



MEDRC Series of R&D Reports
MEDRC Project: 16-DC-020

**Study the Effect of Reeds Tissues on the
Adsorption of Heavy Metals and Bacteria from
Sewage Water**

M. Sc. Thesis

Submitted By

Munjeda Tahseen Salman

Principal Investigator

Dr. Ahmad Abu-Obiad

An-Najah National University

**Middle East Desalination Research Center Muscat,
Sultanate of Oman**

2017

An-Najah National University

Faculty of Graduate Studies

**Study the Effect of *Reeds Tissues* on the
Adsorption of Heavy Metals and
Bacteria from Sewage Water**

By

Munjeda Tahseen Salman

Supervisor

Dr. Ahmad Abu-Obiad

Co-Supervisor

Dr. Raed Alkowni

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

2017

**Study the Effect of *Reeds Tissues* on the Adsorption of
Heavy Metals and Bacteria from Sewage Water**

By

Munjeda Tahseen Salman

This Thesis was defended successfully on / / 2017, and approved by:

Defense Committee Members

Signature

1. Dr. Ahmad Abu-Obiad/ Supervisor

.....

2. Dr. Raed Alkowni / Co-Supervisor

.....

3.

.....

4.

.....

Dedication

All praise to Allah, Lord of creation, the most Merciful and Compassionate, who blessed me with the ability to attain my task in this research work.

I am highly thankful to my dear husband Wael Nassar, and my children Mohammad, Amir, Luna and Sara for sacrificing their time and enjoyment for my studies.

My greatest gratitude to my family, specially my father and mother, sisters and brothers for their support and encouragement.

Acknowledgements

First of all, I am so grateful to Allah, Who gave me the patience and strength to finish my thesis.

I want to express my gratitude to my supervisors, Dr. Ahmad Abu-Obiad and Dr. Raed Alkowni, for their supervision, effort, and the time they spent in correcting and commenting on my work until the last stage.

Thanks also to the technical staff at the Department of Chemistry at An-Najah National University, especially. Mr. Nafeth Dwekat for his help, and to all who helped and encouraged me in any way...

الاقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل عنوان:

Study the Effect of *Reeds Tissues* on the Adsorption of Heavy Metals and Bacteria from Sewage Water

أقر بأن ما اشتملت عليه هذه الرسالة انما هو نتاج جهدي الخاص, باستثناء ما تم الاشارة اليه حيثما ورد, وأن هذه الرسالة ككل, أو أي جزء منها لم يقدم من قبل أي درجة أو بحث علمي أو بحثي لدى أي مؤسسة تعليمية أو بحثية أخرى.

Declaration

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

Student's name:

اسم الطالب:

Signature:

التوقيع:

Date:

التاريخ:

List of Contents

No.	Contents	Page
	Dedication	III
	Acknowledgment	IV
	Declaration	V
	List of contents	VI
	List of tables	VIII
	List of figures	X
	Abstract	XII
	Chapter One: Introduction	1
1.1	Pollution by pathogenic bacteria	2
1.2	Source, Fate and Behavior of Microorganisms	3
1.3	Pollution by heavy metals	4
1.4	Source and behavior of heavy metals	5
1.4.1	Cadmium (II)	7
1.4.2	Copper(II)	8
1.4.3	Iron(III)	8
1.4.4	Lead(II)	9
1.4.5	Nickel (II)	9
1.5	Phragmites Australia characteristic	10
1.6	Phytofiltration	11
1.7	Objective	12
1.8	Novelty	13
1.9	Hypothesis	14
1.10	Previous studies	14
	Chapter two: Methodology	14
2.1	Collection and treatment of biomass	16
2.2	Biological part experiment	17
2.2.1	Preparation sample for Antibacterial Activity	18
2.2.2	Preparation Media	18
2.2.3	Bacteria Preparation	19
2.3	Chemical part experiment	19
2.3.1	Preparation of the solution of metals	20
2.3.2	Preparation of stock solution of metals	20
2.3.3	Preparation of calibration curve	20
2.4	Metal quantification	20
2.5	The instruments	21
2.6	Studied Parameters	21

VII

2.6.1	Effect of initial concentration	21
2.6.2	Competing study	21
2.6.3	Effect of contact time	22
2.6.4	Effect of PH	22
2.6.5	Effect of temperature	22
	Chapter Three: Results and discussion	26
3.1	Results of biological part experiment.	27
3.2	Results of chemical part experiment.	27
3.2.1	Effect of initial metal ion concentration	27
3.2.2	Effect of competing ions	32
3.2.3	Effect contact time	34
3.2.4	Effect of PH	37
3.2.5	Effect of temperature	40
3.3	Adsorption isotherm of pb(II)	44
3.3.1	Freundlich model	44
3.3.2	Langmuir model	46
3.4	Adsorption thermodynamics	49
3.5	Rate order of the adsorption process	50
	Conclusion	55
	Recomendations	56
	References	57
	الملخص	ب

List of Tables

No.	Table	Page
1	Classification of phragmites Australia	11
2	Effect of initial metal ion concentration(5)ppm on the % removal by both Phragmites	27
3	Effect of initial metal ion concentration(10)ppm on the % removal by both Phragmites	28
4	Effect of initial metal ion concentration(15)ppm on the % removal by both phragmites	28
5	Effect of initial metal ion concentration(20)ppm on the % removal by both phragmites	29
6	Effect of the presence of all metals on the percent removal of each other by reed shoot.	30
7	Effect of contact time on the % removal of metals by reed shoot.	33
8	Effect of pH on the % removal of metals by reed shoot.	37
9	Effect of temperature on the % removal of metals by reed shoot.	41
10	Application of Freundlich adsorption isotherm on the % removal of pb by reed shoot.	42
11	Parameters and correlation coefficient of Freundlich isotherm model for adsorption of pb(II) onto reed shoot	43
12	Application of Langmuir adsorption isotherm on % removal of pb by reed shoot.	44
13	Parameters and correlation coefficient of Langmuir isotherm model for adsorption of pb(II) onto reed shoot	45
14	The values of the thermodynamic of pb(II) adsorption at various temperature	46
15	Parameters of thermodynamic for adsorption of pb(II) onto reed shoot	47
16	Applying Pseudo first- order for pb(II) adsorption onto reed shoot at 25°C	48
17	Pseudo first - order parameters for pb(II) adsorption onto reed shoot at 25°C.	50

18	Applying Pseudo second- order for pb(II) adsorption onto reed shoot at 25°C.	50
19	Pseudo second- order parameters for pb(II) adsorption onto reed shoot at 25°C.	51

List of Figures

No.	Figure	Page
1.2	Phragmites Australia (common reed)	17
2.2	Phragmites from sarra purification.	18
3.3	Effect of initial metal ion concentration on the % removal of (Fe) metal by both phragmites	25
4.3	Effect of initial metal ion concentration on the % removal of (Cd) metal by both phragmites	25
5.3	Effect of initial metal ion concentration on the % removal of (Cu) metal by both phragmites	26
6.3	Effect of initial metal ion concentration on the % removal of (Ni) metal by both phragmites	26
7.3	Effect of initial metal ion concentration on the % removal of (Pb) metal by both phragmites	27
8.3	Effect of metal ions on the percent removal of each other by shoot samples.	30
9.3	Effect of contact time on the % removal of (Fe) metal for shoot sample.	31
10.3	Effect of contact time on the % removal of (Cd) metal for shoot sample.	32
11.3	Effect of contact time on the % removal of (Cu) metal for shoot sample.	32
12.3	Effect of contact time on the % removal of (Ni) metal for shoot sample.	33
13.3	Effect of contact time on the % removal of (Pb) metal for shoot sample.	33
14.3	Effect of solution pH on adsorption of (Fe) metal ion by reed shoot sample.	35
15.3	Effect of solution pH on adsorption of (Cd) metal ion by reed shoot sample.	36
16.3	Effect of solution pH on adsorption of (Cu) metal ion by reed shoot sample	36
17.3	Effect of solution pH on adsorption of (Ni) metal ion by reed shoot sample	37
18.3	Effect of solution pH on adsorption of (Pb) metal ion by reed shoot sample	37
19.3	Effect of temperature on the % removal of (Fe) metal	38

	by reed shoot sample	
20.3	Effect of temperature on the % removal of (Cd) metal by reed shoot sample	39
21.3	Effect of temperature on the % removal of (Cu) metal by reed shoot sample	39
22.3	Effect of temperature on the % removal of (Ni) metal by reed shoot sample	40
23.3	Effect of temperature on the % removal of (Pb) metal by shoot sample	40
24.3	Applying Freundlich adsorption isotherm on the adsorption of pb(II) on reed shoot.	43
25.3	Applying Langmuir adsorption isotherm on the adsorption of pb(II) on reed shoot.	45
26.6	Aplot graph of $\ln K_d$ vs. $1/T$ for pb(II), adsorption onto shoot.	47
27.3	Pseudo first- order adsorption kinetics of pb(II) onto shoot.	49
28.3	Pseudo second order adsorption kinetics of pb(II) onto shoot.	50

List of Abbreviation

Symbol	Abbreviation
C _o	Concentration of pb(II) in the sample solution before treatment (µg/L)
C _e	Concentration of pb(II) in the sample solution after treatment (µg/L) at equilibrium
FAAS	Flame atomic absorption spectroscopy (FAAS): is a spectro analytical technique to determine quantity of chemical elements using absorption of optical radiation by free atoms in their gaseous state.
K ₁	The Lagergren's first order rate constant
K ₂	The pseudo second order rate constant
K _d	The distribution coefficient
K _F	Freundlich constant which is an approximate indicator of adsorption capacity of the sorbent (mg/g (L/mg) ^{1/n})
K _L	Langmuir isotherm constant (L/mg)
L	leaves parts for reed common plant
LH	leaves parts for Indian phragmites plant
n	Dimensionless Freundlich constant giving an indication of how favorable the adsorption process
Q _e	The amount of As(III) adsorbed per gram of the adsorbent (mg/g)
Q _m	Maximum monolayer coverage capacity (mg/g)
Q _t	Amount of adsorbate per unit mass of adsorbent at time t (min)
R	The gas constant (8.314 J/mol. K)
R	roots parts for reed common plant
RH	roots parts for Indian phragmites plant
R ²	regression coefficient
R _L	Dimensionless constant separation factor
t	Time
S	plant shoot parts for reed common
SH	shoot parts for Indian phragmites plant
ΔG°	Standard free Gibbs energy
ΔH°	Standard enthalpy
ΔS°	Standard entropy

**Study the Effect of *Reed Tissues* on the Adsorption of Heavy Metals
and Bacteria from Sewage Water**

By

Munjeda Tahseen Salman

Supervisor

Dr. Ahmad Abu-Obiad

Co-Supervisor

Dr. Raed Alkowni

Abstract

Phragmites Australia (reed common) and the other Phragmites from Sarra purification (leaves, shoots and roots) adsorption potential to remove Fe, Cd, Cu, Ni, and Pb from waste water and antibacterial activity were studied.

Initial concentration of metal ion, the effect of the presence of other competing ions, contact time, Ph, temperature, were also studied. Adsorption isotherms were investigated.

The results showed that the maximum percent removal of metal ions was at 20ppm concentration, the results for all metals were Fe (77,5%) by Phragmitesr roots from Sarra (RH), Cd(71,2%) by reed leave(L), Cu (88%)by reed shoot (S)and reed leaves(L), Ni(93%)by reed shoot(S), and by reed shoot. Almost all ions for lead pb were removed (97, 3%).

The optimal conditions of adsorption for lead were studied and the results showed that the highest percent removal of metal ions for Pb(II) was optimum at the initial concentration of 20 mg/L, a temperature range of

XIII

25°C - 40°C, and a contact time range of (10-30) minutes. Flame atomic absorption spectrometry was used to flow equilibrium concentration of metal ions in solution.

The results of the uptake of Pb (II) by reed shoot fit well with the Freundlich adsorption isotherm. Freundlich adsorption isotherm was found to be more applicable for the removal pb (II) The binding of metal ions with shoot followed a second order kinetics. The values of Gibbs free energy were also determined.

Chapter One

Introduction

Chapter One

Introduction

1. Introduction

Environmental pollution is the greatest challenge facing humankind today. Water pollution is one of these greatest challenges, the removal of pollutants from water and soil has been long researched in the fields of environmental science and engineering in order to find ways of eliminating this serious problem in both, the developed and developing worlds.(Jadia and Fulekar, 2009; Lu *et al.*, 2010).

Water pollution may include organic contaminants such as pathogenic bacteria and inorganic contaminants such as heavy metals.

Heavy metals are among the contaminants in the environment. Almost all human activities have produced heavy metals as the side effect beside the natural activities. Transmissions of these contaminants from contaminated areas into non- contaminated areas by dust or leachates through the soil and spreading of heavy metals containing sewage sludge are examples of this pollution towards contamination of the ecosystems (Gaur and Adholeya, 2004).

1.1. Pollution by pathogenic bacteria.

The pollution of water resources and related diseases by water-borne pathogen contamination are the biggest concern regarding water quality

throughout the world. For almost all types of ambient water bodies, pathogen contamination is a serious issue, making its recognition and understanding essential.

3.4 million People each year, mostly children, die from water-related diseases, according to the World Health Organization (WHO) (WHO [2014]). 4000 children, according to an assessment by the United Nations Children's Fund (UNICEF), die each day as a result of contaminated water (UNICEF [2014]). The world Health Organization WHO ([2010]) reports that lack of access to clean water for over 2.6 billion people is responsible for about 2.2 million deaths annually, 1.4 million being children. Improving water quality can minimize the global burden of disease approximately 4% (Pramod et al., 2014).

The pathogens of particular interest, such as *staphylococcus aureus*, *pseudomonas aeruginosa*, *Escherichia coli*, *protesu mirabilis* and *klebsiella sp* have been selected in this project because they are considered of great health significance (Dechesne, 2006).

1.2. Sources, Fate and Behavior of Microorganisms in Water

Water sewage overflow (CSO), and non-collective sewage systems lead to the microbial contamination of water .this contamination is of fecal nature either to humans or from manure spreading, pit stock overflow, from domesticated animals or from wildlife. The discharges of water treatment plants, decontamination stations, hospitals and industries into the natural aquatic resources are the main sources of the microbial contamination of

these resources and are considered as point sources. The correlation between pathogen concentrations and urban activities is well documented (Jung; 2014).

The abundance of pathogens in water depend on factors such as the contamination level, the persistence of pathogens in water bodies, biological reservoirs (including aquatic plants and sediments) and the ability of pathogens to be transported (Dechesne, 2006). The Knowledge of the widespread contamination of water resources necessitate an appraisal of the effect on human of infection caused by pathogen.

The management practices of land use and the size of the watershed also influence the survival of microorganisms (George, 2004)

Streams flowing through areas partly or fully covered with pastures are more contaminated than those running through forests and cultivated areas. (Jung, 2014).

1.3. Pollution by heavy metals

Heavy metals are naturally occurring elements in the environment and they have a specific gravity at least five times the specific gravity of water. The term heavy metal refers to all the metals having density over (6). For example, Cu – 8.93, Cd – 8.65 and Pb has density of 11.34. Therefore, the term “heavy metal” has become interchangeable with toxic metal. (Blaylock, 2000).

The official “term toxic” metal is more valid for the group of metals such as Cd, Cu, and Pb. This is because some of them are essential within limits

for humans, animals, plants and other living organisms, but in excess, they prove to be toxic. The chronic exposure or quantity beyond permissible level makes them toxic for humans and other organisms. (Blaylock, 2000).

This necessitates a demand for sequestration of toxic heavy metal. This is due to the fact that toxic heavy metals are not biodegradable over time and this makes their accumulation in the environment a threat to both, human health and the environment.

1.4. Sources and behavior of toxic heavy metals

Mining operations and domestic waste water effluents containing large quantities of trace metal elements from metabolic waste, detergents or pipe corrosion are the main sources of toxic heavy metals (Csuros and Csuros, 2002). Other sources of high content of heavy metals are storm water runoff, industrial wastes and discharges, and sanitary landfill (Csuros and Csuros, 2002). Besides the natural activities, almost all human activities also have made a potential contribution to the production of heavy metals as side effects. (Gaur and Adholeya, 2004).

Many industrial activities, such as mining, processing minerals and chemical industries, increase harmless and non-essential metal concentration in the water tables in the surrounding regions of their manufacturing plants (Ho and El-Khairi, 2009). Metalliferous soils can contain high amounts of heavy and toxic metals (Gardea-Torresdey, 2003)

Most metals in their metallic or zero valence state are insoluble. Sodium is an exception which reacts with water some metal compounds can be dissolved in water, which may be introduced to soil and thus transferred to the food chains, since these metals are not degradable metabolically, their accumulation in living tissues can cause serious health effects

The researcher has selected metals (Fe,Cu,Cd,Ni,Pb) which are commonly found as pollutants in different habitats in the water tables of Palestine.

Pb, Cu and Cd are considered as heavy metals because they have the characteristics of forming positive ions in the solution and each has a density more than 5 gm/cm³. Each of these metals is discussed below in terms of their properties, significance, and toxicity and effect on health.

1.4.1. Cadmium: Cd (II)

Cadmium is a metal silvery-white color, lustrous, soft, and ductile and has a relatively high vapor pressure. It is divalent when it is in a free condition, and moderately active similar to other stable metals (Csuros and Csuros, 2002). It is a rare metal and it is spread uniformly in the Earth's crust with an average concentration of 0.15 to 0.2 mg/kg. (Naja and Volesky, 2009). Cd is more soluble in the acid medium, increasing the acidity of the solution will increase the dissolution of suspended or sediment bound cadmium. Cd concentration in unpolluted fresh water is found to be less than 0.001 mg/L and in seawater 0.00015 mg/L (Naja and Volesky, 2009).

Main sources of Cd pollution are industrial and municipal wastes. Cd is used in as a protective layer for other metals, in nickel – cadmium, silver–cadmium or solar batteries, electroplating, paint pigments, plastics, and many other uses. (Csuros and Csuros, 2002). Current Cd production in the world is 20,000 tones; the use of Cd is growing at a current annual rate of 5 to 10%. (Bernard and Lauwerys, 1984, Naja and Volesky, 2009). Cd is considered as a very toxic metal because it is not an essential nutrient for animals or humans. Even if it is absorbed in very small quantities by the body, it can cause severe high blood pressure, heart disease and can even lead to death (Pan *et al.*, 2010).

1.4.2. Copper (II)

Cu is a high conductor of electricity. It is a corrosion resistant metal that is reddish brown, malleable and ductile, (Csuros and Csuros, 2002). Cu is mainly used in plumbing and electrical conductors because it is a high conductor of electricity. In the presence of CO₂, it oxidizes slowly in air and its surface exhibits a green color due to a film of Cu₂ (OH)₂ CO₃ (Flemming and Trevors, 1989). It usually exists in the +2 oxidation state. CuO – copper (II) oxide which is black, can also exist in the +1 state Cu₂O – copper (I) oxide which is red. It is essential to life as small amounts because it plays a major role in the enzyme function as a co-enzyme, but in large amounts, it is toxic (Abel, 2002).

1.4.3. Iron (III)

Iron, is the second most common metal on Earth, and the most widely-used. It forms most of the Earth's core, and is the fourth most common element in the Earth's crust. Iron is the most metal used, more than any other metal because it is strong and cheap. It is used to make buildings, bridges, and pipes.

Iron as a chemical reacts with most acids, like sulfuric acid, to make ferrous sulfate, and reacts with air and water to form rust. There are ferrous compounds and ferric compounds: ferrous compounds where iron has two electrons taken and ferric compounds: when iron has three electrons taken. Ferrous compounds have iron in its +2 oxidation state.

Ferric compounds have iron in its +3 oxidation state. Iron compounds can be black, brown, and yellow or green. (Wang *et al.*, 2009).

Iron compounds are used for several things. Iron (II) chloride is used to clean water. Iron (II) sulfate is used to reduce chromates in cement. Some iron compounds are used in vitamins. Iron deficiency is the most common nutritional deficiency in the world. Our bodies need iron to help oxygen get to our muscles, but it is toxic when large amounts in the form of too many iron pills are taken into the body. (Wang *et al.*, 2009).

1.4.4. Lead (II)

Lead (Pb) is a soft, and bluish – grey color metal; it is one of the most common heavy elements and also the most abundant. Pb can resist corrosion and has a low melting point of 327° C. and have two oxidation states, +2 and +4. The main sources of pollution of pb solid and liquid sludge wastes that participate with more than half of the Pb contamination in the environment, mainly through landfills. The other grate pollutant of pb is exhaust fumes of cars which cause atmospheric pollution (Naja and Volesky, 2009).

Lead pollution increased during the industrial age and this pollution has risen rapidly since it was added to the gasoline fuel of vehicles .Therefore we can say lead pollution is a typical example of anthropogenic metal pollution. (Valavanidis and Vlachogianni, 2010). Current Pb annual production in the ward is approx. 3 million tons, of which 40% is consumed by electrical accumulators and batteries, 20%

additives in gasoline, 12% in construction, 6% in cable coatings, 5% in ammunition and 17% in diverse uses. However, there are many countries have stopped lead additive usage in gasoline due to environmental hazards (Naja and Volesky, 2009). Pb has many harm effects on the health of human, it is toxic to the human nervous system and children are more capable to its effects. By absorption Lead can go to the central nervous system directly from the intestinal tract (Abel, 2002; Naja and Volesky, 2009)

1.4.4. Nickel (II)

Nickel (II) chloride is the chemical compound NiCl_2 . The anhydrous salt is yellow, but the more familiar hydrate $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ is green. Nickel (II) chloride, in various forms, is the most important source of nickel for chemical synthesis. The nickel chlorides are deliquescent, absorbing moisture from the air to form a solution. Nickel salts are carcinogenic. Nickel (II) chloride is irritating upon ingestion, inhalation, skin contact, and eye contact. Prolonged exposure to nickel and its compounds have been shown to produce cancer. (Wang *et al.*, 2009)

1.5. *Phragmites australis* characteristic

Kingdom	Plantae
Phylum	Magnoliophyta
Class	Liliopsida
Order	Cyperales
Family	Poaceae
Genus	<i>Phragmites</i>
Species	<i>Austral</i>

Table (1.1): Scientific classification of *Phragmites australis* (Lansdown, 2015).

Phragmites Australia (PA) plant, also known as common reed, is a perennial plant which is widely used and has find great interest for remediating soils and water polluted by multi-metals, due to its ability to thrive with rapid growth and high yields in a wide range of adverse conditions. Furthermore, the most common reed plant species, '*Phragmites australis*' (PA plants) can grow in natural or artificial conditions. (Khaled Al Akeel, 2013)

These plants are found all over the world in various habitats and conditions. These plants are known as common reed or ditch reed in English and Qasab/ Ghaab in Saudi Arabian Arabic.

It is found in many counties in the world; North America, Europe, the Middle East, Africa and Australia. It is generally found in low level coastal plains or riparian areas. This plant can reach a length to 3.5 meters and have the ability to move oxygen through its stems to the roots. The roots can resist difficult conditions it can grow even in moist or water logged soil conditions.(Khaled Al Akeel, 2013; Lansdown, 2015).

1.6. Phytofiltration

The bioremediation technology is the overall term, it is include phytofiltration and phytoremediation. Bioremediation mean using biological agents as bacteria or plants to remove or equalize contaminants

in polluted water. (Gardea-Torresdey, 1996; Volesky, 2001).

Phytoremediation: a friendly (green) technology for the environment that uses living plants to remove contaminants from the environment or rendering them harmless (Berti and Cunningham, 2000; Salt *et al.*, 1994).

Phytoremediation is the efficiency and cheap technology used to extract or remove pollutants from contaminated soil and water.

phytofiltration; the use of dead or inactivated biomass to remove heavy metals from contaminated water (Miller, 1996; Gardea-Torresdey *et al.*, 2004). Phytoremediation can be achieved by phytoextraction, phytovolatilization, phytodegradation, phytostabilization, and rhizofiltration.

Rhizofiltration: is the use of the plant roots as a filter to absorb pollutants, mainly heavy metals, from waste water (Zhu *et al.*, 1999; Dushenkov *et al.*, 1995). Phytoextraction: is the direct uptake of metals from soil into the plant roots that translocate into the upper parts of plant to be harvested later (Cluis, 2004). Phytodegradation, also called phytotransformation, is a contaminant extermination process, it is a Phytoextraction mechanism, but differs in that, after the contaminants are translocated in the aerial portions of the plant, they are converted to a less toxic form, because the plant produced enzymes to metabolize the contaminants (Singh and Labana, 2003). Phytostabilization: is the process by which plants stabilize the contaminants in the soil to prevent the risk of their leaching in ground water or spreading in the air that reducing their bioavailability in the environment (Prasad and de Oliveira Freitas, 2003).

Previous experiments have shown that the dead Biomass has a good ability to bind toxic contaminants from waste water and the dead biomass shows better properties than living organisms. It is not affected by high concentrations of pollutants, and needs no maintenance, in contrast to living organisms, which are affected by high concentrations of pollutants and need nutritional supply (Gardea-Torresdey, *et al.*, 1996).

The demand for new material that is more efficient, inexpensive, biodegradable, and environmentally friendly, as the use of plant material (*phragmites australis*) for the purification of toxic products in aqueous effluents has received a significant credibility in recent years (Laidani *et al.*, 2010).

1.7. Objective

In this research, the objective is to study and determine the potential of *phragmites Australia* plant which collected from Wadi Al Bathan and compare it with the other plant of pragmites which was taken from sewage purification plant in Sarra to remove Pb, cu, Ni, Cd and Fe from aqueous solution, and to investigate the optimal conditions for phytofiltration e.g., temperature, ph, contact time of adsorption, concentration of metal ions, and effect of other competing ions. The kinetics of the biosorption process and the adsorption isotherms will be explored in this study, in addition to the testing of anti-bacterial activity for the *Phragmites Australia*.

1.8. Novelty

Many studies have studied the use of plants and their role in contaminated water treatment, but few of these researched the *phragmites Australia* and no previous studies have examined the leaves, stems and roots of this plant and their ability to adsorb toxic metals and compared the amount of removal of toxic metals from wastewater.

This research studies the adsorption of Pb (II), Cu (II), Cd (II), Ni (II) and Fe (III), by the leaves, stems and roots of *phragmites Australia* at optimum batch conditions. More focus will be given to the shoot of *Phragmites Australia*.

1.9. Hypothesis

This work was managed under the hypothesis that all leaves, stem and root of *Phragmites Australia* are able to adsorb certain amounts of the heavy metals Pb(II), Cu(II), Cd(II), Ni(II) and Fe(III) from their aqueous solutions.

1.10. Previous studies

One study investigated the accumulation of nutrients and heavy metals (Cr, Ni, Cu and Zn) in *Phragmites Australia* and this study confirmed that the accumulation generally increased toward the end of the growing season. (Bragatoa, 2006).

Another study investigated the heavy metal bioaccumulation by the organs of *Phragmites Australis* (common reed) and their potential use as contamination indicators. This study shows that the toxic threshold was exceeded by Cr in roots. (Bonanno and Giudice, 2010)

One of the studies found that the concentration of any one metal in the different tissues was affected by the presence of other metals. That means there are interactions between the metals and this affects their distribution in the tissues of *Phragmites Australis*. (Judith and Weisa, 2004).

Demirezen and Aksoy (2004) found that *Phragmites Australis* is useful to measure concentration of heavy metals such as Iron and Manganese and the PA plants can be used as biological indications in the determination of environmental pressures

Another study examined the removal of cadmium from polluted water using decaying leaves the effects of type of leaves and of the concentration of cadmium which was researched at An-Najah University in corporation with Birzeit University, found that reed leaves are efficient for removing cadmium from aqueous solution. (Sayrafi and Salim, 1996).

Chapter Two

Methodology

Chapter Two

Methodology

2.1 Collection and treatment of biomass

Phragmites Australia plant were collected from Wadi Al Bathan field. Plants were removed from the soil and washed, and the roots were separated from the stems and leaves. The other samples of *phragmites* were collected from the sewage Purification plant from Sarra. Washed, and the roots, stems, and leaves, were separated. All samples were oven dried at 37C for one week. Then the leaves, root and stem of both plant samples were crushed separately.



Figure (1.2): Phragmites Australia (common reed)



Figure (2.2): Phragmites from purification plans in Sarra.

This was followed by two parts of the experiment: The biological part which examined the antibacterial activity for both of two phragmites plants, and the other part in which the chemicals were analyzed to the effects of

both plants on the adsorption of Cu (II), Cd (II), Ni (II), Pb(II), and Fe(III) metals.

2.2. The experiment of Biological part:

2.2.1. Preparing Sample for Antibacterial Activity.

The dried plant material was ground to a fine powder in a blender. A measured amount (7gm) of dried powder from *phragmites australia* and 6gm from the other phragmites were soaked in 100cc of methanol in a round bottom flask and put in a shaker at room temperature for 48 h.

Another measured quantity 7gm and 6gm of dried powder for both of *phragmites* were soaked in 100cc of distilled water in round bottom flask and put in a shaker at room temperature for 48 h.

Extracts of methanol and water sample were filtered using a Buckner funnel and Whatman No 1 filter paper. The filtrate of all of the samples was put in centrifuge.

Then methanol samples were concentrated to dryness in autoclave at (121°C) until dry methanol extract was obtained. But the water samples were put in freezer For the antibacterial test, samples of 50 mg from each plant extract were taken with a concentration of 10% DMSO, which was prepared and used for antibacterial analysis.

2.2.2. Preparation Media

Mueller-Hinton Agar was prepared for this test.

Media powders (36g/L) were added to sterile distilled water. Then the media were heated to boiling to dissolve the media completely. Then the media were poured into sterile petri dishes which were sterilized by autoclaving at 15lbs pressure (121c) for 15 minutes, and then lifted to be dried before being used. Holes were made using heads of sterile glass pipettes.

2.2.3. Bacteria preparation.

At least four morphologically similar colonies were taken from *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Escherichia coli*, *Klebsiella sp* bacteria with sterile loop and transferred into MHA. To affect the performance of the test, the plates were incubated in the incubator for 48hours.

2.3 Chemical parte experiment:

2.3.1. The Preparation of solutions of metals

In this part, solution of the five metals (Pb, Cu, Cd, Ni, Fe) was prepared. $\text{Pb}(\text{NO}_3)_2$, unhydrous (zero H_2O) (2.07 gm/L), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (2.4gm/L), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (4.03gm/L), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.90gm/L), and $(\text{NO}_3)_2$, unhydrous (2.36gm/L) were used to prepare 100 ppm of each metals respectively.

2.3.2. The Preparation of stock solution of metals

Stock solution from the solution of each metals $\text{Pb}(\text{NO}_3)_2$, unhydrous(zero H_2O)(**1.2ml**), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (**3.96ml**), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (**4.487ml**), $(\text{NiNO})_2 \cdot 6\text{H}_2\text{O}$ (**4.27ml**), and $\text{Cd}(\text{NO}_3)_2$ unhydrous (**4ml**).were used to prepare 50ppm in (500ml/L) of each metals.

Then from the stock solution of metals, four concentrations (5ppm, 10ppm, 15ppm, 20ppm).were diluted

2.3.3. The Preparation of standardization curves.

A new 50 ppm metal particle solution was arranged day by day by progressive mitigations of the stock 500ml solution. At that point 5, 10, 15 and 20 ppm solution were set up by weakening 25, 50.75 and 100 ml individually from the 50 ppm standard arrangement into 250 mL volumetric vials. Deionized water was utilized as a clear. All volumetric vials washed with 0.1 M HNO_3 before being used. The concentration of the metal particles was trailed by measuring the absorbance of the solution by flame atomic absorption spectrometry (FAAS). A standardization curve of absorbance versus concentration was formed at the time of investigation. Alignment coefficient (R^2) was no less than 0.999 for all investigations. The instruments were washed with Deionized water prior and then afterward the examination of each sample to avoid the contamination and a different control of 20 ppm for each metal solution was perused for all samples.

2.4. Metals quantification

The percent removal of metal particle by biomass was calculated by applying the equations:

$$\% \text{ Removal} = \frac{C_o - C_f}{C_o} \cdot 100 \quad (1)$$

Where C_o is the underlying metal particle fixation, (mg/L), and C_f is the last particle fixation (mg/L) after the event biosorption.

2.5. The instruments

- (ICE 3000 SERIES, Thermo Scientific) Flame atomic absorption spectrometer with acetylene-air flame was used for absorption measurements.
- JENWAY (3510) pH Meter was used to measure pH.
- Shaker was used to mixing the samples.
- Incubator

2.6. Studied parameters



2.6.1. Effect of concentration dose

Different concentrations solution (5, 10, 15, and 20 ppm) of all metals was fit out from their stock solutions. For each concentration (30gm) of plant samples (leaves, stems and roots) were filed in column and (500ml) of

metal ion solution were added to it. Then the extracts were saved for metal quantification.

2.6.2 The effect of competing test.

$\text{Pb}(\text{NO}_3)_2$ anhydrous (0.1ml), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.35ml), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.36ml), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.34ml), and $\text{Cd}(\text{NO}_3)_2$ anhydrous (1.78ml), were used to prepare 20ppm in a 100ml flask. (30gm) of plant samples (leaves, stems and roots) were filed in column and (500ml) of metal ion solution were added to it. Then the extracts were saved for metal quantification, using Flame atomic absorptions spectrometer (FAAS).

2.6.3 The effect of contact time on shoot samples.

The effect of contact time on shoot samples at binding time intervals of 15,30,60,90 and 120 minutes were studied. For each time interval, the shoot samples were mixed with 20ppm metal ion solutions, and then the extracts were saved for metal quantification using Flame atomic absorptions spectrometer (FAAS).

2.6.4 The effect of pH on shoot samples.

The impact of pH was studied. The plants samples were regulated to pH values (3 – 10) by either including 0.1 M HCl or 0.1 M NaOH for each biomass sample,

The stem samples were blended with (20ppm) metal particle solutions, and then the extracts were saved for metal quantification, using Flame atomic absorptions spectrometer (FAAS).

2.6.5 The Effect of temperature on shoot samples.

The effect of temperature on shoot samples was investigated at different degrees of 15, 25, 40 C°, and 60 C°. For each temperature, the stems samples were mixed with 20ppm metal ion solutions, and then the extracts were saved for metal quantification using Flame atomic absorptions spectrometer (FAAS).

Chapter Three

Results and Discussion

Chapter Three

Results and Discussion

3.1. Results of the experiment of the Biological part:

The results of all samples of antibacterial activity test came out negative. This means that *phragmites Australia* and the other *phragmites* from Sarra have not had the promised effect on the pathogenic bacteria.

3.2. Results of Chemical part experiment:

3.2.1. The Effect of initial concentration

The effect of initial metals, ions concentration on their removal are shown in the figures(3 to 7) for all metals (Fe,Cd,Cu,Ni,Pb) respectively in both *phragmites* biomasses. As seen, increasing the initial metal ion concentration for all metals lead to an increase in the percent removal of the metal ions by both plants. At low concentration, most metal ions were not occupying, yet the available sites of biomassand. These sites will be occupied by increasing the concentration of these ions. The sites will be filled to saturation. More ions have more removal. The removal is increased by increasing the concentration. (Sayrafi and Salim, 1996)

In the 20ppm concentration, as can be seen in table (6) the percent removal for pb metal by shoot sample of *Australia phragmites* is the highest percent (97,3%) .

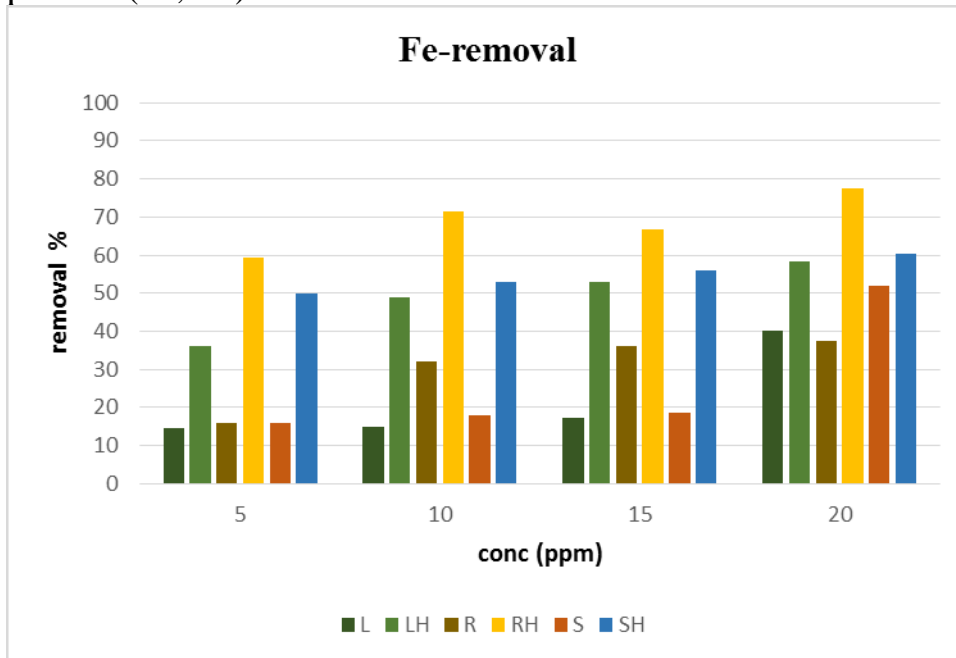


Figure (3): Effect of initial iron metal ions concentration on the % removal by both phragmites.

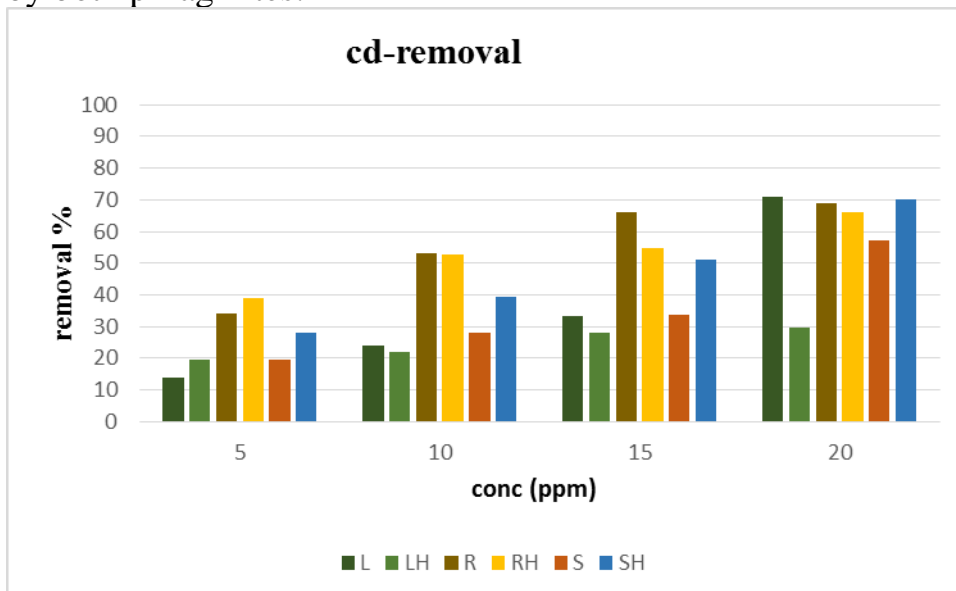


Figure (4): Effect of initial cadmium metal ions concentration on the %removal by both phragmites.

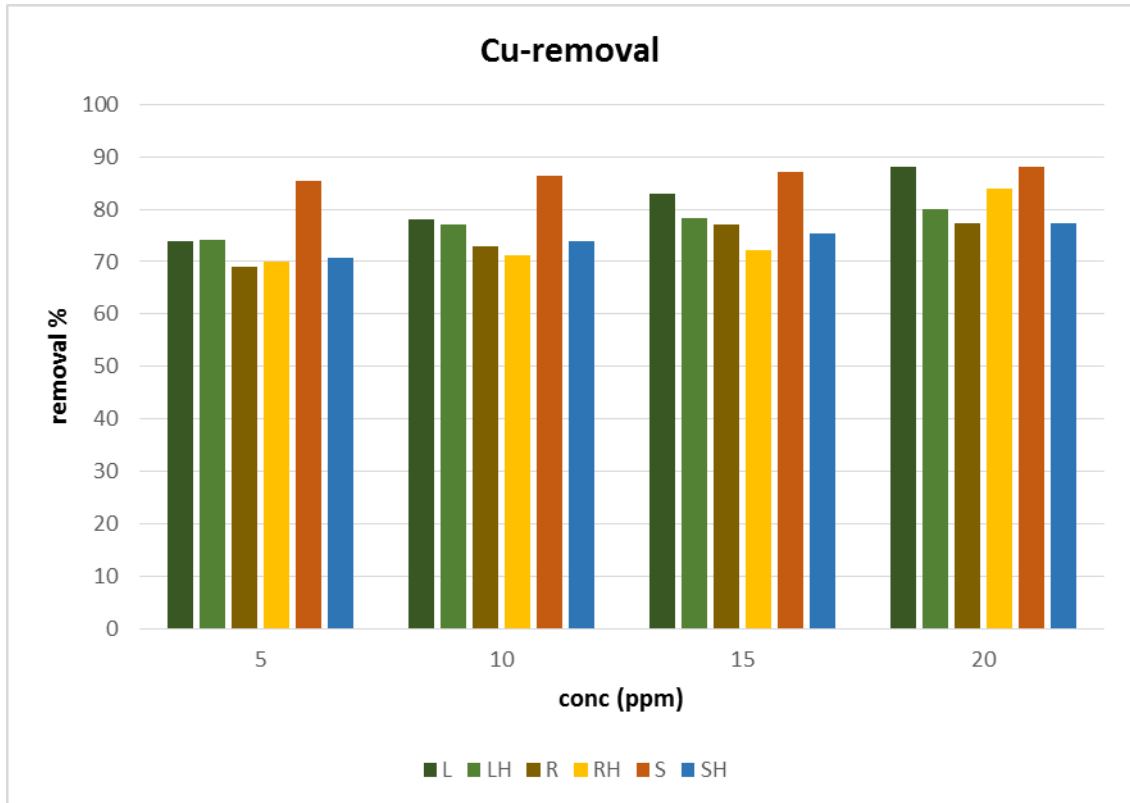


Figure (5): Effect of initial copper metal ions concentration on the %removal by both phragmites

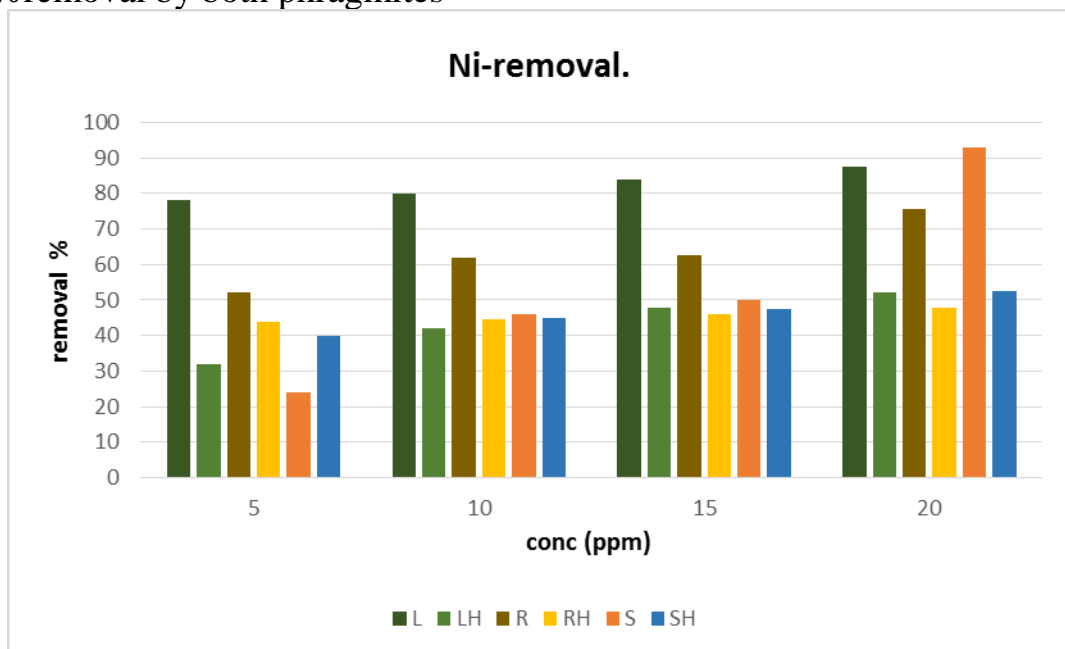


Figure (6): Effect of initial nickel metal ion concentration on the %removal by both phragmites

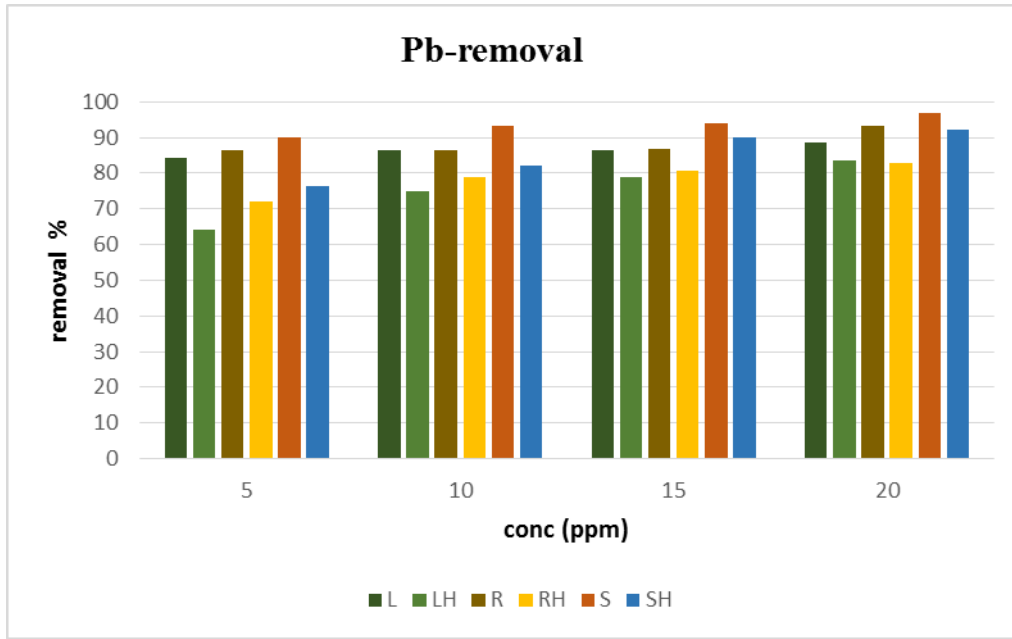


Figure (7): Effect of initial lead metal ion concentration on the %removal by both *phragmites*.

concentration	% Removal	% Removal	% Removal	% Removal	% Removal
5 (ppm)	of Fe	of Cd	of Cu	of Ni	of Pb
L	14,5%	14,%	74,4%	78%	86,4%
LH	36%	9,5%	74,2%	32%	64%
R	16%	34%	69%	52%	86,6
RH	59,5%	38,8%	70,0%	44%	72%
S	16%	19,4%	85,4%	24%	90,1%
SH	50%	28,2%	70,8%	40%	76,2%

Table (2): Effect of (5) ppm metal ion concentration on the % removal of metals by samples of leaves, stems and roots of both *phragmites* biomass, natural pH values, 25 °C.

concentration 10(ppm)	% Removal of Fe	% Removal of Cd	% Removal of Cu	% Removal of Ni	% Removal of Pb
L	15%	24.5%	78,4%	80%	86,4%
LH	49%	22%	77,2%	42%	75%
R	32%	53%	73%	62%	86,6
RH	71,5%	52,8%	71,3%	44,5%	78,8%
S	18%	28,2%	86,2%	46%	93,3%
SH	53%	39,2%	74,0%	45%	82,2%

Table (3): Effect of (10) ppm metal ion concentration on the % removal of metals by samples leaves, stems and roots of both *phragmites*, natural pH values, 25C.

concentration 15 (ppm)	% Removal of Fe	% Removal of Cd	% Removal of Cu	% Removal of Ni	% Removal of Pb
L	17,3%	33,3%	83.2%	83,9%	84,9%
LH	52,9%	28%	78,2%	48%	79,5%
R	36,6%	66,9%	77%	62,6%	86,9
RH	74,6%	54,8%	72,3%	46%	80,8%
S	18,6%	33,6%	87,2%	50%	94,1%
SH	56%	51,32%	75,3%	47,3%	90,1%

Table (4): Effect of (15) ppm metal ion concentration on the % removal of metals by samples leaves, stems and roots of both *phragmites* biomass, natural pH values, 30min., 25C

concentration	% Removal of Fe	% Removal of Cd	% Removal of Cu	% Removal of Ni	% Removal of Pb
20 (ppm)					
L	40,5%	71,2%	88%	87,6%	88,5%
LH	58,5%	29,5%	80%	52,5%	83,7%
R	37,4 %	69,8%	77,4%	75,5%	93,3
RH	77,5%	66%	84%	48%	83%
S	52%	57%	88%	93%	97%
SH	60,3%	70,7%	77,5%	52,5%	92%

Table (5): Effect of (20) ppm metal ion concentration on the % removal of metals by sample leaves, stems and roots of both *phragmites* biomass, natural pH values, 30min., 25C.

As can be seen in tables (2-6) the shoot of *phragmite*, which was collected from Wadi Al Bathan had the most percent of removal for pb and other metals, showing the optimum condition (PH, temperature and contact time) of adsorption studied for shoot samples.

3.2.2. Effect of competing test

As we know, more than one substantial metal particle is brought about by water contamination and the presence of the accumulation of many metals

caused interferences between them. This impact on their connecting to biomass when existing in similar solution, as can be seen in table (6) in the presence of all metals (Fe,Ni,Cd,Cu,Pb) the percent removal of Pb is the best $Pb > Cu > Fe > Ni > Cd$.

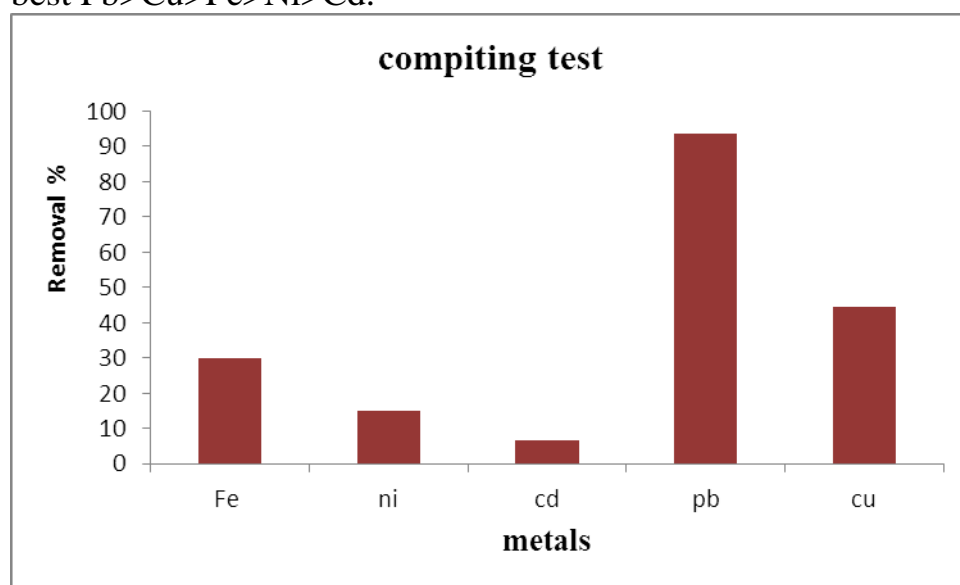


Figure (8): Effect of metal ions on the percent removal of each other by shoot samples. $Pb > Cu > Fe > Ni > Cd$

Metal at 20 ppm conc	% Removal
Fe	30%
Ni	15%
Cd	6,5%
Pb	93,5%

Table(6): Effect of the presence of all metals on the percent removal of each other by reed shoot. (3mg/mL biomass, optimum pH values (for each metal) 25°C

The impact of competing ions is appeared to be subject to the sorption liking of the sorbent and the metal. The results show that the binding sites on *phragmites Australia* shoot have higher affinity for pb compared to that for other metals when they are mixed together.((Sayrafi and Salim, 1996).

3.2.3. Effect of contact Time on reed shoots samples

A amongst the most imperative parameters that is considered for waste water treatment applications is contact time Figures (9-13) show the percent removal of metal ions by shoot samples of *phragmites australia* at different contact times. The data is shown in tables (7).

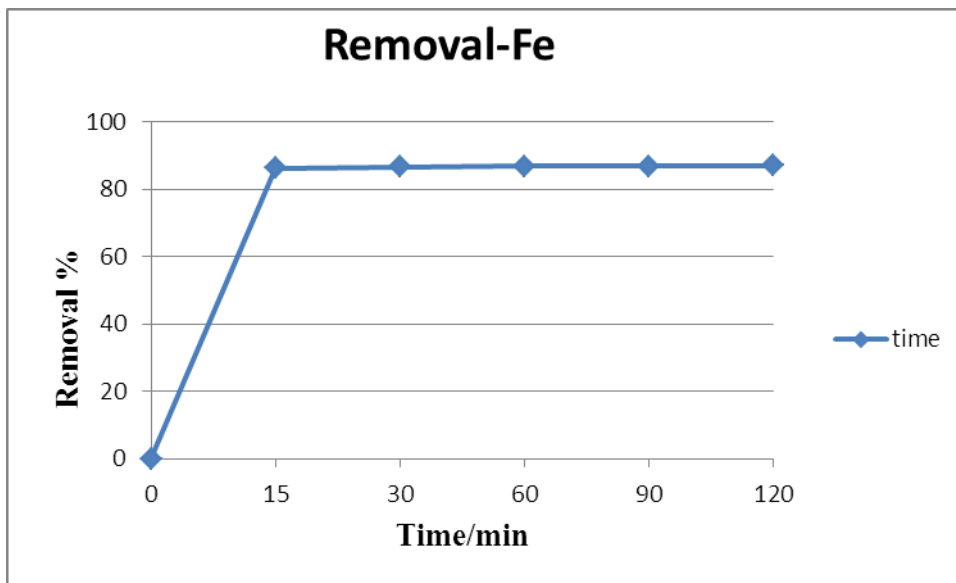


Figure (9): Effect of contact time on the % removal of (Fe) metal for shoot sample.

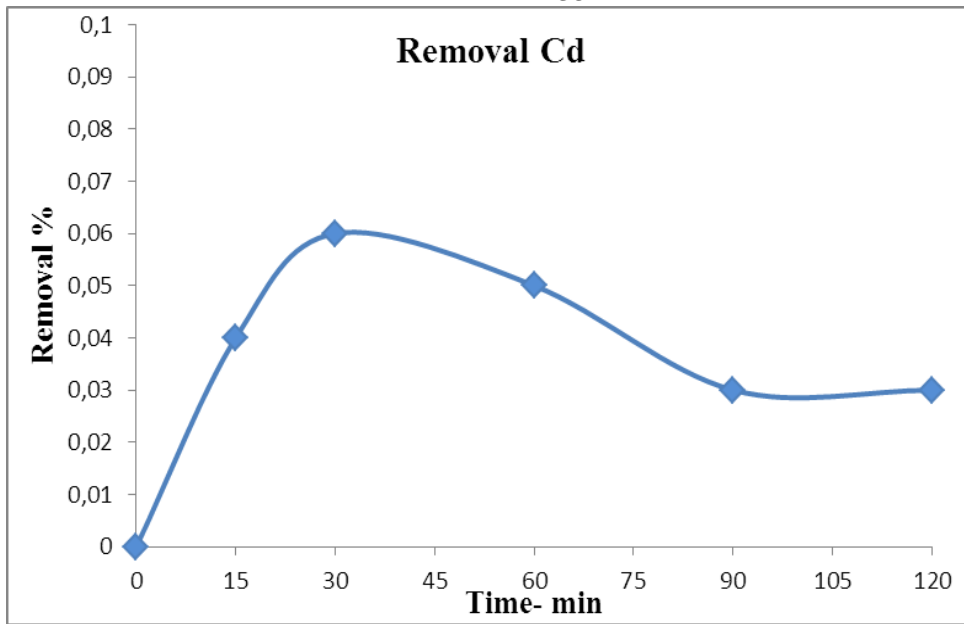


Figure (10): Effect of contact time on the % removal of (cd) metal for stem sample

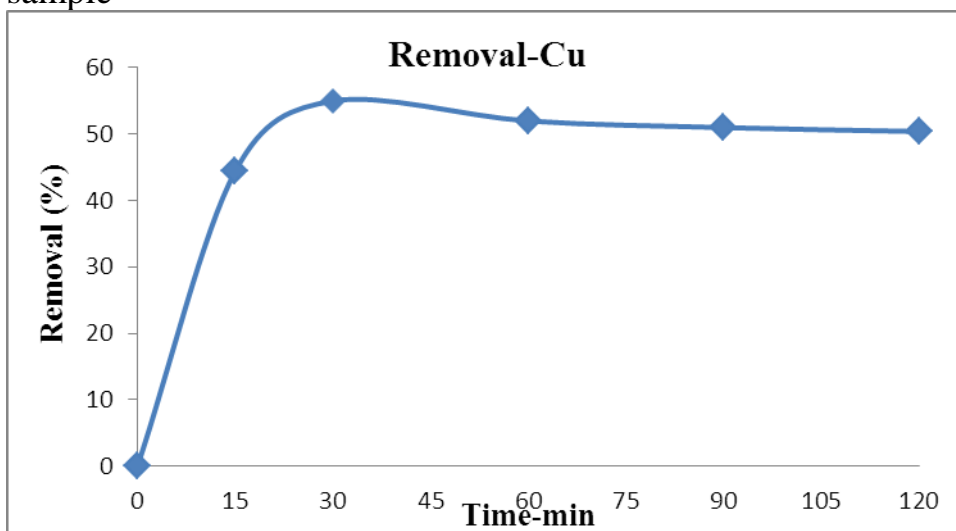


Figure (11): Effect of contact time on the % removal of cu metal for stem sample

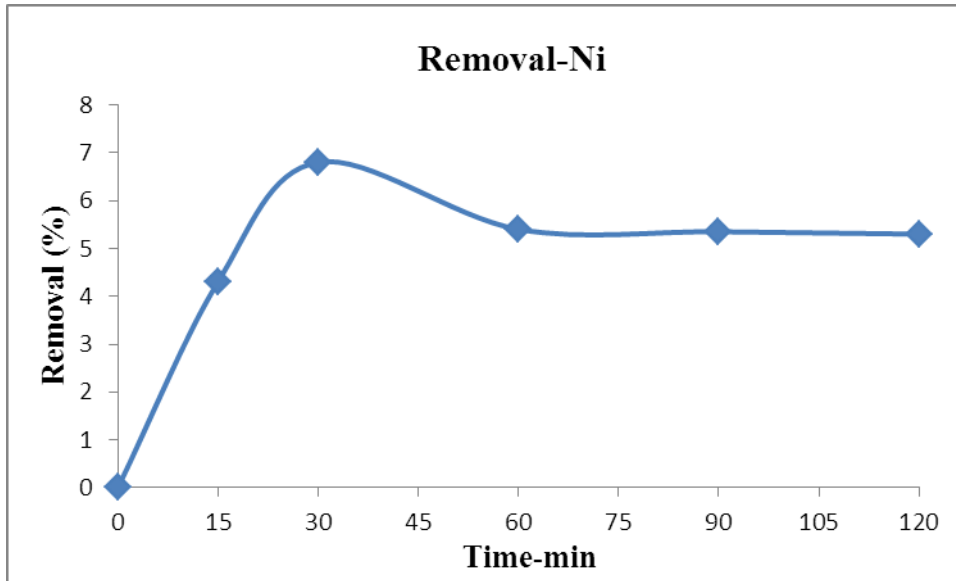


Figure (12): Effect of contact time on the % removal of Ni metal stem for sample

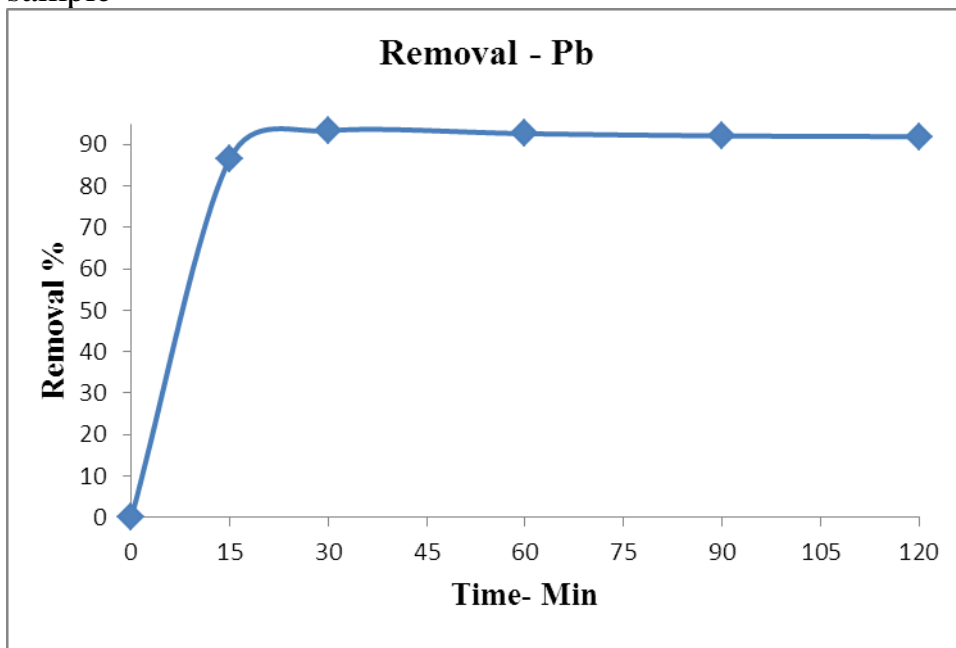


Figure (13): Effect of contact time on the % removal of pb metal for stem sample.

Time/min	%Removal of Fe	%Removal of Cd	%Removal of Cu	%Removal of Ni	%Removal of pb
15	86,3%	50%	44,4%	4,3%	86,5%
30	86,7%	90%	55%	6,5%	93,3%

60	86,79%	90,3%	55,07%	5,4%	92,6%
90	86,8%	90,56	55,2%	5,45%	92,05%
120	87,0%	90,6%	55,5%	5,5%	91,90

Table (7): Effect of contact time on the % removal of metals by shoot samples biomass, 20 ppm metal ion, PH 7, 25 °C).

As can be seen from the tables above, results demonstrate that the percent removal of metals is extensive at little contact times, until harmony is come to after a specific time. At first, a lot of empty sites are accessible for binding , however after a specific time (10 –30min), these destinations get to be involved and soaked with metal particles, The rest of the destinations are hard to be possessed as a result of the awful strengths that shape between metal ions (Lu *et al.*, 2009)

3.2.4. Effect of Solution pH

The pH of the solution has essential impact on sorption procedure as it influences the charge on the surface of biomass in water solution. Studies of the effect of solution pH were carried out in the pH range of 3.0 to 10.0. Figures (14-18) shows the effect of solution pH on the amount of metal ions adsorbed onto the shoots. From Figures 14 to 18, an increase in the solution pH from 3.0 to 7.0 has increased the amount of metal ions (Fe,Cu, Cd,Ni,Pb)adsorbed until pH7.0. The removal of ions was found to decrease at pH 10.0. This can be clarified by the way that the concentration of H particle was high at low pH. This brought about rivalry amongst H and metal particles for dynamic locales on the surface of biosorbents. As the solution pH expanded, the centralization of H particle in the

arrangement diminished, bringing down the opposition of metal particle for dynamic locales. (Yusoff and Kamari, 2014)

The ideal pH for adsorption of (Fe, Cu, Cd, Ni, Pb) was registered at pH7.0. The reduction in removal at pH more than 7.0 might be because of solvation and hydrolysis of metal particle.

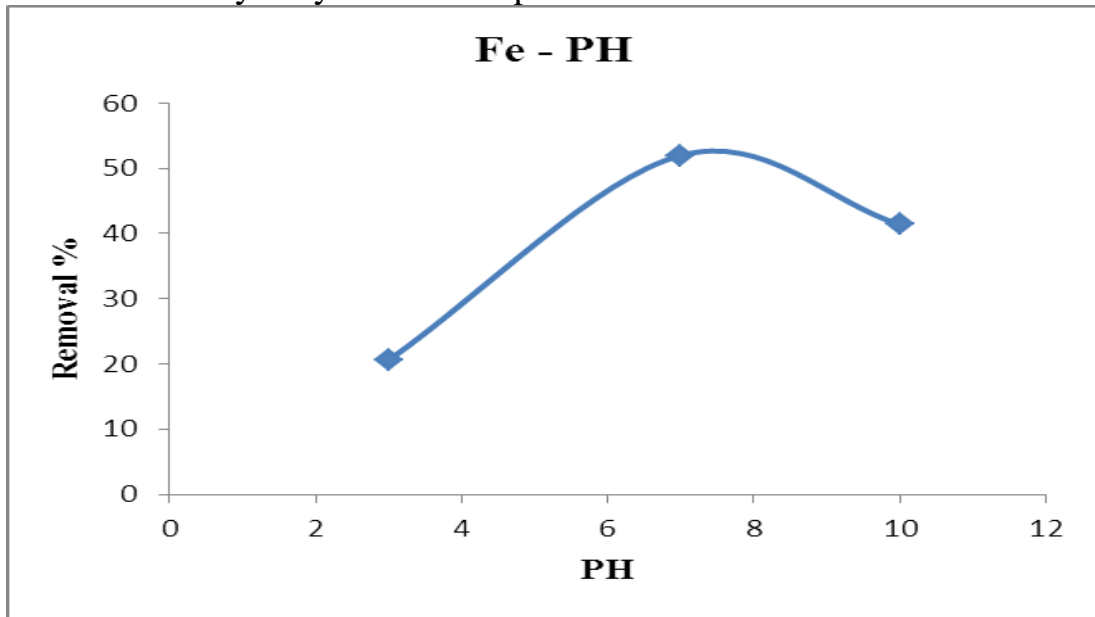


Figure (14): Effect of solution pH on adsorption of (Fe) metal ion by reed shoot sample shoot sample

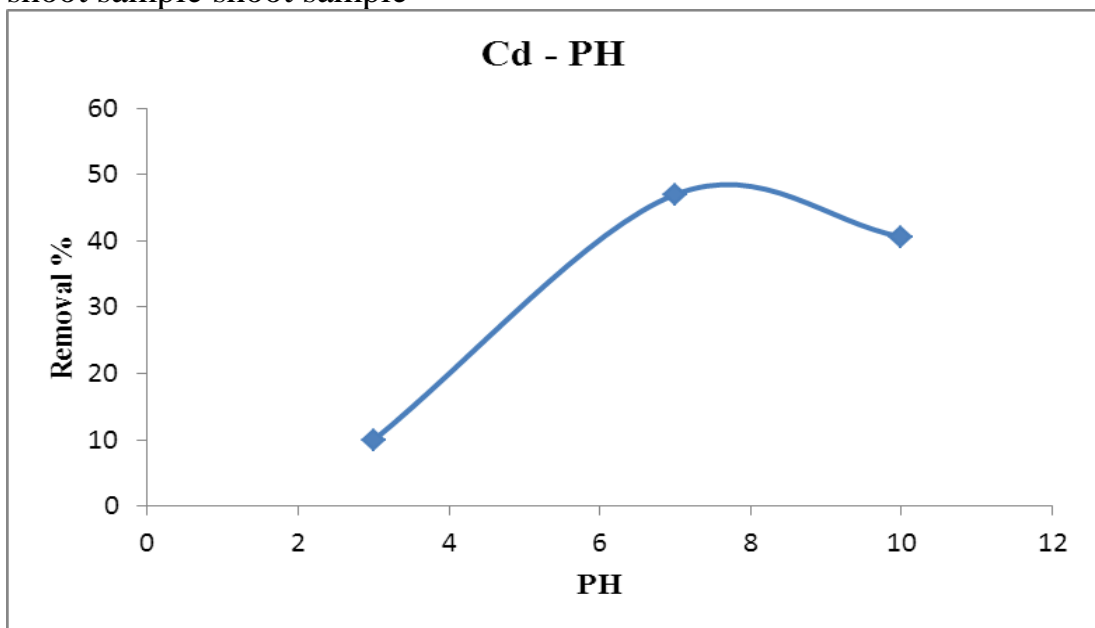


Figure (16): Effect of solution pH on adsorption of (Cd) metal ion by reed shoot sample.

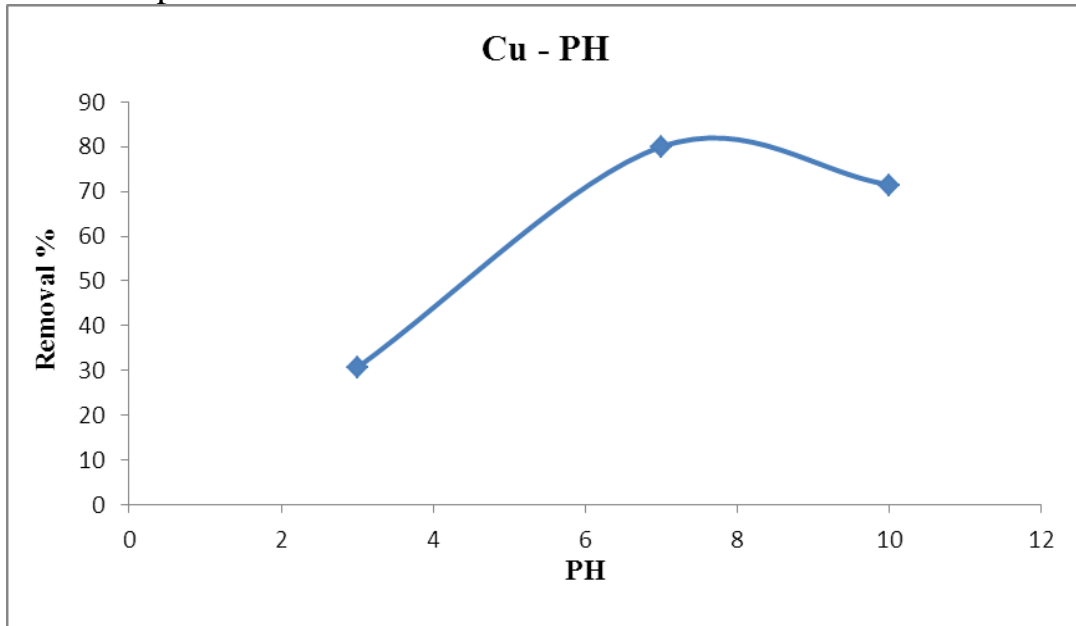


Figure (15): Effect of solution pH on adsorption of (Cu) metal ion by reed shoot sample.

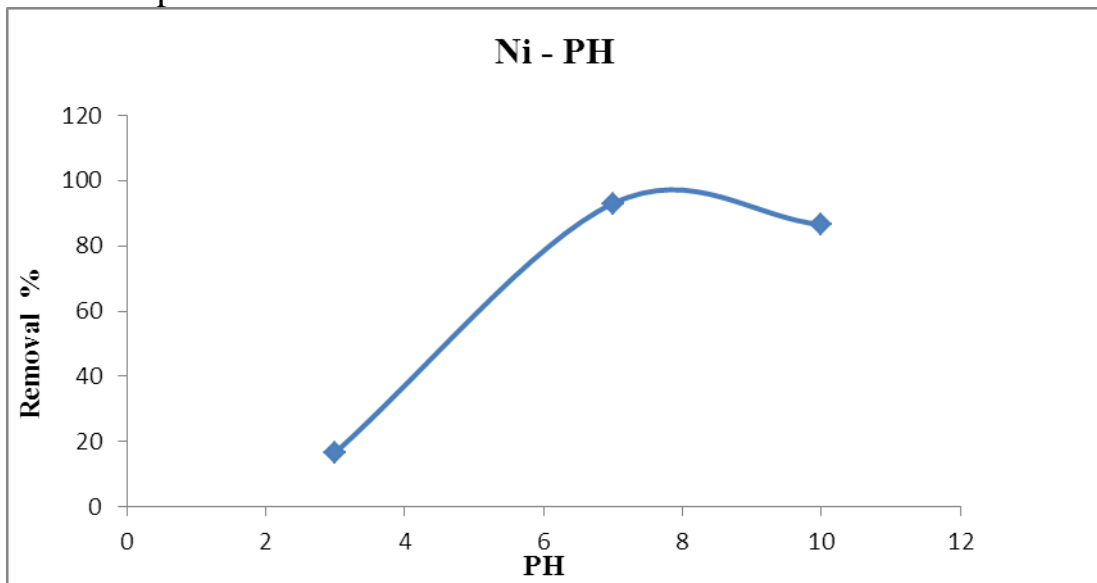


Figure (17): Effect of solution pH on adsorption of (Ni) metal ion by reed shoot sample

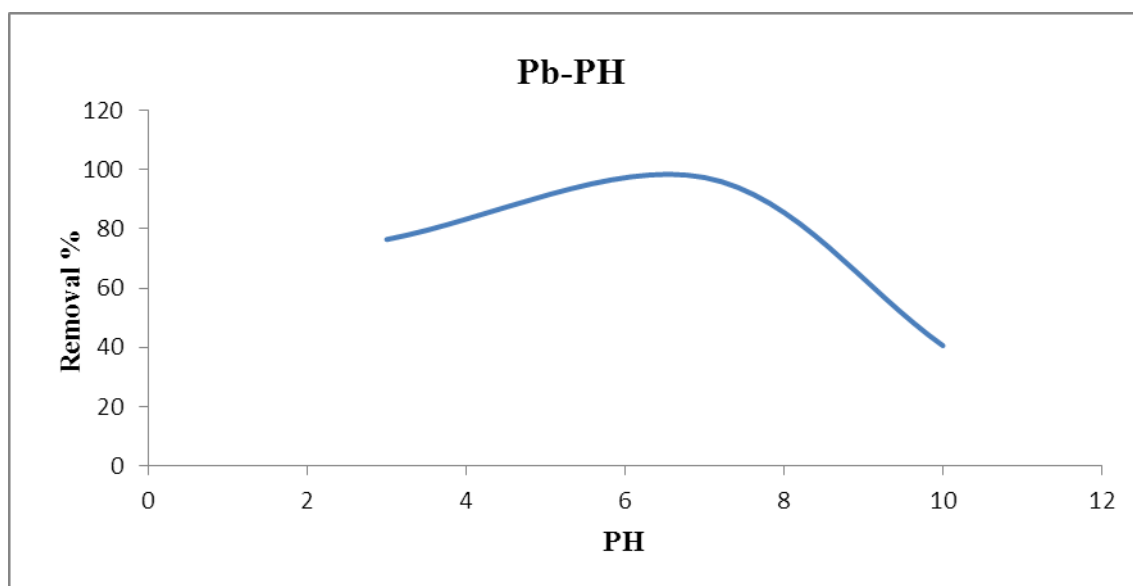


Figure (18): Effect of solution pH on adsorption of (pb) metal ion by reed shoot sample.

PH	%Removal of Fe	%Removal of Cd	%Removal of Cu	%Removal of Ni	%Removal of pb
3	20,6%	10%	30%	16,7%	76,41%
7	52%	47%	80%	93%	97,3%
10	41,39%	40,6%	71,49%	86,5%	40,6%

Table (8): Effect of PH on the % removal of metals by shoot sample biomass, 20 ppm metal ion, 25C⁰

3.2.5. Effect of Temperature

Temperature is a very important parameter that has an effect on the adsorption process, as can be seen in figures (19-23).

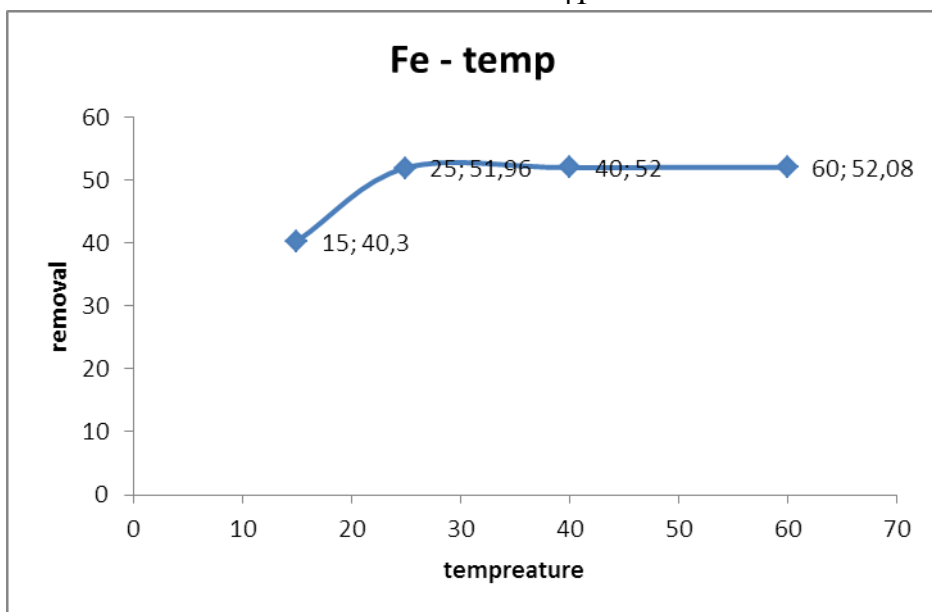


Figure (19): Effect of temperature on the % removal of (Fe) metal by reed shoot sample

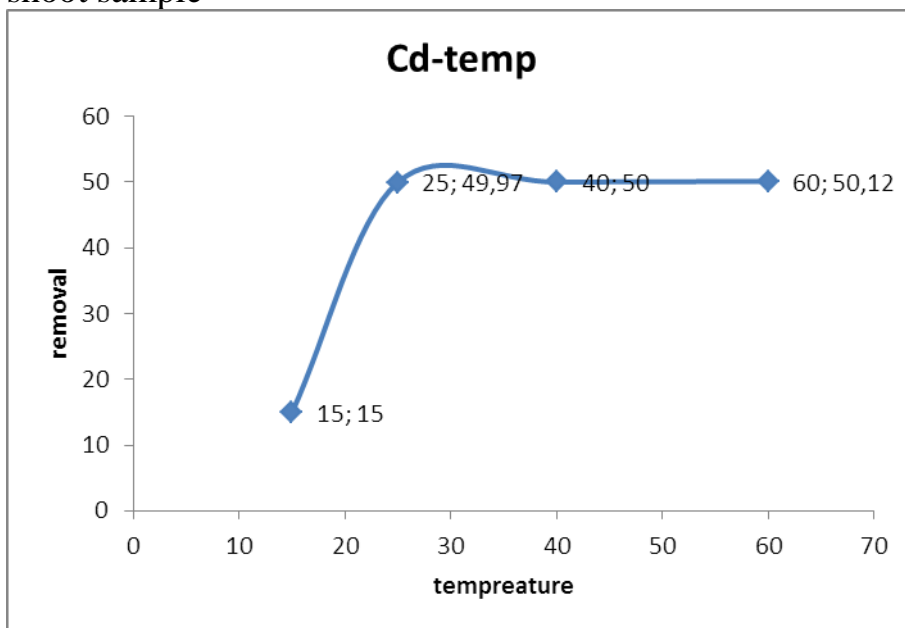


Figure (20): Effect of temperature on the % removal of (Cd) metal by shoot sample.

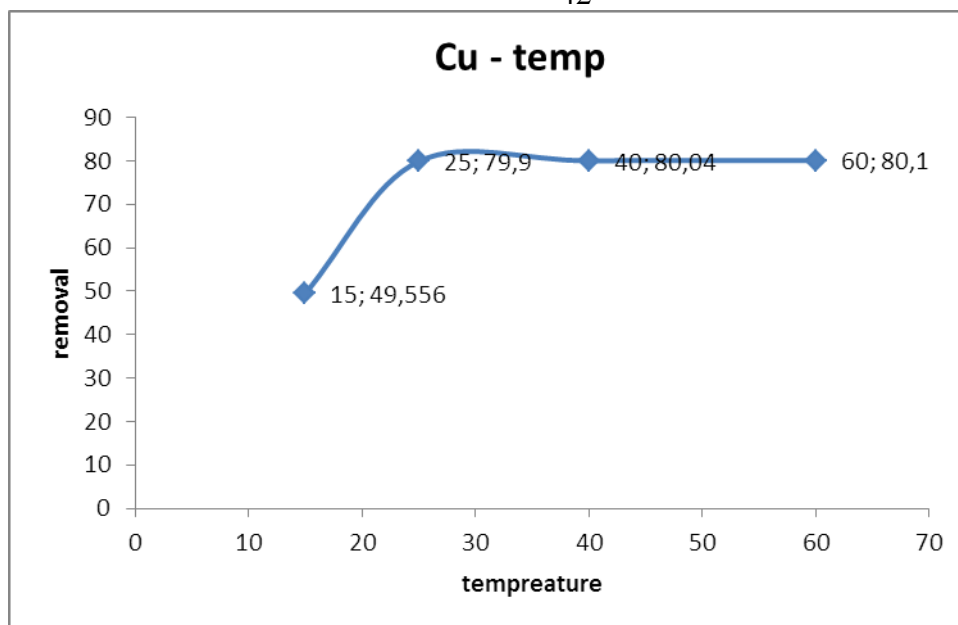


Figure (21): Effect of temperature on the % removal of (Cu) metal by shoot sample

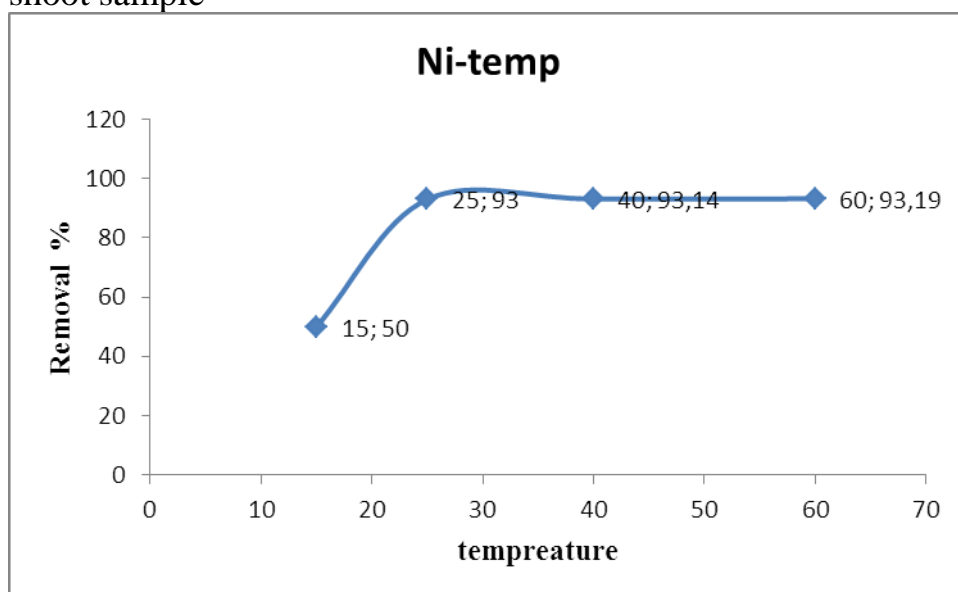


Figure (22): Effect of temperature on the % removal of (Ni) metal by shoot sample.

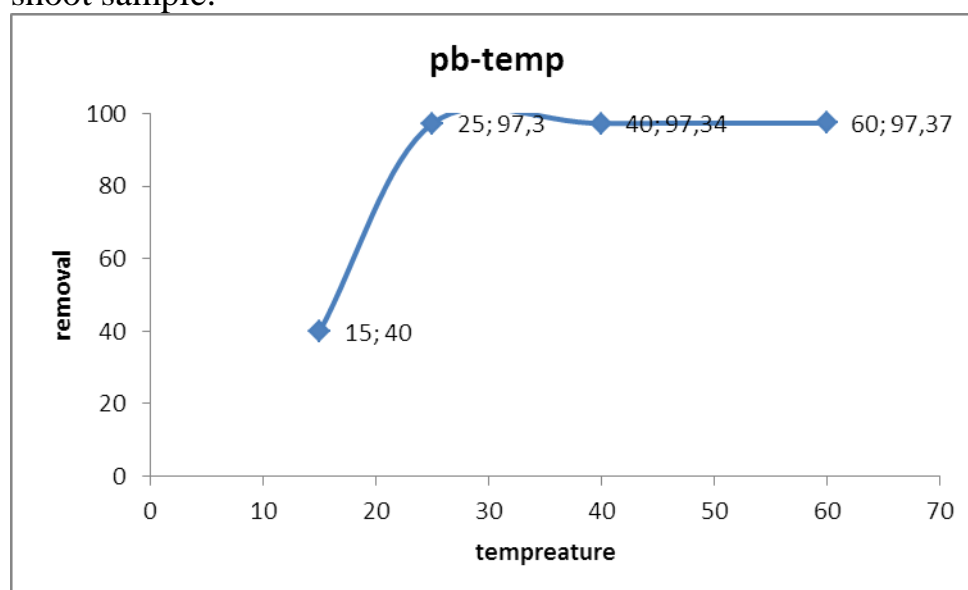


Figure (23): Effect of temperature on the % removal of (Pb) metal by shoot sample.

Tempreture	%Removal of Fe	%Removal of Cd	%Removal of Cu	%Removal of Ni	%Removal of pb
15	40,3%	15%	80,04%	50%	40
25	51,96%	49,97%	80,1%	93%	97,3%
40	52%	50%	68,75%	93,14%	97,34%
60	52,08%	50,12%	69,23%	93,19%	97,37%

Table (9): Effect of temperature on the % removal of metals by shoot sample biomass, 20 ppm metal ion, PH (7)

The rate of dissemination and spreading of metal particles on the external layer and in the internal pores of biomass will rise by expanding temperature. (Babarinde et al., 2006).

And as can be seen, the percent evacuation somewhat increase to breaking point an incentive as the temperature increase. An expansion in temperature brings about an expansion in portability of extensive metal particles, which demonstrates that the adsorption process is endothermic. This induces to a enormity impact inside the inner structure of biomass, that in this way, induces the metal particles to penetrate further and increase the dynamic essentialness of adsorbent particles, growing in the crash among adsorbent and adsorbate iotas that results in overhauls the removal of metals from the adsorbent surface (Guo *et al.*, 2009).

3.3: Adsorption isotherm of pb (II).

Freundlich and Langmuir are two models used in studying the adsorption at equilibrium that describes the characteristics of the adsorbent and the ability in adsorption.

3.3.1: Freundlich Model:

It is an experimental connection between the concentrations of a solute on the surface of an adsorbent to the concentration of the solute in the fluid with which it is in contact. In 1909, Herbert Freundlich gave an expression speaking to the isothermal variety of adsorption of an amount of gas adsorbed by unit mass of strong adsorbent with weight (Mehdi and Mehdi, 2014).

Freundlich model equation is:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

Where:

q_e = Is the amount of metal take-up per unit mass of biomass at equilibrium (mg/g)

K_f = Is the constants that demonstrate the most extreme adsorption limit (L/mg)

n = Is the adsorption adversity indicative of the favorability the adsorption process.

C_e = Is the concentration of metal in solution at equilibrium (mg/L)

A plot of $\ln C_e$ versus $\ln q_e$ gives a straight line of slope $\frac{1}{n}$, intercept $\ln K_f$

If value of n is less than one it indicates a typical adsorption. If n lies between one and ten, this shows an ideal sorption process (Mehdi and Mehdi, 2014) as in figure (24).

$\ln C_e$	$\ln q_e$
-2.0144	0.67
-0.5825	1.32
-0.0778	1.72
-0.0531	2.0

Table (10): Application of Freundlich adsorption isotherm on the % removal of Pb by reed shoot.

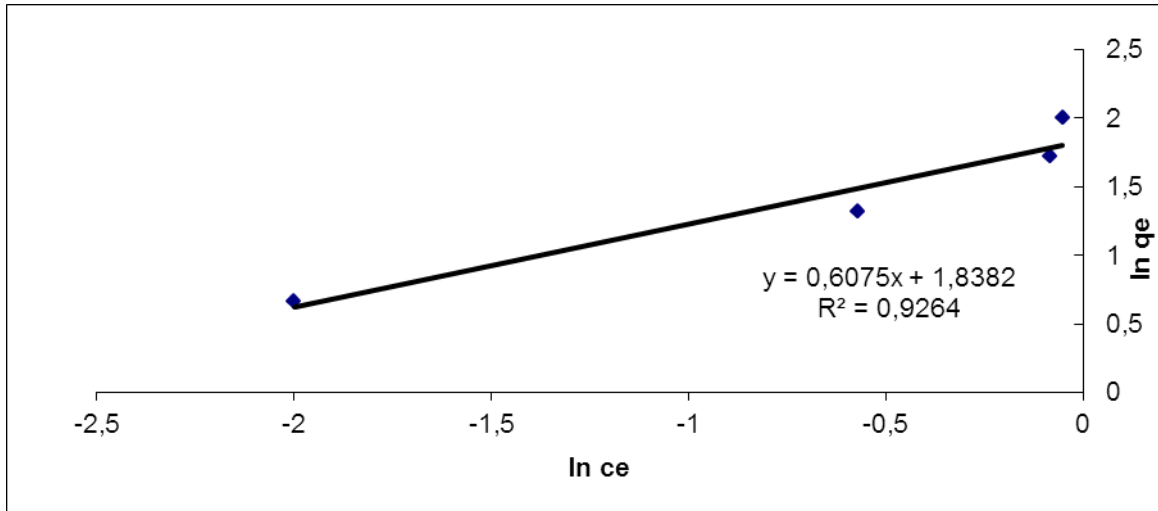


Figure (24): Aplot of ln ce ves lnqe for applying Freundlich adsorption isotherm on the adsorption of pb (II) on reed shoot.

The Parameters Freundlich isotherm model				
Adsorbate	Parameters			
	$\frac{1}{n}$	n	KF=(mg/g)	R ²
Reed shoot	0.6075	1.646	1.8382	0.9264

Table (11): Parameters of Freundlich and correlation coefficient for adsorption of pb (II) onto reed shoot.

From these values of $n=1.646 > 1$ and $1/n=0.6075$, Freundlich isotherm model shows that the sorption of pb (II) on reed shoot is ideal and the R^2 value is 0.9264.

3.3.2: Langumir model:

This model proposes that a solitary adsorbate is adsorbed onto a progression of proportional destinations on the surface of the

solid. At the surface containing the adsorbing locales is a level without any creases (expecting the surface is homogeneous).

Langumir equation:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{Q_m K_L} \quad (3)$$

Where:

C_e = the balance convergence of adsorbate (mg/L)

Q_e = the measure of pb(II) adsorbed per gram of the adsorbent (mg/g)

Q_m = most extreme monolayer scope limit (mg/g)

K_L = Langmuir isotherm consistent (L/mg)

The estimations of Q_m and K_L were registered from the slope and intercept of the Langmuir plot of C_e/Q_e versus C_e . From Langmuir plots which is appeared in Figure (24),the sum adsorbed for monolayer development (Q_m), Langmuir adsorption-desorption harmony steady (K_L) and relapse consistent (R^2) were resolved and values are appeared in the table underneath

C_e/q_e	C_e
0.07	0.1334
0.125	0.56
0.15	0.92
0.16	0.95

Table (12): Application of Langmuir adsorption isotherm on % removal of pb by reed shoot.

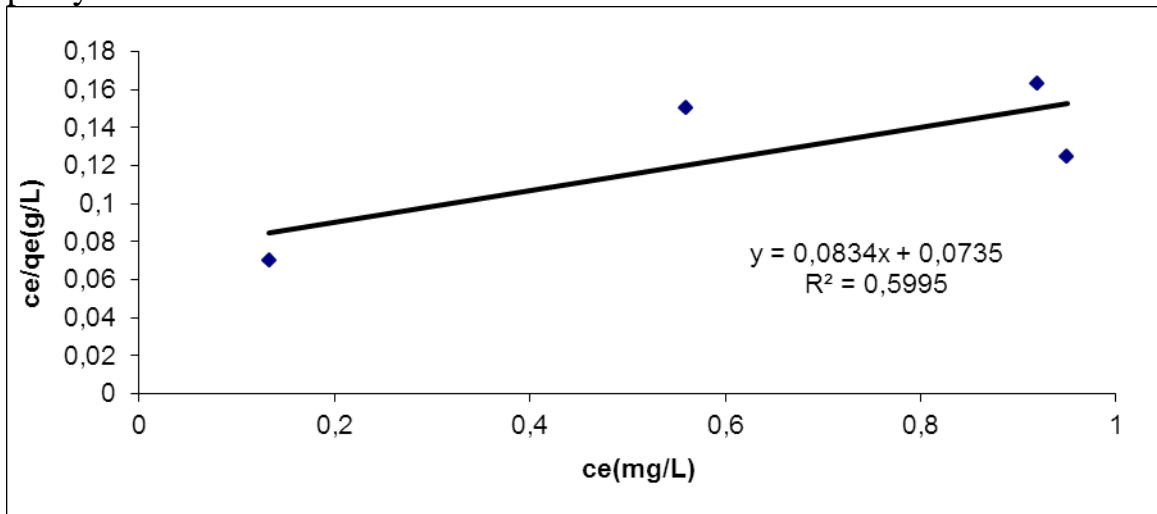


Figure (25): Aplotof ce(mg/L)ves ce/qe(g/L) applying Langmuir adsorption isotherm on the adsorption of pb (II) on reed shoot.

The parameters Langmuir isotherm model				
Adsorbent	Parameters			
	$Q_m(\text{mg/g})$	$K_L(\text{L/mg})$	R_L	R^2
Reed shoot	0.834	0.0735	0.404	0.5995

Table (13): Parameters of Langmuir and correlation coefficient for adsorption of pb(II) onto reed shoot .

From this data for adsorption of pb (II) on reed shoot the exploratory outcomes were better fitted to the Freundlich condition ($R^2 = 0.9264$) as seen in figures 23 and 24 than the Langmuir condition ($R^2 = .05995$).

R_L value can be calculated by the equation:

$$R_L = \frac{1}{(1+K_L C_0)} \quad (4)$$

Where C_0 is the maximum initial concentration of adsorbate (mg/L).

The estimation of R_L shows the state of the isotherm to be either hard (R_L more than 1), straight (R_L equal 1), great (R_L between 0 and 1), or irreversible (R_L equal 0). The R_L values between 0 and 1 show good adsorption. The estimation of R_L in the present examination was (0.404).

3.4: Adsorption thermodynamics

Adsorption thermodynamics were studied at various temperatures and concentration to check conceivable adsorption systems, by utilizing Van't Hoff plot according to equation

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (5)$$

Where K_d is the thermodynamic balance constant ($L \text{ g}^{-1}$).

The thermo chemical parameters ΔH and ΔS can be determined using Van't Hoff's plot from plotting $\ln K_d$ versus $1/T$ were $\Delta H = -R \cdot \text{slope}$ and $\Delta S = R \cdot \text{Intercept}$.

$\ln k_d$	$1/T$
2.67	0.0034
1.9	0.0035
1.8	0.0032
2.0	0.003

Table (14): the values of the thermodynamic of pb(II) adsorption at various temperature.

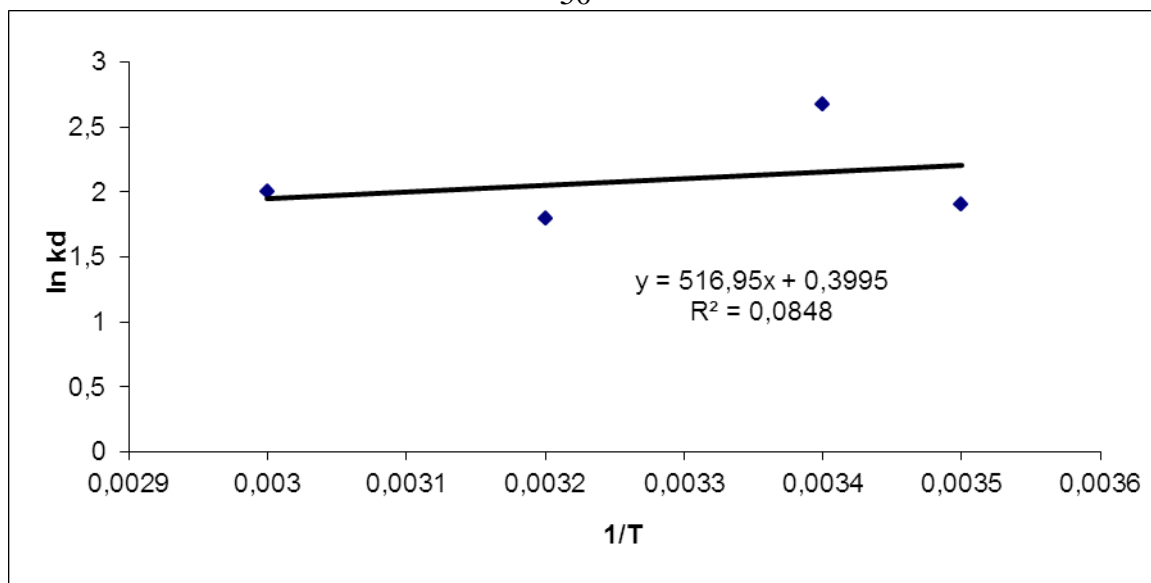


Figure (26): the graph of $\ln K_d$ versus $1/T$ for Pb (II) adsorption on (reed shoot).

The outcome demonstrates that the enthalpy of adsorption ΔH° was $-150.5 \text{ kJ mol}^{-1}$ and the entropy ΔS° was $0.115 \text{ J mol}^{-1} \text{ K}^{-1}$. ΔG° was computed at different temperatures from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

Adsorbent	ΔH° (KJ/mol)	ΔS° (J/mol.K)	ΔG° (KJ/mol)			
			289 K	308 K	318 K	328 K
Reed Shoot	-150.5	0.115	-152.2	-153.3	-154.6	-157.4

Table (15): The parameters of the thermodynamic of pb(II) adsorption at various temperatures.

3.5: Rate order of the adsorption process

The negative ΔG° values exhibit that the adsorption is unprompted, at these temperatures. The negative estimations of ΔH demonstrate an exothermic

adsorption and demonstrate that the adsorption is ideal, at low temperature. On the other hand, the positive estimation of ΔS° prescribes that some assistant changes occur on the adsorbent and the irregular movement at the strong/liquid interface in the adsorption structure increment through the adsorption system.

For the assessment of the kinetics of adsorption pb(II) onto reed shoot, pseudo first and second order were applied and the rate constant for the adsorption, k_1 and k_2 were assessed.

The first-order equation: $\log(Q_e - Q_t) = \log Q_e - \left(\frac{K_1}{2.303}\right)t$ (7)

Where Q_e is the adsorption limit of the reed shoot at balance (mg/g), Q_t is the measure of Pb(II) adsorbed at time t (mg/g) and K_1 is the pseudo first order rate constant (min^{-1}).

A plot of $\log (Q_e - Q_t)$ against time obtains the rate constant K_1

The Lagergren's first order rate constant (K_1) and Q_e determined from the model are given below and from the corresponding correlation coefficients. It was watched that the pseudo first order model did not adjusted well. It was found that the calculated Q_e values did not correspond with the experimental Q_e value. This indicates that the adsorption of pb (II) was not preferred first-order kinetics.

Time	Log ($q_e - q_t$)
15	0.26
30	0.4
60	0.25
90	0.19

120	0.17
-----	------

Table (16): Applying first- order equation on the % removal of (pb) by reed shoot

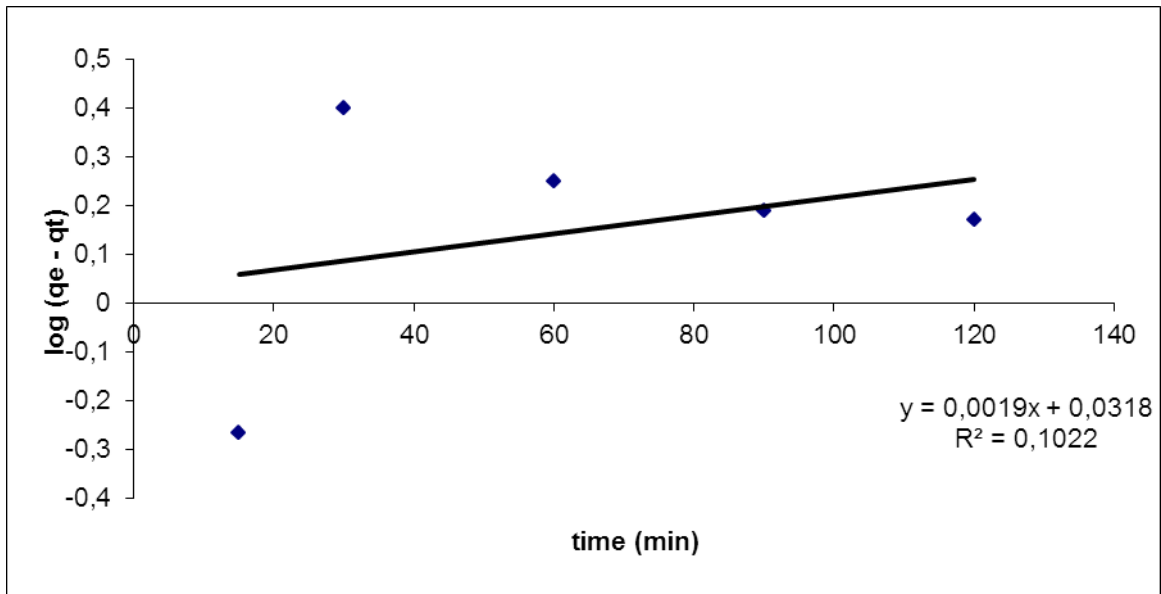


Figure (27): The plot of Pseudo first- order adsorption kinetics of pb(II) onto reed shoot.

From figure 27, the R^2 rate shows that there is no corresponding between adsorption pb(II) onto reed shoot and the pseudo first- order kinetics, and the pseudo first- order model is not suitable for the adsorption

Adsorbent	$Q_{e(\text{exp})}$ (mg/g)	pseudo first- order		
		K_1 min^{-1}	Q_e (calculated) (mg/g)	R^2
Reed Shoot	.95	2.441×10^{-3}	0.235	0.1022

Table (17): Pseudo first- order parameters for pb(II) adsorption onto reed shoot at 25°C.

The pseudo second order equation

$$\frac{t}{Q_t} = \frac{1}{Q_e} t + \frac{1}{K_2 Q_e^2} \quad (8)$$

Where K_2 is the pseudo second order rate constant ($\text{g mg}^{-1}\text{min}^{-1}$).

Pseudo second - order adsorption model for Pb(II) adsorption onto reed shoot was applied and the rate constant for the adsorption K_2 was evaluated as shown in figure (28).

Time	T/q_t
15	5.35
30	22.4
60	40
90	56.6
120	74.0

Table (18): Applying second- order equation on the % removal of (pb) by reed shoot.

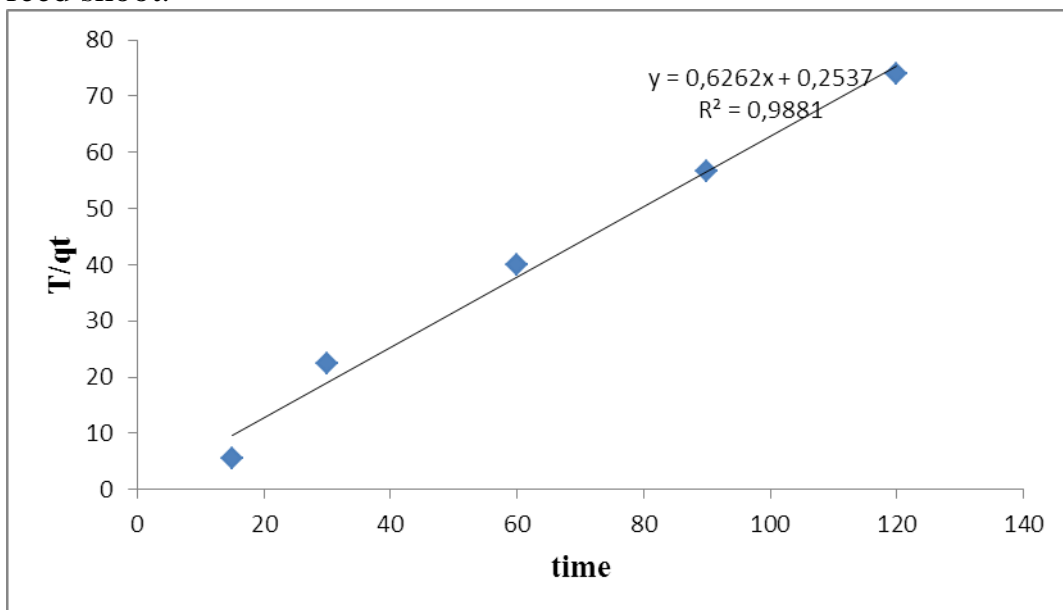


Figure (28): plot of Pseudo second- order adsorption kinetics of pb(II) onto reed shoot.

Adsorbe	q _e (exp) (mg/g)	pseudo second – order		
		K ₂ min ⁻¹	q _e (calculated) (mg/g)	R ²
Reed Shoot	0.95	6.9×10 ⁻³	1.39	0.9881

Table (19): Pseudo second- order parameters for pb(II) adsorption onto reed shoot at 25°C.

As can be seen there is a harmonization between experimental and calculated values for pseudo second order model. This means the Pseudo second – order kinetic model accord, and it was appropriate for the adsorption.

Conclusion

These results show an efficient capability of *Phragmites Australia* and the other type phragmites which from Sarra in removing all metals which were studied in this work, and increasing the concentration of biomass leading to an increase in the removal of metals by both plants, this study shows that concentration (20 ppm) is the highest removal percentage.

As can be seen from results the *phragmites Australia* (common reed) is more efficient, as it almost completely removed lead from the shoot sample.

Adsorption parameters such as pH, initial concentration of metal ion, temperature and contact time, have been to have an effect on the removal of (Fe,Cu,Cd,Ni,Pb)The optimal percent removal of Pb ions by reed shoots was 97,3%.The suitable conditions for binding of biomasses is at pH 7for pb ions, initial concentration of 20 mg/L, temperature (25°C -) and contact time(30 minutes).

The results of the uptake of Pb (II) by reed shoot fit well with the Freundlich adsorption isotherm more than Langmuir adsorption isotherm. And Pseudo second – order kinetic model fit better than pseudo first order model.

Recommendations

Findings in this thesis show that phragmites Australia plants from Wadi Al Bathan can absorb multiple metals more than the other phragmites which imports from other country; hence it is recommended to utilize them for pollution removal from water. And recommended to carry out research in detail and find if this plant can be useful to extract other metal than these metals studied in this research.

References

1. Abel, P. D., 2002, Water pollution biology, 2/e, London: Taylor and Francis
- Acar, Y. B., Gale, R. J., Alshawabkeh, A. N., Marks, R. E., Puppala, S., Bricka, M., Parker, R., 1995, Electrokinetic remediation – Basic and technology status, *Journal Hazardous Matter*, 40, 117 – 137
2. Adesola Babarinde, N.,A., Oyebamiji Babalola,J., Olalekan Sanni S.,2007 Isotherm and thermodynamic studies of the biosorption of Cd(II) from solution by maize leaf
3. Al, Akeel, k., 2013 emipircal investigation of water pollution Control through use of *Phragmites australis*
4. . Bernard, A., and Lauwerys, R., 1984, Cadmium in human populations, *Experientia*, 40, 143 – 152
5. Bernard, A., and Lauwerys, R., 1984, Cadmium in human populations, *Experientia*, 40, 143 – 152
6. Berti, W., Cunningham, S. D., 2000. Phytostabilization of metals. IN Raskin, I. & Ensley, B. D. (Eds.) *Phytoremediation of toxic metals: using plants to clean-up the environment*. New York, John Wiley & Sons.
7. Blaylock, M., J., and J., W., Huang. 2000, *Phytoremediation of ToxicMetals: Using Plants to Clean Up the Environment*, John Wiley and Sons Inc., New York, p. 53.
8. Bonanno, G., Guidice, R. L., 2010, Heavy Metal Bioaccumulation by the Organs of *Phragmites Australis* (Common Reed) and Their Potential Use as Contamination Indicators

9. Bragatoa, C., Brixb, H., Malagolia, M., 2006, Accumulation of nutrients and heavy metals in *Phragmites australis* (Cav.) Trin. ex Steudel and *Bolboschoenus maritimus*(L.) Palla in a constructed wetland of the Venice lagoon watershed Environmental Pollution Volume 144, Issue 3, December 2006, Pages 967–975
10. Cluis, C., 2004. Junk-greedy Greens: phytoremediation as a New Option for Soil Decontamination. BioTeach Journal, 2, 61-67.
11. Csuros, M., Csuros, C., 2002, Environmental sampling and analysis for metals, London: Lewis publishers.
12. Dechesne, M.; Soyeux, E.; Loret, J.F.; Westrell, T.; Stenström, T.A.; Gornik, V.; Koch C.; Exner, M.; Stanger, M.; Agutter, P.; 2006, Pathogens in Source Water, Microbiological Risk Assessment: A Scientific Basis for Managing Drinking Water Safety from Source to Tap; Microrisk European Project: Nieuwegein, The Netherlands, pp. 1–42.
13. Demirezen, D., Aksoy, A., 2004, Accumulation of heavy metals in *Typha angustifolia* (L.) and *Potamogeton pectinatus* (L.) living in Sultan Marsh (Kayseri, Turkey), Chemosphere, 56, 685 – 696
14. Flemming, C.A. and Trevors, J.T., 1989, Copper toxicity and chemistry in the environment: a review, Water, Air, and Soil Pollution, 44, 143 – 158 following uptake by hybrid poplar trees. Int J Phytoremediation, 1999, 1, 139 – 51
15. Gardea-Torresdey, J. L., Cano-Aguilera, I., Webb, R., Tiemann, K. J., Gutierrez- Corona, F., 1996. Journal of Hazard Materials , **48**, 171–180

16. Gardea-Torresdey, J. L., 2003, Phytoremediation: Where does it stand and where will it go?, *Environmental Progress*, 22, 1, A2 – A3 Editorial
17. Gaur, A., and Adholey, A., 2004, "Prospects of arbuscular mycorrhizal fungi in phytoremediation of heavy metal contaminated soils," *Current Science*, vol. 86, no. 4, pp. 528–534.
18. George, I.; Anzil, A.; Servais, P. 2004, Quantification of fecal coliform inputs to aquatic systems through soil leaching. *Water Res.* 38, 611–618.
19. Gibbs, J., W., 1873, "A Method of Geometrical Representation of the Thermodynamic Properties of Substances by Means of Surfaces," *Transactions of the Connecticut Academy of Arts and Sciences* 2, Dec. pp. 382-404 (quotation on p. 400)
20. Hlavsa, M.C.; Roberts, V.A.; Anderson, A.R.; Hill, V.R.; Kahler, A.M.; Orr, M.; Garrison, L.E.; Hicks, L.A.; Newton, A.; Hilborn, E.D.; et al. 2001 Surveillance for waterborne disease outbreaks and other health events associated with drinking water—United States, 2007–2008. *MMWR Surveill. Summ.* , 60, 1–32.
21. Ho, Y., El-khaiary, M. I., 2009, Metal research trends in the environmental field, in Wang et al (eds) 2009 'Heavy metals in the environment', London: CRC Press, Taylor and Francis Group
22. Jadia D, Chhotu and Fulekar, M.H., 2009, Phytoremediation of heavy metals: Recent techniques. *African Journal of Biotechnology*, 8 (6): 921-928.10

23. Judith, S., Weisa, T., Gloverb, P., Weis, 2004, Interactions of metals affect their distribution in tissues of *Phragmites australis* Volume 131, Issue 3, October 2004, Pages 409–41
24. jung, A.,V., Caan, P., Roig,B., Thomas, O., E., Baurès, E., Thomas, M.,F., 2014, Review Microbial Contamination Detection in Water Resources: Interest of Current Optical Methods, Trends and Needs in the Context of Climate. 11, 4292-4310
- 25.Laidani, Y., Hanini, S., Henini, G., 2010. Valorization of Luffa for Water Treatments Copper Chargers. Study of the Possibility of Regeneration by Chemical Desorption. Oman, pp. 1.
- 26.Lansdown, R.V. 2015. *Phragmites australis*. The IUCN Red List of Threatened Species e.T16449A79857020.
- 27.Lu, D., Cao, Q., Cao, X., Luo, F., 2009. Removal of Pb (II) using the modified lawny grass, Mechanism, Kinetics, Equilibrium and Thermodynamics studies. Journal Hazardous Materials, 166 (1): 239-
- 28.Mehdi, R., Mehdi, V., 2014, Langmuir, Freundlich and Temkin Adsorption Isotherms of Propranolol on Multi-Wall Carbon Nanotube, journal of modern drug discovery and drug delevary research.
29. Miller, R., 1996. Phytoremediation: Technology Overview report, Ground Water Remediation Technologies Analysis Center.r, R., 1996. Phytoremediation: Technology Overview report, Ground Water Remediation Technologies Analysis Center.

30. Naja, G. M., Volesky, B., 2009, Toxicity and sources of Pb, Cd, Hg, Cr, As,, and Radionuclides in the environment, chapter 2 in Wang, L. K., Chen, J. P., Hung, Y.
31. Pan, J., Plant, J. A., Voulvoulis, N., Oates, C. J., Ihlenfeld, C., 2010, Cadmium levels in Europe: implications for human health, *Environ Geochem Health*, 32, 1 – 12
32. Pramod, K., Pandey, Philip, H., Kass, Michelle, L., Soupir, S., Biswas, and Vijay, P., Singh, 2014, Contamination of water resources by pathogenic bacteria. *AMB Express*. Jun 28. doi: 10.1186/s13568-014-0051-x
33. Prasad, M. N. V., De oliveira freitas, H. M., 2003. Metal hyperaccumulation in plants - Biodiversity prospecting for phytoremediation technology. *Electronic Journal of Biotechnology*.
34. Salt, D. E., Kumar, P. B. A. N., Dushenkov, S., Raskin, I. 1994 *Phytoremediation: A New Technology for the Environmental Cleanup of Toxic Metals. International Symposium Research on Conservation and Environmental Technology for Metallic Industry*. Toronto, Canada.
35. Sayrafi, O., Salm, R., Sayrafi, S., A., 1996 ,Removal of cadmium from polluted water using decaying leaves-effects of type of leaves and of concentration of cadmium , *J. Environ. Sci. Health*, A31 (10), 2503-2513.
36. Singh, V., Labana, S., 2003. Phytoremediation: an overview of metallic ion decontamination from soil. *Appl. Microbiol. Biotechnol.*, 61, 405-412.

37. Tangahu, B., V., Sheikh Abdullah, S., R., H., Basri, H., Idris, M., Anuar, N., Mukhlisin, M., 2011, Article ID 939161, 31 pages Review Article International Journal of Chemical Engineering
38. Tsezos, M., Deutschmann, A. A., 1990. Journal of Chemical Technology Biotechnology, 48, 29-39.
39. Valavanidis, A. And Vlachogianni. T. 2010, Metal pollution in ecosystems: ecotoxicology studies and risk assessment in the marine environment, Science advances on Environment, Toxicology and Ecotoxicology issues, Available at www.chem-tox-ecotox
40. Volesky, B., 2001. Hydrometallurgy .59, 203–216.
41. Wang, L. K., Chen, J. P., Hung, Y., Shamas, N. K. (ed), 2009, Heavy metals in the environment, Boca Raton: CRC Press
42. Yusoff, S., N., M., Kamari, A., Putra, W.P., Ishak, C.F., Mohamed, A., Hashim, N. and Md Isa, I. 2014, Removal of Cu(II), Pb(II) and Zn(II) Ions from Aqueous Solutions Using Selected Agricultural Wastes: Adsorption and Characterization Studies. Journal of Environmental Protection, 5, 289-300.
43. Zhu, Y. Z., Pilon-Smits, E. A. H., Tarun, A. S., Weber, S. U., Jouanin, L., Terry, N., 1999 . Cadmium Tolerance and Accumulation in Indian Mustard is Enhanced by Overexpressing g-Glutamylcysteine Synthetase1. Plant Physiol., 121, 1169-1177.

جامعة النجاح الوطنية
كلية الدراسات العليا

دراسة تأثير نبات البوص على أمتصاص المعادن السامة ونشاط البكتيريا الموجودة في المياه الملوثة

إعداد

منجدة تحسين ياسين سلمان

إشراف

د. أحمد أبو عبيد

د. رائد الكوني

قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في العلوم البيئية بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس - فلسطين.

2017

دراسة تأثير نبات البوص على أمتصاص المعادن السامة وعلى نشاط البكتيريا الموجودة في المياه الملوثة

إعداد

منجدة تحسين ياسين سلمان

إشراف

د. أحمد أبو عبيد

د. رائد الكوني

الملخص

في هذا البحث تم دراسة نبات البوص الاسيوي والبوص المستخدم في محطه التنقيه في قرية صره (اوراق وسيقان وجدور) وقدرتهما على امتصاص المعادن السامة الموجودة في المياه العادمة وعلى قدرتهما في التأثير على نشاط البكتيريا الموجودة فيها .

وتم دراسة عدة عوامل تؤثر على قدره امتصاص هذا النبات منها عامل تركيز المعادن المراد امتصاصها من المياه العادمة وعامل وجود اكثر من معدن واحد في المياه وتأثيره على المعادن الاخرى وعامل الحرارة ودرجة الحموضة للمياه العادمة والامتصاص مع مرور الوقت. اظهرت النتائج ان افضل نسبه امتصاص كانت عند تركيز 20 في كلا النباتين المدروسين.

وكانت أعلى النسب للمعادن في كلا النباتين كما يلي :الحديد 77%أمتصته جدور البوص الكادميوم 71%أمتصته اوراق البوص الاسترالي،النحاس 88% أمتصته اوراق وسيقان البوص الاسترالي،النكل 93%أمتصته سيقان البوص الاسترالي والرصاص تم امتصاصه بأعلى نسبه وهي 97 % من قبل سيقان البوص الاسترالي، لذلك تم دراسته امتصاص عنصر الرصاص تحت تأثير ظروف ومقاييس مختلفه مثل الحرارة ودرجة الحموضة والوقت .

وقد أ اظهرت النتائج ان افضل ظروف امتصاص لرصاص هي عند تركيز (20) ودرجه حراره 25 مئوية ودرجه حموضه (7) وبعد مرور من 10 الي 30دقيقة، تم متابعة تراكيز أيونات العناصر باستخدام جهاز طيف الامتصاص الذري باستخدام اللهب ووجد ان النظام Freundlich adsorption isotherm الافضل لإزالة ايونات الرصاص، وقد تم تحديد رتبة التفاعل بين ايونات العنصر والساق من الدرجة الثانيه .