

Adsorption of Heavy Metals by Reed (*Phragmites australis*) as a Potential Clean Water Technology

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Abstract

In this study the adsorption behavior of reed tissues has been investigated in a batch system in order to determine its applicability in treating wastewater. The optimum conditions for the treatment process were investigated by observing the influence of organ of plant (leaf, stem, root), pH levels, the presence of competing ions, initial concentration and of the reed tissues.

The results indicated that the adsorption capacity was strongly affected by the initial concentration, pH levels and organ of plant. Optimum adsorption of Pb (II) was observed at pH 7.0, initial Pb(II) concentration 20 mg/L, temperature 25-45 °C and contact time 30 minute. It has a good fit for the Freundlich compared with Langmuir isotherm models. As well as, Pseudo second – order kinetic model was fit better than pseudo first order model. *Phragmites Australia* shows that it is feasible for this plant material as a novel adsorbent for Pb(II) removal in the future.

Key words: Reed tissues, Pb(II), Adsorption, Freundlich, Langmuir; Stem.

1. Introduction

Groundwater is considered a vital source of drinking water. Even worse, this source is now decreasing due to the continuous pollution resulting from industrial technologies, urban, agricultural, and human activities, chiefly in the third world countries (Robert (2008); Fu & Wang (2011)). Moreover, these actions have led to the continuous disposal of huge quantities of wastewater to the environment. This wastewater contains a notable concentration of heavy metal ions which has constituted a significant potential threat to human health (Garcia-Reyes & Rangel-Mendez (2010); Demirbas (2008)). Their potential for health effects in at least two major ways: first, by environmental transport, that is, by human or anthropogenic contributions to air, water, soil, and food, and second by altering the speciation or biochemical form of the element (Beijer. & Jernelov 1986).

The concept of heavy metal ions refers to the elements having atomic weights between 63.5 and 200.6, and specific gravity more than 5.0 such as transition elements (Srivastava & Majumde 2008). Toxic heavy metals of particular concern in treatment of wastewaters include copper, iron, nickel, cadmium and lead.

Copper is essential for animal metabolism. But the extreme ingestion of copper brings about serious toxicological concerns, such as vomiting, cramps, convulsions, or even death (Paulino *et al.* 2006). Nickel exceeding its critical level might bring about serious lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis and it is known that nickel is human carcinogen (Borba *et al.* 2006). Cadmium has been classified by U.S. Environmental Protection Agency as a probable human carcinogen. Cadmium exposes human health to severe risks. Chronic exposure of cadmium results in kidney dysfunction and high levels of exposure will result in death. Lead can cause central nervous system damage. Lead can also damage the kidney, liver and reproductive system, basic cellular processes and brain functions. The toxic symptoms are anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damages (Naseem & Tahir 2001). 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).

In this context, it should be pointed out that most of heavy metal ions salts are very soluble in aqueous solutions. Hence, it is not easy to separate these ions from aqueous solutions or wastewater using simple separation processes (Hussein *et al.* 2004). Moreover, for the reason that these ions are persistent in the environment and are not being degradable to form harmless products, it is of primary safety concerns to treat and remove these toxic ions from all wastewater effluents before their disposal to the environment (Egila *et al.* 2011). Recently to

meet the increased more and more stringent environmental regulations, appropriate technologies have initiated to assess the presence and mobility of metals in soil, water and wastewater.

Presently, phytoremediation technologies have reached such a state that they are not only comparable with other technologies in terms of cost, but they are also more efficient and more effective. Ultimately, it is great attention to use these methods in treatment of water/wastewater owing its attractive advantages such as environmental compatibility, versatility, safety, cost effectiveness as well as take the advantage of the unique and selective uptake capabilities of plant root systems, together with the translocation, bioaccumulation, and contaminant degradation abilities of the entire plant body (Cho-Ruk *et al.* 2006). Phytoremediation is the use of plants to clean up a contamination from soils, sediments, and water. Many species of plants have been successful in absorbing contaminants such as lead, cadmium, chromium, arsenic, and various radionuclides from soils. Recently, 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 (Laidani *et al.* 2010).

Here, *Phragmites australis* are known for their accumulator power, can response to the pollution in a sensitive and effective manner, hence the importance of their use in phytoremediation. It has a high tolerance to heavy metals.

Based on literature reviews, so far no other studies have taken into account the ability of *phragmites Australia* to adsorb toxic metals (Pb, Cu, Ni, Cd, Fe) by their roots, stems and leaves from wastewater.

This paper was carried out to determine the optimum operating conditions of heavy metals removal by phytoremediation technique. In addition, it was investigated the influence of the variables such as temperature, pH solution, contact time, concentration of metal ions and the effect of competing ions on treatment efficiency. And also, the kinetics of the biosorption process and the adsorption isotherms explored in this study, in addition to the testing of anti-bacterial activity for the *Phragmites Australia*.

2. Materials and methods

2.1 Methodology

The raw biomass of *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 others samples of *Phragmites* were obtained from the sewage wastewater treatment plant from Sarra. Washed, and the roots, stems, and leaves, were separated. All samples were oven dried at 370C for one week. Then the leaves, root and stem of both plant samples were crushed separately.

This was followed by two parts of experiments: the potential of *Phragmites australis* plant which collected from Wadi Al- Bathan to remove (Fe^{2+} , 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 antimicrobial activity for the *Phragmites australis* was examined in the biological part.

2.2 Biological experiments

In this study, we prepared Mueller-Hinton Agar in order to examine the antibacterial activity. In this context, the dried plant materials were conducted to a fine powder in a blender. 7 gm of dried powder from *phragmites australia* and 6gm from the other *phragmites* were soaked in 100cc of methanol either distilled water in a round bottom flask and put in a shaker at room temperature for 48 h. Then methanol samples were concentrated to dryness in autoclave at (121⁰C) 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. Here, 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 experiments

HCl and NaOH (analytical grade from Merck) were used to adjust the solution pH. The Pb, Cu, Cd, Ni, and Fe stock solutions were prepared respectively by dissolving their corresponding nitrate salts ($Pb(NO_3)_2$.anhydrous ,

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2$.anhydrous, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, analytical grade from Merck) in distilled water, and standardized by atomic absorption spectrophotometry. The ion concentrations in stock solutions were about 5 g/l. Thus, batch adsorption experiments were carried out at an ambient temperature of about 20 °C. However, Absorption measurements were carried out by (ICE 3000 SERIES, Thermo Scientific) Flame atomic absorption spectrometer with acetylene-air flame. The solution pH values were measured by JENWAY (3510) pH Meter.

3. Results and discussion

3.1 Effect of initial concentration

Heavy metal removal efficiency by the organs of *Phragmites australis* is shown in Figs.2-6. It can be noticed that the removal efficiencies of these heavy metals (Fe, Cd, Cu, Ni and Pb) increased with an increasing initial concentrations of all metals in all organs (stem, leaf, root) of plant in two sites. This may be related to not occupancy of most metals ions at low concentration, so increasing of these metal ions concentration lead to fill all sites and saturation.

Regarding Pb the removal efficiency increased according to the order of stem > root > leaf for both sites. This may be due to the fact that the exhaust fumes of the vehicular traffic are primary sources of Pb pollution and, as a result, aboveground organs are directly affected. Indeed, the purification wastewater plant under study presences in a town and the other site located in a city. In particular, the aboveground organs are the main sink for many pollutants. In the second case of study area (sewage purification plant), it showed that the stem can remove about 97% of Pb ions. In this context, it can be pointed out that the second site in the study area compared with first site (Wadi Al-Bathan) has approved a good efficient for removing of most metal ions by the shoot of *P. Australia*.

3.2 Effect of solution pH

For obtaining an optimum pH for heavy metals adsorption by our modified shoots plant adsorbents, a series of experiments were investigated at different pH. Fig. 7 illustrates a relationship between heavy metals removal and pH by different adsorbents. It is observed that increasing pH values from 3 to 7 leads to higher heavy metals removal. As pH increases there are fewer hydrogen protons in solution, this means that there is less competition for binding sites and more binding sites are released, which results in the increase of adsorption amount of heavy metals. While at pH 10 it is concluded that removal of ions was low. 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 *et al.* 2014). It can pointed out that at pH more than 7 leads to lower heavy metal ions due to solvation and hydrolysis of metal particle.

3.3 Effect of competing ions on the adsorption process

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 Fig. 8 in the presence of all metals (Fe, Ni, Cd, Cu, Pb) the percent removal of Pb is the best $\text{Pb} > \text{Cu} > \text{Fe} > \text{Ni} > \text{Cd}$. 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 *et al.* 1996).

3.4 Effect of Temperature on the adsorption process

Temperature may play an important role in the process of heavy metals removal. So batch experiments are performed under different temperatures from 15 °C to 60 °C to examine the effect of temperature on heavy metals adsorption by the modified shoot adsorbents. The results are presented in Fig. 9, 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 an 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 ions that results in overhauls the removal of metals from the adsorbent surface.

3.5 Effect of contact time on the adsorption process

Fig.3 shows contact time profiles of the modified shoots adsorbents on heavy metal ions adsorption. It can be seen from the fig. 10, 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.

3.6 Adsorption Isotherms of Pb(II)

The constants of Langmuir and Freundlich isotherms models for the Pb(II) adsorption by P. Asturilia are presented in Table 1. Based on the correlation coefficient R^2 , the Freundlich isotherm model was the best model to describe the experimental data.

3.6.1 Adsorption thermodynamics of Pb (II)

Adsorption thermodynamics were studied at various temperatures and concentration to check conceivable adsorption systems as in table 2, by utilizing Van't Hoff plot according to equation

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (1)$$

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 $\Delta H = -R \cdot \text{slope}$ and $\Delta S = R \cdot \text{Intercept}$.

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

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

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 suggest that the nature adsorption is a physical process.

3.6.2 Rate order of Pb (II)

The negative ΔG_o 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:

$$\log(Q_e - Q_t) = \log Q_e - \left(\frac{K_1}{2.303}\right) t \quad (3)$$

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 seen from figure 11 and table 3 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.

The pseudo second order equation
$$\frac{t}{Q_t} = \frac{1}{Q_e} t + \frac{1}{K_2 Q_e^2} \quad (4)$$

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 12

As can be seen from table 4 there is a harmonization between experimental and calculated values for pseudo second order model. The results of uptake of Pb (II) by reed shoot fit well the Langmuir adsorption isotherm more than Freundlich adsorption isotherm, and Pseudo second - order kinetic model fit better than pseudo first order model.

4. Conclusion

The adsorption of the heavy metal ions from solution onto *Phragmites Australia* was determined. The adsorption was increased for increasing the concentration of biomass. Efficiency of metal removal from solution by *Phragmites Australia* is directly proportional to the initial solution concentration. The rate of adsorption was fit at natural pH value of the solution. Adsorption decreased in more acidic solutions, due to hydrogen ion competition. In this work, Pb (II) was efficiently removed at optimum condition for binding of biomass. Pb (II) removal efficiency was achieved as 97.3% by shoot samples, and it has a good fit for the Freundlich compared with Langmuir isotherm models. As well as, Pseudo second – order kinetic model was fit better than pseudo first order model.

Ultimately, *Phragmites Australia* shows that plants were collected from Wadi Al- Bathan can absorb metals more other phragmites which imports from other country. Hence, *Phragmites Australia* shows that it is feasible for this plant material as a novel adsorbent for Pb(II) removal in the future. And it can be used as a substitute for the more expensive adsorbents like activated carbon or other treatment methods like electro-dialysis, due to its availability and low cost.

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Fig.1. *Phragmites Australia* (common reed) from sewage purification plant

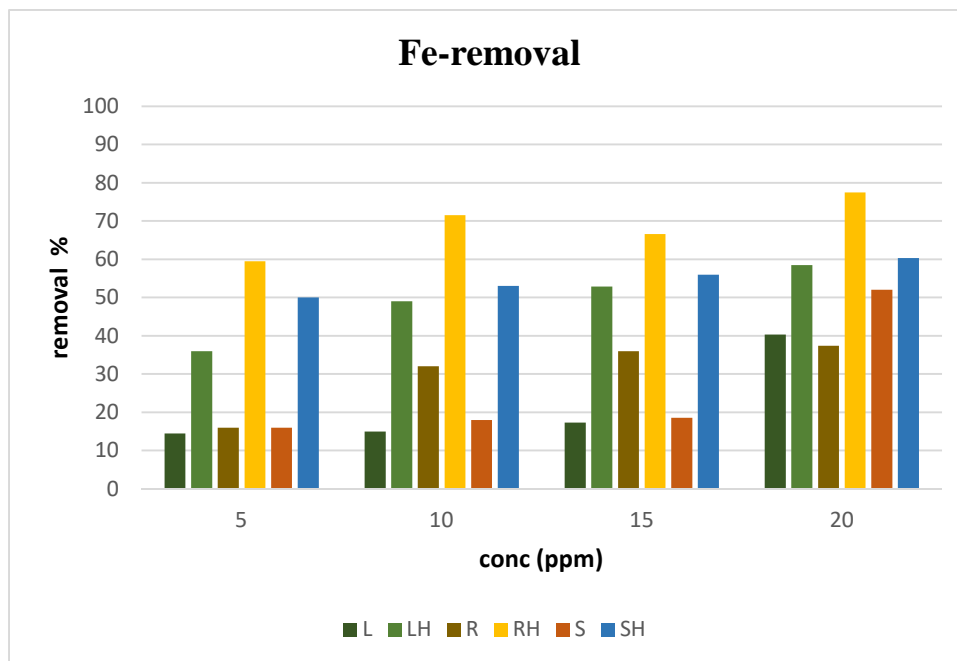


Fig. 2. Effect of initial iron metal ions concentration on the removal efficiency by root, stem and leaf of both *P. australis*; (pH 7, time, 30 minutes, temperature 25 °C), * L: leaf; R: root; S: stem; H: purification wastewater part

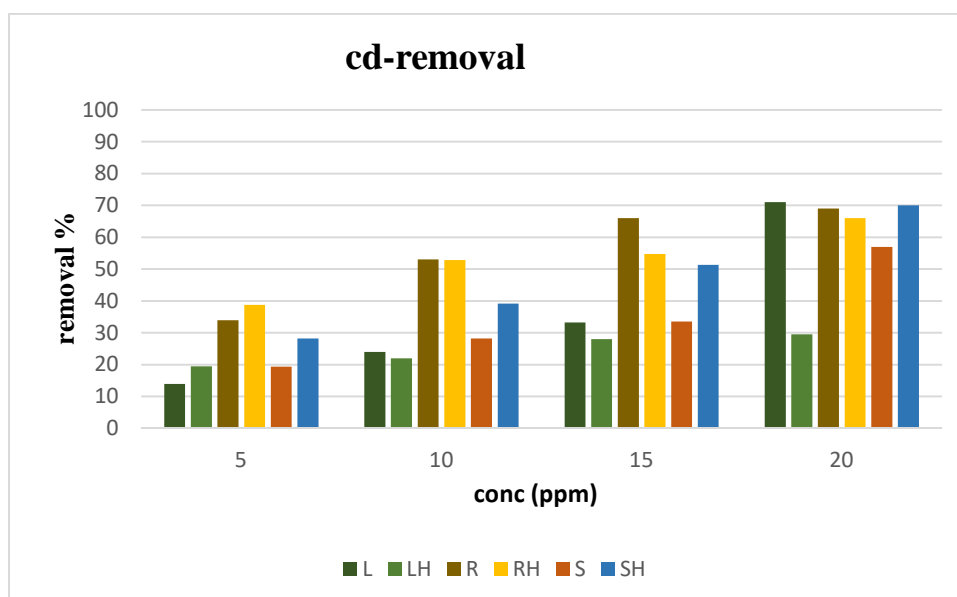


Fig. 3. Effect of initial cadmium metal ions concentration on the removal efficiency by root, stem and leaf of both *P. australis*; (pH 7, time, 30 minutes, temperature 25 °C)

* L: leaf; R: root; S: stem; H: purification wastewater part

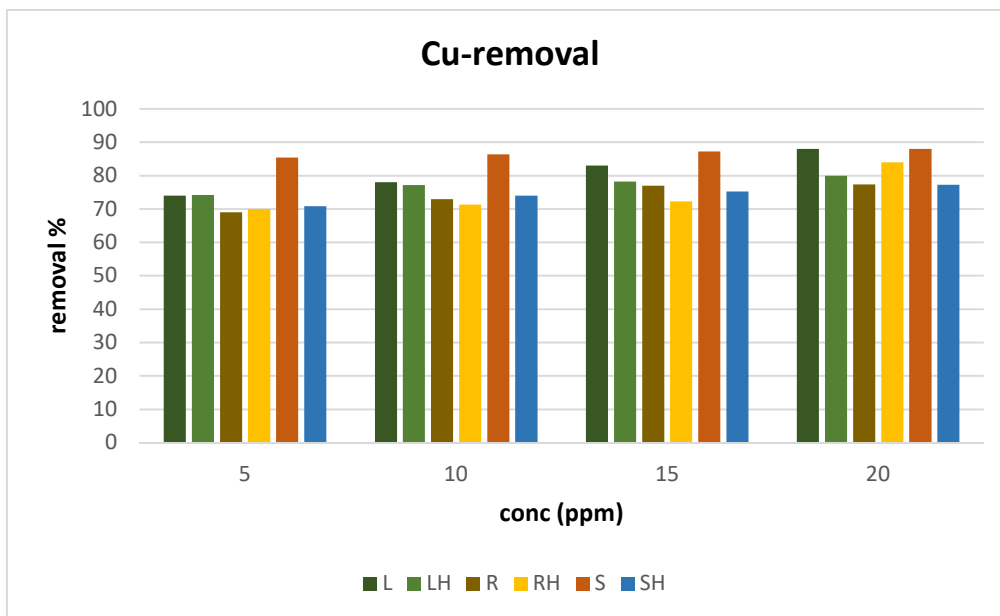


Fig. 4. Effect of initial copper metal ions concentration on the removal efficiency by root, stem and leaf of both *P. australis*; (pH 7, time, 30 minutes, temperature 25 °C)

* L: leaf; * R: root; * S: stem; * H: purification wastewater part

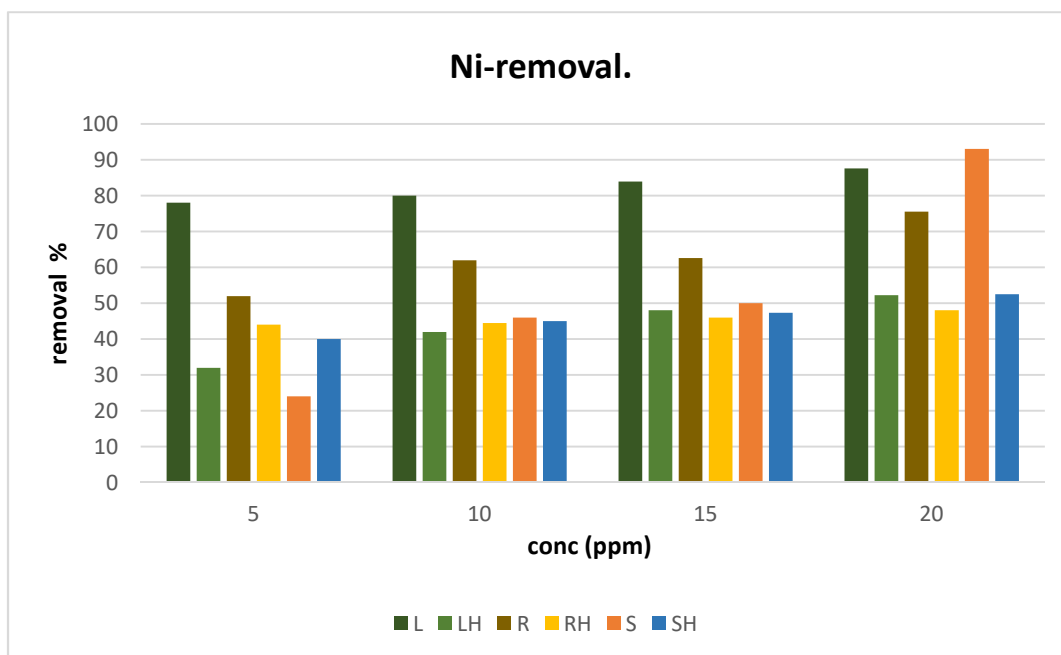


Fig. 5. Effect of initial nickel metal ions concentration on the removal efficiency by root, stem and leaf of both *P. australis*; (pH 7, time, 30 minutes, temperature 25 °C)

*L: leaf; R: root; S: stem; H: purification wastewater part)

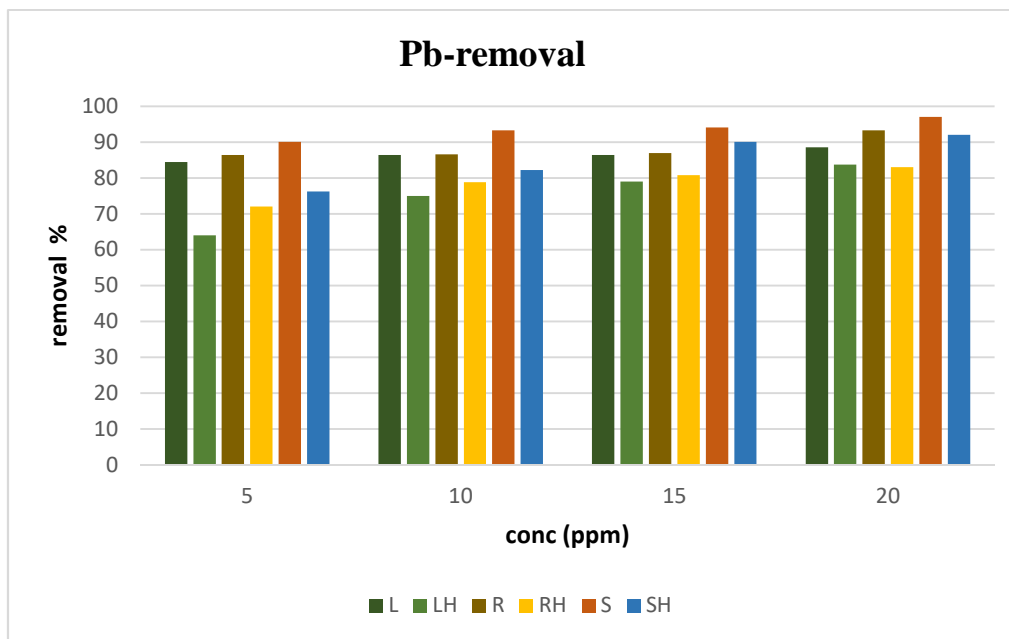


Fig. 6. Effect of initial iron metal ions concentration on the removal efficiency by root, stem and leaf of both *P. australis*; (pH 7, time, 30 minutes, temperature 25 °C)

* L: leaf; R: root ; S: stem; H: purification wastewater part

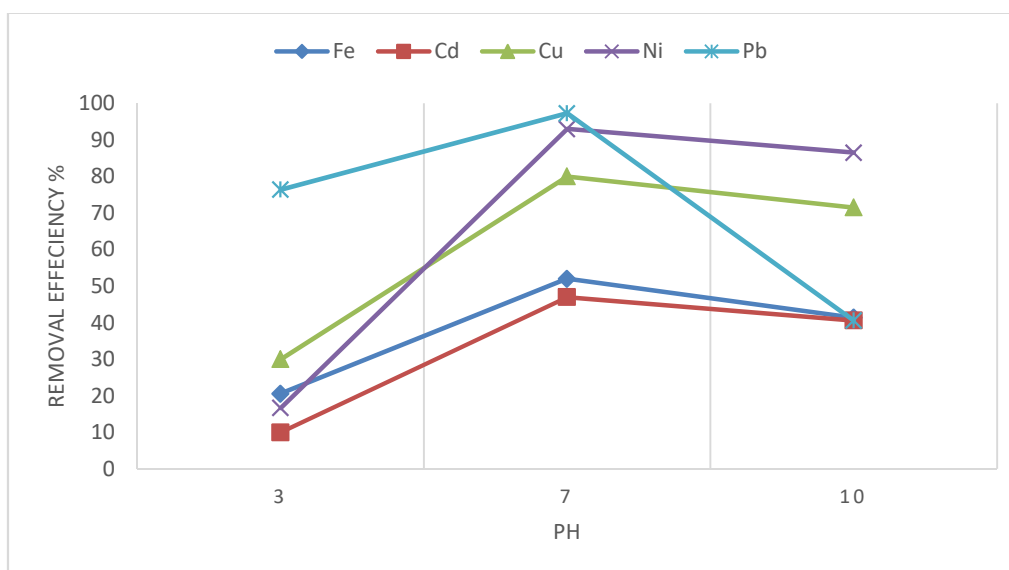


Fig. 7. Effect of solution pH on adsorption of heavy metal ions by reed shoot sample (20 ppm metal ion, 25°C)

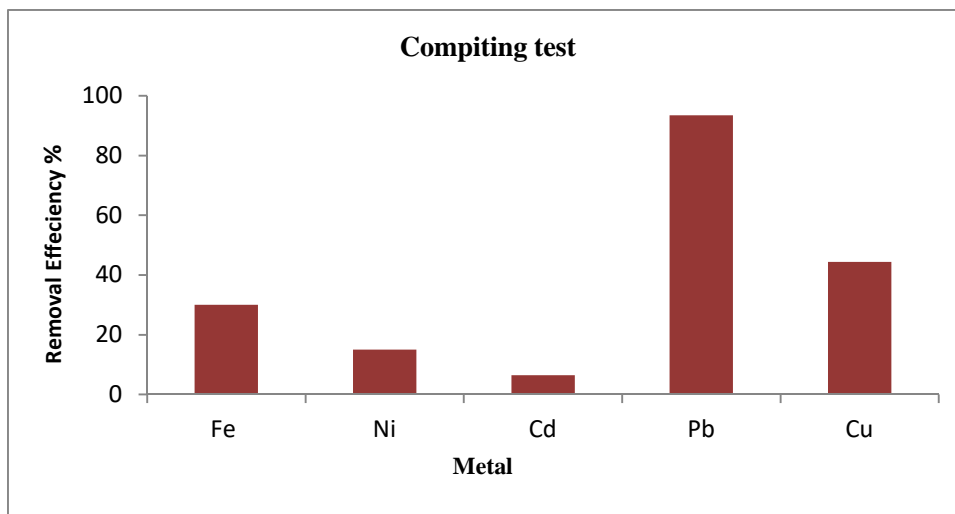


Fig.8. Effect of metal ions on the percent removal of each other by reed shoot samples (20 ppm metal ion, 25⁰C)

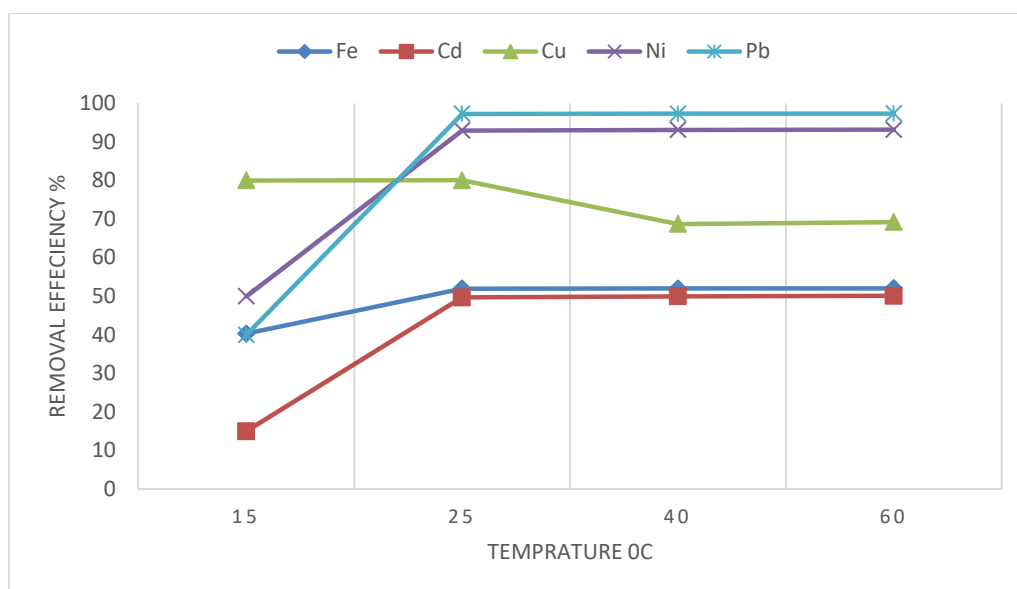


Fig. 9. Effect of temperature on the percent removal of heavy metal ion by reed shoot sample (20 ppm metal ion, 25⁰C)

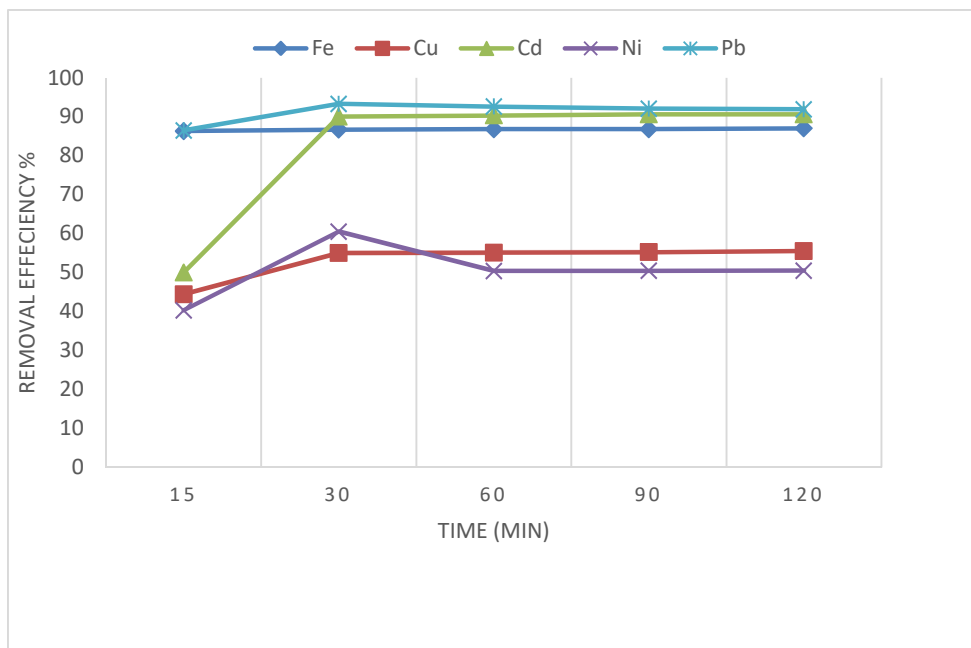


Fig.10. Effect of contact time on the percent removal of metals by shoot samples biomass, 20 ppm metal ion, PH 7, 25 °C).

Table 1. Langmuir, and Freundlich isotherms for Pb(II) adsorption equilibrium.

Models	Fitting equations	Corresponding parameters
Langmuir	$y = 0.0834x + 0.0735$	$R^2 = 0.5995$
Freundlich	$y = 0.6075x + 1.8382$	$R^2 = 0.9264$

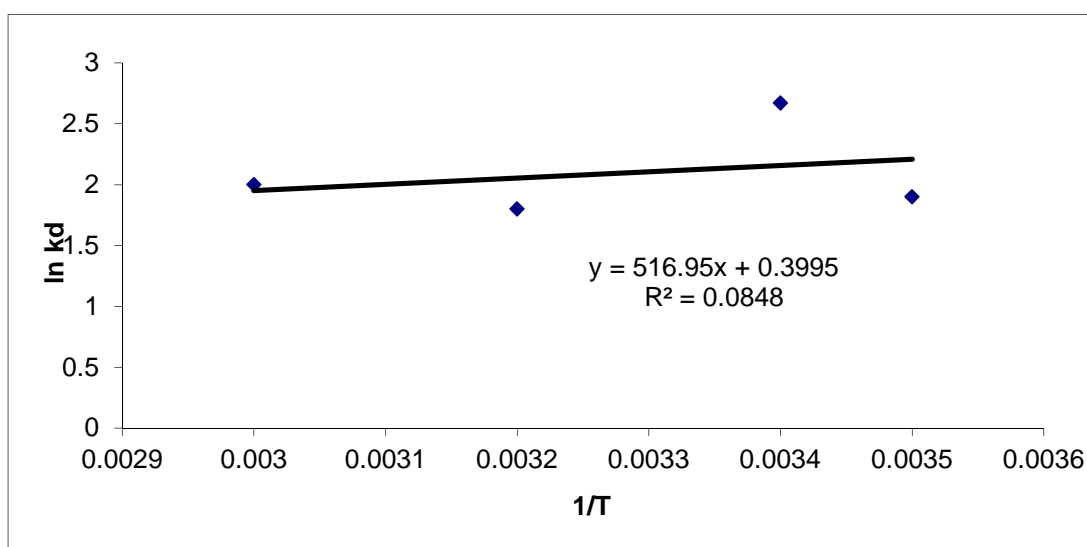


Fig. 11. The graph of $\ln K_d$ versus $1/T$ for Pb (II) adsorption on (reed shoot)

Table 2
 The parameters of the thermodynamic of pb(II) adsorption at various temperatures.

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

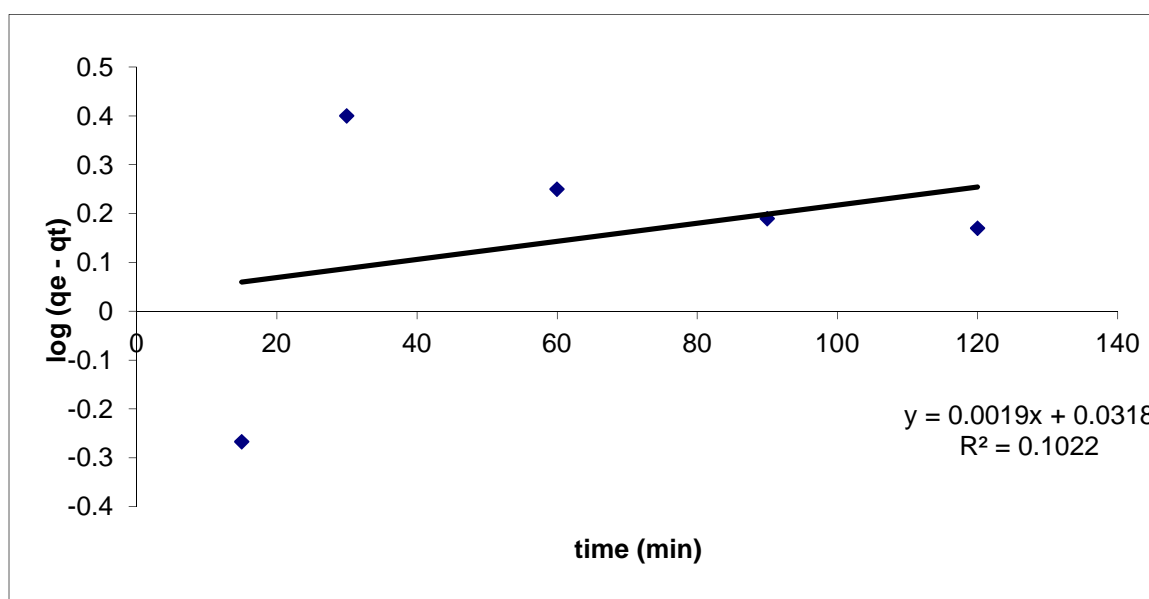


Fig.12. The plot of Pseudo first- order adsorption kinetics of pb(II) onto reed shoot

Table 3
 Pseudo first- order parameters for pb(II) adsorption onto reed shoot at 25°C

Adsorbent	Qe(exp) (mg/g)	pseudo first- order		
		K1 min ⁻¹	qe (calculated) (mg/g)	R ²
Reed Shoot	0.95	2.441×10^{-3}	0.235	0.1022

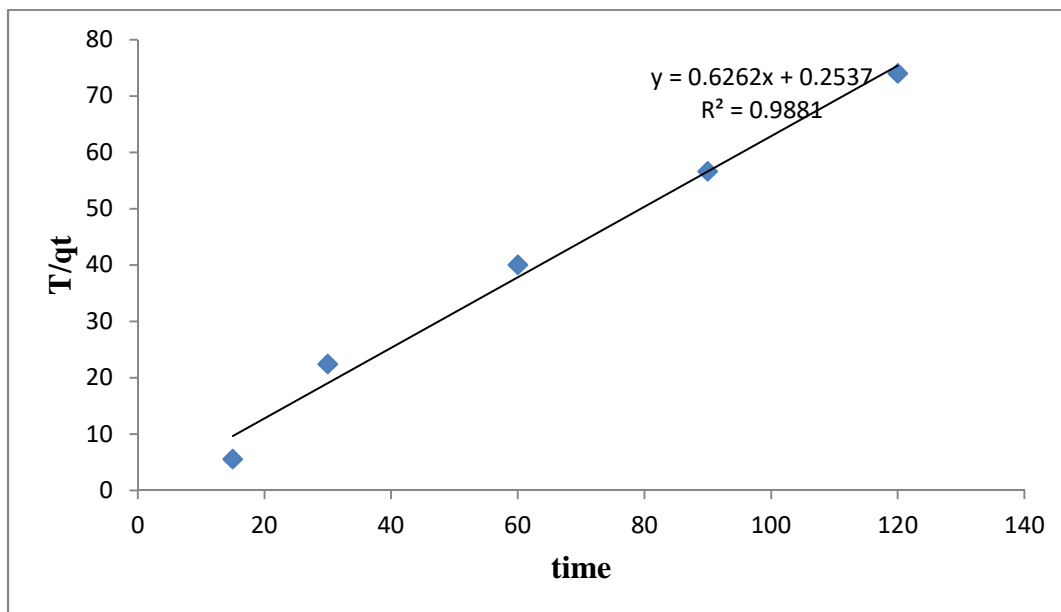


Fig. 13 plot of Pseudo second- order adsorption kinetics of pb(II)onto reed shoot.

Table 4

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

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