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Adsorption of lead by modified *Eucalyptus camaldulensis* barks: equilibrium, kinetic and thermodynamic studies

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ABSTRACT

In order to remove lead ions from aqueous solutions, the potential use of a modified form *of Eucalyptus camaldulensis* bark (ECB) through acrylic acid grafting (EAA) was investigated through several methods. On one hand, the adsorbent was characterized by Fourier Transformed Infrared Spectroscopy (FTIR), X-Ray diffraction (XRD) and bohemian method. The bulk density and the zero-charge point (p_{zch}) were also determined. The results showed that EAA is rich in COOH and OH groups and $p_{zch is acid}$. The remove of Pb (II) is highly dependent on the solution pH, which increases with increasing of the pH of the solution while the adsorption capacity increases with the increasing of initial metal concentration and the weight of the adsorbent. The adsorption rate of Pb^{2+} decreases with the increasing of temperature. On the other hand, the kinetic measurements using Lagergen pseudo-first order model, pseudo-second order model and diffusion intra particle model have explained that the process is fast following the pseudo-second order model. The studies of adsorption equilibrium, using several isotherm models such as Freundlich, Langmuir, Temkin, Elovich, Dubinin-Radushkevich (DR) and Redlich-Peterson, have shown that the adsorption of lead ions by EAA obeys Langmuir model and the maximum adsorption amount of EAA is 82 mg/g at 25°C. Finally, various thermodynamic parameters indicate that the adsorption process is spontaneous and exothermic.

Keywords: Eucalyptus bark; Chemical treatment; Acrylic acid; Characterization; Adsorption capacity; Pb(II) ions; Adsorption isotherm

1. Introduction

Despite the undeniable progress in chemical depollution nowadays, lead is still widely dispersed in the environment and the most significant contamination levels are highlighted in water. It is considered as a dangerous metal due to its non-biodegradation, persistence in nature, food chain accumulation and toxicity [1,2]

In spite of the presence of different depollution techniques such as membrane systems, precipitation, ion-exchange resins [3] and electro dialysis, they are still very expensive [4]. Recently, the fight against metallic pollution has stimulated the search for clean technologies and particularly processes by using natural, ecofriendly and low costs materials. In order to remove heavy metals from industrial wastewater. Several studies have been recently developed for the adsorption of heavy metals by plants [4–12], more particularly by the eucalyptus bark [11–15]. In this regard in the present study we used a material based on eucalyptus bark because of its availability and its richness in compounds which able to fix heavy metals (cellulose, hemicellulose and Lignin). The chemical modification of *Eucalyptus bark* can greatly increase the binding capacity of heavy metals. Among all possible treatments, there is the chemical modification of bark through the grafting of acrylic acid [16,17] or formaldehyde cross linking [18,19]. These treatments have the particular aim of reducing the wood hydrophilicity and stabilizing it dimensionally [23].

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In this study, we grafted the *Eucalyptus bark* with acrylic acid and applied it in the decontamination of aqueous solutions loaded with lead ions.

The aim of the present work is to investigate the ability of EAA as a lead ions removal from aqueous solutions, after its characterization by several spectroscopic techniques [23]. The adsorption parameters such as pH, adsorbent mass, contact time, initial ions concentration and temperature were investigated using SAA and ICP analysis to evaluate interactions between EAA and Pb (II). Finally the equilibrium kinetic and thermodynamic studies were realized in order to characterize the equilibrium relationship between the amounts of adsorbed ions by adsorbents and its equilibrium concentration in the solution.

2. Materials and methods

2.1. Preparation of the adsorbent material

Eucalyptus barks which were collected from the region of Gharb-Kenitra-Morocco (near Ibn Tofail University) were washed to remove the impurities such as sand and dust and dried at 50°C in order to prevent any possible alteration of the material physicochemical properties and then crushed and sieved. The particles whose diameter varies between 112 and 250 µm were retained and used for analysis.

The extracts which are able of inhibiting the prehydrolysis of the eucalyptus have been removed through extraction with Soxhlet technic by a continuous refluxing process. The solvents tend to solubilize the extractable contained in the plant material which are finally concentrated in the recovery flask [24].

The chemical treatment of eucalyptus bark was carried out first with a mixture of organic solvents: ethanol/toluene (ratio 1/2) for 16 h, according to the experimental protocols presented in previous studies[22–25], then by using acetone for 8 h to remove the extractable substances. The choice of solvents is made in such way to extract the greatest quantity of those substances. Finally, the eucalyptus bark was dried in an oven at 100ºC for 2 d. A mass of 50 g of *Eucalyptus bark*-weighed in a cellulose cartridge and placed in the Soxhlet apparatus. The extraction was carried out at 1 to 4 cycles (dipping/leaching) per hour in 600 ml of organic solvent.

The copolymerization reaction with acrylic acid was done with two steps: preliminary oxidation of the wood leading to the formation of macro-radicals and then copolymerization with acrylic acid.

- The first step: pretreatment with $KMnO_4$: 0.5 g of bark is stirred with 25 ml of a 0.016 M aqueous solution of $KMnO_4$ for 30 min at room temperature. The bark was filtered and then washed to remove the remainder of the permanganate.

- The second step: grafting the monomer on the eucalyptus bark. The pre-treated bark is putted into a 100 ml flask and then mixed with 0.5 g of acrylic acid in 30 ml of hexane. The reaction is continued for 2 h. The bark was then filtered by a Buchner, washed with 10% hydroxylamine hydrochloride solution in H_2SO_4 (1.0 M) and then rinsed with double distilled water while the final mixture was filtered. The wet powder is finally extracted in Soxhlet with dioxane for 6 h before drying in an oven at 100°C overnight.

The reaction scheme adopted for the grafting of acrylic acid on eucalyptus bark is as follows [29].

2.2. The preparation of metal solution

Lead is chosen as a representative ion of heavy metals because of its high toxicity and use in electroplating and industrial plants.

The metal solution was prepared by using lead nitrate (Pb (NO_3)) while the preparation of various diluted solutions was made using double distilled water. The various concentrations of metal ion were analyzed by inductively coupled plasma (ICP) in the University Center for Analysis, Expertise, Transfer of Technology and Incubation, Ibn Tofail University, Kenitra, Morocco.

All chemical products were purchased from Sigma-Aldrich (France) with a high quality.

2.3. Adsorption experiments

The extraction experiments were realized by adding the given quantity of adsorbent with 100 mL of aqueous solution with known lead ion concentration, in 250 mL beaker. The flask was intermittently stirred for an adequate period of time, depending on the purpose of the experiment. All experiments were done at room temperature (25°C). After each extraction test, the solution was filtered by using a cellulose nitrate filter paper with a diameter of 0.45 µm, and finally the obtained solutions were analyzed to measure the different concentrations. The capacity of yield and extraction were calculated by the following equations:

$$R(\%) = \frac{C_0 - C_f}{C_0} \times 100 \tag{1}$$

$$q_t(mg/g) = \frac{C_0 - C_f}{m} \times V \tag{2}$$

where C_0: initial concentration of the metal in solution in mg/l, C_f: final concentration of the metal in solution in mg/l, R: extraction yield in%, q_t: extraction capacity in mg/g of the support, m: the mass of the support in g and V: the volume of the solution in L.

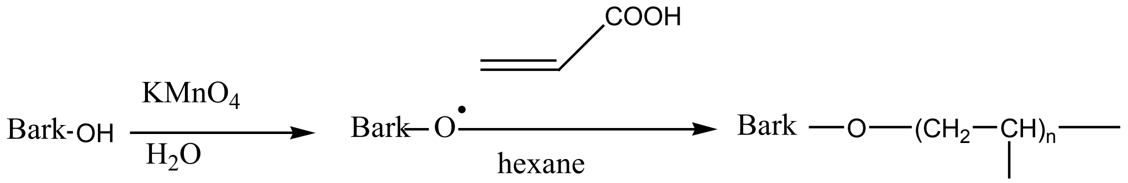


Fig. 1. Scheme adopted of the reaction for the grafting carboxylic functions on the Eucalyptus bark.

2.4. Characterization of the material

The eucalyptus bark has been characterized by different methods: the surface functions have been defined by the Boehm method [23,30], which corresponds to the acid-base titration of the surface functional groups. The various materials were analyzed by Fourier Transform Infrared (FTIR) spectroscopy which was performed by using a VERTEX 70 type apparatus in the wavelength ranging from 400 cm^{-1} to 4000 cm^{-1}; the spectral resolution is 4.0 cm^{-1}. The pellets were made from an intimate mixture of sieved samples (1 mg) and potassium bromide (100 mg) under a pressure of 4.5 10^{8} Pa. The crystallinity index (CrI) was calculated by the ratio of the surface area of the crystalline phase, the total area (crystalline phase (SCP) and amorphous phase (SAP)), using Eq. (3) [31]:

$$CrI = \frac{SCP}{SCP + SAP} X100 \tag{3}$$

The powder samples were scanned using a X-ray diffractometer type XPERT-3, the wave number and the scanning degree are ranging between 0–4000 cm^{-1} and 0–50° respectively. The analysis was on a continuous scanning mode using a monochromatic Kα1 radiation of copper (CuKα- radiation) (λ = 0.154 nm) at 35 kV and 30 mA.

3. Results and discussions

3.1. Characterization of the material

Table 1 summarizes the different characteristics of the crude eucalyptus bark grafted with acrylic acid while the chemical composition of crude eucalyptus bark was determined according to TAPPI standards [32] :

- TAPPI T-204 om-88. Flight. 1. TAPPI Test Methods. Atlanta. GA: TappiPress. (1992).
- TAPPI T 222 om-06. Acid-insoluble Lignin in Wood and Pulp. (2006) 5.
- TAPPI T 204 cm-97. Solvent extractives of wood and pulp. T 204 cm-97, (2007).
- TAPPI T 211 cm-86. Ash in wood and pulp (2003).

The results of the determination of materials surface functions by the Boehm method are illustrated in Table 2.

At first, it is found that the surface chemistry of material is slightly affected by the performed chemical treatment.

Table 1
Physico-chemical characteristics of Eucalyptus bark before and after chemical treatment

Material	EB	EAA
Humidity (%)	5.19	4.81
Mineral materials (%)	14.92	1.51
pH$_{zch}$	4.25	3.60
Apparent density (g/cm^{3})	0.75	0.77
Hollo cellulose (%)	57	–
Lignine of klason (%)	26	–
Extractable material (%)	4.03	–

On one hand, the *Eucalyptus bark* (raw and treated) has an acidic character (pH < 5), which can be explained by the presence of acid functions and the absence of basic functions on the surface of both of materials. The results in Table 2 have shown a clear increase of carboxyl functions in the surface of the adsorbent after treatment of *Eucalyptus bark* with acrylic (0.57 mmol/g).

The spectra which are obtained by infrared analysis (FTIR) of the raw and the treated *Eucalyptus bark* samples (EB, EAA) are shown in (Fig. 2). Characteristic vibration bands have been assigned to different chemical functions (Fig. 3) in accordance with the literature data. The FTIR spectra of EB and EAA have almost the same form but the bark treated with acrylic acid (EAA) had an increased intensity.

All infrared spectra reveal the presence of a broad band at 3400 cm^{-1} which corresponds to the stretching vibrations of the OH bond of the aromatic and aliphatic phenol structures (lignin and cellulose group) with the exception of the bark treated with Acrylic acid (EAA).There is an important increase of EAA spectra intensity due to the grafting by the acrylic acid. The band which is about 2930 cm^{-1} corresponds to the asymmetric elongation of the cellulose C-H bond. As for the band located at 2850 cm^{-1}, it corresponds to the symmetrical elongation vibration of the C-H bond of the methoxy groups of the lignin.

The peak at 1720 cm^{-1}characterizes the (C = O) valence vibration of carboxylic acids and/or esters of xylans present in hemicelluloses [29–31]. For the compound which is treated with acrylic acid, this same peak appears with a marked increase in intensity due to the appearance of the

Table 2
Surface functions of materials with different states

Material	EB	EAA
Functions carboxyl (mmol/g)	0.09	0.57
Functions lactones (mmol/g)	0.12	0.14
Functions phenols (mmol/g)	0.45	0.55
Total of functions acids (mmol/g)	0.66	1.26
Functions basic(mmol/g)	0.00	0.00

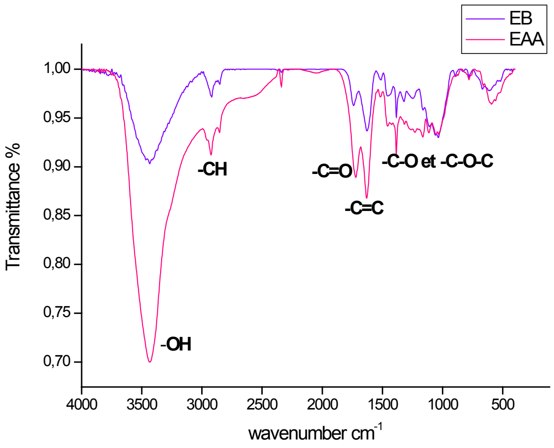


Fig. 2. FTIR spectra of rough (EB) and modified (EAA) Eucalyptus bark.

carboxylic acids C = O bond of the acrylic acid grafted onto the bark.

Furthermore, the band which is observed around 1630 cm^{-1} corresponds to the C = C deformation of the aromatic cycles of the lignins. The bands observed at 1380 cm^{-1} and 1230 cm^{-1} are attributed to the ν (C-O) vibration of the methoxy groups of lignin and the bond which is formed by the action of formaldehyde on cellulose (C-O-C). The band which is around 1159 cm^{-1} in the bark spectrum treated with acrylic acid corresponds to the elongation of the C-O bond of the acid group because of the grafting of the acid functions on the eucalyptus bark.

The peak around 1030 cm^{-1} corresponds to the valence vibrations of the C-O and C-O-C bonds of cellulose [36].

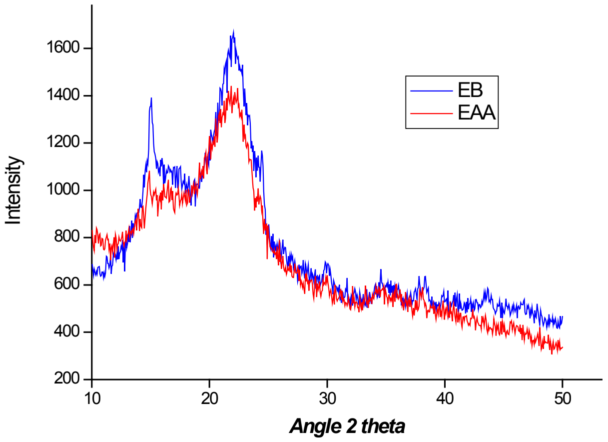


Fig. 3. X-ray diffraction patterns of both the raw and the treated Eucalyptus bark.

Table 3
Crystallinity index of EB and EAA

Biomass	Crystallinity index CrI (%)
Rough bark (EB)	46.57
Bark copolymerized with acrylic acid (EAA)	41.44

The X-ray diffraction patterns of the rough and modified *E. camaldulensis* bark samples are shown in Fig. 3. It appears that all the samples have the characteristic shape of a native cellulose of lignocellulosic materials with a clear domination of the amorphous form [37].

The analysis of these curves allowed us to deduce the overall crystallinity of the raw and the treated eucalyptus.

The data in Table 3 shows that the bark was affected by the treatment, where the crystallinity index of EAA decreased from 46.57% for EB to 41.44% for EAA, which is due to the reaction of the cellulose OH groups with the acrylic acid. As a result, their hydrogen is no longer available to form intermolecular hydrogen bonds. So, the cellulose loses its crystalline form.

3.2 Kinetics of adsorption

The kinetics of adsorption describes the contact time required to attain the extraction equilibrium by studying the simultaneous evolution of the concentration of Pb^{2+} versus time (Fig. 4) and the variation of the aqueous solution pH. The concentration of lead ions has decreased from 20 ppm to 0.5 ppm. The extraction equilibrium is reached after 40 min with an adsorption amount equal to 19.5 mg/g.

The pH evolution of the metal solution during the kinetic study was followed and a decrease in the initial pH of the contact solution during the first minutes was obtained. The pH values increased from 5 to 3.93. The decrease in pH indicates that the adsorbent releases protons in order to fix the Pb^{2+} ions.

3.3. Effect of initial pH of aqueous solution

It is well known that pH is an important factor for heavy metal adsorption, which was in the range of 2–6 in this study to prevent precipitation of Pb^{2+} in the form of metal hydroxides. The relationship between the initial pH values and the amounts of Pb^{2+} adsorbed on the material is shown in Fig. 5. It is found that the adsorption amount increases as the pH of the solution increases but its values are lower at pH (<4), which is attributed to the fact that the sites of the material are protonized and therefore the formation of bonds between active sites and metal ions is no longer possible. When pH

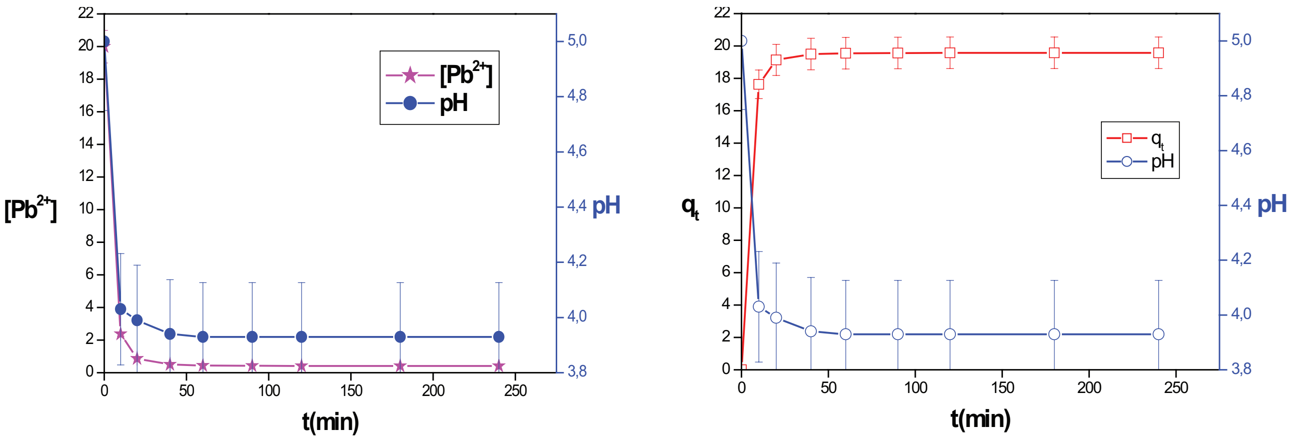


Fig. 4. Variation of the Pb^{2+} concentration, the adsorption amount and the pH vs. time.

≥ 4, the adsorption capacity of Pb^{2+} has increased slightly and afterwards remains constant and at this time connections can be made between the metal and the vacant sites, in addition the electrostatic repulsive forces decrease at high pH between heavy metal ions and the positive charge of the surface. Therefore, the pH ranging from 4 to 6 could be considered as the favorable pH in the adsorption process, or the maximum value of the adsorption amount is 20 mg/g at pH = 5.5. Thus, the optimum pH for Pb^{2+} adsorption is 5.5, which have been selected for the following experiment.

3.4. Effect of initial concentration of lead ions

The initial concentration of the metal has an important influence on the retention capacity of the adsorbent. In order to study its effect, the following values were considered: 20, 40, 60, 80, 100, 200 and 300 ppm.

The obtained results are shown in Fig. 6. The adsorption amount increases with the increase of the initial concentration of Pb^{2+}. However, at high concentrations, the driving force, due to the higher concentration gradient, and the amount of Pb^{2+} adsorbed per unit of mass of adsorbent, q_t, is greater, which causes the adsorbent saturation and thus an amount of the ions remains free in the solution, giving a low yield [38].

Accordingly, it can be concluded that the treated eucalyptus bark is an efficient adsorbent of low and high concentrations of lead ions from aqueous solutions.

3.5. Effect of mass of extraction medium

In this study, quantities of increasing EAA (0.02, 0.05, 0.07, 0.1, 0.2, 0.3, 0.4 and 0.5 g) were plunged into 100 ml of each aqueous solution of Pb (II), with a concentration equal to 20 ppm. The pH of each solution was set at 5.5. According to the results of Fig. 7, it can be seen that the extraction efficiency of the Pb^{2+} ions increases progressively as the mass of the support contacted with the metal solution increases and as a result,the contact surface becomes larger. Moreover, the availability of the active sites responsible for the metal ions complexation increases. An optimum yield of 100% is obtained at a mass of 0.1 g. Consequently, it can be concluded that under the operating conditions used, a mass of 0.1 g of the support is

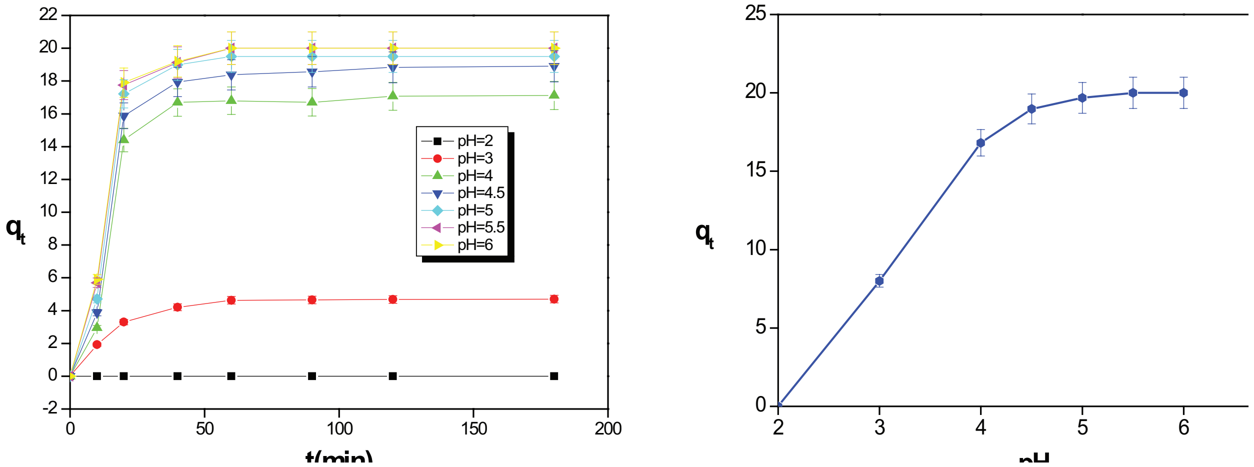


Fig. 5. Effect of initial pH on the adsorption amount of Pb^{2+} by EAA.

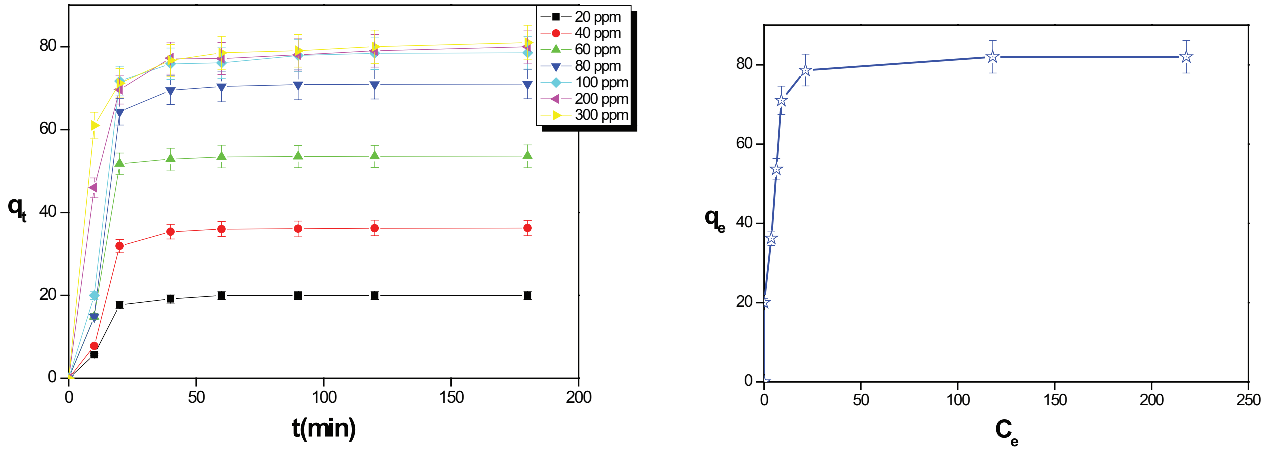


Fig. 6. Effect of the initial concentration on the capacity of extraction of $Pb^{2+}$by EAA.

sufficient to purify a metallic solution of Pb^{2+} with a concentration equal to 20 ppm.

3.6. Influence of temperature

Temperature was a major factor in the adsorption process. The influence of this parameter on the extraction efficiency was studied by using temperatures ranging from 25 to 55°C. It can be seen from Fig. 7 that the temperature has a slight influence on the extraction yield. From Fig. 8, the lead removal percentage decreases by 100% (q = 20 mg/g) to 95.4% (q = 19.08 mg/g), when the temperature increases from 25 to 55°C, respectively. These results indicate that the adsorption may be exothermic and may be explained by the fact that the rise in temperature may not be in favor of any agglomeration of the lead ions on the solid surface.

3.7. Adsorption isotherms

Adsorption isotherms characterize the equilibrium relationship between the amounts of adsorbed ions by adsorbents and its equilibrium concentration in the solution [39]. There are several isotherms for analyzing experimental adsorption equilibrium data. The equation parameters of these isotherms often provide some insight into the adsorption mechanism [40].

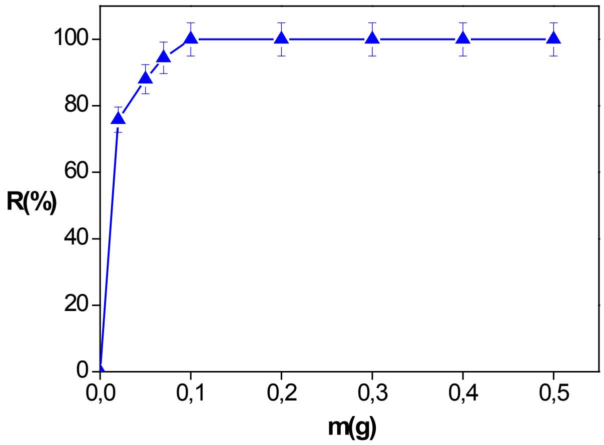


Fig. 7. Effect of the mass on the extraction rate of Pb^{2+} by EAA.

In order to identify the retention mechanism for the initial concentrations (C_0 = 20–300 mg/L), and the isotherm that represents better the adsorption of Pb (II) ions on the eucalyptus bark (EAA), six theoretical models were tested on the obtained experimental results, namely Freundlich, Langmuir, Temkin, Elovich, Dubinin-Radushkevich (DR) and Redlich-Peterson.

From the graphical representation of each isotherm (Fig. 9 and Table 4), which have given the correlation factors as well as the constants of each model, it is evident that the Pb (II) ion retention mechanism is represented by Langmuir isotherm which has the highest correlation factor, compared to the other models. Thus, according to Langmuir theory, the adsorbent solid has a limited adsorption capacity (q_m), all active sites are identical,which implies that they can complex only one solute molecule (mono layer adsorption) also there is no interactions between the adsorbed molecules.

3.8. Validation of kinetic models

The kinetic data obtained for the adsorption process were analyzed using the three most common models such as Lagergen pseudo first order, pseudo second order and intra-particle diffusion. A concentration equal to 20 ppm was used in this study.

3.8.1. Lagergen pseudo first and second order model

The validity of the Lagergren equation is first tested by plotting ln ($q_e - q_t$) as a function of time (t).

From Fig. 10 it is clear that the Lagergren equation is not applicable in the case of lead retention for the support under study.

From the equation representative of pseudo-second order kinetics and its linear form, the rate constant k_2 can be calculated graphically by plotting t/q_t as a function of t.

Fig. 11 shows that the experimental results obtained follow perfectly the linear variation given by the equation representative of pseudo-second order kinetics.

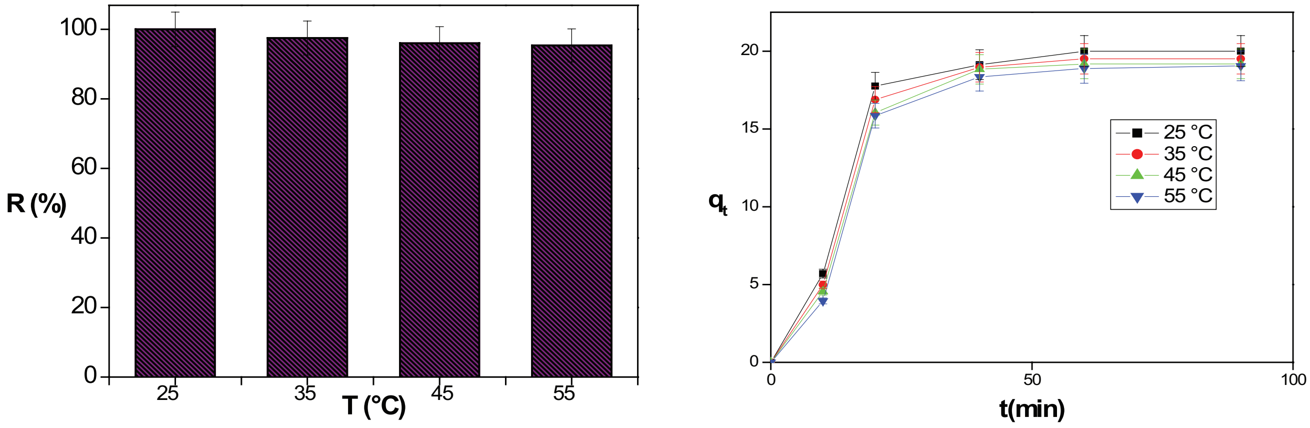
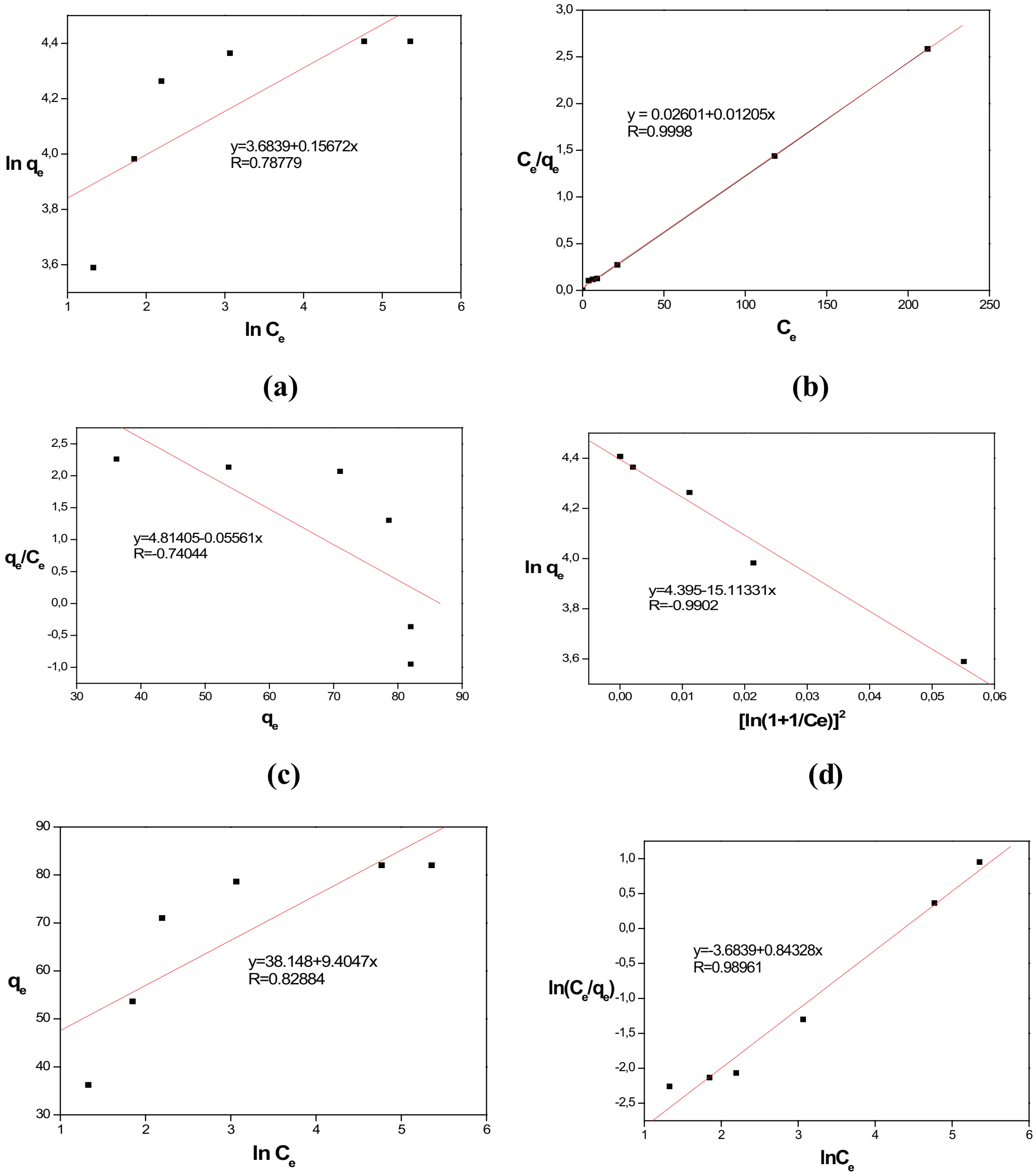


Fig. 8. Effect of temperature on yield and Pb^{2+} extraction capacity by EAA.



(a) **(b)**

(c) **(d)**

(e) **(f)**

Fig. 9. The adsorption isotherm modeling by (Freundlich (a), Langmuir (b), Elovich (c), Dubnin-Radushkevich (d), TemkinE) and Redlich-Peterson (f)).

3.8.2. Intra-particle scattering model

The application of the equation of this model to the experimental data by plotting q_t for $t^{0.5}$ suggests the applicability of the intra-particle diffusion model, governing the adsorption kinetics. Thus, the curves present (Fig. 12) the kinetics of the intrinsic diffusion for the studied support.

From Fig. 12, It can be seen that there is no continuous linearity along the process. Therefore, it is enough to apply the linear regression on the most linear edge as shown in Fig. 13.

The linear regression was only done on the edge where the straight line is linear as shown in Fig. 13.

The model of intra particle diffusion based on the linear regression data of various models shown in Table 5 and according to the values obtained for the correlation coefficients close to unity, it can be concluded that the lead retention kinetics are described better by the pseudo-second order model than the other two models. Therefore, the adsorption depends on the ions concentration onto the adsorbent surface in accordance with chemiso rption nature.

Table 4
Kinetic constants and correlation factors of different adsorption isotherms of Pb (II) on EAA

Type of isotherm	Constants		Equations
Freundlich	K_f ($mg^{1-n}·l^n·g^{-1}$)	39.8013	$\ln q_e = \ln K_f + n \ln C_e$
	n_f	0.15	
	R	0.78779	
Langmuir	q_m(mg/g)	82.98	$C_e/q_e = C_e/q_m + 1/(q_m K_L)$
	K_L (L/mg)	0.46	
	R	0.9998	
Temkin	B_T (mg/g)	9.4047	$q_e = B_T \ln K_T + B_T \ln C_e$ $(B_T = q_m RT/dq)$
	K_T (L/mg)	57.76	
	R	0.82884	
Elovich	K_E ((L/mg)	6.8537	$\mathrm{Ln}(q_e/C_e) = \ln(K_E q_m) + q_e/q_m$
	q_m (mg/g)	17.98	
	R	−0.74044	
Dubinin-Radushkevich	q_{mDR} (mg/g)	81.04	$\mathrm{Ln}\, q_e = \ln q_{mDR} - (RT/E)^2 (\ln(C_s/C_e))^2$ $E = 1/(\beta)^{0.5}$
	β (mol²/Kj²)	2.46	
	R	−0.9902	
Redlich-Peterson	n	0.84	$C_e/q_e = 1/(K_L q_m) + K_L^{(n-1)}.(C_e)/q_m$
	$\mathrm{Ln}(K_L^{n-1}/q_m)$	−3.6839	
	R	0.98961	

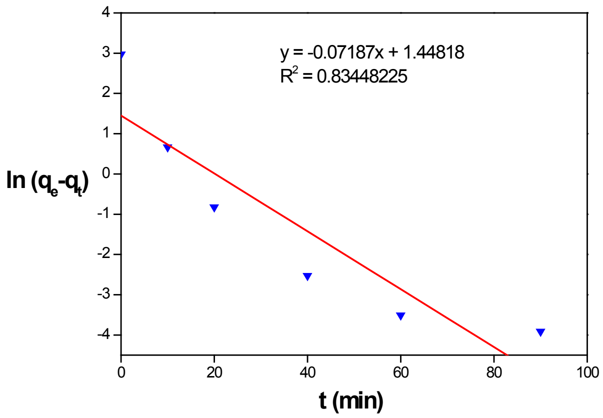


Fig. 10. Linearization of the retention kinetics of the lead of the first order-model of the pseudo second order kinetics.

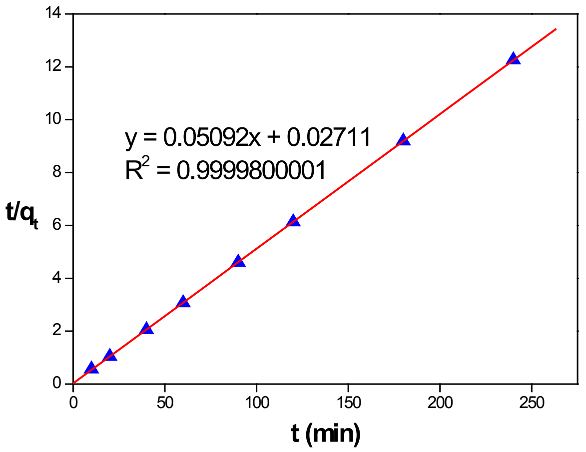


Fig. 11. Second order linearization of lead retention kinetics.

3.9. Thermodynamic study

Thermodynamic analysis of the adsorption process is essential to determine the spontaneity of the adsorption process. The feasibility and the spontaneous nature of the adsorption process are reflected in the thermodynamic parameters (Fig. 14). To calculate the Gibbs free energy variation (ΔG°), values of enthalpy variation (ΔH°) and entropy variation (ΔS°) were calculated using the equations below:

$$\Delta G° = \Delta H° - T\Delta S° \text{ and}$$

$$\mathrm{Ln}\,(q_e/C_e) = (\Delta S°/R) + (-\Delta H°/RT)$$

In addition, the corresponding values for free energy variation (ΔG°), enthalpy variation (ΔH°) and entropy variation (ΔS°) for treated eucalyptus bark are presented in Table 6. It was found that Gibbs free energy (ΔG°) and enthalpy (ΔH°) were negative at all temperatures associated to the exothermic and spontaneous nature of the process, while the positive value of the entropy (ΔS°) probably indicates that the adsorption of Pb^{2+} increases in a random manner.

3.10. Comparative study

Table 7 shows various studied adsorbents used previously for the removal of Pb (II). It is found that the bark adsorption capacity of the modified *Eucalyptus* is among the highest capacities, which makes it among the suitable adsorbents for the removal of metals from actual wastewater facilities.

In spite of the activated charcoal mentioned in Table 7 gives a good capacity that the bark of modified eucalyptus, we can say that our support have several advantages:

- The mode of preparation of the material it is an essential parameter. For the grafting of the acrylic acid is made in two stages: the first one is the elimination of extracts by solvents which are not very expensive and reusable for several times after their recoveries (recycling) by means of the distillation. In addition, extracts are valued in the field of the inhibition of the corrosion in two acid media and give good results and be the object of a several publication. The second is the copolymerization of the material by means of the acrylic acid and KMnO4 as precursor and hexane as solvent that we can also get back him after the reaction. Thus, this reaction is made with simple, available products, less dear, and in moderate temperatures. By basing itself on this last parameter which is the temperature, we can say that the preparation of the activated charcoal is made with higher temperatures (more of 500°C) what returns this very expensive support because it requires more energy on one hand and the use of very concentrated acids (H_3PO_4 85%) of one somewhere else.

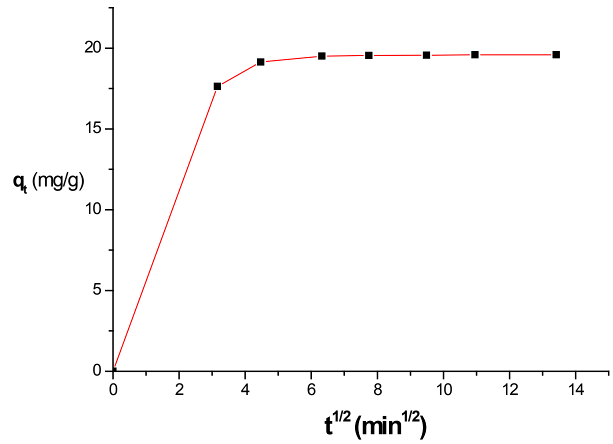


Fig. 12. Graphical representation of the intra particle diffusion model for the retention of the Pb (II) by EAA.

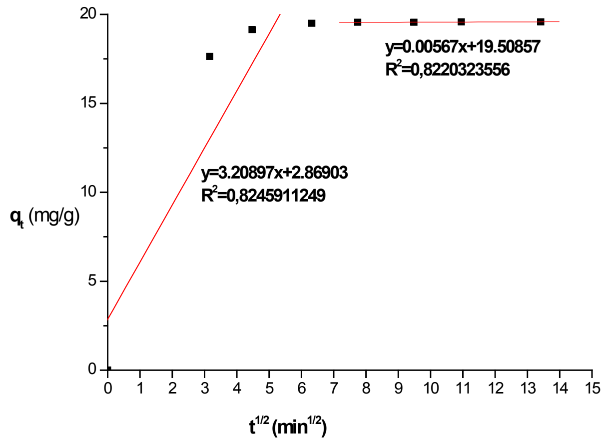


Fig. 13. Linearization of the right slice of lead retention kinetics.

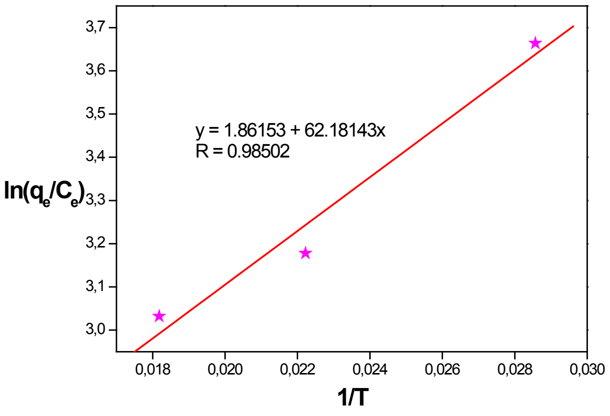


Fig. 14. Van'tH off curve for the adsorption of Pb^{2+} by EAA.

Table 6
Thermodynamic parameters of Pb^{2+} adsorption at different temperatures by EAA

Adsorbent	Temperature (K)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol.K)
Modified eucalyptus bark	298	–5.13	–0.517	0.0155
	308	–5.207		
	318	–5.439		
	328	–5.594		

Table 5
Kinetic models parameters studied for lead

Lagergen pseudo 1st order			Pseudo 2nd order		Intra-particle diffusion	
Constants	k_1(min^{-1})	0.07187	k_2(g·mg^{-1}·min^{-1})	0.0956	k_{int} (mg/g·min$^{0.5}$)	0.00687
						3.20887
	q_e (mg/g)	4.25	q_e (mg/g)	19.64	R²	0.82220
	R²	0.83448	R²	0.99998		0.82468
Equations	$\ln(q_e - q_t) = \ln q_e - K_1 t$		$t/q_t = t/q_e + 1/(K_2 q_e)^2$		$q_t = K_{int} t^{1/2} + C$	

Table 7
The adsorption amount of lead ions by different natural adsorbents

Adsorbent	Adsorption capacity (m mol/g)	Reference
Modified Eucalyptus bark	0.39	Present study
Activated carbon of eucalyptus bark	0.53	[41]
Activated charcoal from a new shell of hazelnut	0.065	[42]
Bagasse of sugar cane	0.015	[43]
Sawdust	0.0154	[44]
Cloth-activated carbon	0.15	[45]
Coconut-granular activated carbon	0.11	[46]
Apricot stone-activated carbon	0.11	[47]
Coal-activated carbon	0.15	[48]
Peanut shell-activated carbon	0.74	[49]
Cucumber Peel	0.56	[50]

- For the stability and the reusable of the support is also important, for the activated charcoal mentioned in the table 7, this parameter is not studied. On the other hand, our support was already made, but is not mentioned in this article and the results found are very encouraging. The reusable of the support was studied for 5 cycles with a decrease of efficiency of the 5% of support, after wash of the support with the nitric diluted acid HNO_3 0.1M (it is the désextraction) and the time of désextraction is 7 times is faster than extraction. Which confirms the feasibility of the applied treatment and the rigidity and the mechanical stability of our support.
- For the time of balance, which is a determined factor, we can say that our support gives better yields (efficiencies) in times lower than 40 min, thus is fast, for the study made in table 7, this parameter is not studied.
- For the pH of the solution, our support gives a good yield in a wide range of pH going from 4 to 6 what returns this favorable support.
- For the temperature, our support gives the best yield (efficiency) to ambient temperatures between 20 and 25°C.
- For the mass, our support gives a good yield (efficiency) to lower masses of 0.1 g.

Thus to compare two supports, it is necessary to affect all the parameters which check the process of extraction. What shows that our support has several advantages namely: it is a friendly process of nature, stable, reusable and effective in the low masses, effective at room temperature, profitable in a wide range of pH and give a very good capacity of 82 mg/g, which is close to that of activated charcoal. However, the study of the activated charcoal mentioned in Fig. 7 is not studied several parameters such as: the time of balance, the pH of the solution, the temperature, the mass of the support and the reusable of the support, which returns the comparison in this case difficult.

Symbols

C — Constant (mg/g).
C_e — Pb^{2+} concentration at equilibrium.
K_1 — Pseudo first order constant.
K_2 — Pseudo second order constant.
K_E — Elovich constant.
K_f — Freundlich adsorption constant.
K_{int} — Intra-particle diffusion constant.
K_L — Langmuir constant.
K_T — Temkin constant.
q_e — Equilibrium binding capacity.
q_m — Maximum adsorption capacity (mg / g).
R — Coefficient of linear regression.
β — Constant connected to the adsorption energy.

4. Conclusion

The chemical modification of the *Eucalyptus bark* made it possible to influence the micro structure of the ligno cellulosic material, which leads to a change in the surface functions properties of the material (grafting of the COOH functions). These results were verified by FTIR, Bohemian method and DRX. The adsorption of Pb (II) by eucalyptus bark was evaluated, the best extraction was recorded at pH = 5.5 at a mass of 0.1 g. The extraction equilibrium is reached at about 40 min. The extraction capacity increases with the increasing initial concentration and reaches a value of 82 mg/g. The temperature has a slight influence on the extraction yields. The kinetic measurements show that the process follows pseudo-second order model. The thermodynamic study shows that the process is spontaneous and exothermic.

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