



REMOVAL OF Pb(II) FROM WASTEWATERS BY ACTIVATED CARBON FROM LEBANESE *CYMOPOGON CITRATUS* (LEMONGRASS): A COMPARATIVE STUDY

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This study is made to prove the efficiency of the activated carbon (AC) of Lebanese *Cymbopogon citratus* in the adsorption of lead (Pb(II)) from aqueous medium. The adsorption was found to be dependent on initial metal ion concentration, pH of the solution, temperature, contact time and adsorbent dose. The maximum adsorption capacity was found for the concentration of 450 mg L⁻¹, pH 4, temperature 25 °C, contact time 2 h, and adsorbent dose 1g. The equilibrium adsorption was better described by Freundlich isotherm model rather than Langmuir model. The kinetic data were better represented by the pseudo-second-order than the pseudo-first-order kinetic model. Thermodynamic studies showed that the process was exothermic and spontaneous. The results of this study reveal that the activated carbon (AC) of Lebanese *Cymbopogon citratus* is a very effective and environmentally friendly adsorbent, with low cost for Pb(II) removal.

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Introduction

The problem of pollution have attracted increasing interest with the growth and development of the industrial sector, since it affects several vital sectors.¹ Heavy metals are among the factors that contribute to the pollution, their toxicity and the danger of their bioaccumulation in the food chain represent one of the major environmental and health problems of our modern society.² The term heavy metal refers to elements that have a relatively high density greater than 5.0 g cm⁻³ and exhibit metallic properties, it includes transition metals and metalloids arsenic and antimony.³

Lead is one of the most toxic heavy metals, it has several fields of application, including battery storage, production of insecticides and plastic water pipes.⁴ Lead is emitted into the atmosphere after the combustion of fossil fuels and the smelting of sulfide ores, it is also emitted in lakes and streams by acid mine drainage.⁵ According to the guidelines of World Health Organization (WHO) and American Water Works Association (AWWA), the quantity recommended for lead in drinking water is 0.05 mg L⁻¹.⁶ The U.S. Environmental Protection Agency has set the maximum dose of lead allowable in drinking water to be 15 ppb.⁷

Several techniques have been used for the decontamination of heavy metals.⁸ Adsorption has been recently recognized as an effective and economic method for heavy metal wastewater treatment. The adsorption

process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process.⁹ Many studies have been conducted to find low-cost adsorbents as replacement for costly current methods, an adsorbent is considered as low-cost if it is naturally abundant, requires little processing or is a by-product of waste material from industry according to Bailey et al.¹⁰ Many types of low-cost adsorbents have been used such as clay adsorbents,¹¹ marine sponges,¹² algae,¹³ activated carbon,¹⁴ biomass of plants^{15,16} and activated carbon.⁹

More recently, many studies have been made about the conversion of solid waste into porous materials,¹⁷⁻¹⁹ especially activated carbon.²⁰ The efficiency of the bio-adsorption of Pb(II) by Lebanese *Cymbopogon citratus* is demonstrated by Hijazi et al.¹⁶

In this work, we have studied the benefits of natural by-products of Lebanese *Cymbopogon citratus*, and the effectiveness of use of activated carbon (AC) resulted from these plants as adsorbent. The effect of different parameters on the adsorption process such as initial concentration of the pollutant, pH, temperature, contact time and dose of the adsorbent has been investigated. Isotherms, kinetic and thermodynamic studies have also been performed.

Experimental

Adsorbent preparation

Crude Lebanese *C. citratus* plant was washed several times with deionized water and dried for one week at room temperature and then left in an oven at 60 °C for 2 days. Then, they were ground and sieved at 0.25 mm. After milling, pyrolysis of the raw material was realized in a

temperature-programmed oven (WiseTherm Furnace) at 600 °C. After pyrolysis, the char was cleaned from the ash and dried in the oven for 2 hours at 90 °C.

For every 10 g of charcoal, 100 ml of H₂O₂ (15 %) were added. They were stirred for 24 h before washing until neutralization of the rinsing water by regular check of pH. Finally, they are kept in the oven at 95 °C for 24 h to obtain a dry AC.

Batch adsorption studies

1000 mg L⁻¹ stock solution of Pb(II) (1000 mg L⁻¹) was prepared by dissolving Pb(NO₃)₂ (supplied by Aldrich, in analytical grade and without further purification) in deionized water. Other solutions with different concentrations were then prepared by mixing a determined volume of the stock solution with deionized water.

Batch experiments were carried out using Erlenmeyer flasks (50 ml) where 50 ml of solution of Pb(II) were mixed with 0.5 g of AC of *C. citratus* at room temperature (25 °C ± 2 °C) except studies concerning the effect of temperature.

To study the effect of pH, small amounts of nitric acid (0.1 mol) or sodium hydroxide (0.1 mol) solutions were added to the mixtures until the target pH was reached. All the experiments were conducted without adjusting the solution pH, except when the effect of pH on Pb(II) removal was studied. In this particular study, the solution pH was adjusted to the desired value throughout the experiment. Solutions are then stirred under a speed of 350 rpm for one hour, whereas, for studies of the effect of the contact time, stirring time was different.

Different batch operational conditions were examined including AC of *C. citratus* dose (0.2–2 g), initial Pb(II) concentration (25–600 mg L⁻¹), temperature (0–75 °C), contact time (5–180 min) and pH (2–12).

At the end of an experiment, the adsorbent was filtered out with filter-paper by Buchner filtration followed by a second filtration using a 0.45 μm syringe micro-filters. The filtrate was collected and analysed by atomic adsorption spectrometer (AAS) at 217 nm, for the determination of Pb(II) content.

The percentage removal efficiency *R* (%) was determined using Eqn.1.

$$R = 100 \frac{C_0 - C_e}{C_0} \quad (1)$$

where

*C*₀ is the initial concentration of Pb(II),
*C*_e is the equilibrium concentration of Pb(II).

The equilibrium adsorption capacity *q*_e (mg g⁻¹), and the adsorption capacity at time *t*, *q*_t (mg g⁻¹), were evaluated according to the Eqns. 2 and 3.

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (3)$$

where

*C*_t is the concentration of Pb(II) at time *t*,
V is the volume of Pb(II) solution and *m* is the weight of adsorbent.

Adsorption isotherms

Adsorption isotherms are an essential way for the understanding of the mechanism of an adsorption system, since they represent the amount of compounds adsorbed on a surface as a function of concentration at a constant temperature.²¹

Langmuir isotherm is based on the assumption that predicts monolayer coverage of the adsorbate on the outer surface of the adsorbent. This model also suggests that there is no lateral interaction between the adsorbed molecules.²² Linear form of Langmuir isotherm is presented by Eqn. 4.

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (4)$$

where

*C*_e is the equilibrium pollutant concentration,
*q*_e is the amount of pollutant adsorbed onto adsorbent at equilibrium,
*q*_{max} is the maximum monolayer capacity of the adsorbent and
*K*_L is Langmuir isotherm constant.

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter,²¹ “*R*_L” is expressed as follows.

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

Four cases are possible. If *R*_L = 0, the adsorption is irreversible, if 0 < *R*_L < 1, the adsorption is favorable, if *R*_L = 1, the adsorption is linear and if *R*_L > 1, the adsorption is unfavourable.

Freundlich isotherm

Freundlich isotherm model is the well-known earliest relationship which describes the adsorption process. It can be applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption.²¹ This model assumes an exponential decrease in the adsorption energy with the increase in surface coverage. Adsorption is considered to

occur with negligible interaction between sorbed molecules.²³ linear form of Freundlich isotherm is expressed as Eqn. 6.

$$\log q_e = \log K_F + \frac{1}{n \log C} \quad (6)$$

where

K_F is the Freundlich constant indicating adsorption capacity,

n is the adsorption intensity and

n value indicates the degree of non-linearity between solution concentration and adsorption as follows, three cases are possible.

If $n = 1$ the adsorption is linear, if $n < 1$ the adsorption is a chemical process and if $n > 1$ the adsorption is a physical process.

Kinetic study

In order to evaluate the rate and mechanism of Pb(II) adsorption, the experimental kinetic data were examined with two reaction rate models i.e., pseudo-first-order kinetics and pseudo-second-order kinetics.

The pseudo-first-order kinetic model is based on the assumption that the sorption rate is proportional to the number of free available sites. It is usually used to determine the kinetic behaviour at the initial stage of the adsorption process.²⁴ The pseudo-first-order rate equation of Lagergren is presented as Eqn. 7.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

where k_1 is the pseudo-first-order rate constant.

The pseudo-second-order kinetic model covers the entire range of the adsorption process.²⁵ The pseudo-second-order rate equation given as Eqn. 8.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

where k_2 is the pseudo-second-order rate constant. The two kinetic models were tested for a time up to 180 min.

Thermodynamic Study

The thermodynamic parameters, of the adsorption of Pb(II) onto the AC of *C. Citrates*, such as the enthalpy of adsorption ΔH^0 , Gibbs free energy ΔG^0 , and entropy ΔS^0 , were determined following the equations:

$$\Delta G^0 = -RT \ln K_c \quad (9)$$

$$\Delta G^0 = \Delta H - T\Delta S \quad (10)$$

where

T is the temperature in Kelvin,

R is the gas constant ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$) and

K_c is the distribution coefficient determined as²⁶: $K_c = q_e / C_e$, ΔH^0 and ΔS^0 were determined respectively from the intercept and gradient from the plot of ΔG^0 versus T .

Results and Discussion

Effect of initial concentration of Pb(II)

The removal percentage and adsorption capacity of Pb(II) were evaluated at different initial metal concentrations (Figure 1), between 25 and 600 mg L⁻¹. At low concentrations, the adsorption of the metal ion on the adsorbent increases rapidly with increasing concentration of the metal and is slowed when the metal concentration reached 300 mg L⁻¹ for an adsorption capacity of 29.98 mg g⁻¹. The rapid increase in the adsorption capacity can be attributed to the interaction between the metal ions and the active sites of the adsorbent as well as to an increase in the driving force for the mass transfer between the aqueous phases and the solid phase.²⁷ Beyond this value, the adsorption capacity increases slowly with the increase of the metal concentration, this is due to the filling of the majority of sorption sites of surface at higher initial concentrations.

There is no large difference between the removal percentages for different concentrations, it is between 99.46 and 99.95 %, with the highest removal being 99.95 % for a concentration of 450 mg L⁻¹. This indicates that the AC can eliminate efficiently a large amount of metal.

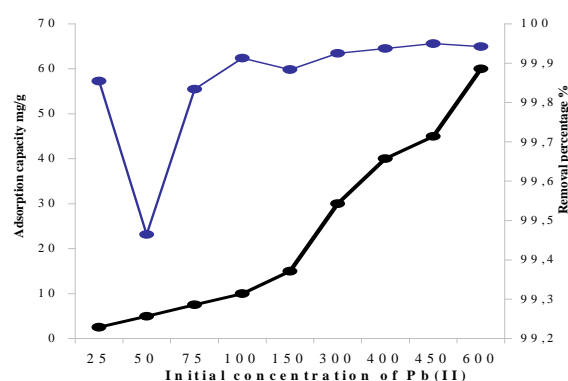


Figure 1. Effect of initial Pb(II) concentration on adsorption capacity (black) and extent of its removal (blue).

Effect of pH

pH is an important parameter affecting the adsorption process and surface properties as well as degree of ionization and speciation of the metal ions in aqueous solution²⁶ Hence, we have studied the effect of pH on the

removal percentage of Pb(II) by the AC of *C. citratus*, in the pH range of 2-12. Figure 2 shows that the removal percentage increases with the pH of medium until pH 6 corresponding to the optimal pH for adsorption of Pb(II), with a removal of 99.97 %.

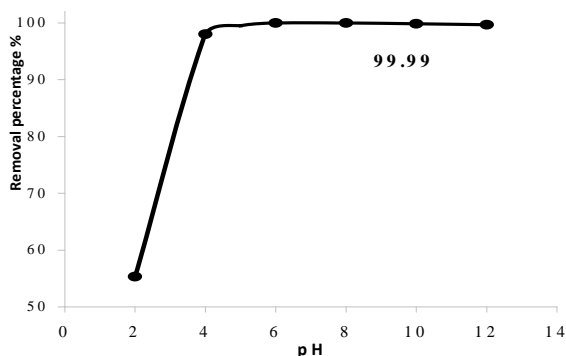


Figure 2. Effect of pH on the removal of Pb(II).

This is explained by the fact that at $\text{pH} < 4$, the active sites on the surface of AC are protonated, thus no interaction occurs with metal ions. At pH between 4 and 6, H^+ ions are released from the active sites and the adsorbed amount of the metal cation is usually found to increase. At higher pH values ($\text{pH} > 6$), the formation of hydroxyl Pb(II) species may cause a decrease of the concentration of free Pb(II), thereby decreasing the removal of Pb(II) by adsorption.²⁸

This is demonstrated by the percentage removal of 99.99 % at pH 8 greater than 99.97 % at pH 6, which is due to the removal of metal by precipitation in addition to adsorption.

Effect of temperature

Temperature is likely to affect on the adsorption process. We have studied the effect of temperature on the percentage removal of Pb(II) in a range between 0 and 75 °C (Figure 3). The effect of temperature is not striking. When the temperature increases from 0 to 25 °C, the removal percentage increases until it reaches 99.96 % at 25 °C. This may be explained by the increase in the rate of diffusion of metal ions across the external boundary and the internal pores of the adsorbent particle.²⁹ It was also observed that with an increase in temperature from 25 to 40 °C, there is a slight decrease in the percentage removal of metal ions which indicates that the adsorption is an exothermic process. The low temperature (25 °C) of maximum adsorption demonstrates the domination of a physical adsorption phenomenon. We noted that there is a small increase of the removal percentage at 60 °C, which may be due to the presence of a chemisorption process.

Effect of contact time

We have studied the effect of the contact time for a range between 0 and 180 min. As it can be shown on the Figure 4, AC can eliminate 99.8 % of the Pb(II) with a contact time of 120 min. It can be seen that the rate of adsorption was high within the first 5 minutes, then it decreases when equilibrium was reached after 20 min. Afterwards, a slight

increase from 99.62 to 99.8 % of the percentage removal of Pb(II) was detected as contact time passes from 30 to 120 minutes. After reaching the equilibrium at 120 min, the removal percentage remained constant with increasing contact time because of the saturation of the sorption sites. The rapid adsorption during the initial stage can be attributed to the availability of a large number of vacant sorption sites for adsorption at this stage.³⁰

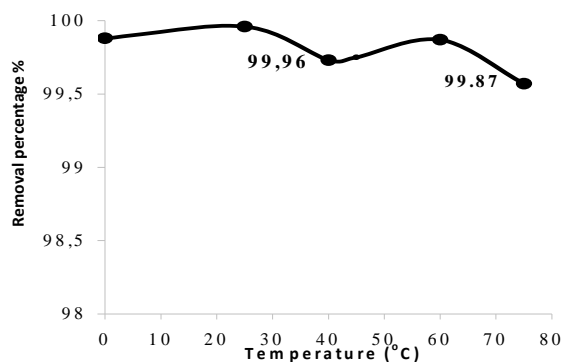


Figure 3. Effect of temperature on the removal of Pb(II).

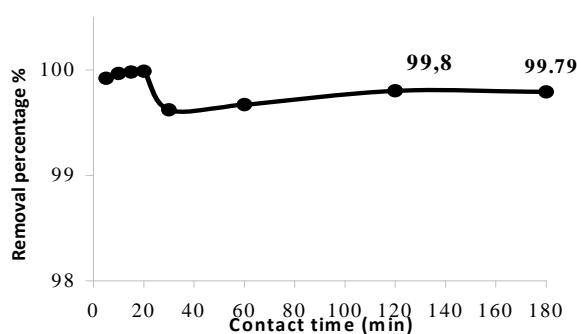


Figure 4. Effect of contact time on the extent of removal of Pb(II).

Effect of amount of adsorbent

The percentage removal of the metal ion increases with increasing amount of the adsorbent (Figure 5). This is due to an increase in the effective surface area, hence making it easier for Pb(II) to access the specific sorption sites. The graph shows that 1g of adsorbent is needed to remove substantially all of the metal ions (150mg L^{-1} of Pb(II)).

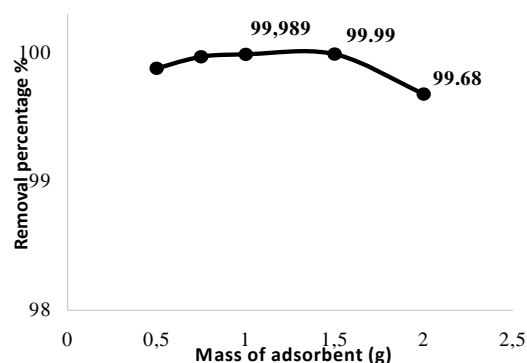


Figure 5. Effect of mass of adsorbant on the removal of Pb(II).

However, after equilibrium was reached, increasing the amount of the adsorbent has no effect on the Pb(II) removal, however the small decrease of the percentage removal corresponding to 2 g of mass adsorbent may be attributed to the formation of adsorbent aggregates at higher solid mass leading to a decrease in the surface area and an increase in diffusion path length.³¹

Isotherms

The experimental data were fitted to Langmuir and Freundlich models (Figures 6 and 7).

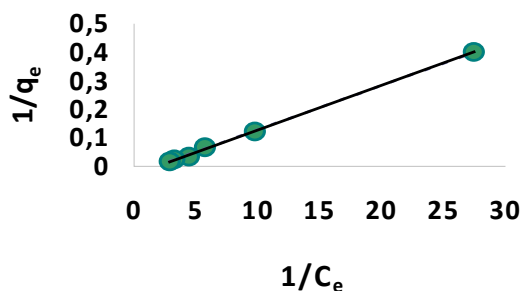


Figure 6. Langmuir isotherm of adsorption of Pb(II) on AC.

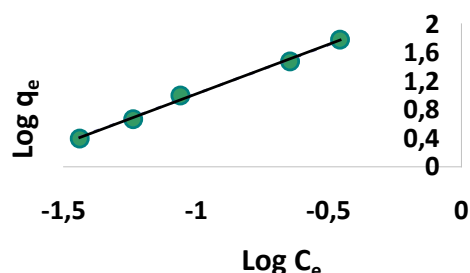


Figure 7. Freundlich isotherm of adsorption of Pb(II) on AC.

The linear plot of $1/q_e$ versus $1/C_e$ has a correlation coefficient $R^2 = 0.999$ for Langmuir isotherm. Freundlich isotherm represented by the plot of $\log q_e$ versus $\log C_e$ shows linearity with a correlation coefficient $R^2 = 0.995$. Langmuir model provided the best correlation for the experimental data. However, the maximum amount adsorbed, q_{max} , could not be calculated because the straight line $1/q_e = f(1/C_e)$ has a negative y-intercept. This negative value is most probably due to the weight of the points of the isotherm corresponding to very low concentrations of pollutant. Hence the adsorption of Pb(II) does not follow the Langmuir model.³²

The application of Freundlich isotherm showed a high correlation coefficient of 0.995 with the adsorption intensity $n = 1.3875$ and $K_F = 254.68$, indicating that the adsorption corresponds to a physical process. The Freundlich isotherm thus better models the adsorption of Pb(II) by the AC of *C. citratus* as compared to that by the Langmuir isotherm.

Kinetic study

To determine the kinetic for Pb(II) adsorption on the AC of *C. citratus*, the experimental data were analysed by the pseudo-first-order and pseudo-second-order kinetic models (Figures 8 and 9). The pseudo-first order model showed a very poor correlation coefficient ($R^2 = 0.6306$) and the value of q_e is 0.00327. In comparison, the pseudo-second order plot has an excellent coefficient correlation ($R^2 = 1$). The values of k_2 and q_e are 4.0566 and 14.97 respectively. These values obtained are comparable with the experimental ones. These observations indicate the applicability of the second kinetic model to the adsorption of Pb(II) onto the AC.

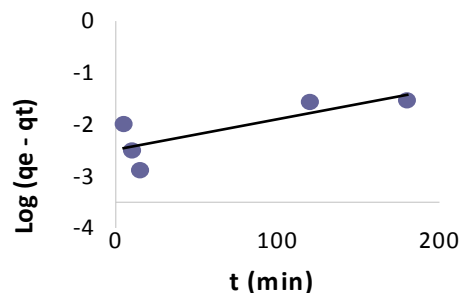


Figure 8. First order plot of the adsorption of Pb(II) on AC.

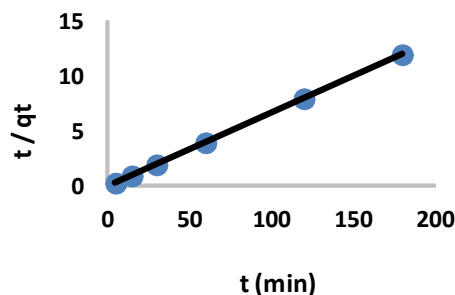


Figure 9. Second order plot of the adsorption of Pb(II) on AC.

Thermodynamic study

The thermodynamic parameters are recorded in Table 1. ΔH^0 is negative suggesting that the process is exothermic and it is not necessary to increase the temperature to be favourable, this is verified by the effect of the temperature (Figure 3) on the adsorption where the maximum capacity is at 25 °C. ΔS^0 is negative due to a decrease in randomness at the solid-liquid interface. However, its very small value suggests that there is no material change in randomness.

Table 1. The thermodynamic parameters.

T (K)	ΔG^0	ΔH^0	ΔS^0
298	13.91	-40.7	-0.09
333	-12.09		
348	-9.07		

Comparative study

We have earlier studied the removal of Pb(II) with the stem of *C. Citrates*.¹⁶ It is useful to compare the efficiency of the AC derived from the plant and the plant itself.

The maximum adsorption capacity, for the same concentrations of Pb(II), is shown to be greater for the AC than the original plant. This indicates the saturation of the surface of the crude *C. citratus* at lower concentration of Pb(II) than that of AC. The study of the effect of pH showed that the removal of Pb(II) by *C. citratus* requires a more acidic medium than the one required for the AC. Further, at the respective optimum pH values, the removal of Pb(II) the AC removed 99.97 % of Pb(II), which is greater than that by crude *C. citratus*. The adsorption of metal ions by *C. citratus* requires gentle heating while the AC can remove a larger amount at room temperature. The percentage removal of Pb(II) after 2 h by *C. citratus* is lower than that by AC and this shows a higher efficiency of the AC to eliminate almost whole of the metal in a relatively short time. Finally, weight to weight the AC is more efficient than the plant itself for the removal of Pb(II).¹⁶

Conclusion

This study was performed to determine the influences of batch parameters on the removal of Pb(II) in aqueous solution by the activated carbon of *C. Citrates*. We have demonstrated that it is better to transform *C. Citratus* to activated carbon to ensure more efficient removal of Pb(II). Therefore the AC of Lebanese *C. citratus* can be considered as a low cost, eco-friendly and effective adsorbent for treatment of waste water containing Pb(II).

The adsorption process was best described by the Freundlich model. The kinetic data were in good agreement with the pseudo-second-order kinetic model. Thermodynamic parameters which included Gibbs free energy, enthalpy and entropy of adsorption have also been determined.

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