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Faculty of Graduate Studies

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

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

2017

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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.

To my family; father, mother, sisters and brothers, my greatest gratitude 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. Also I would like to thank Prof. Dr. Shehdeh Jodeh for his supporting and advice in my research work.

Many thanks to Middle East Desalination Research Center (MEDRC) who funded my project through the Palestinian Water Authority whom our thanks go as well to them for their follow up the project.

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:**

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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
DMSO	Dimethyl sulfoxide
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.
MHA	Mueller-Hinton Agar
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)
Lb	Leaves parts for reed common plant from Wadi Al-Bathan
Ls	Leaves parts for Phragmites plant from Sarra
n	Dimensionless Freundlich constant giving an indication how favorable the adsorption process of wastewater purification treatment
OPT	Occupied Palestinian Territories
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)
Rb	Roots parts for reed common plant from Wadi Al-Bathan
Rs	Roots parts for Phragmites plant from Sarra
R^2	Regression coefficient
R_L	Dimensionless constant separation factor
t	Time
Sb	Shoot parts for reed common plant from Wadi Al-Bathan
Ss	Shoot parts for Phragmites plant from Sarra
$\Delta G°$	Standard free Gibbs energy
$\Delta H°$	Standard enthalpy
$\Delta S°$	Standard entropy

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

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Abstract

The main problem here is to study the potential of *Phragmites australis* and Phragmites used in the purification plant in Sarra village (leaves, stems and roots) to absorb a specific heavy metal ions (Fe^{3+}, Cd^{2+}, Cu^{2+}, Ni^{2+} and Pb^{2+}) and their ability to stop bacterial activity in sewage water.

Several experiments were conducted under different conditions and variables such as temperature, pH, concentration of metal ions, plant biomass and contact time to determine the optimal conditions for the best adsorption of the metal ions specified in the research. It was observed that the removal of these ions from the aqueous solutions was at a concentration of 20mg / L and a temperature of 25°C and acidity around pH = 7 and within 15-30 minutes.

The highest uptake rates under the optimum conditions for metal ions were obtained using the biomass of both plants as follows: Iron 77% absorbed by roots, Cadmium 72% absorbed *Phragmites australis* leaves, 88% copper absorbed by *phragmites australis* leaves and stalks, 93% nickel absorbed by *phragmites australis* and lead absorbed with the highest percentage which was 97% by the stalks of *Phragmites australis*, so the absorption of lead element was studied under the influence of different conditions of temperature, pH and contact time.

Experiments were done to examine the behavior of absorption under competitive conditions in the presence of ions together in water. The results showed that the order of percentages for the removal of metal ions was as follows: $Pb^{+2} > Cu^{+2} > Fe^{+3} > Ni^{+2} > Cd^{+2}$.

The results and analysis showed that the adsorption process can be described according to the Langmuir model, indicating that the adsorption process is monolayer. The negative ΔG values indicate that the adsorption process is appropriate and spontaneous at the specified temperatures. The negative value of $\Delta H°$ indicates that the adsorption process is exothermic and is favored at low temperatures not more above room temperature, and the value of $\Delta H°$ is much lower of those associated with chemical adsorption, confirming the physical nature of the adsorption process. The small positive value of $\Delta S°$ indicates structural changes on the biomass surface, and that the disorder has increased near the adsorption surface during the adsorption process.

The results confirm that the biomass of the plant is effective, suitable and safe in removing heavy metal ions from sewage water. Phragmites from Sarra (leaves, shoots and roots) had been tested for their antibacterial activity and the result was negative.

Chapter One

Introduction

Chapter One

Introduction

1.1. Introduction

Environmental pollution is the greatest challenge facing human 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 world [1][2].

Water contamination 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. Transportation 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 [3].

1.2. Objectives

1. To study and determine the potential of *Phragmites australis* plant which collected from Wadi Al Bathan and compare it with the other plant of Phragmites which was taken from sewage purification plant in Sarra to remove (Fe^{3+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+}) from aqueous solution

2. 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.
3. To explore the kinetics and the adsorption isotherms of the biosorption process.
4. To test the anti-bacterial activity for the Phragmites Australia.

Beside the major objective of removal Heavy Metals from Sewage Water; other objectives will be like screening the Sewage Water for other pollutants and to give an idea to different ministries in Palestine like ministries of health, agriculture and water.

1.3. Novelty

Many studies have studied the use of plants and their role in contaminated water treatment, but few of these researched the *Phragmites australis* 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 australis* at optimum batch conditions. More focus will be given to the shoot of *Phragmites australis*.

1.4. Hypothesis

This work was managed under the hypothesis that all leaves, stem and root of *Phragmites australis* 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.

1.5. Previous studies

One study investigated the accumulation of nutrients and heavy metals (Cr, Ni, Cu and Zn) in *Phragmites australis* and this study Confirmed that the accumulation generally increased toward the end of the growing season [4].

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 [5].

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 the in tissues of *Phragmites australis* [6].

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 [7].

Chapter Two

Background and Literature review

Chapter Two

Background and Literature review

2.1. Sewage and wastewater in the Palestinian Territories

An essential tool in the management of hazardous waste is an inventory of national hazardous waste substances. No such inventory exists in the Occupied Palestinian Territories (OPT), and its absence makes it difficult to determine what types of waste are being generated, and where they are being disposed of. OPT has inadequate facilities for sewage and wastewater treatment and disposal. There are very few estimates of the amounts of hazardous waste generated in the OPT. In the West Bank, the amount has been estimated at 2,500 tons per year. The true amount is likely to be much higher. Heavy metals, which are used for fixing colors in the dye, are also present. Estimates of annual solid and liquid hazardous waste are 290 and 600 tons respectively. Tanneries consume large quantities of scarce freshwater, and generate and release corresponding amounts of wastewater with significant pollution loads, and sometimes with extreme pH values. The disposal of wastewater containing untreated tannery effluent presents a high risk of groundwater pollution, as wastewater infiltrates through the limestone into the aquifer. A range of hazardous substances are used in the manufacturing processes such as organic compounds, various acids, metals, hazardous isomers, and alcohols. Estimates of annual solid and liquid hazardous waste generation are 8 and 201 tons respectively. About 2,500 million m^3 of used mineral oil are released annually in the OPT without any collection systems or adequate treatment. The mini steel mills in the OPT use a range of hazardous substances, such as heavy metals, phenol (and its salts), dioxins, furans, cyanides, and several dangerous halogenated hydrocarbons. Estimates of annual solid and liquid hazardous waste generation are 1,016 and 1,200 tons respectively. Medical waste covers several categories: infectious waste, pathological waste, pharmaceutical waste, genotoxic waste, chemical waste, wastes with high heavy metal content, pressurized containers, and radioactive waste. In the West Bank, 330 tons of contagious waste, 65 tons of biological waste and 2 tons of sharp objects are generated each year. The quantity for Gaza has been estimated at only 0.2 tons. The low value of this figure is that it refers to amounts that are collected, rather than total amounts including the waste that enters the domestic waste stream. Israeli colonies are also reported to release quantities of hazardous waste without treatment, such as Barqan industrial zone are release 810,000 cubic meters of industrial wastewater per year, including hazardous waste [8][9].

The discharge of untreated wastewater into the shallow waters of Gaza strip is a serious problem for the status of the marine ecological system. The input of raw sewage water into the sea can cause a number of detrimental effects Table (7.1). About 80% of the wastewater generated in Gaza strip is currently discharged without treatment into the sea (50,000 m3 per day). The untreated sewage discharge affects the complete marine food chain ranging from phytoplankton, via zooplankton, crustaceans, macro-benthos, and macro-algae to fish and mammals. A Wadi Gaza flooding in winter, caused by intense rainfall, will bring large amounts of heavily polluted water into the marine environment. The status of the water quality on the Gaza part collects raw sewage from adjacent refugee camps and has a very poor water quality [10].

Some 2.8 million people currently live in the West Bank and Jerusalem. The wastewater of two million of them - from settlements, the city of Jerusalem, and Palestinian towns and villages - is not treated. The prolonged neglect of Wastewater Treatment in the West Bank has created various hazards and environmental nuisances throughout the West Bank and is liable to pollute the Mountain Aquifer, the main water source of the area. Of the 17.5 million cubic meters of wastewater created annually by the settlements, 5.5 mcm flow as raw sewage into West Bank streams and riverbeds. The Jerusalem Municipality produces 17.5 mcm of wastewater that flows eastward into the West Bank. Of this amount, 10.2 mcm are raw sewage that flows into the Kidron Stream Basin. Palestinian towns and villages in the West Bank produce 56 mcm of wastewater annually, 62 percent of all wastewater in the West Bank. Some 90-95 percent of Palestinian wastewater is not treated at all. The first victims of the neglect of wastewater treatment are Palestinians, primarily residents of small towns and villages, which depend on water from natural sources whose pollution cause disease and harms crops. Because settlements are generally at higher altitudes, their untreated wastewater flows down to nearby Palestinian communities [11].

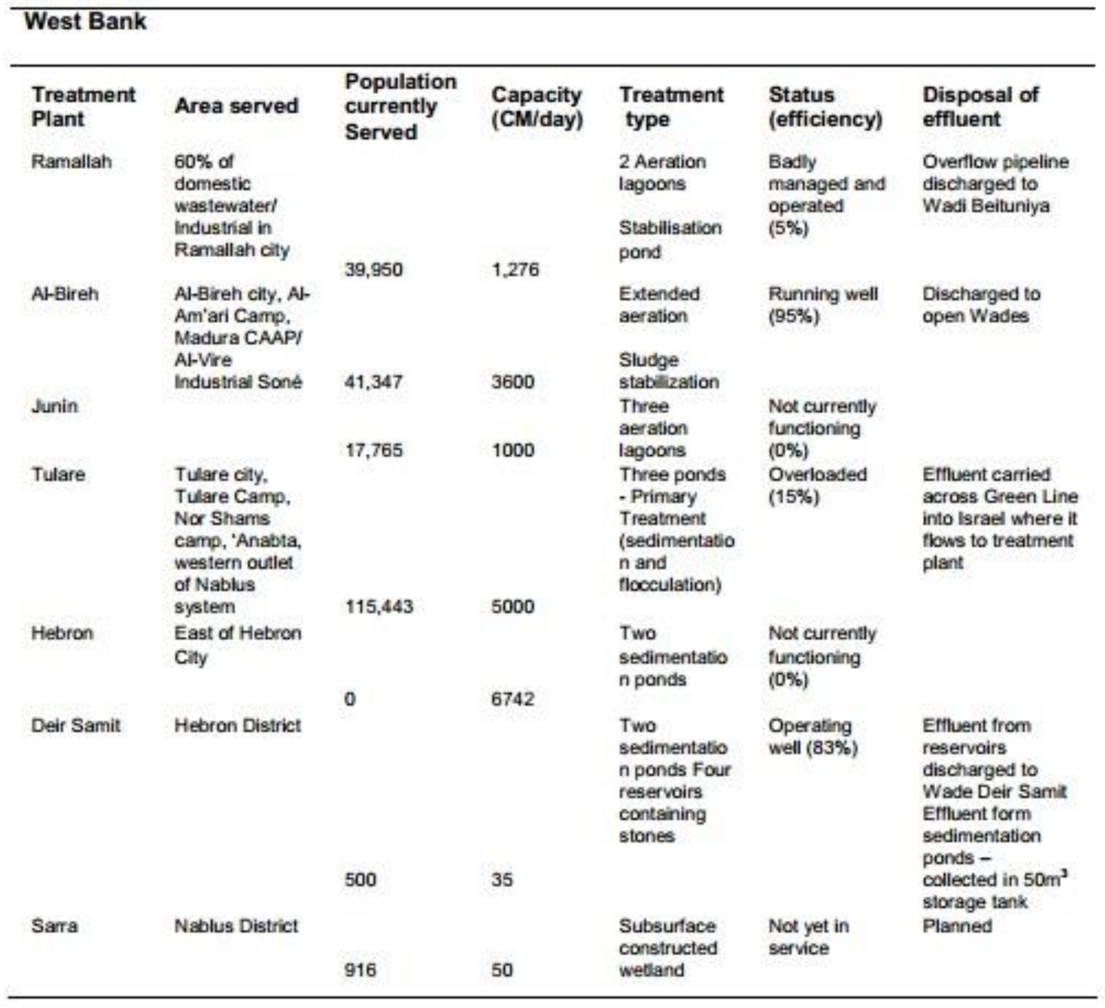
2.2. Small scales wastewater treatment plants in West Bank of Palestine

Palestine is suffering from severe shortages of fresh water caused by Israelis exploitation of Palestinian water resources. Wastewater is an invaluable resource that may successfully be used for irrigation upon treatment. Small-scale reuse of treated wastewater for agriculture would play a major role in increasing agricultural area in Palestine as well as help to conserve the environment. As a response to such a situation, Small-Scale Wastewater Technology could be the most appropriate solution to replace current cesspit systems in rural areas of the West Bank. Recently, in 2003 the Palestinian Water Authority started to collect information on the type of the plants used in order to prepare strategy for small-scale plants. Several small-scale wastewater treatment plants have been constructed in the rural areas of the West Bank. Different types of small plants have been installed in the West Bank, including:

1. UASB (Up flow And Anaerobic Sludge Blanket)
2. Sequencing Batch Reactors
3. Contact Stabilization
4. Septic Tank-Anaerobic Filter

Table (2.1) shows data related to existing wastewater treatment plants in West Bank [12].

Table (1. 1): Data related to wastewater treatment plants in West Bank



West Bank

Treatment Plant	Area served	Population currently Served	Capacity (CM/day)	Treatment type	Status (efficiency)	Disposal of effluent
Ramallah	60% of domestic wastewater/ Industrial in Ramallah city	39,950	1,276	2 Aeration lagoons Stabilisation pond	Badly managed and operated (5%)	Overflow pipeline discharged to Wadi Beituniya
Al-Bireh	Al-Bireh city, Al-Am'ari Camp, Madura CAAP/ Al-Vire Industrial Soné	41,347	3600	Extended aeration Sludge stabilization	Running well (95%)	Discharged to open Wades
Junin		17,765	1000	Three aeration lagoons	Not currently functioning (0%)	
Tulare	Tulare city, Tulare Camp, Nor Shams camp, 'Anabta, western outlet of Nablus system	115,443	5000	Three ponds - Primary Treatment (sedimentation and flocculation)	Overloaded (15%)	Effluent carried across Green Line into Israel where it flows to treatment plant
Hebron	East of Hebron City	0	6742	Two sedimentation ponds	Not currently functioning (0%)	
Deir Samit	Hebron District	500	35	Two sedimentation ponds Four reservoirs containing stones	Operating well (83%)	Effluent from reservoirs discharged to Wade Deir Samit Effluent form sedimentation ponds – collected in $50m^3$ storage tank
Sarra	Nablus District	916	50	Subsurface constructed wetland	Not yet in service	Planned

Sarra is one of the villages of the West Bank. It is located in the west of Nablus. It is located only a few kilometers away from old Nablus. Sarra currently has about 3,700 inhabitants. The village has three mosques. There is a Diwan of more than 170 years old, which was restored by the people of the village and there are two olive machines in the village, which work seasonally and meet the needs of the village. A power plant and a wastewater treatment plant were built there.

2.3. Pollution by pathogenic bacteria.

The pollution of water resources and related diseases by water-borne pathogen contamination are concerned 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. Each year 3.4 million of People, mostly children, die from water-related diseases, according to the World Health Organization (WHO). According to an assessment by the United Nations Children's Fund (UNICEF) 4000 children die each day as a result of contaminated water. WHO 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% [13].

The pathogens of a particular interest, such as *Staphylococcus aureus, Pseudomonas aeruginosa, Escherichia coli, Protesu mirabilis and Klebsiella spp* have been selected in this project because they are associated with human disease [14].

2.4. Sources, fate and behavior of microorganisms in water

Water Sewage Overflow 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 [15].

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. The Knowledge of the widespread contamination of water resources necessitate an appraisal of the effect on human of infection caused by pathogen [14].

There appears to be a microenvironmental link between heavy metals and bacteria as research has reported that heavy metals have been found at increasing levels within bacterial environments [16][17]. Metals like copper (Cu), iron (Fe), manganese (Mn), nickel (Ni) and zinc (Zn) are essential micronutrients in bacterial metabolism [16][18] where they are involved in redox processes and stabilize molecules through electrostatic interactions. In addition, they are co-factors in enzymatic reactions and regulate osmotic balance [18][20]. Essential metals are also involved in the expression of genes and stabilize DNA structure. However, a physiological role by heavy metals like Cadmium (Cd) and Lead (Pb) is not known as they are toxic to bacterial cells, even at low concentration [21].

A major impact of urbanization is the long term impacts on water quality as a result of urban runoff. Urban development causes an increase in the pollutants in storm water. These pollutants can vary widely from event to event and over the course of the year. These pollutants are a normal byproduct of modern urban life and include such pollutants as road salt, fertilizers, pesticides, heavy metals, oils, nutrients, oxygen-demanding substances, and bacteria [22].

2.5. Heavy metals and pollution

Heavy metals are naturally occurring elements in the environment and they have a specific gravity at least five times the specific gravity of water [23]. The term heavy metal refers to all the metals having density over (5 g/cm^3). For example, Cu – 8.93 g/cm^3, Cd – 8.65 g/cm^3 and Pb has density of 11.34 g/cm^3. Therefore, the term “heavy metal” has become interchangeable with toxic metal. 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 [24].

In recent years, there has been an increasing ecological and global public health concern associated with environmental contamination by these metals. Also, human exposure has risen dramatically as a result of an exponential increase of their use in several industrial, agricultural, domestic and technological applications [25]. Reported sources of heavy metals in the environment include geogenic, industrial, agricultural, pharmaceutical, domestic effluents, and atmospheric sources [26].

The hazardous ill effects of heavy metals on the environment and public health is a matter of serious concern. Heavy metals in water resources are one of the most important environmental problems of countries. The intensification of industrial activity and environmental stress greatly contributes to the significant rise of heavy metal pollution in water resources making threats on terrestrial and aquatic life. The toxicity of metal pollution is slow and interminable, as these metal ions are non-biodegradable [27].

2.6. 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. Other sources of high content of heavy metals are water runoff, industrial wastes and discharges, and dump sites [28]. Beside the natural activities, almost all human activities also have made a potential contribution to the production of heavy metals as side effects [3].

Many industrial activities, such as mining, processing minerals and chemical industries, increase harmless and non-essential metal concentration to the water tables from the surrounding regions of their manufacturing plants [29].

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater. Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer (International Occupational Safety and Health Centre1999) [30].

The majority of heavy metals are transition metals. Whether metalloids or light metals, their toxicity varies according to the metal oxidation state and the concentration. Some heavy metals at specific oxidation state are trace elements, while in another oxidation state they become highly toxic. Therefore, not all heavy metals are toxic to organisms. Some heavy metals at a lower concentration are essential elements and become toxic with concentration increase. However, there are some heavy metals, such as Pb and Hg, which are highly toxic even at a low concentration. Toxicity of some heavy metals exists when they are in a specific form. For example, in soluble form, some heavy metals become toxic, affecting the physiologic state of organisms. The toxicity occurs when heavy metals are in the form of cations which enable them to bind to proteins and other biomolecules. Therefore, accumulation of non-essential heavy metal in organism tissue was used as bioindicators of environmental pollution [31].

Based on the above, the researcher has selected metals ions (Fe^{3+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+}) which are commonly found as pollutants in different habitats in the water tables to remove them using *Phragmites australis* (reed common) from wastewater. 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/cm^3. Each of these metals is discussed below in terms of their properties, significance, and toxicity and effect on health.

2.6.1. 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 [28]. 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 . 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 [32].

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 [28]. 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% [32][33]. 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 [34].

2.6.2. Copper: Cu (II)

Cu is a high conductor of electricity. It is a corrosion resistant metal that is reddish brown, malleable and ductile, [28]. Cu is mainly used in plumbing and electrical conductors because it is a high conductor of electricity. In the presence of CO_2, it oxidizes slowly in air and its surface exhibits a green color due to a film of $Cu_2(OH)_2CO_3$ [35]. It usually exists in the +2 oxidation state. CuO – copper (II) oxide which is black can also exist in the +1 state Cu_2O – 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 [36].

2.6.3. Iron: Fe (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 uses, 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 from rust. There are ferrous compounds and ferric compound: 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. Iron compounds are used for several purposes. 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 disorder 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 [37].

2.6.4. Lead: Pb (II)

Lead 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 . Landfills is 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. The other grate pollutant of Pb is exhaust fumes of cars which cause atmospheric pollution [32]. 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

[38]. Current Pb annual production in the ward is 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 [32]. 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 [32][36].

2.6.5. Nickel: Ni (II)

Nickel (II) chloride is the chemical compound $NiCl_2$. The anhydrous salt is yellow, but the more familiar hydrateNiCl2•6H2O 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 [37].

2.7. *Phragmites australis* characteristic

A tall perennial wetland grass in the Grass family (Poaceae) ranging in height from 3 to 20 ft. Strong leathery horizontal shoots, called rhizomes, growing on or beneath the ground surface give rise to roots and tough vertical stalks. Canelikem stems, 1 inch in diameter, support broad sheath-type leaves that are .5 to 2 inches wide near the base, tapering to a point at the ends. Large dense, featherlike, grayish purple plumes, 5 to16 inches long, are produced in late June to September. The plant turns tan in the fall and most leaves drop off, leaving only the plume-topped shoot. The root system is comprised of rhizomes that can reach to 6 feet deep with roots emerging at the nodes. Common reed reproduces by spreading rhizomes that form large colonies [39]. Scientific classification of *Phragmites australis* is shown in Table (2.2).

Table (2. 1): Scientific classification of *Phragmites australis* [40]

Kingdom	Plantae
Phylum	Magnoliophyta
Class	Lilliopsida
Order	Cypearales
Family	Poaceae
Genus	*Phragmites*
Species	*Australis*

Phragmites australis 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* can grow in natural or artificial conditions. 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 countries 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 [40][41].

Figure (2. 1): *Phragmites australis* (common reed)

2.8. Phytofiltration

The bioremediation technology is the overall term; it is include phytofiltration and phytoremediation. Bioremediation means using biological agents as bacteria or plants to remove or equalize contaminants from polluted water [42][51]. Phytoremediation: a friendly (green) technology for the environment that uses living plants to remove contaminants from the environment or rendering them harmless [43][44]. Phytoremediation is the efficiency and cheap technology used to extract or remove pollutants from contaminated soil and water**.** Phytofiltration is the use of dead or inactivated biomass to remove heavy metals from contaminated water [45][46]. Phytoremediation can be achieved by phytoextraction, phytovolatization, phytodegradation, phytostabilization, and rhizofiltration. Rhizofiltration: is the use of the plant roots as a filter to absorb pollutants, mainly heavy metals, from waste water [47]. 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 [48]. 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 [49]. 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 [50].

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 [51].

The use of plant material *Phragmites australis* for the purification of toxic products in aqueous effluents has received a significant credibility in recent years because it is more efficient, inexpensive, biodegradable, and environmentally friendly [52].

Chapter Three

Methodology

Chapter Three

Methodology

3.1 Chemicals and Materials

All solvents and chemicals were of analytical scale and used without additional purification. $Pb(NO_3)_2$ anhydrous (≥99.0%, Sigma-Aldrich), $Cu(NO_3)_2.3H_2O$ (99-104%, Sigma-Aldrich), $Fe(NO_3)_3.9H_2O$ (≥99.95%, Sigma-Aldrich), $Ni(NO_3)_2.6H_2O$ (≥99.999%, Sigma-Aldrich), and $Cd(NO_3)_2$ anhydrous (≥98.0%, Sigma-Aldrich) were used to prepare 100 ppm of each metals respectively. Methanol, 10% DMSO and deionized water were used. HNO_3 (0.1M) and KOH (0.1M) for pH adjustment were used.

Mueller Hinton Agar, petri dishes and four morphologically similar colonies were taken from *Staphylococcus aureus, Pseudomonas aeruginosa, Escherichia coli, Klebsiella spp* bacteria were used for antibacterial activity test.

Phragmites australis plant was collected from Wadi Al Bathan field and samples of phragmites were collected from the sewage wastewater treatment plant from Sarra.

The required apparatus are: glassware, scale, Whatman No 1 filter paper, pH meter (model: 3510, JENWAY), centrifuge (model:1020 DE, Centurion Scientific), Shaking Water Bath (Daihan Labtech, 20 to 250 rpm

Digital Speed Control), desiccator and incubator (Memmert incubator, Germany).

3.2 Collection and treatment of biomass

Phragmites australis plant was 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 wastewater treatment plant from Sarra. Washed, and the roots, stems, and leaves, were separated. All samples were oven dried at 37°C for one week. Then the leaves, root and stem of both plant samples were crushed separately.

Figure (3. 1): Phragmites from purification plans in Sarra.

This was followed by two parts of the experiment: The potential of *Phragmites australis* plant which collected from Wadi Al Bathan to remove (Fe^{3+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+}) from aqueous solution was studied and compared with other plant of Phragmites which was taken from sewage purification plant in Sarra. The antibacterial activity for the *Phragmites australis* was tested in the biological part.

3.3. The experiment of biological part:

3.3.1. Preparation of samples for antibacterial activity

The dried plant material was ground to a fine powder in a blender. A measured amount 7 gm of dried powder from *Phragmites australis* and 6 gm from the other phragmites were soaked in 100 cc of methanol in a round bottom flask and put in a shaker at room temperature for 48 h. Another measured quantity 7 gm and 6 gm of dried powder for both of phragmites were soaked in 100 cc 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^{o}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 [53][54][55].

3.3.2. Preparation of media

Mueller-Hinton Agar was prepared for this test. Media powders 36 g/L were added to sterile distilled water. 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 15 lbs pressure 121°C for 15 minutes, and then lifted to be dried before being used. Holes were made using heads of sterile glass pipettes [56].

3.3.3. Bacteria preparation

Four morphologically similar colonies were taken from *Staphylococcus aureus, Pseudomonas aeruginosa, Escherichia coli, Klebsiella spp* bacteria with sterile loop and transferred into MHA. The plates were incubated at 37°C for 48 hours [53][55].

3.4. Chemical part of experiment:

3.4.1. Preparation of solutions of the metals

Solutions of the five metals' salts of (Pb, Cu, Cd, Ni, Fe) was prepared. 3.31 gm/L $Pb(NO_3)_2$ anhydrous ($\geq$99.0%, Sigma-Aldrich), 2.42 gm/L $Cu(NO_3)_2.3H_2O$ (99-104%, Sigma-Aldrich), 4.04 gm/L $Fe(NO_3)_3.9H_2O$ ($\geq$99.95%, Sigma-Aldrich), 2.91 gm/L $Ni(NO_3)_2.6H_2O$ ($\geq$99.999%, Sigma-Aldrich), and 2.36gm/L $Cd(NO_3)_2$ anhydrous ($\geq$98.0%, Sigma-Aldrich) were used to prepare 100 ppm of each metals respectively.

3.4.2. Preparation of stock solutions of the metals

Stock solution from the solution of each metals' salts; 1.2 ml $Pb(NO_3)_2$ anhydrous, 3.96 ml $Cu(NO_3)_2.3H_2O$, 4.487 ml $Fe(NO_3)_3.9H_2O$, 4.27 ml $Ni(NO_3)_2.6H_2O$, and 4 ml $Cd(NO_3)_2$ anhydrous were used to prepare 50 ppm in (500 ml/L) of each metals. Then from the stock solution of metals, four concentrations (5 mg/L, 10 mg/L, 15 mg/L, and 20 mg/L) were diluted

3.4.3. Preparation of standardization curves

A new 50 ppm metal particle solution was arranged in every work day by progressive mitigations of the stock 500 ml solution. From the 50 ppm standard which was prepared, solutions of 5, 10, 15 and 20 ppm were set up by diluting 25, 50, 75 and 100 ml individually into 250 mL volumetric vials with deionized water. All volumetric vials washed with 0.1 M HNO_3 before being used. The concentration measured by Flame Atomic Absorption Spectrometry (FAAS) (type: ICE 3000 SERIES, Thermo Scientific). A standardization curve of absorbance versus concentration was formed at the time of investigation. Alignment coefficient (R^2) was in the range of 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.

3.5. Metals quantification

The percent removal of metal particle by biomass was calculated by applying the equations [57]:

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

Where C_0 is the underlying metal particle fixation, (mg/L), and C_f is the last particle fixation (mg/L) after the event biosorption.

3.6. Studied parameters

3.6.1. Effect of initial concentration of the metal

Different concentrations solution (5, 10, 15 and 20 ppm) of all metals was fit out from stock solutions. For each concentration 30 gm of plant samples (leaves, stems and roots) were filed in column and 500 ml of metal ion solution were added to it. Then the extracts were saved for metal quantification, using Flame atomic absorptions spectrometer (FAAS).

3.6.2. 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 20 ppm metal ion solutions, and then the extracts were saved for metal quantification using (FAAS). The exploratory results of the batch experiments indicated that the reed stem which was obtained from Wadi Al-Batahan had the optimum absorption value of Pb^{+2} at concentration of 20 ppm. Consequently, these results were followed as a hint to complete the study and determine the other optimum conditions for absorption

3.6.3. Effect of pH on shoot samples

The impact of pH was studied. The plants samples were arranged to (3–10) pH values using 0.1 M HCl or 0.1 M NaOH for pH adjustment for each biomass sample. The stem samples were blended with (20ppm) metal ions solutions, and the extracts were saved for metal quantification using (FAAS).

3.6.4. Effect of temperature on shoot samples

The effect of temperature on shoot samples was investigated at different degrees of 15, 20, 25, 30, 35 and 40 ^{o}C. For each temperature, the stems samples were mixed with 20 ppm metal ion solutions, and the extracts were saved for metal quantification using (FAAS).

3.6.5. Interaction of metal ions (matrix effect)

The solutions emitted by industrial processes and wastewaters usually contain more than one metallic species. Therefore, it is essential to investigate the sorption behaviour under competitive conditions when several metallic species are present. In the evaluation of metal ion competition batch tests were conducted employing equal concentrations (20 mg/L) of the metal ions at optimum condition (pH=7, Temp=25^{o}C) using 30 gm of plant samples (leaves, stem and roots).

$Pb(NO_3)_2$ anhydrous (0.1ml), $Cu(NO_3)_2.3H_2O$ (0.35ml), $Fe(NO_3)_3.9H_2O$ (0.36ml), $Ni(NO_3)_2.6H_2O$ (0.34ml), and $Cd(NO_3)_2$ anhydrous (1.78ml) were used to prepare 20 ppm in a l00 ml flask. 30 gm 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 (FAAS).

Chapter Four

Results and Discussion

Chapter Four

Results and Discussion

4.1. Results of the experiment of the biological part:

The results of all samples of antibacterial activity test reveal that is negative. This means that *Phragmites australis* and the other *phragmites* from Sarra have not realized the impact on the pathogenic bacteria. This result indicates that the plant extracts have no antibacterial effect on the Gram-negative and Gram-positive bacteria, showing that they do not contain active ingredients against the organisms.

4.2. Results of the experiment chemical part:

4.2.1. The Effect of initial concentration

The metal ions concentrations and their % removal are shown in Figures (4.1 to 4.5) for all metals (Fe, Cd, Cu, Ni and Pb) respectively in both phragmites biomasses. Results revealed that their 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 lower concentration, the ratio of the initial number of metal ions to the available surface area is low and the available sites are high, but at high concentrations of ions, the available sites are fewer. Amount of metal ions adsorbed per unit mass of adsorbent increased with increasing metal ions concentration from 5 to 20 mg/L. When all sites are occupied, the adsorption becomes nearly constant whatsoever concentration of metal ions is increased. The removal is increased by increasing the concentration this agreed with study by (Sayrafi and Salim, 1996)[7]. In the 20 ppm concentration, as shown in Table (4.5) the percent removal for Pb^{+2} by shoot sample of *Phragmites australis* is the highest percent with (97.3%).

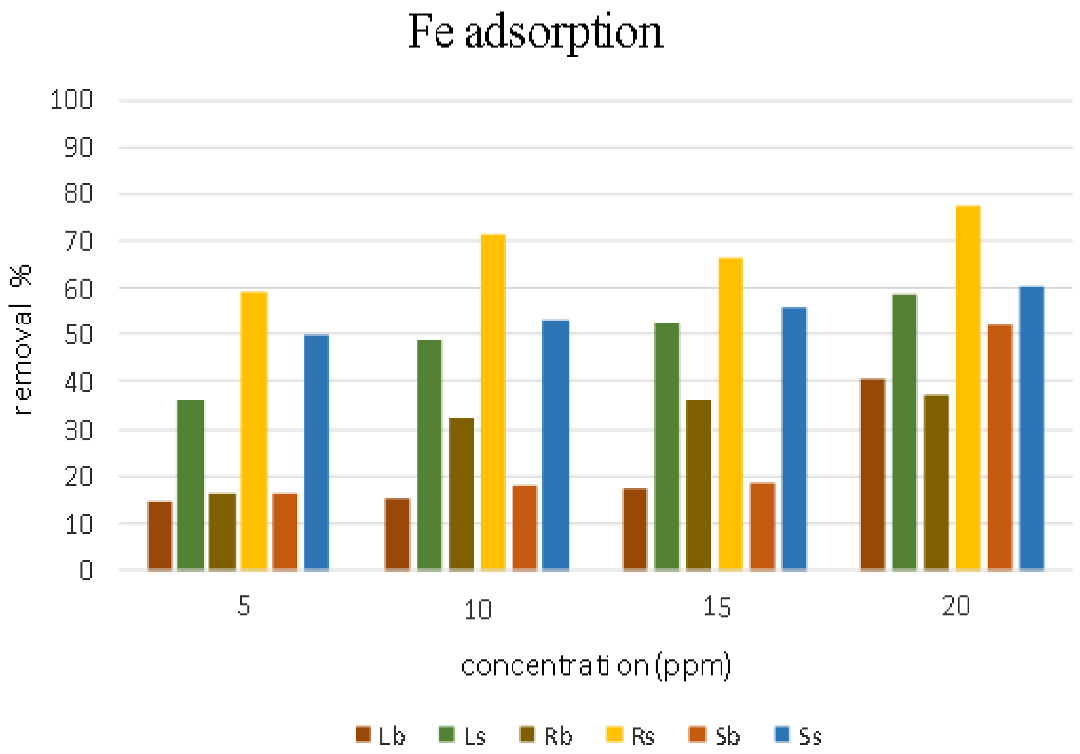


Figure (4. 1): Effect of initial iron metal ions concentration on the % removal by both phragmites**.**

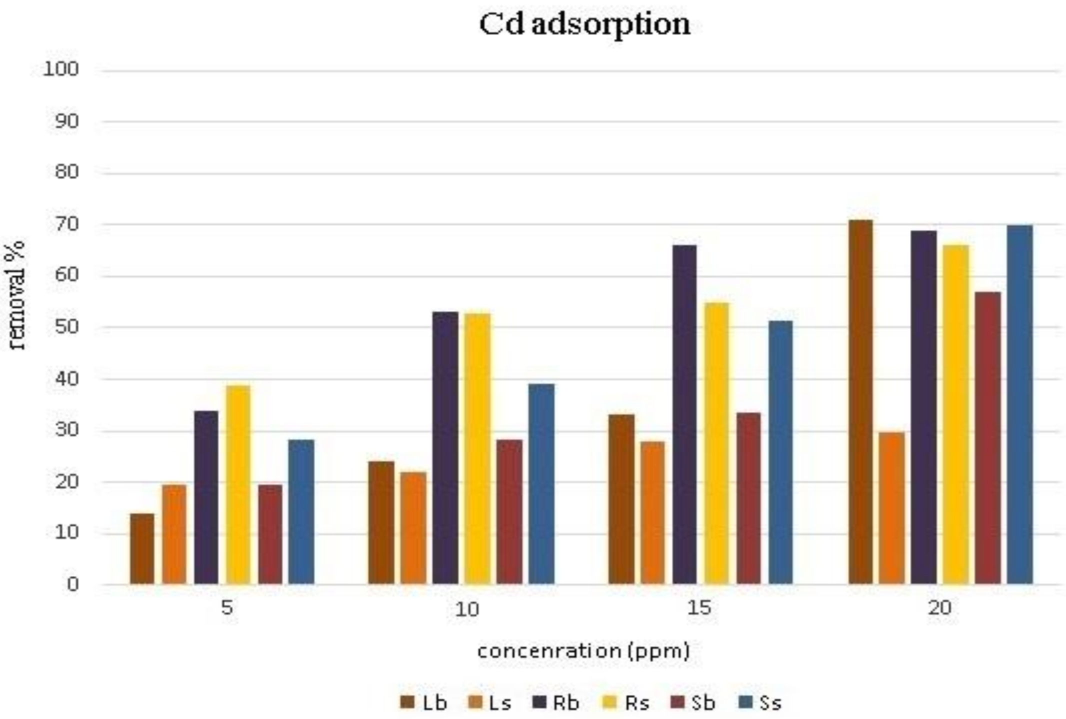


Figure (4. 2): Effect of initial cadmium metal ions concentration on the % removal by both phragmites.

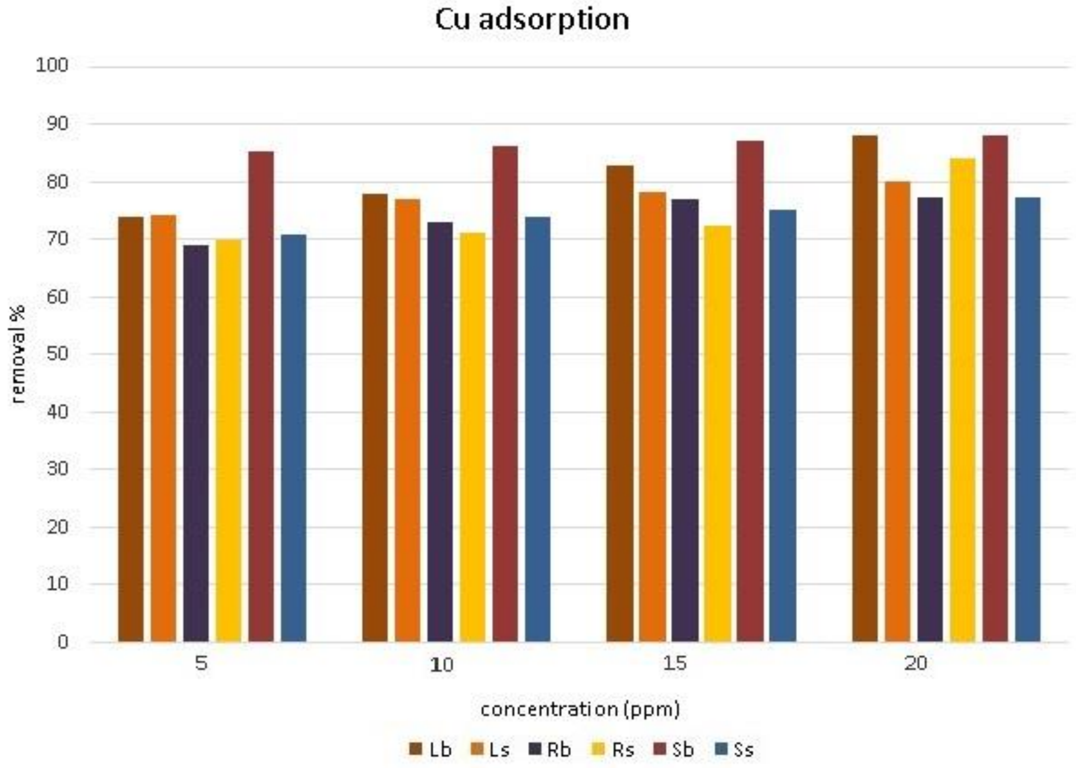


Figure (4. 3): Effect of initial copper metal ions concentration on the % removal by both phragmites

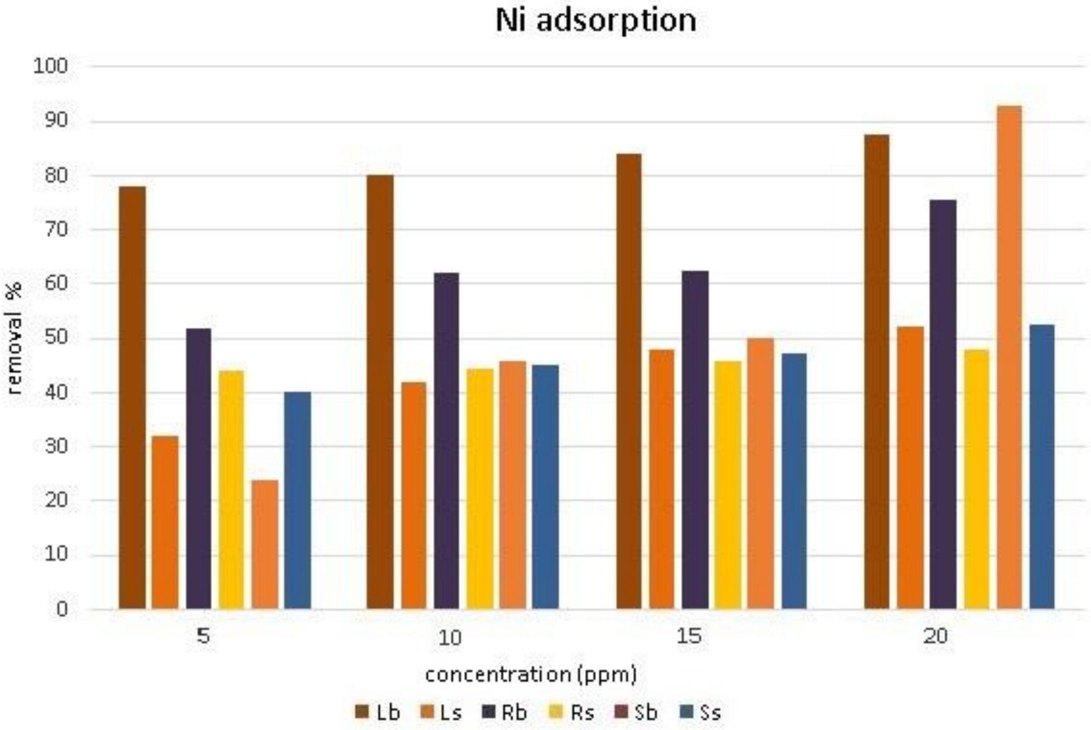


Figure (4. 4): Effect of initial nickel metal ion concentration on the %removal by both phragmites

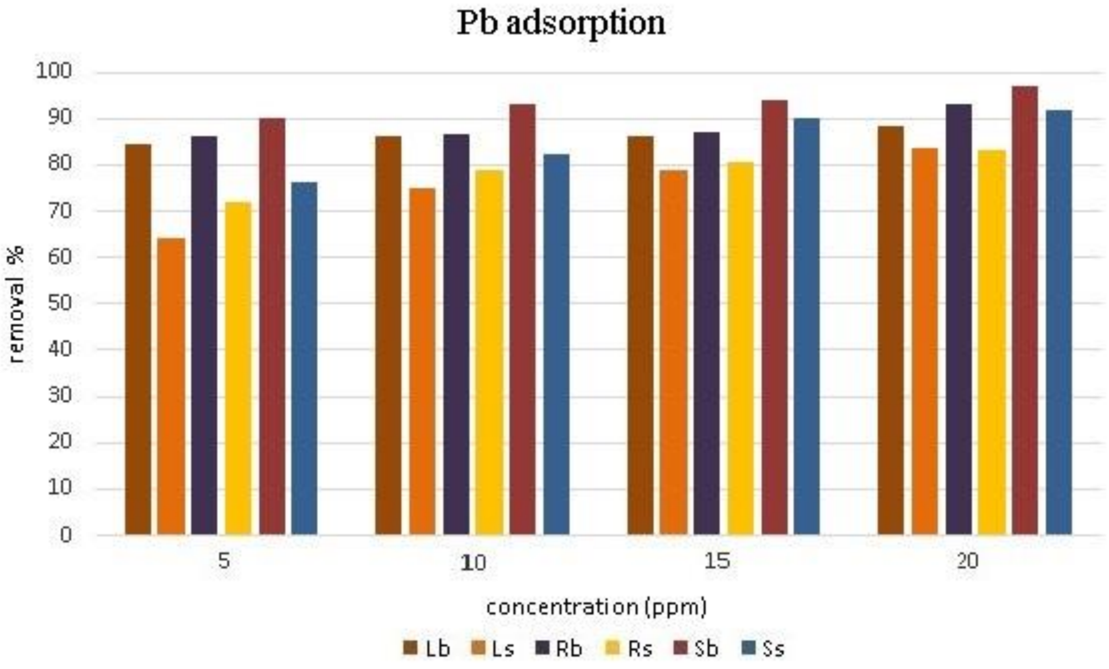


Figure (4. 5): Effect of initial lead metal ion concentration on the %removal by both phragmites

Table (4. 1): Effect of (5) ppm metal ion concentration on the % removal of metals by samples of leaves, stems and roots of both phragmites biomass, pH=7, 25°C

concentration 5 (ppm)	% Removal of Fe	% Removal of Cd	% Removal of Cu	% Removal of Ni	% Removal of Pb
Lb	14.5	14.0	74.4	78.0	86.4
Ls	36.0	9.5	74.2	32.0	64.0
Rb	16.0	34.0	69.0	52.0	86.6
Rs	59.5	38.8	70.0	44.0	72.0
Sb	16.0	19.4	85.4	24.0	90.1
Ss	50.0	28.2	70.8	40.0	76.2

Table (4. 2): Effect of (10) ppm metal ion concentration on the % removal of metals by samples leaves, stems and roots of both phragmites, pH=7, 25°C

concentration 10(ppm)	% Removal of Fe	% Removal of Cd	% Removal of Cu	% Removal of Ni	% Removal of Pb
Lb	15.0	24.5	78.4	80.0	86.4
Ls	49.0	22.0	77.2	42.0	75.0
Rb	32.0	53.0	73.0	62.0	86.6
Rs	71.5	52.8	71.3	44.5	78.8
Sb	18.0	28.2	86.2	46.0	93.3
Ss	53.0	39.2	74.0	45.0	82.2

Table (4. 3): Effect of (15) ppm metal ion concentration on the % removal of metals by samples leaves, stems and roots of both phragmites biomass, pH=7, 25°C

concentration 15 (ppm)	% Removal of Fe	% Removal of Cd	% Removal of Cu	% Removal of Ni	% Removal of Pb
Lb	17.3	33.3	83.2	83.9	84.9
Ls	52.9	28.0	78.2	48.0	79.5
Rb	36.6	66.9	77.0	62.6	86.9
Rs	74.6	54.8	72.3	46.0	80.8
Sb	18.6	33.6	87.2	50.0	94.1
Ss	56.0	51.3	75.3	47.3	90,1

Table (4. 4): Effect of (20) ppm metal ion concentration on the % removal of metals by sample leaves, stems and roots of both phragmites biomass, pH=7, 25ºC

concentration 20 (ppm)	**% Removal of Fe**	**% Removal of Cd**	**% Removal of Cu**	**% Removal of Ni**	**% Removal of Pb**
Lb	40.5	71.2	88.0	87.6	88.5
Ls	58.5	29.5	80.0	52.5	83.7
Rb	37.4	69.8	77.4	75.5	93.3
Rs	77.5	66.0	84.0	48.0	83.0
Sb	52.0	57.0	88.0	93.0	97.0
Ss	60.3	70.7	77.5	52.5	92.0

Results revealed that 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=7, temperature=25ºC and contact time=30 min) of adsorption studied for shoot samples.

4.2.2. Matrix effect

As known, wastewaters usually contain more than one metallic species and the presence of the accumulation of many metals caused interferences between them. The impact of competing to be adsorbed to biomass can be seen in Table (4.5). In the presence of all metal ions (Fe^{+3}, Ni^{+2}, Cd^{+2}, Cu^{+2} and Pb^{+2}) the percent removal of the metal ions was in the order of $Pb^{+2}>Cu^{+2}>Fe^{+3}>Ni^{+2}>Cd^{+2}$. The percent removal for Pb^{+2} is the highest percent with (97.3%).

Table (4. 5): Effect of interaction of metal ions (matrix effect) by shoot sample of Phragmites australis, (3mg/mL biomass, pH=7 and 25°C)

Metal ions (20 ppm)	**% Removal**
Fe^{+3}	30.0
Ni^{+2}	15.0
Cd^{+2}	6.5
Pb^{+2}	93.5
Cu^{+2}	43.2

The impact of competing ions is appeared to be subject to the sorption liking of the sorbent and the metal.

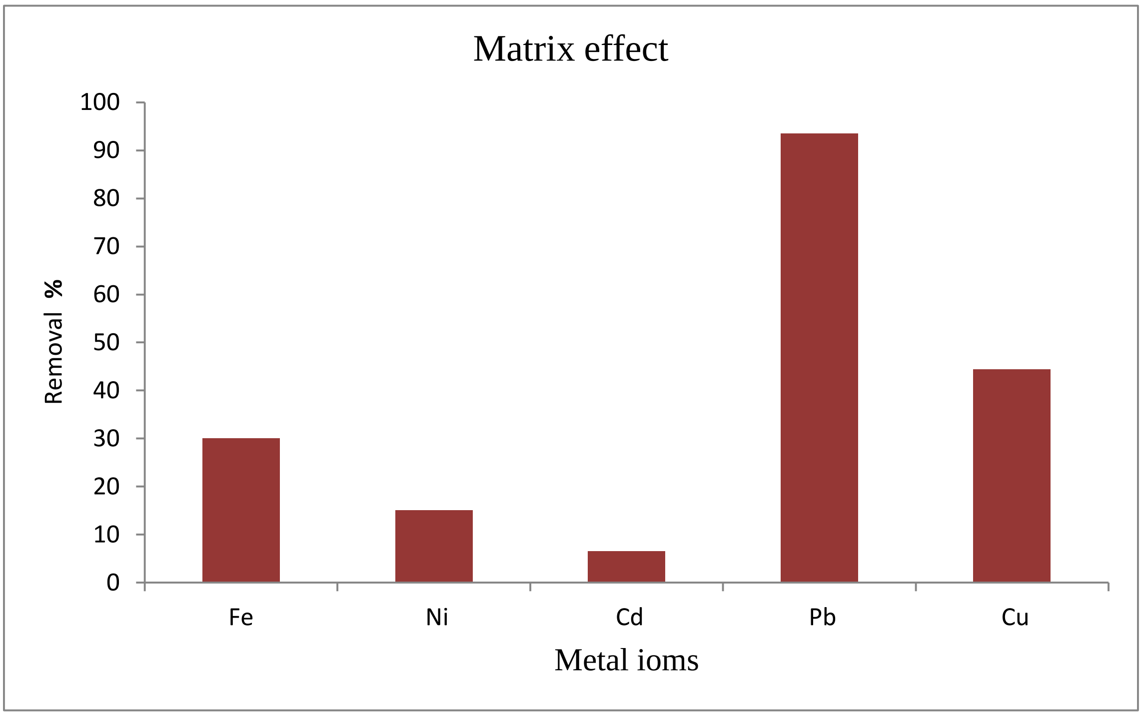


Figure (4. 6): Effect of metal ions on the percent removal of each other by shoot samples, (Pb+2>Cu+2>Fe+3>Ni+2>Cd+2)

4.2.3. Effect of contact time on adsorption

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 australis* at different contact times. The data is shown in Table (4.6).

Table (4. 6): Effect of contact time on the % removal of metals by shoot samples biomass, (20 ppm metal ion, pH 7 and 25 ºC)

Time/min	%Removal of Fe	%Removal of Cd	%Removal of Cu	%Removal of Ni	%Removal of pb
15	86.3	50.0	44.4	4.3	86.5
30	86.7	90.0	55.0	6.5	93.3
60	86.8	90.3	55.1	5.4	92.6
90	86,8	90.6	55.2	5.5	92.1
120	87.0	90.6	55.5	5.5	91.9

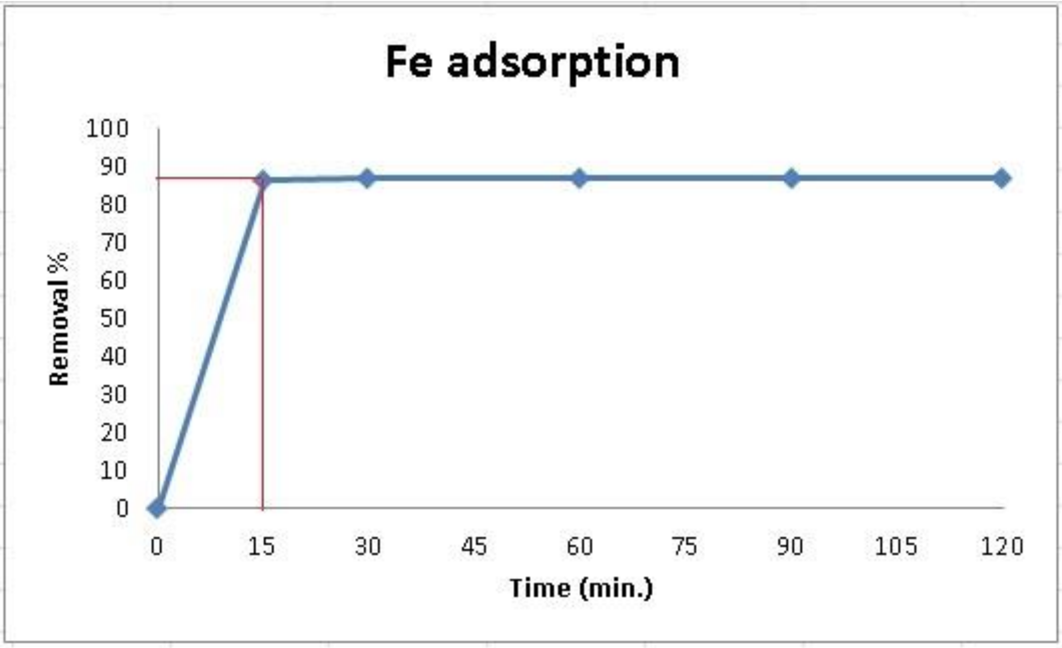


Figure (4. 7): Effect of contact time on the % removal of Fe+3 for shoot sample

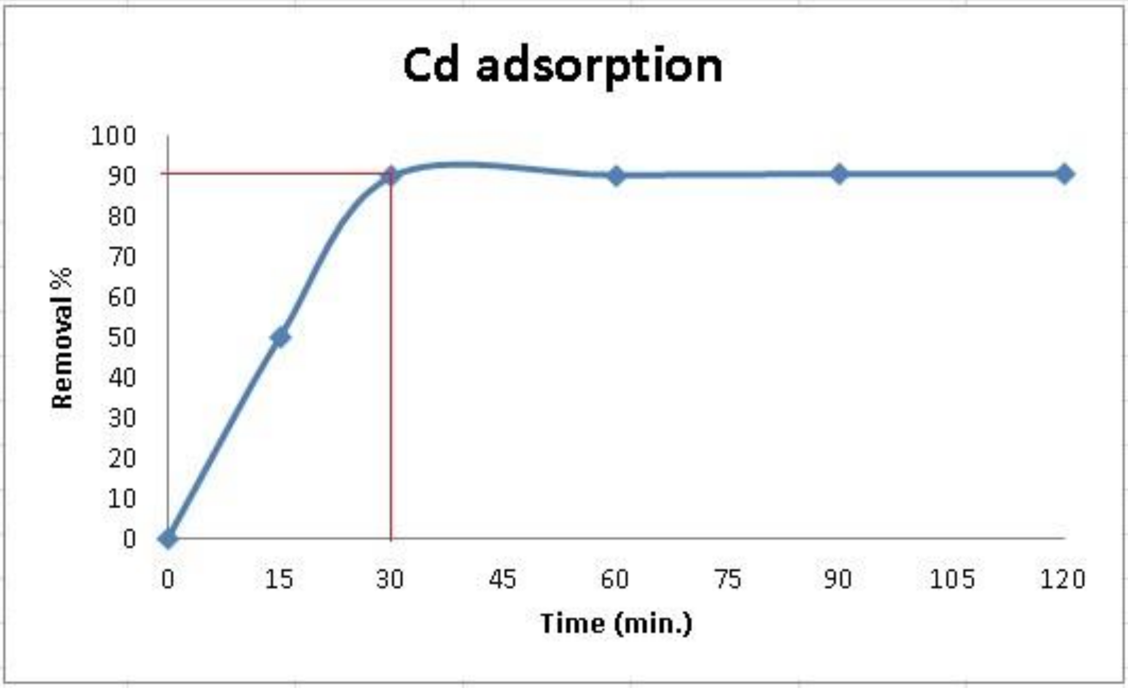


Figure (4. 8): Effect of contact time on the % removal of Cd+2 for stem sample

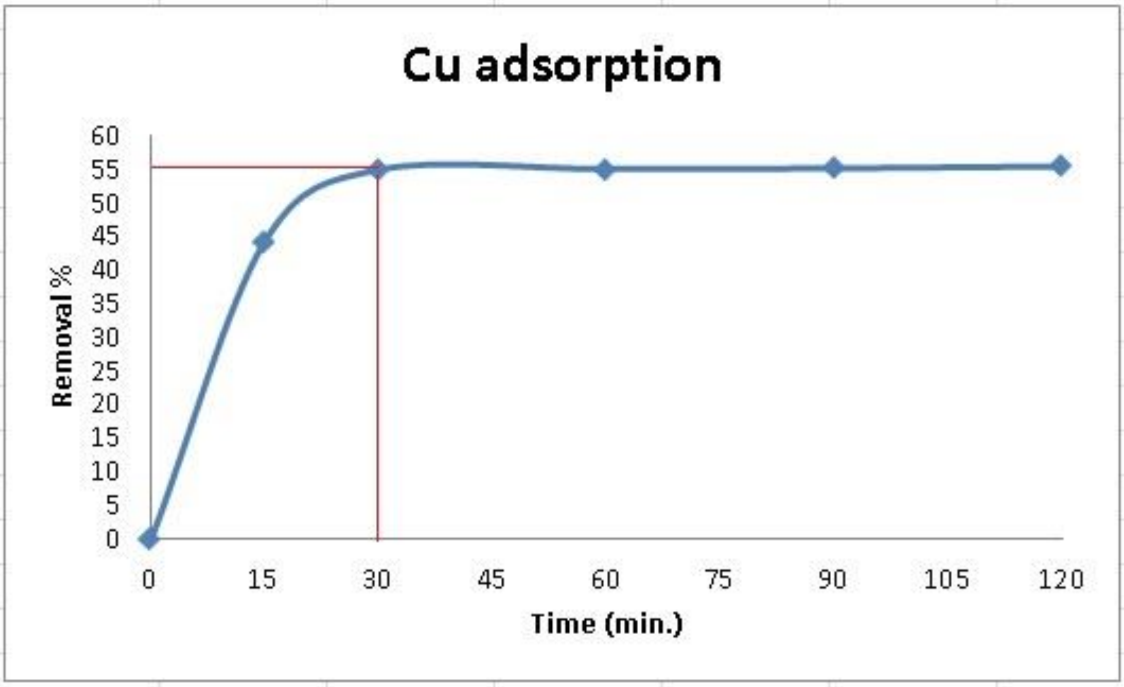


Figure (4. 9): Effect of contact time on the % removal of Cu+2 for stem sample

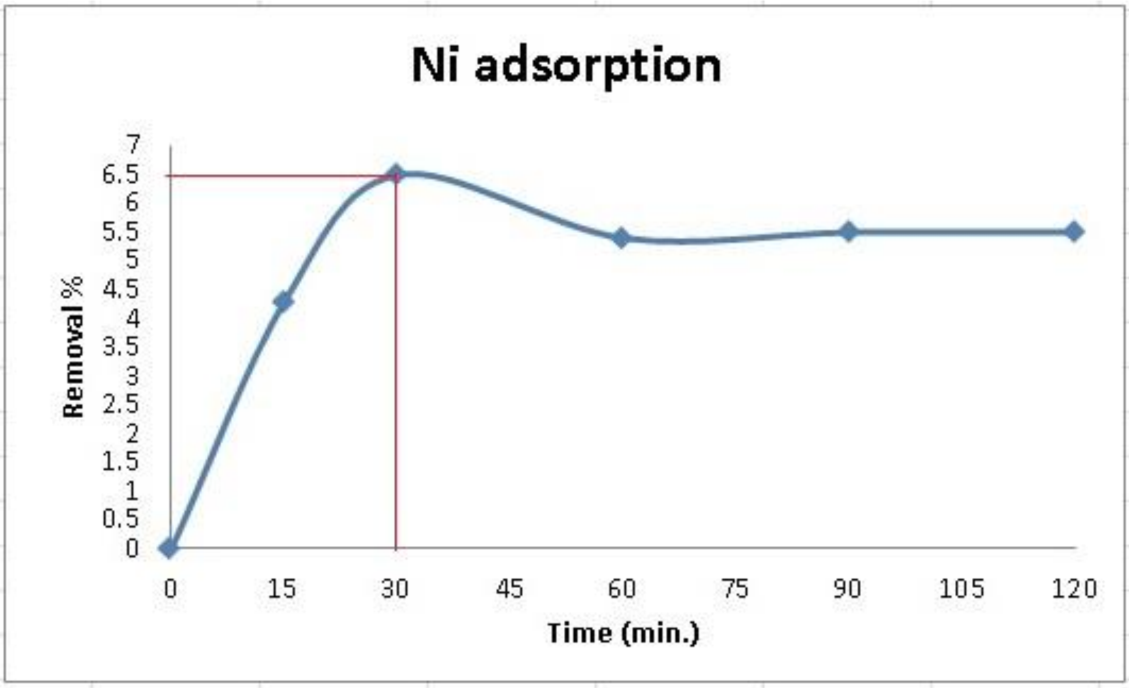


Figure (4. 10): Effect of contact time on the % removal of Ni+2 stem for sample

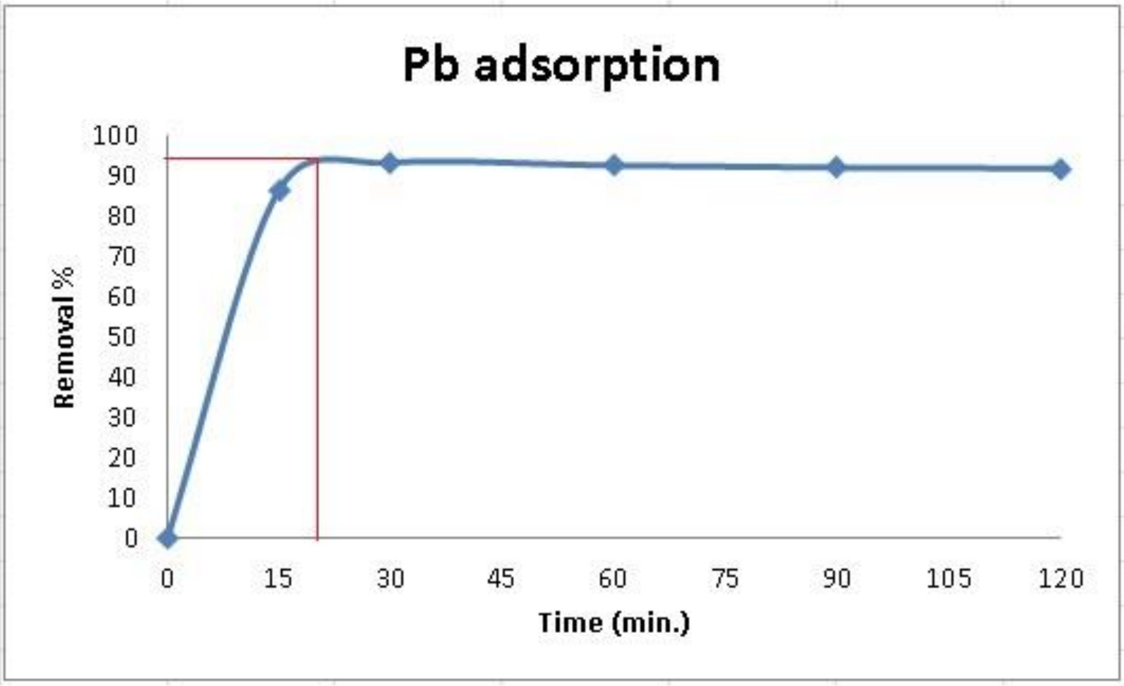


Figure (4. 11): Effect of contact time on the % removal of Pb+2 for stem sample

Results demonstrate that the percent removal of metals is extensive at the beginning of experiment, and then it becomes almost insignificant after that. At first, a lot of empty sites are accessible for binding, however after a specific time (15 –30 min), these sites get to be involved and soaked with metal ions. The rest of the sites are hard to be possessed as a result of the awful strengths that shape between metal ions [2].

4.2.4. Effect of pH of the solution

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 (4.12-4.16) shows the effect of solution pH on the amount of metal ions adsorbed onto the shoots. From Figures (4.12 to 4.16), an increase in the solution pH from 3.0 to 7.0 has increased the amount of metal ions (Fe^{+3}, Ni^{+2}, Cd^{+2}, Cu^{+2} and Pb^{+2}) adsorbed until pH about 7.0. 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 [58].

The ideal pH for adsorption of metal ions (Fe^{+3}, Ni^{+2}, Cd^{+2}, Cu^{+2} and Pb^{+2}) was registered at pH 7.0. The reduction in removal at pH more than 7.0 might be because of solvation and hydrolysis of metal particle.

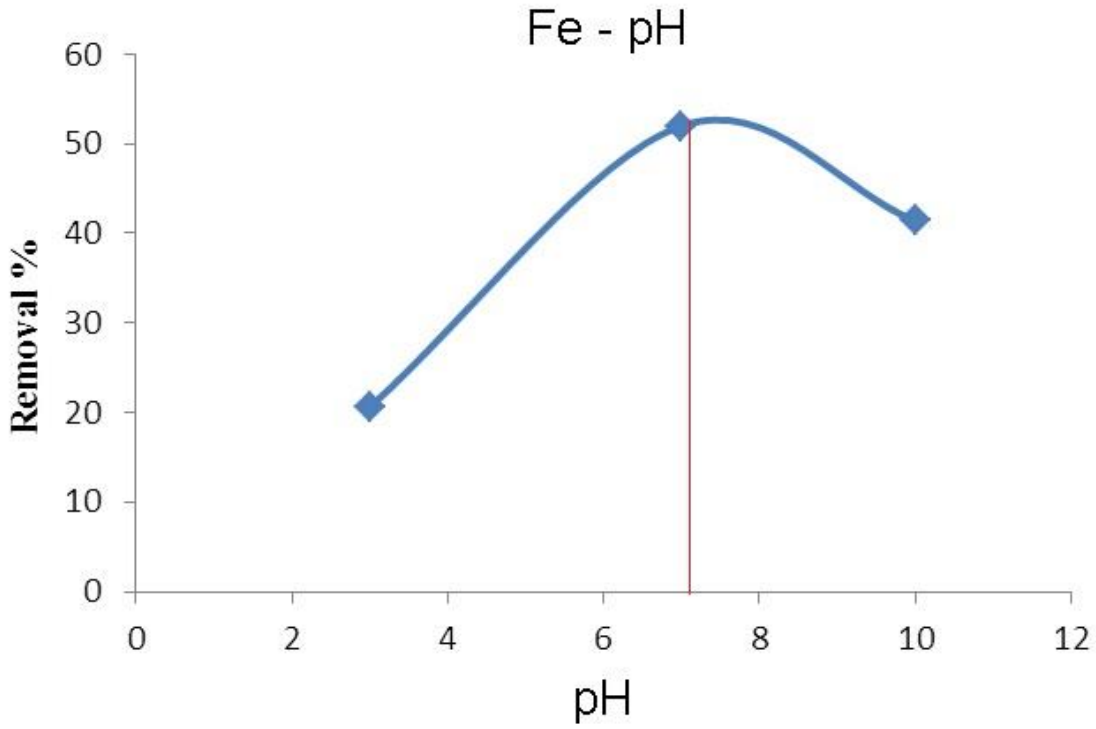


Figure (4. 12): Effect of solution pH on adsorption of Fe+3 by reed shoot sample shoot sample

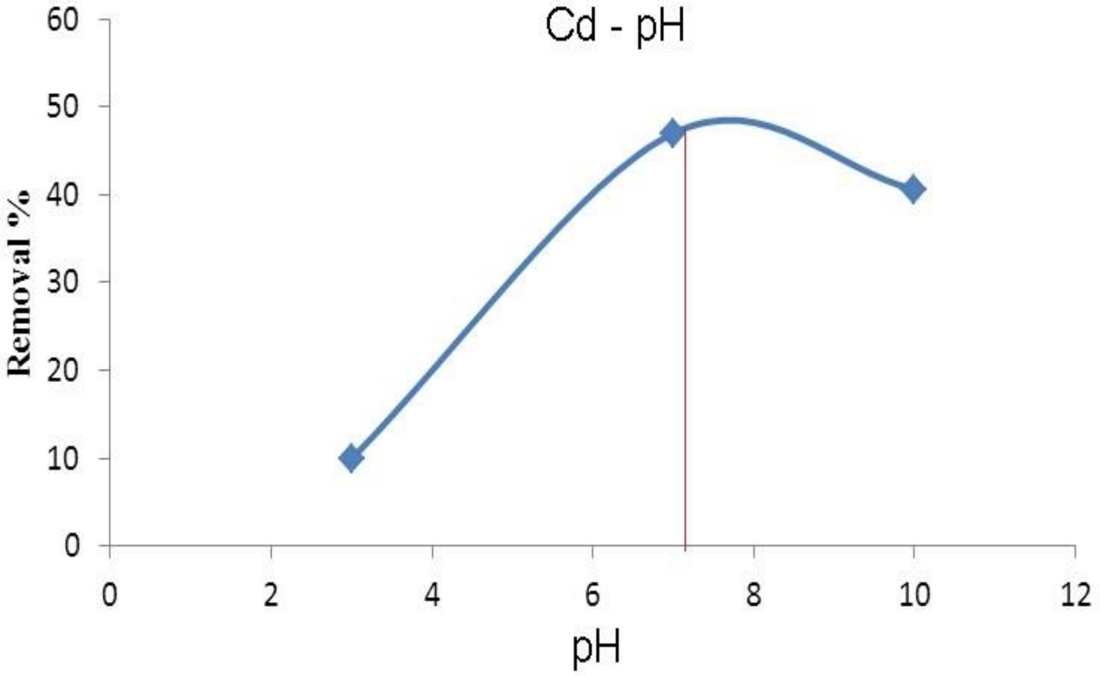


Figure (4. 13): Effect of solution pH on adsorption of Cd+2 by reed shoot sample

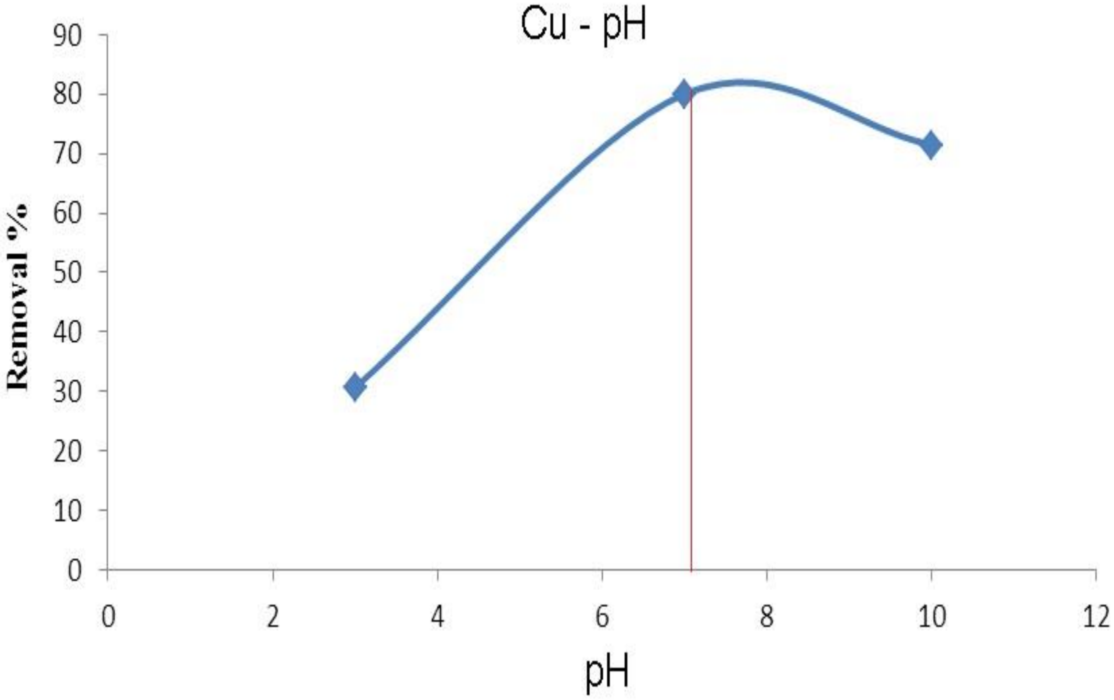


Figure (4. 14): Effect of solution pH on adsorption of Cu+2 by reed shoot sample

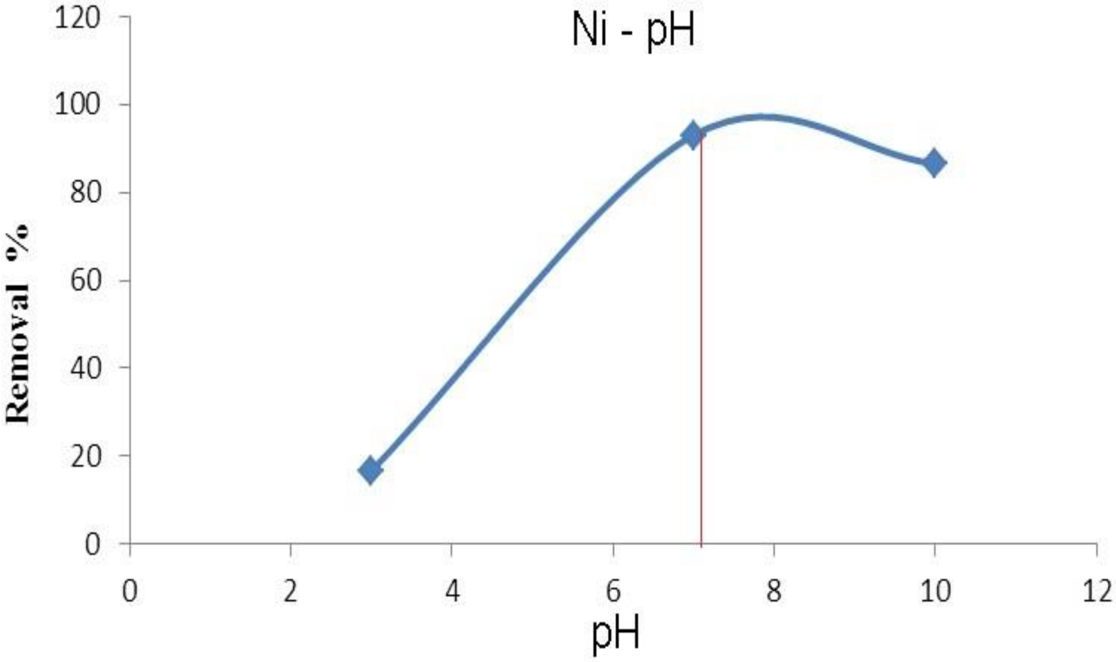


Figure (4. 15): Effect of solution pH on adsorption of Ni+2 by reed shoot sample

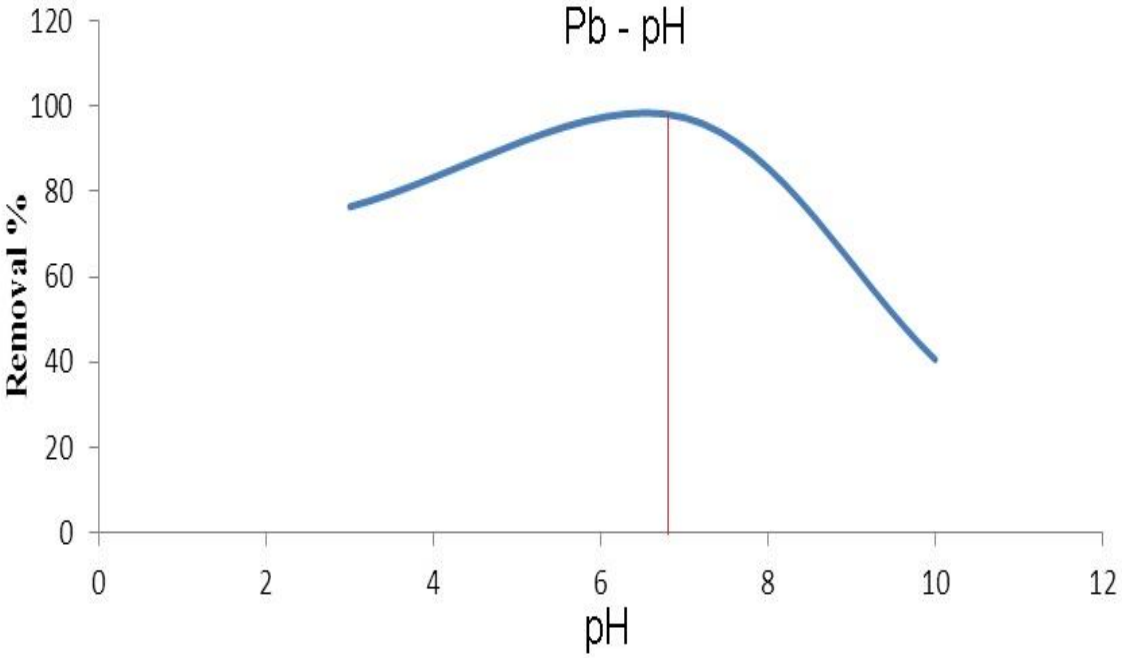


Figure (4. 16): Effect of solution pH on adsorption of Pb+2 by reed shoot sample

Table (4. 7): Effect of pH on the % removal of metals by shoot sample biomass, 20 ppm metal ion, 25oC

pH	%Removal of Fe	%Removal of Cd	%Removal of Cu	%Removal of Ni	%Removal of pb
3	20.6	10.0	30.0	16.7	76.4
7	52.0	47.0	80.0	93.0	97.3
10	41.4	40.6	71.5	86.5	40.6

4.2.5. Effect of Temperature

Temperature is a very important parameter that has an effect on the adsorption process, as can be seen in Figures (4.17-4.21).

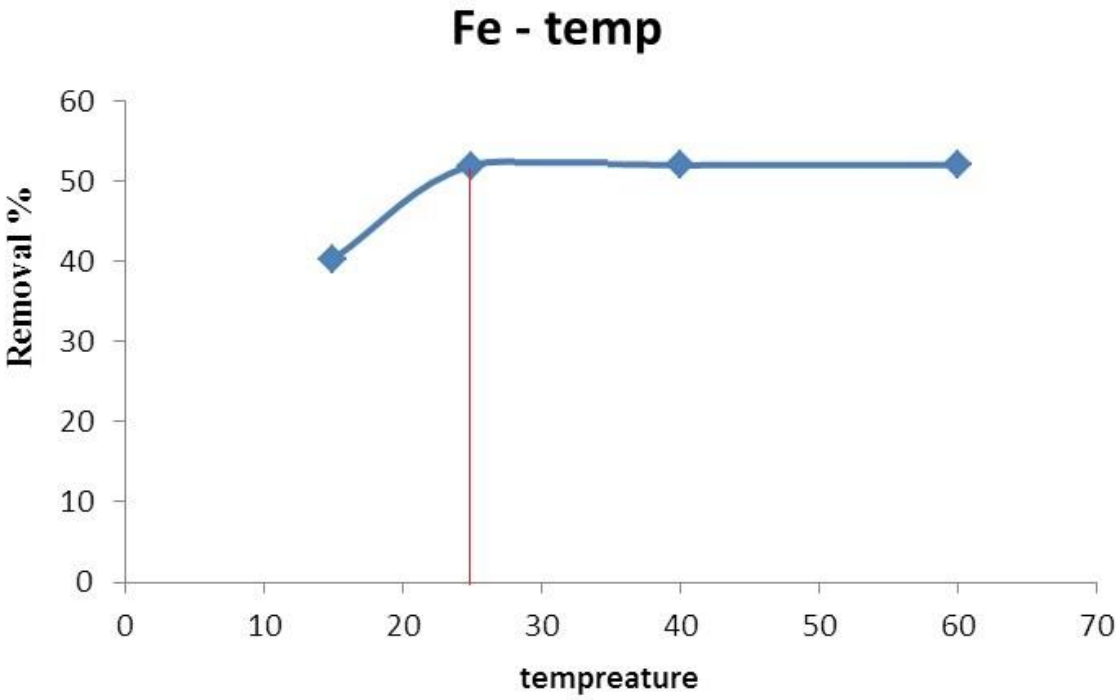


Figure (4. 17): Effect of temperature on the % removal of Fe+3 by reed shoot sample

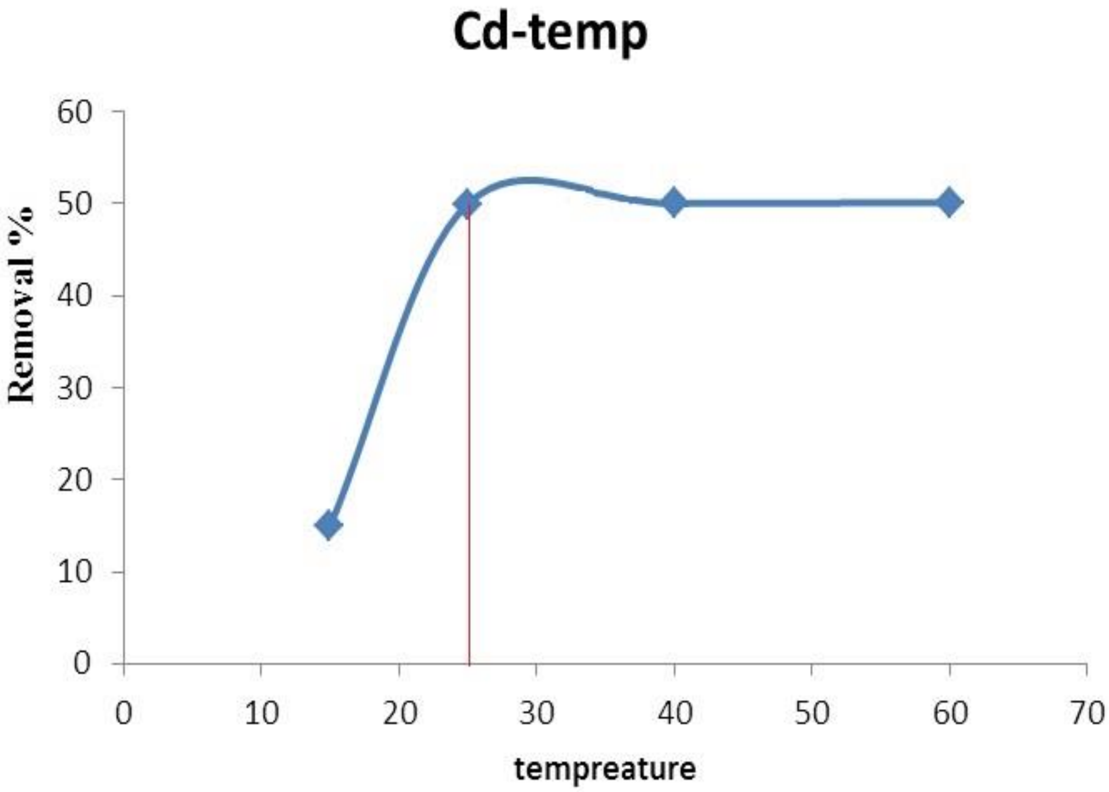


Figure (4. 18): Effect of temperature on the % removal of Cd+2 by shoot sample

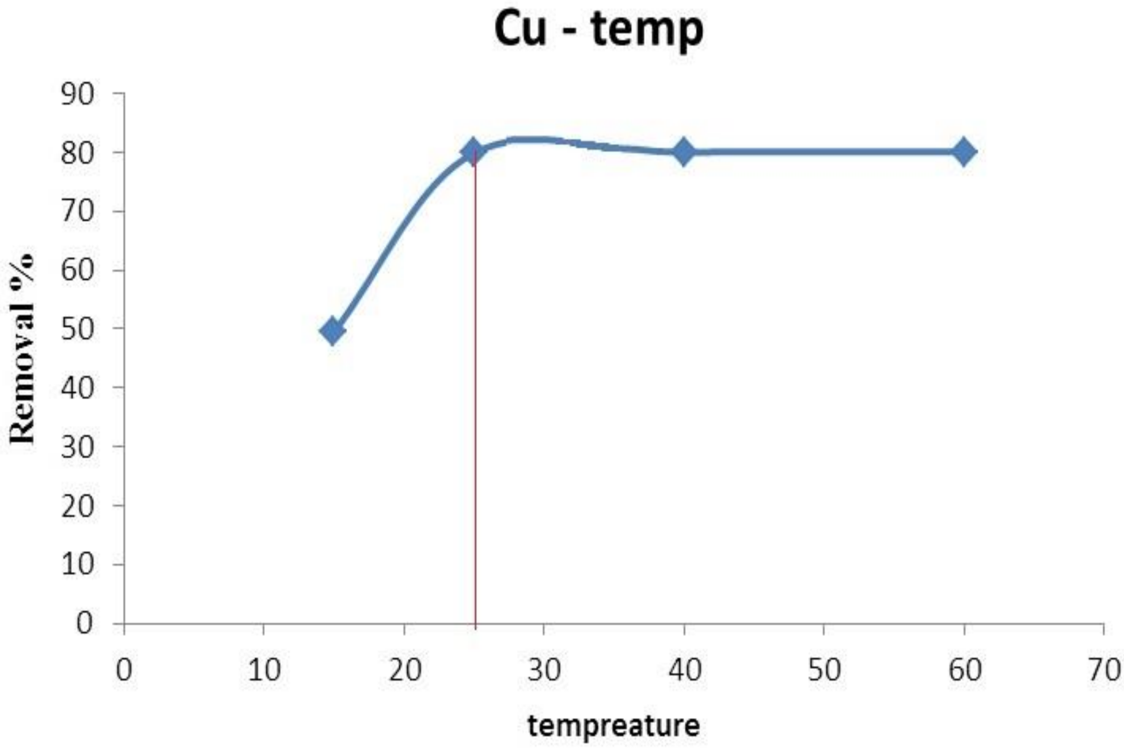


Figure (4. 19): Effect of temperature on the % removal of Cu+2 by shoot sample

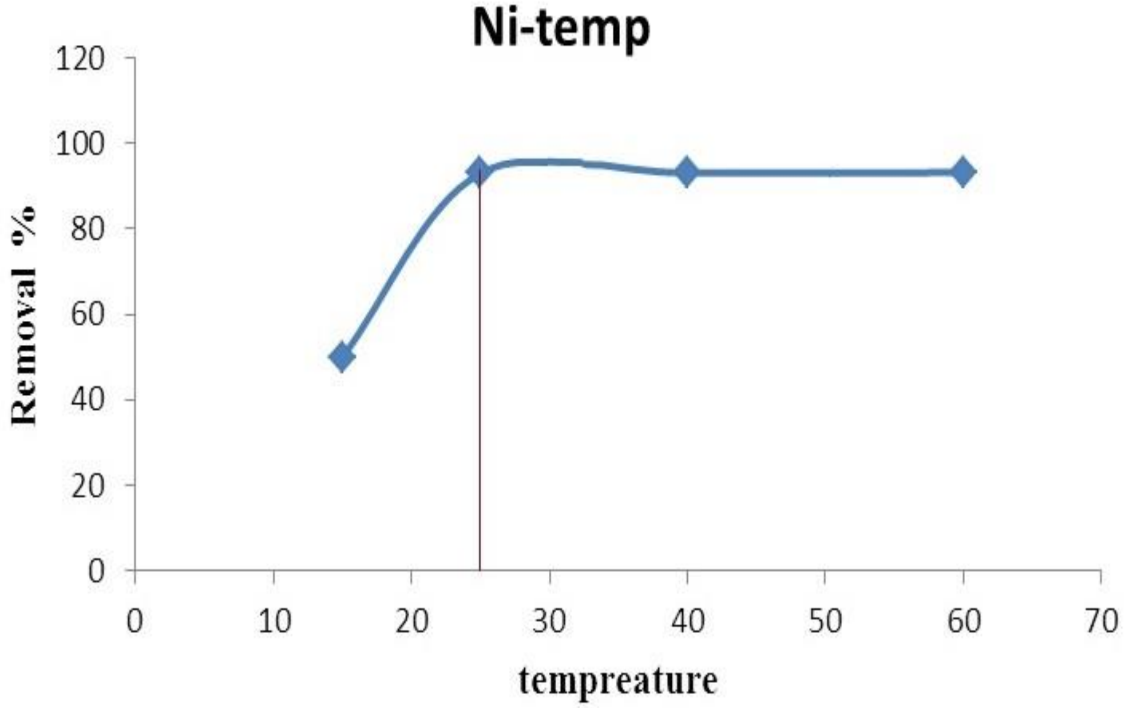


Figure (4. 20): Effect of temperature on the % removal of Ni+2 by shoot sample

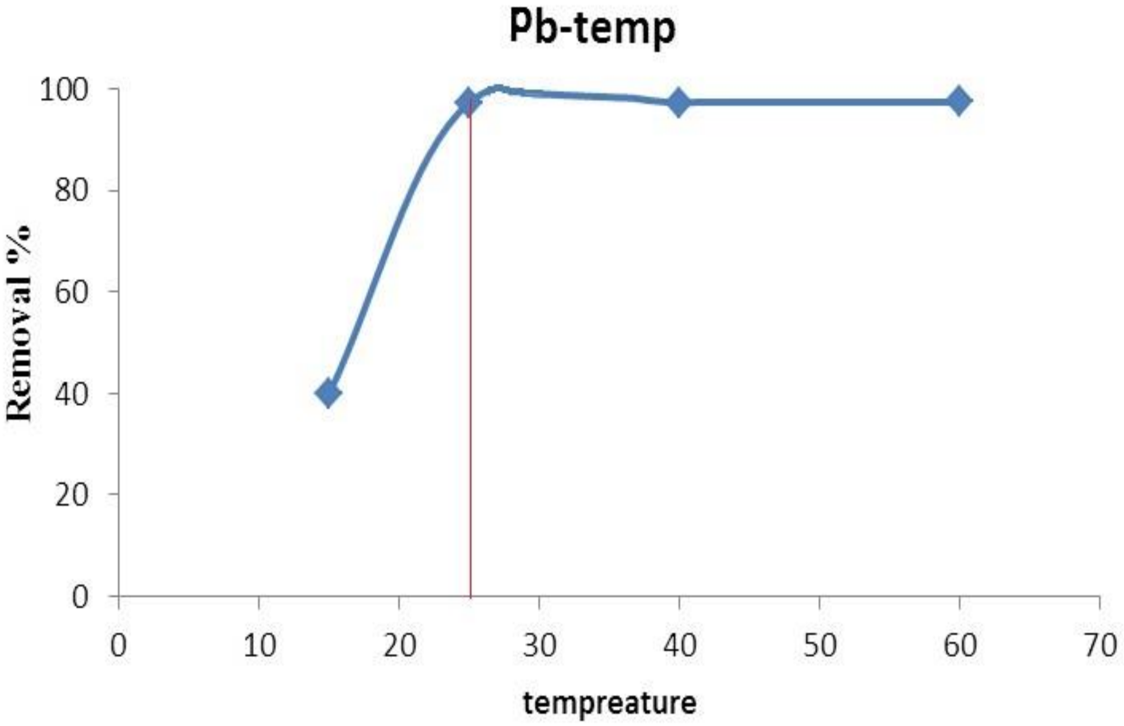


Figure (4. 21): Effect of temperature on the % removal of Pb+2 by shoot sample

Table (4. 8): Effect of temperature on the % removal of metals by shoot sample biomass, (20 ppm metal ion and pH =7)

Tempreture °C	%Removal of Fe	%Removal of Cd	%Removal of Cu	%Removal of Ni	**%Removal of Pb**
15	40.3	15.0	80.0	50.0	40.0
25	52.0	50.0	80.1	93.0	97.3
40	52.0	50.0	68.8	93.1	97.3
60	52.1	50.1	69.2	93.2	97.4

The effect of temperature on the uptake % of metal ions by biomass was studied at (15-60°C) as represented in Figures (4.17-4.21). Results revealed that in general the % removal of metal ions increases with increasing the temperature up to room temperature. Increasing the temperature above the room temperature has very insignificant effect on increasing the adsorption capability of the biomass surface. The maximum adsorption was achieved around 25°C. This indicates that the adsorption of metal ions by biomass follows exothermic process.

4.3. Adsorption isotherm of Pb (II)

Adsorption study at equilibrium gives ideas about the ability of the adsorbent. Equilibrium data can be tested using commonly known adsorption methods. Several mathematical models can be used to describe the experimental data of adsorption isotherms. Models Freundlich and Langmuir are used in the data analysis of the adsorption isotherm experiment [59].

4.3.1. 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 related 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 [60]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (4.1)$$

Where:

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

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

$n =$ The adsorption adversity indicative of the favorability the adsorption process

C_e = 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 $\frac{1}{n}$ and with intercept $\ln K_f$

If value of n is less than one it indicates a typical adsorption and if n lies between one and ten this shows an ideal sorption process (Mehdi and Mehdi, 2014) as in Figure (4.22).

Table (4. 9): Freundlich adsorption isotherm on the % removal of Pb+2 by reed shoot

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

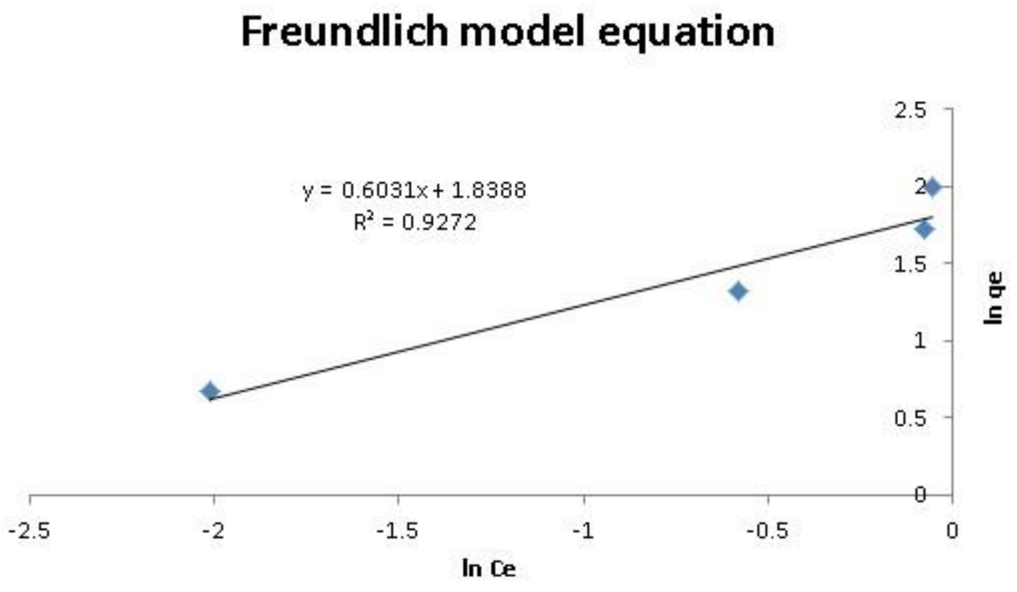


Figure (4. 22): A plot of lnCe vs lnqe for applying Freundlich adsorption isotherm on the adsorption of Pb (II) on reed shoot.

Table (4. 10): Parameters of Freundlich and correlation coefficient for adsorption of Pb (II) onto reed shoot.

The Parameters Freundlich isotherm model				
Adsorbate	Parameters			
	$\frac{1}{n}$	n	K_F (mg	R^2
Reed shoot	0.6031	1.6581	6.2889	0.9272

From these values of n=1.6581 $>$ 1 and $1/n$ = 0.6031, Freundlich isotherm model shows that the sorption of Pb (II) on reed shoot is ideal and the R^2 value is 0.9272.

4.3.2. Langmuir 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). Langmuir equation [61]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{Q_m K_L} \qquad (4.2)$$

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 constant (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 regression coefficient (R^2) were resolved and values are appeared in the next table.

Table (4. 11): Application of Langmuir adsorption isotherm on % removal of Pb+2 by reed shoot

C_e	C_e/q_e
0.133	0.07
0.560	0.125
0.920	0.15
0.950	0.16

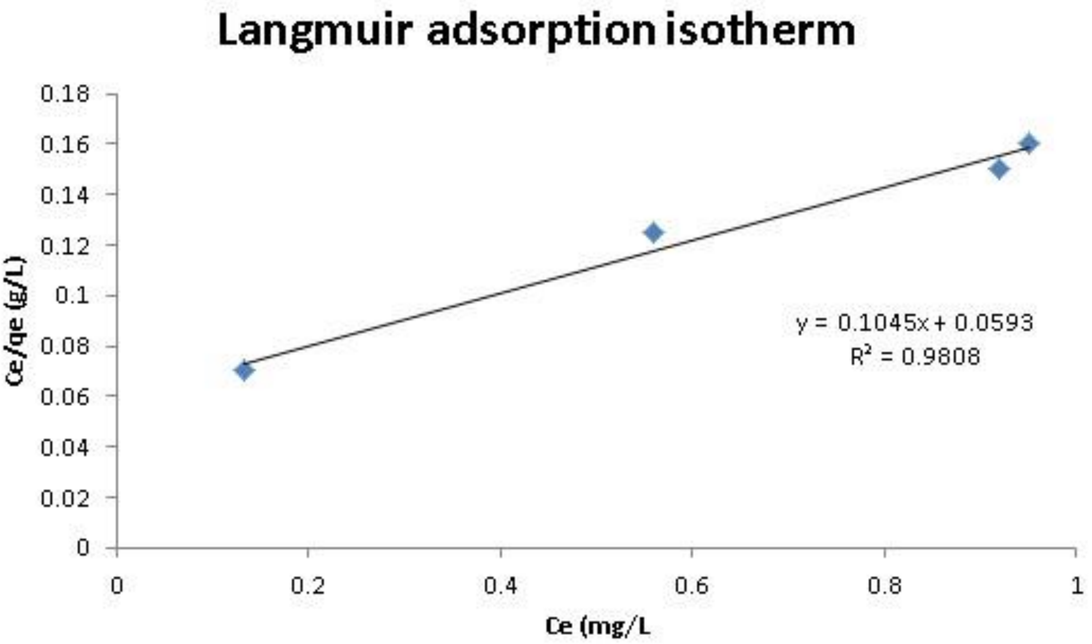


Figure (4. 23): A plot of Ce (mg/L) vs Ce/qe(g/L) applying Langmuir adsorption isotherm on the adsorption of Pb (II) on reed shoot

Table (4. 12): Parameters of Langmuir and correlation coefficient for adsorption of Pb(II) onto reed shoot

The parameters Langmuir isotherm model

Adsorbent	Parameters			
	Qm (mg/g)	KL (L/mg)	RL	R^2
Reed shoot	9.5694	1.7622	0.0276	0.98 08

From this data for adsorption of Pb (II) on reed shoot the exploratory outcomes were better fitted to the Langmuir condition (R^2= 0.9808) as seen in figures 23 and 24 than the Freundlich condition (R^2= 0.9272).

R_L value can be calculated by the equation [61]:

$$R_L = \frac{1}{(1+K_L C_o)} \qquad (4.3)$$

Where C_o 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 (0.0276).

4.4. 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 [62]:

$$lnK_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (4.4)$$

Where K_d is the thermodynamic balance constant (L 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 ΔH=-R*slope and ΔS=R*Intercept.

Table (4. 13): The values of the thermodynamic of Pb(II) adsorption at various temperature

1/T	**Ln kd**
0.0034	2.67
0.0035	1.90
0.0032	1.80
0.0030	2.00

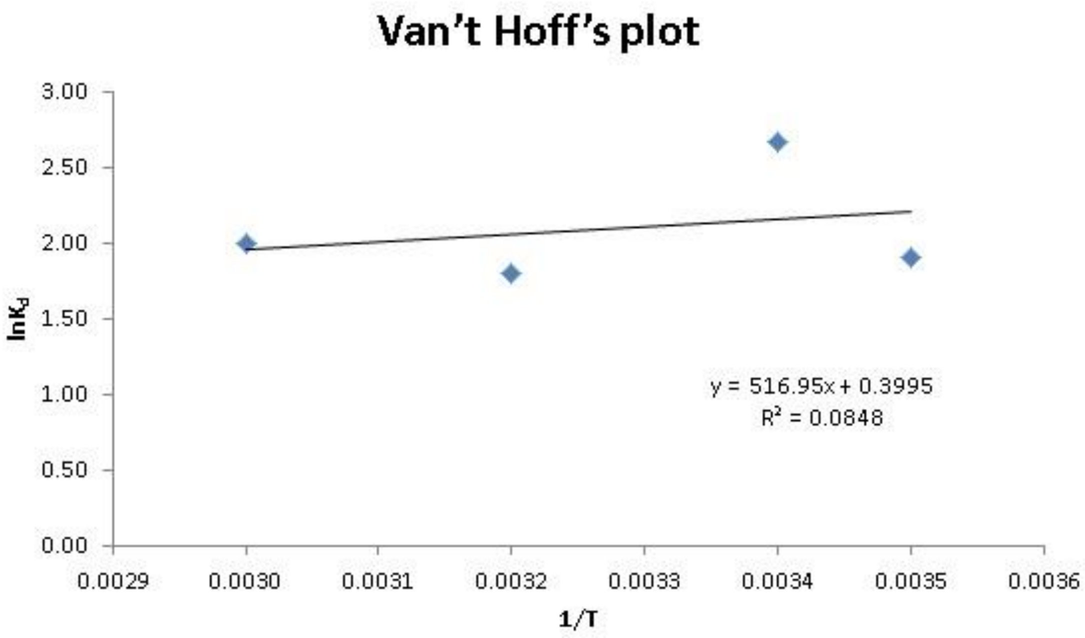


Figure (4. 24): Van't Hoff's plot of lnKd vs 1/T for Pb (II) adsorption on (reed shoot)

The outcome demonstrates that the enthalpy of adsorption $\triangle H^\circ$ was −4.30 kJ mol^{-1} and the entropy $\triangle S^\circ$ was +3.32 J mol^{-1} K^{-1}. $\triangle G^\circ$ was computed at different temperatures from the following equation [63]:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (4.5)$$

Table (4. 14): The parameters of the thermodynamic of Pb(II) adsorption at various temperatures

Adsorbent	**$\triangle H^o$**	**$\triangle S^o$**	**$\triangle G^o$**

	(KJ/mol)	(J/mol.K)	(KJ/mol)			
			289 K	308 K	318 K	328 K
Reed Shoot	-4.30	+3.32	-5.25	-5.32	-5.35	-5.39

4.5. Rate order of the adsorption process

The negative ΔG^o values exhibit that the adsorption is spontaneous, at these temperatures. The negative value of ΔH demonstrates an exothermic adsorption and the adsorption is ideal at room temperature. 0n 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. . In general enthalpy change value ΔH for physical adsorption is lower than that of the chemical adsorption. Generally, ΔH for physical adsorption reaches up to 40 KJ/mol which is much less than that of chemical adsorption which varies from 40 to 800 KJ / mol. This suggests that the nature of adsorption is a physical process.

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 [61]:

$$\log(Q_e - Q_t) = \log Q_e - \left(\frac{K_1}{2.303}\right)t \qquad (4.6)$$

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.

Table (4. 15): Applying first- order equation on the % removal of Pb(II) by reed shoot

Time (min)	Log (q_e_q_t)
15	0.26
30	0.40
60	0.25
90	0.19
120	0.17

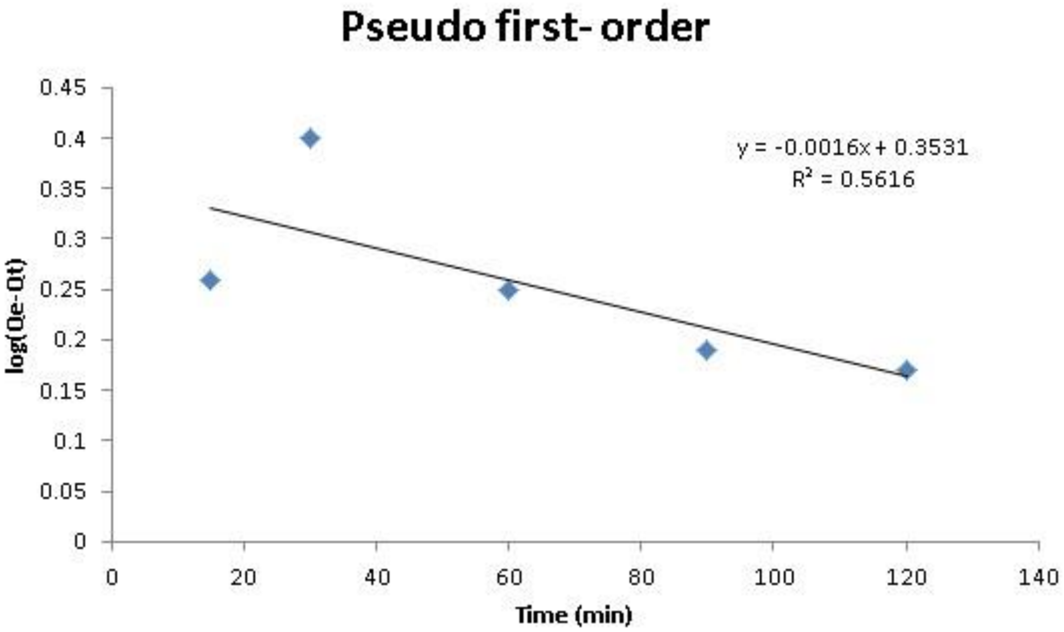


Figure (4. 25): The plot of Pseudo first- order adsorption kinetics of Pb(II) onto reed shoot

From Figure (4.25), 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 this adsorption

Table (4. 16): Pseudo first-order parameters for Pb(II) adsorption onto reed shoot at 25°C

Adsorbent	$Q_{e(exp.)}$ (mg/g)	Pseudo first-order		
		K_1 min^{-1}	$Q_{e\ (cal.)}$ (mg/g)	R^2
Reed Shoot	1.213	3.68×10^{-3}	0.235	0.5616

The pseudo second order equation [61]:

$$\frac{t}{Q_t} = \frac{1}{Q_e}t + \frac{1}{K_2 Q_e^2} \qquad (4.7)$$

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

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 (4.26).

Table (4. 17): Applying second-order equation on the % removal of Pb(II) by reed shoot

Time (min)	**t/q_t**
15	5.35
30	22.4
60	40.0
90	56.6
120	74.0

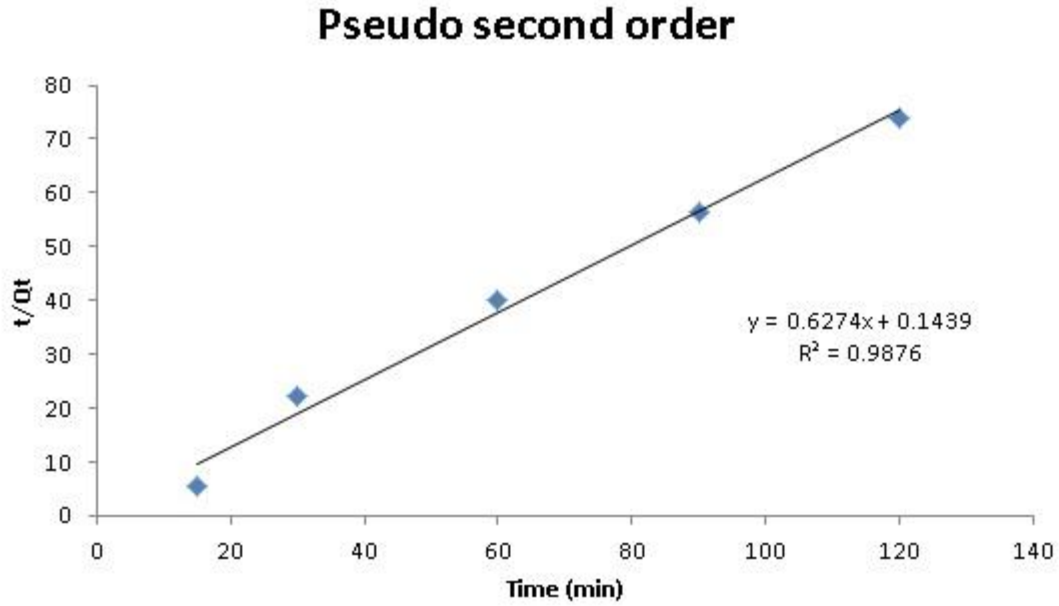


Figure (4. 26): A plot of Pseudo second- order adsorption kinetics of Pb(II) onto reed shoot

Table (4. 18): Pseudo first-order parameters for Pb(II) adsorption onto reed shoot at 25°C

Adsorbent	$Q_{e(exp.)}$ (mg/g)	Pseudo second-order		
		K_2 (g/mg min)	$Q_{e\ (cal.)}$ (mg/g)	R^2
Reed Shoot	1.213	2.735	1.594	0.9876

As can be seen there is a harmonization between experimental and calculated values for pseudo second order model. This means that Pseudo second – order kinetic model accord is appropriate for this adsorption. The results confirm that the pseudo second order kinetic model perfect fit the experimental data with linear regression coefficient which equals 0.9876 (Figure 4.26).

Q_e experimental and Q_e calculated values for the pseudo second order model are illustrated in Table (4.18). It can be observed the agreement between Q_e experimental and Q_e calculated values for the pseudo second order model. Also K_2 is much greater than $K_{1.}$ Hence, the pseudo second order model well represented the adsorption kinetics.

Conclusion

These results show an efficient capability of *Phragmites Australis* and the other type phragmites which from Sarra in removing all metals were studied in this work. The removal of metals by both plants increases by increasing the amount of biomass.

The biomass was able to remove metal ions rapidly within 15-30 min. with high removal efficiency at pH around 7, 25°C temperature and initial concentration of 20 mg/L of metal ions. Around 97.3% removal efficiency of Pb^{+2} was achieved within the first 30 min. at the optimum condition. As can be seen from results the *Phragmites australis* (common reed) is more efficient, as it almost completely removed lead from the shoot sample.

Investigation the sorption behaviour under competitive conditions when several metallic species are present in the presence of all metal ions the percent removal of the metal ions was in the order of $Pb^{+2}>Cu^{+2}>Fe^{+3}>Ni^{+2}>Cd^{+2}$.

Negative values of ΔG at different temperatures point that adsorption is spontaneous at these temperatures. The negative ΔH° denotes that this adsorption is an exothermic process. ΔH° value is lower than 40 KJ/mol which suggests that the nature of adsorption is a physical process.

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

The results of all samples of antibacterial activity test reveal that is negative. This indicates that the plant extracts have no antibacterial effect on the Gram-negative and Gram-positive bacteria

Recommendations

Findings in this thesis show that *Phragmites australis* plants from Wadi Al- Bathan can absorb metals more than other phragmites which imports from other country; hence it is recommended to utilize them for pollution removal from water. It is recommended to carry out research in detail to test if this plant can be useful to extract metal other than those have been studied in this research.

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جامعة النجاح الوطنية

كلية الدراسات العليا

دراسة تأثير نبات البوص على أمتصاص المعادن السامه ونشاط البكنيريا الموجوده في المياه الملوثة

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

2017

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الملخص

مشكلة البحث الرئيسية هي دراسة نبات *Phragmites australis* والبوص المستخدم في محطه التنقية في قرية صره (أوراق وسيقان وجذور) وقدرتهما على امتصاص مجموعة محددة من أيونات المعادن السامه (Fe^{3+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}) التي يمكن تواجدها في المياه العادمة وتأثير هذا النبات على وقف النشاط البكتيري فيها.

أجريت تجارب عديدة تحت ظروف ومتغيرات مختلفة مثل: درجة الحرارة, درجة الحموضة, تركيز أيونات المعادن، كمية الكتلة الحيوية للنبات ووقت الاتصال لتحديد الظروف المثلى لأفضل نسبة امتزاز لأيونات المعادن المحددة في البحث، كما تمت دراسة قدره امتصاص هذا النبات لأيونات المعادن المحددة من المياه العادمة في حالة وجود اكثر من معدن واحد في آن واحد في هذه المياه، وقد لوحظ من خلال هذه التجارب أن نسبة ازالة هذه الأيونات من المحاليل المائية كانت عند تركيز 20mg/L ودرجه حراره 25^oC ودرجه حموضه حول pH=7 وخلال فترة زمنية 15–30 دقيقة.

وكانت أعلى نسب امتصاص تحت الظروف المثلى لأيونات المعادن باستخدام الكتلة الحيوية لكلا النباتين كما يلي: الحديد 77% امتصته جذور البوص, الكادميوم 71% امتصته أوراق *Phragmites australis* ، النحاس88% امتصته أوراق وسيقان *Phragmites australis* ، النيكل 93% امتصته *Phragmites australis* والرصاص تم امتصاصه بأعلى نسبه وهي 97 % من قبل سيقان *Phragmites australis* ، لذلك تمت دراسة امتصاص عنصر الرصاص تحت تأثير ظروف مختلفة من درجة الحرارة ودرجة الحموضة وزمن الاتصال.

تجارب فحص سلوك الامتصاص في ظل ظروف تنافسية في وجود أيونات المعادن معا في المياه أظهرت أن ترتيب النسب المئوية لإزالة أيونات المعادن على النحو الآتي:

$Pb^{+2}>Cu^{+2}>Fe^{+3}>Ni^{+2}>Cd^{+2}$.

كما أظهرت النتائج وتحليلاتها أن عملية الامتزاز يمكن وصفها وفقا لنموذج Langmuir مما يشير إلى أن عملية الامتزاز من نوع أحادي. قيم $\Delta G°$ السالبة تشير إلى أن عملية الامتزاز مناسبة وتلقائية على درجات الحرارة المحددة، كما ان القيمة السالبة لِ $\Delta H°$ تشير إلى أن عملية الامتزاز طاردة للحرارة ومحبذة على درجات حرارة منخفضة لا تتجاوز كثيرا حرارة الغرفة، وكذلك قيمة $\Delta H°$ أقل بكثير من تلك المصاحبة للامتزاز الكيميائي مما يؤكد الطبيعة الفيزيائية لعملية الامتزاز. القيمة الصغيرة الموجبة لِ $\Delta S°$ تشير إلى حصول تغيرات هيكلية على سطح الكتلة الحيوية، وأن الفوضى قد ازدادت بالقرب من سطح الامتزاز أثناء عملية الامتزاز.

تؤكد النتائج أن الكتلة الحيوية لنبات البوص مادة فعّالة ومناسبة وآمنة في إزالة أيونات المعادن الثقيلة من مياه الصرف الصحي. كما دلت النتائج أن نبات البوص الذي أحضر من قرية صرة (الأوراق، والسيقان والجذور) ليس له فاعلية ضد البكتيريا.