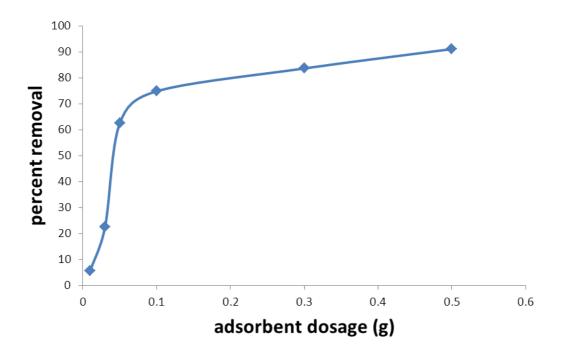


Figure 7: percentage removal of lead (II) on polystyrene trisamine dithiocarbamate as a function of adsorbent dosage by ICP-MS spectroscopy. T= 28°C, pH= 3, initial conc.=100 ppb, contact time=120 minutes.

From [figure 7] it is obvious that the optimum adsorbent dosage is 0.5~g in which the percentage removal reached at maximum value of 91.06~% but 0.05~g of polystyrene trisamine dithiocarbamate was used in the experiments according to the literature data.

#### 3.6. Effect of initial lead (II) concentration

The initial lead (II) concentrations were tested from 100-1000 ppb at pH=3, adsorbent dosage=0.05 g, T=28°C and contact time=120 minutes. [Figure 8] shows the percentage removal of lead (II) increase with decrease in the concentration of lead (II) solution. The highest removal (62.5%) occurs when the concentration of lead (II) solution is 100 ppb. At low initial lead (II) concentrations (less than 200 ppb) the ratio of lead ions to the available surface area is small so the adsorption process shows stronger concentration dependence, while at high initial lead (II) concentration (from 200ppb on), the percentage removal shows weaker dependence since there are fewer active sites for adsorption.

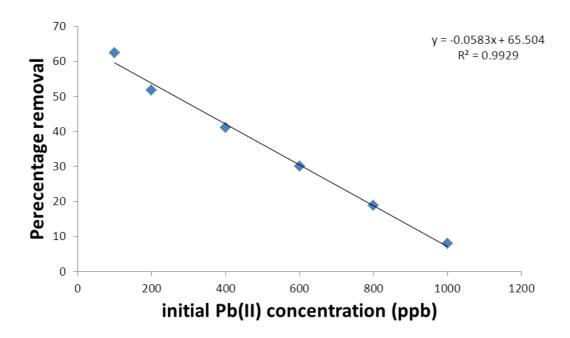


Figure 8: percentage removal of lead (II) on polystyrene trisamine dithiocarbamate as a function of initial lead (II) concentration by ICP-MS spectroscopy. T= 28°C, pH= 3, adsorbent dosage= 0.05 g, contact time=120 minutes.

#### 3.7. Regeneration of the adsorbent

The concentration of lead (II) desorbed into the KCl solution after agitation of adsorbent-lead (II) complex with 1M KCl was determined using the ICP-MS. The concentration of lead (II) in the KCl solution was 53.125 ppb. The initial concentration of lead (II) solution is 100 ppb and after agitation with adsorbent became 37.5 ppb determined by ICP-MS. The difference between initial concentration and final concentration represented the concentration of lead (II) that adsorbed on the adsorbent which is 62.5 ppb. The percent desorption was calculated and appeared at 85%.

Initial concentration of lead (II) solution	100 ppb
Concentration of lead (II) after agitation	37.5 ppb
Concentration of lead (II) adsorbed off the	62.5 ppb
adsorbent	
The percent desorption	85%

Table (1): Regeneration of the adsorbent

#### 3.8. Testing the removal of lead (II) by the regenerated adsorbent

The regenerated adsorbent was agitated with 100 ppb lead (II) solution for 2 hours and the percentage removal was calculated by determining the initial and the final concentration of lead (II) in the solution using ICP-MS instrument. The percent removal of lead (II) was 60%. The regenerated adsorbent had almost the same binding ability for lead (II) as the original adsorbent which was 62.5%.

Initial concentration of lead (II) solution	100 ppb
Concentration of lead (II) after agitation	40 ppb
The percentage removal of lead (II) by the	60%
regenerated adsorbent	
The percentage removal of lead (II) by the	62.5%
original adsorbent	

Table (2): Testing the removal of lead (II) by the regenerated adsorbent

#### 3.9. Adsorption isotherms

To model the adsorption behavior, two adsorption isotherms were studied and their correlation with experimental data was assessed.

#### 3.9.1. Langmiur isotherm

The Langmiur model was used to explain the observed phenomenon. The equilibrium data was analyzed using the following linear equation: [27]

$$C_e \setminus q_e = 1 \setminus Q_{max} K + C_e \setminus Q_{max}$$

Where:

Ce is the equilibrium concentration of solute in the bulk solution (mg\L)

qe is the amount of solute adsorbed per unit weight of adsorbent (mg\g)

 $Q_{max}$  is the adsorption capacity (mg\g)

K is the thermodynamic equilibrium constant related to the free adsorption energy

A plot of Ce\qe versus Ce was linear and the constants Qmax and K were determined from the slope and the intercept of the plot, which was found to be 319.49 mg\g and 0.4742 at  $28^{\circ}$ C and pH=3 with 0.05g adsorbent dosage. The correlation coefficient obtained with the Langmur equation was high  $R^2$ = 0.9992, which indicated a good fit with Langmur isotherm [figure 9].

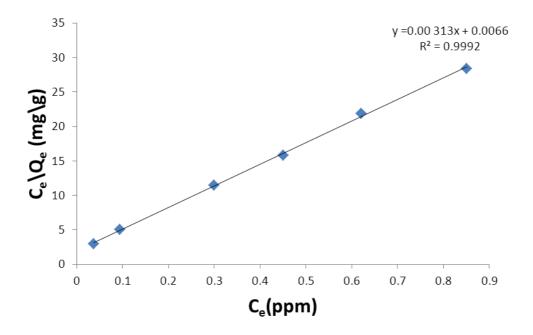


Figure 9: Langmiur isotherm for the adsorption of lead(II) on polystyrene trisamine dithiocarbamate using ICP-MS spectroscopy at T = 28°C, pH = 3, contact time= 2 hrs, adsorbent dosage=0.05 g.

Compared with other adsorbents [table 3], polystyrene trisamine dithiocarbamate showed high adsorption capacity.

#### 3.9.2. Freundlich isotherm

The adsorption behavior was also tested by Freundlich model .[28]

 $Log x\mbox{\em m} = Log K_f + 1\mbox{\em hog } C_e$ 

Where: x\m is the amount of solute adsorbed per unit weight of adsorbent (mg\g)

C<sub>e</sub> is the equilibrium concentration of solute in the bulk solution (mg\L)

K<sub>f</sub> is a constant indicative of the relative adsorption capacity of the adsorbent (mg\g)

1\n indicates the intensity of the adsorption

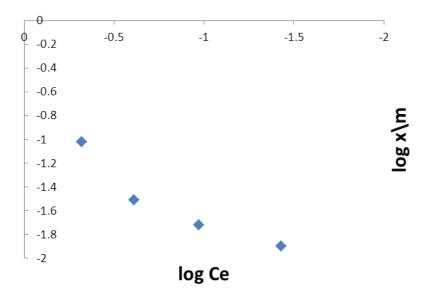


Figure 10: Freundlich isotherm for the adsorption of lead (II) on polystyrene trisamine dithiocarbamate using ICP-MS spectroscopy at T= 28°C, pH= 3, contact time= 2 hrs, adsorbent dosage= 0.05g

A plot of log x\m versus log  $C_e$  was non linear, which is indicative of bad fit between parameters. The regression coefficients ( $R^2$ ) were 0.9992 for Langmiur isotherm and 0.8828 for Freundlich isotherm. The  $R^2$  values indicated that Langmiur isotherm model is the best to describe the removal process of lead (II) ions by polystyrene trisamine dithiocarbamate. The Freundlich isotherm model does not agree well with the adsorption process.

#### 3.10. Proposed mechanism of adsorption

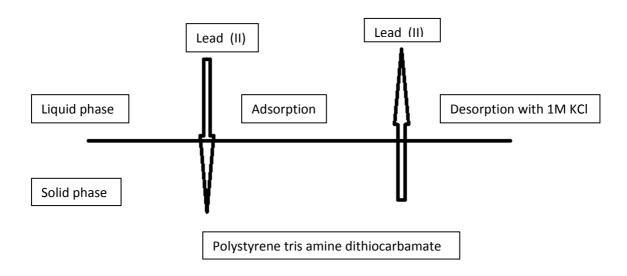


Figure 11: Proposed mechanism of adsorption of lead (II) on polystyrene trisamine dithiocarbamate

Initially, lead (II) was adsorbed on polystyrene trisamine dithiocarbamate as shown in [figure 11]. The entire N-C-S<sub>2</sub> group forming a resonance structure in dithiocarbamate molecules, leading to its characteristically different physical and chemical properties, such as a strong affinity to metals including lead. Lead (II) can be removed by using DTC due to the strong metal affinity of sulfur toward lead (II) by the formation of Pb-S bond. Upon addition 1M KCl to the adsordent, desorption of lead took place and was determined by ICP-MS.

#### 3.11. Comparison of adsorption capacity of various adsorbents

The adsorption capacity of the adsorbent polystyrene trisamine dithiocarbamate under ambient pH and 28° C was found to be 319.49 mg/g of adsorbent.

As [table 3] shows that the adsorption capacity of polystyrene trisamine dithiocarbamate is largest than the others, and this is 30% increase from the most efficient adsorbents reported [Oil palm fiber and Oil palm empty fruit bunch].

Adsorbent	Adsorption capacity (mg/g)	Reference
Palm shell activated carbon	1.337	29
Calcareous soil	2.34	30
Waste tire rubber ash	22.35	31
Poly dithiocarbamate resin supported on polystyrene	27.3	23
Activated carbon	54.945	32
Nipa palm nut (NPN)	125	32
Palmyra palm nut (PPN)	142.85	32.
Oil palm shell (OPS)	200	32
Oil palm fiber(OPF)	250	32
Oil palm empty fruit bunch	250	32
Polystyrene trisamine dithiocarbamate	319.49	This work

Table 3: Adsorption capacity of various adsorbents

# Conclusion

#### **Conclusion**

It is desirable to detect the lead concentration in drinking water and also to provide a suitable, environment friendly and cost effective lead removal process to save millions of people in all over the world from lead poisoning. It is concluded from this study that the adsorption is a valuable tool for controlling the level of aqueous lead pollution. The utilization of low cost adsorbents for the treatment of wastewater containing heavy metals is helpful as a simple, effective and economical means of water treatment.

The potential of polystyrene trisamine dithiocarbamate as low cost adsorbent for the removal of lead from aqueous solutions was established. The amount of lead (II) adsorbed was found to vary with adsorbent dosage, pH, contact time and initial lead (II) concentration. The optimal removal of lead was at pH=3, 120 minute as a contact time and at 100 ppb initial lead (II) concentration. Isotherm for the adsorption of lead (II) on polystyrene trisamine dithiocarbamate was developed and the equilibrium data fitted well to the Langmiur isotherm model, in which the maximum adsorption capacity was 319.49 mg/g which is considered to be very high compared to other adsorbents. Regeneration of adsorbent was studied and the desorption test indicated 85% removal of lead from the adsorbent. polystyrene trisamine dithiocarbamate is a good candidate to be used as an adsorbent for the removal of lead (II) from water because of its low cost and high efficiency.

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# Appendices

# **Appendices:**

#### A1: Determination of lead (II) Calibration curve

Ratio of analyte to standard	Concentration of lead (II) ppb
8.479	10
26.231	25
51.341	50
99.482	100

#### **A2:** Effect of Contact time

Contact Time (minute)	Final concentration of lead (II)	% removal of
	(ppb)	lead (II)
30	95.33	4.7%
60	64.24	35.8%
90	45.62	54.4%
120	37.50	62.5%
150	37.98	62.02%
180	40.20	59.8%

# A3: Effect of pH

pН	Final concentration of lead (II)	%removal of lead
	(ppb)	(II)
3	3.66	96.34%
4	6.58	93.42%
5	9.11	90.89%
6	10.81	89.19%
7	12.20	87.78%

# A4: Effect of adsorbent dosage

Adsorbent dosage (g)	Final concentration of lead (II)	% removal of lead (II)
	(ppb)	
0.01	94.30	5.7%
0.03	77.44	22.6%
0.05	37.50	62.5%
0.1	25.23	74.8%
0.3	16.40	83.6%
0.5	8.94	91.06%

### A5: Effect of Initial lead (II) concentration

Initial concentration (ppb)	Final concentration of lead (II)	% removal of lead (II)
	(ppb)	
	Ce	
100	37.5	62.5%
200	106.6	51.7%
400	243.9	41.1%
600	473.9	30.2%
800	785.7	18.8%
1000	850.22	8.08

### **A6: Langmiur isotherm**

C <sub>e</sub> (ppb)	C <sub>e</sub> \Q <sub>e</sub>
37.5	3
106.6	5
243.9	11.44
473.9	15.81
785.7	21.86
850.22	28.38

#### **A7: Freundlich isotherm**

Log C <sub>e</sub>	Log x\m
-1.43	-1.90
-0.97	-1.72
-0.61	-1.51
-0.32	-1.02
-0.10	-2.54
-0.07	-1.52

#### إزالة الرصاص الثنائي من المياه باستعمال بولى ستيرين ترس أمين ديثيوكربميت

اعداد: ايمان يوسف مخارزة

اشراف د. فؤاد الريماوي

المشرف المساعد: د. عماد عودة

#### الملخص باللغة العربية:

في هذا البحث، تم دراسة عملية إزالة الرصاص (الثنائي) من المياه باستخدام مادة مبلمرة وهي بولي ستيرين ترس امين ديثيوكربميت. تمت دراسة اثر درجة الحموضة ، وقت الاتصال، كمية المادة الرابطة و تركيز الرصاص (الثنائي) الابتدائي على عملية الامتصاص السطحي. تم حساب درجة الحموضة المثالية لعملية الامتصاص وهي 3. كما تم حساب وقت الامتصاص المثالي للرصاص (الثنائي) وهو 120 دقيقة. نسبة الرصاص المزالة انخفضت من 62.5% الى 8.08 % عندما تم رفع تركيز محلول الرصاص الثنائي من الرصاص المزالة انخفضت من 62.5% الى 8.08 ودرجة حرارة 28 مئوية وذلك عن طريق جهاز الامتصاص بواسطة البلازما. تم تقييم عملية ربط الرصاص الثنائي على بولي ستيرين ترس امين ديثيوكربميت باستخدام نموذج لانغمير الايسوثيرمي و نموذج فريندلش الايسوثيرمي. أظهرت النتائج ان نموذج لانغمير الايسوثيرمي يتناسب جيدا مع المعلومات التجريبية وكانت قدرة الامتصاص السطحي تساوي نموذج لانغمير الايسوثيرمي يتناسب جيدا مع المعلومات التجريبية وكانت قدرة الامتصاص السطحي تساوي معهد. 319.48