

The Use of *Acacia tortilis* Leaves as Low Cost Adsorbent to Reduce the Lead Cations from an Aquatic Environment

Mohamed Ackacha^{1,+} and Layla A. Elsharif²

Department of Chemistry, Faculty of Science, Sebha University, Libya

Abstract. *Acacia tortilis* leaves was used as adsorbent material. The influence of initial pH and contact time on adsorption capacity was studied. The batch experiments were used to predict the adsorption capacity of lead cations onto *Acacia tortilis* leaves. The adsorption process was tested with Langmuir and Freundlich isotherm models. Thermodynamic parameters such as ΔG° , ΔH° and ΔS° were calculated for predicting the nature of adsorption. The maximum adsorption capacities were 704.8, 632.3, 437, 332 mg/g at 293, 303, 313, 323, 333 K, respectively.

The aim of the study is to use *Acacia tortilis* leaves as low cost agriculture waste for removal of lead cations from aqueous solution.

Keywords: Biosorption; lead cations; *Acacia tortilis* leaves; Langmuir isotherm; Freundlich isotherm.

1. Introduction

Heavy metals such as lead, mercury, cadmium, cobalt and zinc are toxic and cause environment pollution specially water pollution. Many industries, such as batteries and steel industries discharge various concentrations of lead into water media [1,2]. Because of high toxicity of lead, its removal from water environment is very important. Lead can accumulate mainly in bones, kidney, muscles and brain. Lead cause too much health problems for instance hypertension, brain damage and kidney damage [3]. Even low concentration of lead present in waste water, may cause hepatitis and anemia [3]. The recommended levels of lead in waste water as reported by Environmental Protection Agency (EPA) and World Health Organization (WHO) are 0.05 and 0.01 mg/l, respectively [3].

There are different techniques were used to reduce heavy metal cations from polluted water, namely solvent extraction, ion exchange, precipitation, membrane process, oxidation, reduction, electrolysis and adsorption [4]. Among all these techniques, adsorption is widely used due to low operating costs and high efficiency [5]. Different agricultural materials such as rice husk [6], tree fern [7] and cotton [8] were used as low-cost adsorbents.

In the present work, the ability of *Acacia tortilis* leaves to reduce lead cations from aqueous media have been studied. The parameters such as initial pH of lead cation solution and contact time was also studied. The adsorption isotherm as well as kinetic adsorption and thermodynamic adsorption have been investigated.

2. Materials and methods

2.1. Reagents and equipments

All chemical reagents grade were obtained from Merck, Germany. A pH meter, model 3505 was delivered from Jenway Felsted, Dunmow, Essex C.46 SLB, United Kingdom. The shaker of orbital shaker model number 501 was purchased from Stuart Scientific, United Kingdom.

⁺ ackacha57@yahoo.com

2.2. Preparation of *Acacia tortilis* leaves

Acacia tortilis leaves were washed several times with distilled water to remove impurities. The washed leaves were filtered then dried in a drying oven at 93 °C for 2 hours. The dried leaves were grounded and particles diameter of 50-125 µm were obtained. The obtained fine powder was stored in plastic container to be used later without any pretreatment.

2.3. Preparation of lead cations

Stock solution (2000 mg/l) of lead cations was prepared by dissolving lead acetate salt in distilled water. The stock solution was diluted to the work solutions before use. The pH of work solutions was controlled using 0.1 M HCl or 0.1 M NaOH solutions.

2.4. Batch adsorption experiments

The batch adsorption experiments were carried out by adding a fixed amount of *Acacia tortilis* leaves (0.04 g) to each stopper conical flask filled with 100 ml of lead cation solution of required concentration. The content of the flasks were shaken (400 rpm) with required contact time at required contact temperature and pH. The content of the flasks were filtered. The initial lead concentration as well as final lead concentration after adsorption was calculated by titration with EDTA using xylenol orange as indicator. The amount of adsorbed lead cations onto *Acacia tortilis* leaves was calculated using the following expression:

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

where q_e , adsorption capacity per unit mass of *Acacia tortilis* leaves at equilibrium (mg/g); C_o , initial concentration of lead cations in aqueous solution (mg/l); C_e is the final concentration of lead cations after adsorption (mg/l); V is the volume of lead cations solution in contact with *Acacia tortilis* leaves, (l); W is the dry weight of *Acacia tortilis* leaves, (g).

3. Results and discussions

3.1. Effect of initial pH on adsorption capacity

The pH of adsorption media is the most important factor influencing the adsorption capacity [3]. The study of this effect was preformed at initial lead cations concentration of 300 mg/l, contact time of 2 hours and temperature of 303 K. As shown in Figure 1, the initial pH was varied between 2.9 and 4. The optimum initial pH was found to be 4. At low pH values, the decrease of the vacancies for lead cations due to the intensive concentration of H^+ ions causes a decrease in adsorption capacity of lead cations onto the surface of *Acacia tortilis* leaves. At pH higher than 4, lead cations may be precipitated and adsorption studies could not be performed.

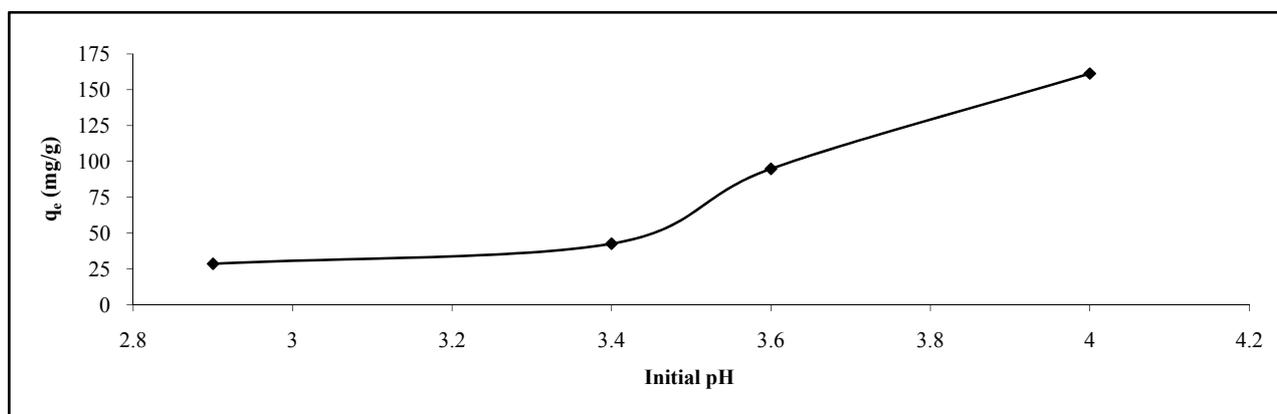


Figure 1: Effect of initial pH on adsorption capacity.

3.2. Effect of contact time on adsorption capacity

The results in Figure 2 show that, the adsorption capacity was fast within 15 min, then increased slowly with contact time before reaching a plateau value after 60 min. Therefore, it is very clear to consider 60 min as equilibrium time. The study was conducted at initial lead cations concentration of 309.2 mg/l, initial pH of 4 and temperature of 303 K.

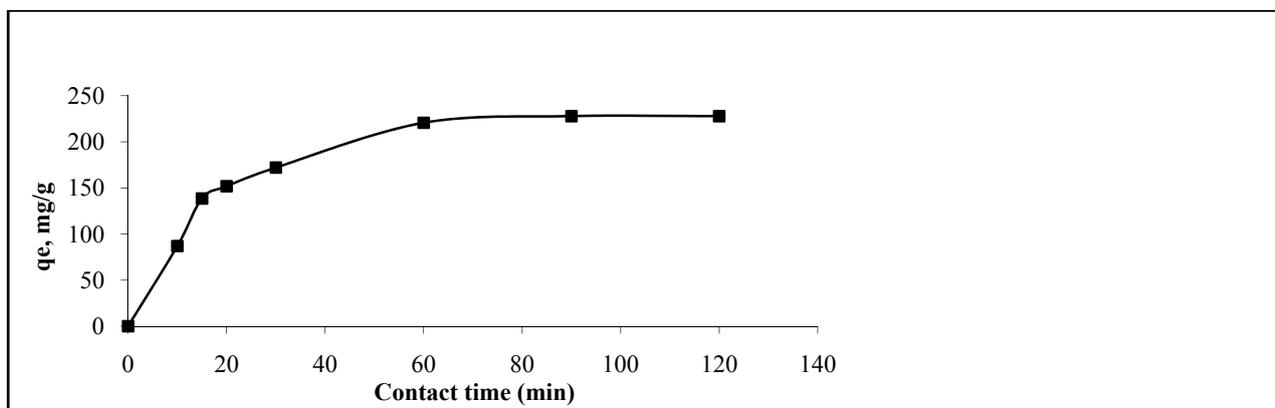


Figure 2: Effect of contact time on adsorption capacity.

3.3. Adsorption isotherm

Figure 3 presented the plotting of adsorption isotherm by the use of adsorbent amount (q_e) and concentration of adsorbate (C_e) at equilibrium.

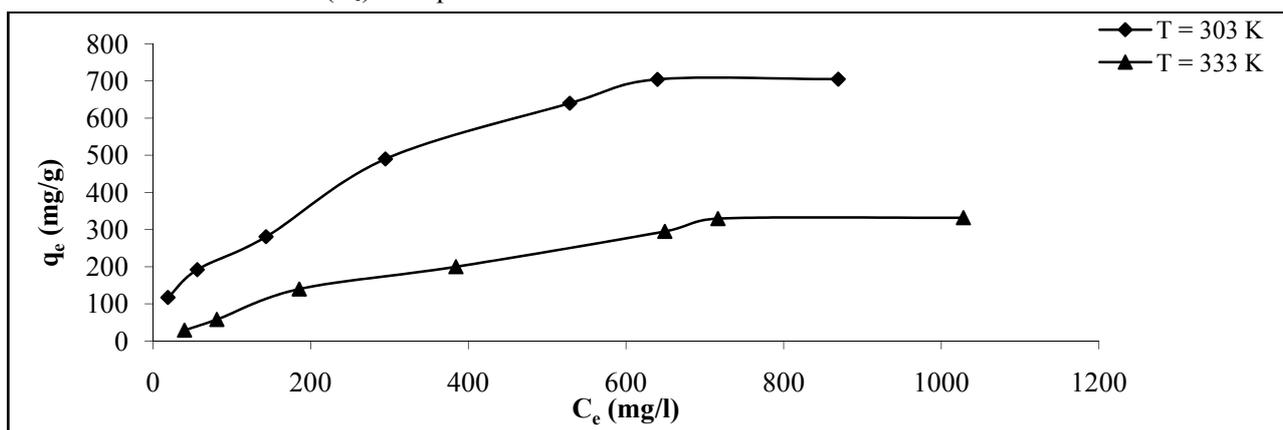


Figure 3: Adsorption isotherm of lead cations onto *Acacia tortilis* leaves at two different temperatures.

The analysis of isotherm data should be fitted into any of isotherm models, to find a suitable isotherm model could be used to design the adsorption process. Langmuir [10] and Freundlich [11] isotherm models were applied in the present study.

The Langmuir equation expressed as follows:

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

where q_{\max} (mg/g) and b (l/mg) are related to the maximum adsorption capacity and energy of adsorption, respectively. These constants were obtained from the plots of $\frac{C_e}{q_e}$ versus C_e and used to calculate the Langmuir constant (K_L) according to the following equation:

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

The Freundlich equation can be expressed as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where K_F and n are the Freundlich constants which determined from the plots of $\log C_e$ versus $\log q_e$.

Table 1 presented the isotherm parameters for both Langmuir and Freundlich models. It is noted from the linear coefficients (R^2) of the adsorption isotherm, that the Freundlich isotherm model showed a better fit to the present work. The values of n (1-10), indicating that the adsorption of lead cations onto *Acacia tortilis* leaves is favorable [12].

Table 1: The Langmuir and Freundlich isotherm parameters at two different temperatures.

T (K)	Langmuir isotherm			Freundlich isotherm		
	b (l/mg)	K_L (l/g)	R^2	K_F	n	R^2
303	0.0045	4.11	0.9660	23.97	1.9204	0.9912
333	0.0013	0.78	0.9488	1.47	1.2134	0.9982

3.4. Thermodynamic studies

The type of the adsorption can be determined through the quantities of thermodynamic parameters such as Gibbs free energy ΔG^0 , standard enthalpy ΔH^0 and entropy change ΔS^0 for the adsorption of lead cations onto the surface of *Acacia tortilis* leaves. These parameters are given in Table 2. ΔG^0 was calculated using the following equation:

$$\Delta G^0 = -RT \ln K_L \quad (5)$$

Where R is the universal gas constant (8.314 j/mol k)

ΔH^0 and ΔS^0 were calculated respectively from the slop and intercept of the plots of $\frac{1}{T}$ versus $\ln K$ (Figure not shown) using the Van't Hoff equation [13]:

$$\ln k = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)$$

The negative values of ΔG^0 showed that, the adsorption process was spontaneous thermodynamically. However, the decrease of the values of ΔG^0 with increase temperatures proved that, the adsorption was not favorable at higher temperatures. The negative value of ΔH^0 indicated the exothermic nature of the adsorption process. The negative value of ΔS^0 suggest the decrease of randomness through the interface during the adsorption of lead cations onto the surface of *Acacia tortilis* leaves.

Table 2: Thermodynamic parameters for adsorption of lead cations from aqueous solution At two different temperatures.

ΔG^0 (kJ/mol. K)				ΔH^0 (kJ/mol. K)	ΔS^0 (kJ/mol. K)
303 K	303 K	303 K	303 K	-43.56	-0.13
-3.55	-2.04	-1.48	0.62		

4. Conclusion

The adsorption capacity was initial pH dependent and the optimum pH was 4. The adsorption of lead cations onto the *Acacia tortilis* leaves was very fast within 15 min and reached equilibrium after 60 min. Freundlich adsorption isotherm was better fitted for adsorption of cations than Langmuir adsorption isotherm. The process is exothermic in nature due to the negative value of ΔH^0 . At temperatures 303 K and 333 K, the system was spontaneous and the spontaneously decrease as the temperature increase. The randomness is decrease through the interface during the adsorption of lead cations onto the surface of *Acacia tortilis* leaves

5. References

- [1] M. Gavnlescu, Removal of heavy metals from environment by biosorption, *Eng. Life Sci.* 2004, **4**: 219-232.
- [2] T. Bahadir, G. Bakan, L. Atals, H. Buy Kgungor, The investigation of lead removal by biosorption: An application at storage battery industry wastwaters, *Enzyme and Microbial Technology*, 2007, **41**: 98-102.

- [3] H. Lalhrualtuanga, K. Jayaram. M. N. V. Prasad, K. K. Kumar, Lead adsorption from aqueous solutions by raw and activated charcoals of melocanna baccifera roxburgh (bamboo)- A comparative study, *J. Hazard. Mater.* 2010, **175**: 311-318.
- [4] P. Chakravarty, N. Sen Sarma, H. P. Sarma, Removal of lead(II) from aqueous solution using heartwood of Areca catechu powder, *Desalination*, 2010, **256**: 16-21.
- [5] O. S. Lowal, A. R. Sami, I. A. Ajayi, O. O. Rabio, Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead (II) ions onto the seed husk of calaphyllum inophyllum, *J. Hazard. Mater.* 2010, **177**: 829-835.
- [6] M. Akhtar, S. Iqbal, A. Kausar, M. I. Bhanger, M. A. Shabeen, An economically viable method for the removal of selected divalent metal ions from aqueous solutions using activated Rice husk, *Colloids and surfaces B: Biointerfaces*, 2010, **75**: 149-155.
- [7] Y. S. HO, W. T. Chiu, C. T. Huang, Sorption of lead ions from aqueous solution using tree fern as adsorbent, *Hydrometallurgy*, 2004, **73**: 55-61.
- [8] E. J. Roberts, S. P. Rowland, Removal of mercury from aqueous solutions by nitrogen containing chemically modified cotton, *Environ. Sci. Technol.* 1973, **7**: 552-555.
- [9] [9] M. M Rao, G. P. Rao, K. Seshiah, N. V. Choudary, M. C. Wang, Activated carbon from ceiba pentandrg hulls, an agriculture waste, as an adsorbent in the removal of lead and zinc from aqueous solutions, *Waste Manage.* 2008, **28**: 849-858.
- [10] I. Langmuir, The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.* 1916, **38**: 2221-2295.
- [11] H. M. F. Frundlich Über die adsorption in IÖsungen, *J. Phys. Chem.*, 1906, **57**: 370-382.
- [12] K. Kadivelu, C. Namasivayan, Agriculture by-products as metal adsorbents: sorption of lead(II) from aqueous solutions onto coir-pith carbon, *Environ. Technol.* 2009, **21(10)**: 1091-1097.
- [13] E. Eren, B. Afsin, Y. Onal, Removal of lead ions by acid activated and manganese oxide-coated bentonite, *J. Hazard. Mater.* 2009, **161**: 677-685.