Adsorption Study of Pb(II) Ions from Aqueous Solution Using *Medicago sativa* Roots: Equilibrium Studies

Mariam Bakkory[1], Hamdy Esmael[2] and Mohamed Ackacha[3]

Abstract— Biosorption of Pb(II) ions from aqueous solution was investigated using Medicago sativa roots. Characterization of some physiochemical methods showed the following results: cellulose content (65.41%), lignen content (15.72%), ash content (2.46%), solubility content of adsorbent in water after treatment (4.12%) and pH (5). The adsorption capacity was pH, initial Pb(II) concentration, contact time and contact temperature dependent. The equilibrium adsorption of Pb(II) ions data was well fitted with Langmuir isotherm more than Freundlich isotherm according to their correlation coefficient range of 0.9997-0.9999 and 0.8218-0.9604 , respectively. The results of D-R isotherm study proved that the adsorption of Pb(II) ions onto Medicago sativa roots is physical adsorption on nature because the values of mean free energies within the range 0.065-0.069. The interference of co-present hard ions Ca(II) and Mg(II) on the Pb(II) biosorption was also studied. It was determined that at highest Pb(II) concentration (500mgl^{-1}) Ca(II) and Mg(II) ions caused 33% and 27% decreasing in Pb(II) uptake, respectively. The obtained results could be useful in prospective application of Medicago sativa roots as an alternative biosorbent for Pb(II) removal from aqueous solution.

Index Terms—Medicago sativa, Langmuir, Freundlich , D-R isotherm.

I. Introduction

Heavy metals such as lead which present in water environment has been a major preoccupation for researchers for many years ago due to its toxicity towards aquatic life, human beings and the environment [1]. Lead can accumulates mainly in kidney, muscles, brain, bones and cause health problems such as hypertension, brain damage, nerve damage and kidney damage [2]. The recommended level of lead in waste water as indicated by Water Health Organization (WHO) is 0.01 mgl^{-1} [2]. There are several traditional techniques have been utilize for lead removal from contaminated water involve filtration, ion exchange resins, flocculation, chemical precipitation or liquid extraction [3]. Among all the techniques adsorption is highly economical and highly effective [4]. However, the main disadvantage of adsorption treatment is the high cost of adsorbents. Thus, adsorbents of low cost and high efficiency such as agriculture materials may be useful in the adsorption process due to the presence of polar functional groups such as ketones, aldehydes, carboxylic and phenolic acids in their structure [5].

A good number of studies have been reported in literature for metal ion removal by different agriculture materials as a low cost adsorbents such as almond green hull [6], rice bran [6], walnut shell [6], neam leaf powder [7], bael leaves [7], coconut husks [8], peanut skins [8] and waste tea leaves [8].

In the present work, the sorption of Pb(II) ions from aqueous solution in the present of hard cations such as Ca(II) and Mg(II) was investigated.

II. Materials And Methods

A. Materials

The *Medicago sativa* roots was acquired from sebha area, south of Libya, in September 2012, washed several times with tap water then distilled water. To speed up the dissolution of undesirable materials, the sample was heated with distilled water at 333 K, oven dried at 393 K for 2 hours and sorted according to the particle diameter of less than 125 µm.

The stock solution of Pb(II) ions at analytical reagent grad was prepared by dissolving $Pb(NO_3)_2$ (Fluka, Germany) in de ionized water to reach the target concentration.

The oven of Naber model was obtained from Germany. The sensitive balance was obtained from Mettler, China. The pH meter of 3505 model was procured from Jenway, England. The shaker water bath was obtained from Clifon, Italy.

Zinc stock solution of 1000 mgl^{-1} was prepared by dissolving the required amount of zinc acetate in double distilled water. Working solutions were prepared by dilution of stock solution.

B. Batch Adsorption

Batch adsorption technique was used out for the study of Pb(II) adsorption from aqueous solution. The effect of initial pH (2.5-6.5) and contact time (5-40 min) were studied. In analytical experiments 0.02 g sorbent with 125 µm was contacted with 100 ml of the 200 mg/l Pb(II) solution and mixed in a water shaker bath (Stuart Scientific) at 400 rps. Contact temperatures of 303, 313 and 323 K were tried. The sorbent and solution were separated by filtration after each run. The Pb(II) concentration in the solutions were determined by titration with ethylene tetra amin acetic acid (EDTA) produced by Lancaster, England using xylenol orange as indicator (Merck, Germany). Uptake capacity was calculated according to the following equation [9]:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

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Where C_o and C_e are Pb(II) concentration (mgl^{-1}) before and after adsorption, respectively, V is the volume of Pb(II) solution (l), W is the weight of *Medicago sativa* roots (g).

III. Results And Discussion

A. Characterization of Adsorbent

In case to use *Medicago sativa* roots as an efficient adsorbent, some physic-chemical properties of this absorbent was studied (Table 1). The surface of adsorbent contain 65.41% cellulose indicating that the adsorbent possess high ability for adsorption. The low solubility of adsorbent after preparation (4.11%) proved that the adsorbent can be used in aqueous solutions.

TABLE I
PHYSICO-CHEMICAL PROPERTIES OF MEDICAGO SATIVA

Parameter	Obtained result
Cellulose content	65.41%
Lignen content	15.7%
Ash content	2.46%
Solubility of adsorbent in water before preparation	17.6%
Solubility of adsorbent in water after preparation	4.11%
pH of adsorbent solution	5

B. Effect of Initial pH on Adsorption

The pH parameter has been identified as a very important parameter that is effective on metal sorption [10]. The effect of initial pH on the adsorption of Pb(II) ions onto *Medicago sativa* roots was studied by varying pH values in the range of 2.5-6.5 and the results were presented in Fig. 1. The adsorption capacity was increased and reached the maximum value at 196 mg/g as pH was increased from 2.5 to 5. At low initial pH value (2.5), the number of negatively charge surface sites decreased and number of positively charge surface sites increased, which did not favor the sorption of positively charged Pb(II) ions due to the electrostatic repulsion. As the initial pH increase from 2.5 to 5, the electrostatic repulsion decreases owing to the reduction of positive charge density on the adsorbent which leads to increase in adsorption capacity. On the other hand, the decrease in adsorption capacity after initial pH of 5 is due to the formation of soluble lead hydroxide and adsorption studies at these initial pH values could not be performed.

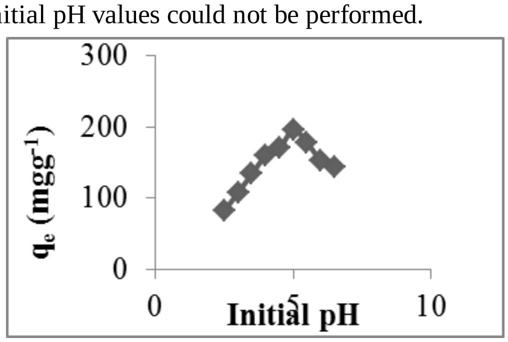

Fig. 1. : Effect of Initial pH on Adsorption. Note: Co = 200 mgl^{-1}, dose = 0.02 gl^{-1}, t = 30 min, T= 303 K, speed = 400 rps.

C. Effect of Contact Time and Initial Concentration of Pb(II) on Adsorption

The dependence of adsorption of Pb(II) ions on *Medicago sativa* roots with contact time for different initial Pb(II) concentration, adsorbent dosage of 0.2 g/l at 30 oC and pH 5 are shown in Fig. 2. The adsorption capacity was found to increase with increasing contact time and reached maximum value at 25 min for all different initial Pb(II) concentrations. The results showed that a rapid increase in Pb(II) adsorption was observed within 5 min. There was no significant change in equilibrium state after 25 min and hence, for further studies, the time for attaining equilibrium could be set at 25 min for adsorption of Pb(II) ions on *Medicago sativa* roots.

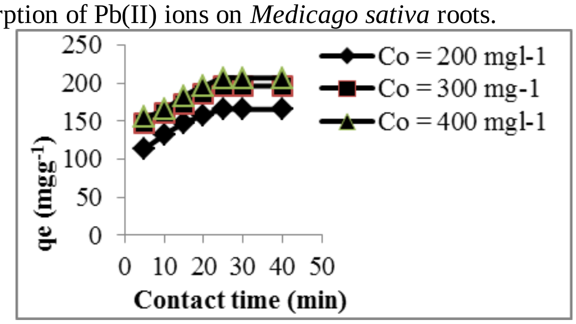

Fig. 2. : Effect of Contact time on Adsorption at Different Initial Pb(II) Concentration. Note: Co = 200, 300 and 400 mgl^{-1}, dose = 0.02 gl^{-1}, pH = 5, T = 303 K, speed = 400 rps.

D. Effect of Contact Temperature on Adsorption

Effect of contact temperature on the adsorption capacity of *Medicago sativa* roots was studied at temperatures of 303, 313 and 323 K. The results are shown in Figure 3. As can be seen from the Figure, adsorption capacity decreased with increase in contact temperature indicating that the adsorption of Pb(II) ions on *Medicago sativa* roots was exothermic.

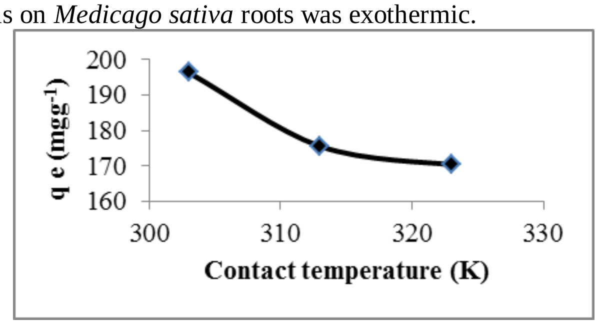

Fig. 3.: Effect of ContactTemperature on Adsorption. Note: Co = 200 mgl-1, dose = 0.02 gl-1, pH = 5, t = 30 min, speed = 400 rps.

E. Adsorption Isotherm Analysis

The adsorption isotherm is usually represent the relationship between the amounts of adsorbate that adsorbent on the surface of adsorbent and the amount of adsorbate remaining in solution at equilibrium [11]. The adsorption capacity at equilibrium, q_e and adsorbate concentration at equilibrium, C_e allows plotting the adsorption isotherm, q_e versus C_e at different temperatures as shown in Figure 4.

Langmiur and Freundlich isotherms are more frequently used to describe the adsorption equilibrium. The Langmuir adsorption isotherm is based on the assumption that the surface of adsorbent is homogeneous, the adsorption sites having the same adsorbate affinity and adsorption at one site not effect to adsorption at an adjacent site. The Langmuir isotherm is used to calculate the maximum adsorption capacity and Langmuir constant and was presented by the following equation [12]:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}.b} + \frac{1}{q_{\max}} C_e \qquad (2)$$

where q_{max} (mgg^{-1}) and b (lmg^{-1}) are the Langmuir constants related to the maximum adsorption capacity and affinity of the binding sites, respectively. The energy of adsorption expressed as K_L which can be determined as follows:

$$K_L = q_{\max} \times b \qquad (3)$$

The Langmuir model can be expressed in terms of dimensionless constant; separation factor (R_L) which defined by the relationship:

$$R_L = \frac{1}{1 + b \times C_O} \qquad (4)$$

The value of R_L indicates the type of Langmuir isotherm to be irreversible (R_L = 0), favourable (0< R_L <1), linear (R_L = 1) or unfavorable (R_L>1) [11].

The Freundlich adsorption isotherm describes hetrogeneaus surface adsorption and does not assume that the surface is monolayer. The Freundlich isotherem was linearized according to the following equation [13]:

$$log\, q_e = log\, K_F + \frac{1}{n} loqC_e \qquad (5)$$

where K_F and 1/n are Freundlich isotherm constants related to adsorption capacity and intensity of adsorption, respectively. The plots of $logq_e$ versus $logC_e$ are presented in Fig. 6. The adsorption is favourable if the value of n is greater than 1 [14] The linearized forms of the Langmuir and Freundlich isotherms are presented in Fig. 5 and 6, respectively.

The calculated model constants and correlation coefficients for Langmuir and Freundlich are given in Table 2 and Table 3, respectively. The experimental data fitted better to Langmuir model compared to Freundlich model according to the values of R^2 obtained. The values of experimental maximum adsorption capacity ($q_{max\ exp.}$) and theoretical maximum adsorption capacity ($q_{max\ theo.}$) are a little similar incase of Langmuir isotherm at all contact temperatures confirming that the experimental data of this work are well fitted with Langmuir isotherm. The adsorption of Pb(II) ions onto *Medicago sativa* roots is also favorable because the values of n are greater than 1 (Table 2) and the values of R_L at different temperatures (Table 3) lie between 0 and 1.

The linearized forms of the Langmuir and Freundlich isotherms are presented in Figures 5 and 6, respectively.

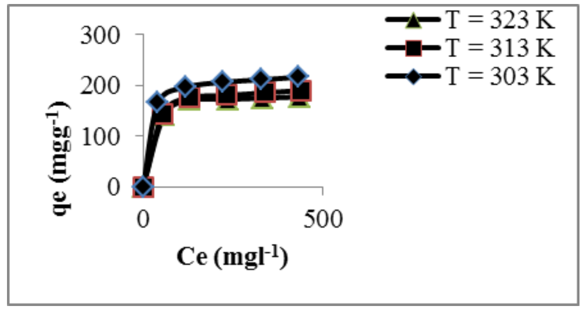

Fig. 4: Equilibrium adsorption isotherm of Pb(II) onto *Medicago sativa* roots at different temperatures. Note: C_o = 100-500 mgl^{-1}, dose = 0.02 gl^{-1}, pH = 5, t = 25 min, speed = 400 rps.

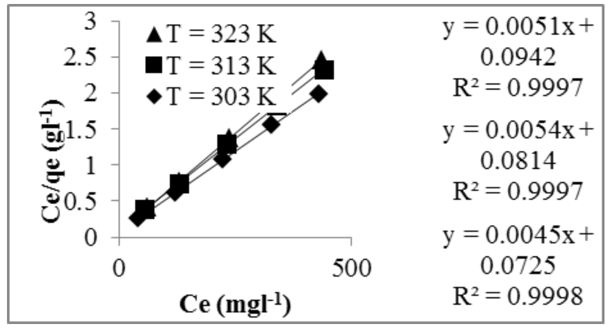

Fig. 5: Linear plot of Langmuir Isotherm at Different Temperatures.

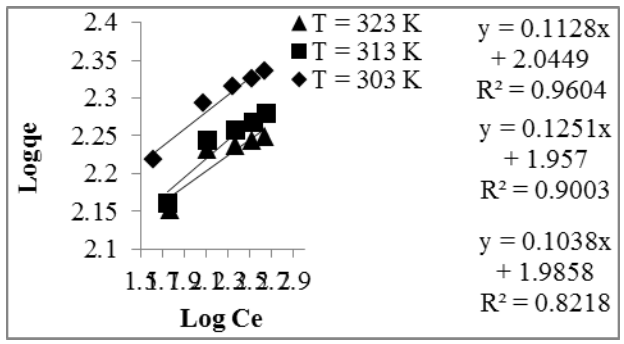

Fig. 6: Linear plot of Freundlich Isotherm at Different Temperature.

TABLE II
LANGUMIR ISOTHERM PARAMETERS

T (K)	q_{max} exp (mgg^{-1})	q_{max} theo. (mgg^{-1})	b (lmg^{-1})	K_L (lg^{-1})	R_L	R^2
303	216.45	222.22	0.062	13.78	0.036-0.280	0.9998
313	190.54	196.08	0.054	10.59	0.040-0.249	0.9997
323	177.61	185.18	0.066	12.22	0.034-0.204	0.9997

The Dubinin-Radushkevich (D-R) isotherm model was applied in this work to estimate the nature of adsorption process weather a physical or chemical adsorption [15]. The following equation represent the D-R isotherm:

$$\ln q_e = \ln q_D - B_D \varepsilon^2 \qquad (6)$$

Where q_D is the theoretical maximum adsorption capacity, B_D is the adsorption energy and Ɛ is the Polanyi potential which determined as follows:

$$\varepsilon = RT\ln\left(1+\frac{1}{C_o}\right) \tag{7}$$

where R is the gas constant (8.314 $jmol^{-1}K^{-1}$) and T is the absolute temperature (K).The constant B_D give an idea about the mean free energy (E) of adsorption per mol of adsorpate. E is usually determines as follows:

$$E = \frac{1}{\sqrt{2B_D}} \tag{8}$$

The slop of the plot of $\ln q_e$ versus ε^2 gives B_D and intercept yields the theoretical adsorption capacity (Figure 7). The values of B_D, E and R^2 are presented in Table 4. From this table, it can be observed that E are within in the range 0.065-0.069 $Kjmol^{-1}$ (E< 8 $Kjmol^{-1}$) [16], indicating that the adsorption of Pb(II) ions onto is physical adsorption. The theoretical maximum adsorption capacities are similar to experimental adsorption capacities (Table 2 and Table 4) indicating that the adsorption of Pb(II) ions onto *Medicago sativa* roots is favorable.

TABLE III
FRUNDLICH ISOTHERM PARAMETERS

T (K)	$q_{max\ exp}$ (mgg^{-1})	$q_{max\ calc\ exp}$ (mgg^{-1})	Log K_F	n	R^2
303	216.45	100.21	2.01	8.87	0.9604
313	190.54	85.11	1.93	7.99	0.9003
323	177.61	97.72	1.99	9.63	0.8218

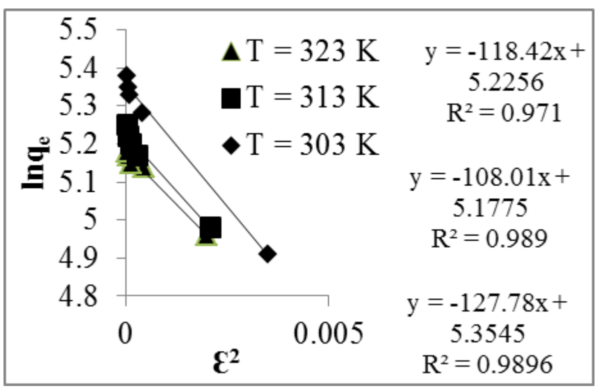

Fig. 7: Linear Plot of D-R isotherm at Different Temperatures

TABLE IV
D-R ISOTHEM PARAMETERS

Parameter			
T (K)	303	313	323
q_D (mgg^{-1})	211.45	186.05	177.33
B_D (mol^2K^{-2})	127.787	118.42	108.01
E ($Kjmol^{-1}$)	0.067	0.065	0.069
R^2	0.9896	0.9710	0.9890

F. *Effect of Interfering Hard Ions on Pb(II) Biosorptions*

Most biosorption experiments carried out in single-ion system; however, , some wastewaters are usually polluted with more than one heavy metal such as hard metals e.g. Ca(II) and Mg(II) ions. For this reason, from a practical of view it is very important to study the effect of these hard ions, onto Pb(II) removal (Figure 8). The concentration of Ca(II) and Mg(II) ions in Pb(II) solution were 300 and 250 mg/l, respectively. Assume that 100% represents the maximum adsorption capacity of Pb(II) ions only. It could be seen that the present of Ca(II) and Mg(II) ions in Pb(II) solution decrease the adsorption capacity of Pb(II) ions onto *Medicago sativa* roots. When the initial Pb(II) concentration was 100 mgl^{-1}, the presence of Ca(II) and Mg(II) ions caused 20% and 14% decrease in adsorption capacity of Pb(II) ions, respectively. On the hand, when the initial Pb(II) concentration was 500 mgl^{-1}, the presence of Ca(II) and Mg(II) ions caused 33% and 27% decrease in adsorption capacity of Pb(II) ions, respectively.

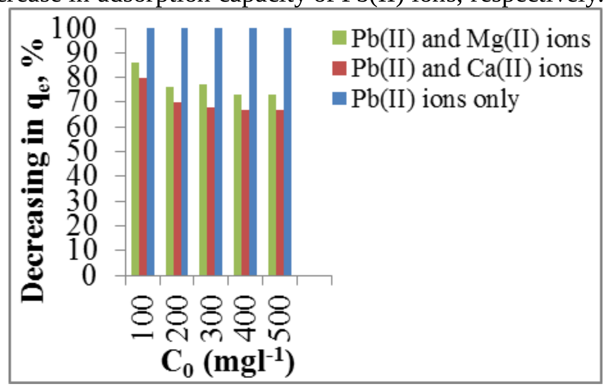

Fig.8: Effect of Ca(II) and Mg(II) Ions on Adsorption Efficiency Pb(II) Ions onto *Medicago Sativa* Roots

IV. Conclusion

The maximum adsorption capacity was obtained at pH 5 after 25 min. The optimal process was pH, initial Pb(II) concentration, contact time and contact temperature dependent. The experimental data at the studied condition fitted well to the Langmuir adsorption isotherm and maximum Pb(II) uptake of 216.45, 190.54 and 177.61 mgg-1 at different contact temperatures were obtained. The decrease of adsorption capacity with the increase of contact temperatures proved that the adsorption system is exothermic. The adsorption of Pb(II) onto Medicago sativa roots is physical adsorption because the values of the mean free energy of adsorption were less than 8 Kjmol-1. There is a decrease in adsorption capacity of Pb(II) ions if hard ions such as Ca(II) and Mg(II) are present in the solution.

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