

*Dedicated to Professor Luminița Silaghi-Dumitrescu
on the occasion of her 65th anniversary*

THE USE OF CHEMICALLY ACTIVATED FIR CONE CARBON IN THE REMOVAL OF Pb²⁺ CONTAMINATED AQUEOUS SOLUTIONS

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ABSTRACT. Fir cone biomass was used as a precursor for the preparation of activated carbon by sulfuric acid treatment and activation. It is known that the activated carbon from different biomass sources has a wide range of applications in water treatment. Therefore, fir cone activated carbon (FCAC) was prepared from raw fir cone by chemical treatment and used in various experiments to test its functions for the removal of Pb²⁺. The influences of different parameters like contact time, initial lead concentration, initial pH, biomass quantity and temperature were studied. Adsorption isotherm and kinetic models were used to analyze the equilibrium data. It was found that the Freundlich isotherm model and pseudo-second-order model describe better the Pb²⁺ biosorption process. The changes in morphological structure after lead ions-biomass interactions were evaluated by SEM analysis. From these studies, it can be concluded that the fir cone activated carbon could be a promising and effectively employed bioadsorbent for the removal of Pb²⁺ ions from aqueous solutions.

Keywords: *Fir cone activated carbon, Lead, Biosorption, Isotherms*

INTRODUCTION

Nowadays, the heavy metal pollution has become one of the most serious environmental problems. Unlike organic pollutants, heavy metals are non-biodegradable and so their removal is extremely important regarding the

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health of living specimens [1]. The heavy metal ions are stable and persistent environmental contaminants, since they cannot be degraded and destroyed. These metal ions represent a threat for human health as well for the aquatic ecosystem [2].

Among all the existing metals, Pb^{2+} may be found in wastewaters from many industries involving metal plating, painting, mining operations, battery manufacture and mining operations [3, 4]. Industrialists and environmentalists usually have the challenge of developing safe and effective disposal methods for these wastewaters containing heavy metals [5]. The long term Pb^{2+} exposure may cause several diseases such as: mental disturbance, retardation, semi-permanent brain damage, liver damage and can accumulate in animal tissues such as kidneys [6, 7, 8, 9, 10]. The World Health Organization (WHO) recommends that the amount of Pb^{2+} should be 0.01 mg/L for safe drinking water while the permissible level of Pb^{2+} in wastewater given by the Environmental Protection Agency (EPA) is 0.05 mg/L [11, 12].

Many physico-chemical methods such as extraction, ion exchange, chemical precipitation, membrane filtration, adsorption, and electro dialysis have been developed for the removal of heavy metals from aqueous solutions, but most of these methods have significant disadvantages (high operational costs and high specific consumption of reagent and energy) [13, 14].

Among the methods noted above, biosorption is preferred as a well-organized technique for the removal of heavy metals from aqueous wastes [15, 16]. This biosorption technique has advantages over other conventional methods due to its unique properties, such as simple design, the use of non-toxic and low cost materials, and the high efficiency in removing pollutants at low level concentrations, fast operation and favorable performance [17].

The biosorption with activated carbon is widely used to remove contaminants in water treatment processes because of its huge specific surface area, heterogeneous surface and well-developed pore structures [18, 19]. One of the major advantages of using activated carbon is that many water treatment and remediation facilities already have granular activated carbon (GAC) filtration systems in place [20].

The removal of heavy metals from aqueous waters using different biomasses [21] such as waste tea leaves [13], orange peel [14], hazelnut shell sago [22], sawdust [23], waste banana, orange peels [24], cocoa shells [25], coffee residue [26], rice husk [27], olive stone waste [28], grape stalk [29] as well as modified papaya seed [30] were also reported to have good biosorption abilities for Pb^{2+} but the potential of other waste agricultural by-products after chemical modification is yet to be entirely explored [31].

Wood products, especially products of fir wood have been treated using different kinds of chemical solutions to improve their surface properties, mechanical strength, chemical resistance and the ability to incorporate organic and inorganic compounds. Many of the recent studies show that these methods

have been applied for wood materials used as bioadsorbents for the removal of heavy metals [32]. Frequently, activated carbon surfaces are modified by oxidation, acidic treatment, ammonization or heating to enhance the biomass adsorption capacity [33, 34].

The main objective of the present work is to investigate the potential biosorption of the FCAC prepared by sulfuric acid treatment and activation from the fir cone biomass. The influence of contact time, initial Pb²⁺ concentration, initial pH, biomass quantity and temperature were investigated in detail. SEM microscopy studies were also used for the extensive characterization of the biomass surface morphology. This study also evaluates the use of the FCAC as a new, low cost and effective bioadsorbent material for the removal of Pb²⁺ from aqueous solutions.

RESULTS AND DISCUSSION

Biosorption experiments

SEM analysis

The SEM micrographs of FCAC carbon samples, before and after the Pb²⁺ biosorption, are given in Fig. 1. SEM enables a direct observation of any surface microstructure changes in the samples that would have occurred due to the biosorption of Pb²⁺. Some slight differences at the micrographs are noticeable. The number and shape of cracks and attached fine particles over the carbon surface clearly differ before (Fig. 1a) and after biosorption (Fig. 1b). A minor decrease in the size of the particles after biosorption is visible.

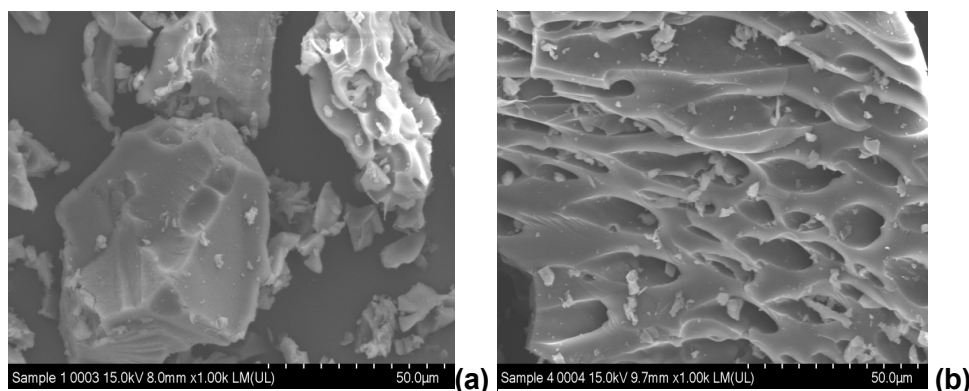


Figure 1. Scanning electron microscope (SEM) images of the (a) unloaded FCAC and (b) FCAC loaded with Pb²⁺.

The effects of contact time and initial Pb^{2+} concentration

The effects of contact time and initial concentration on biosorption of Pb^{2+} by FCAC are presented in (Fig. 2). The amount of Pb^{2+} adsorbed increased with the increase in contact time and reached equilibrium in about 240 min. The equilibrium time is independent of initial Pb^{2+} concentration, but in the first 20 min, the initial rate of biosorption was greater for higher initial Pb^{2+} concentration. After that, it gradually decreases until equilibrium is reached. The rate of percent metal removal is higher at the beginning due to the large number of biosorption sites available and high surface area of the FCAC, while towards the end of the experiment fewer sites are available for biosorption. Therefore an equilibrium time of 240 min was assumed for all further experiments.

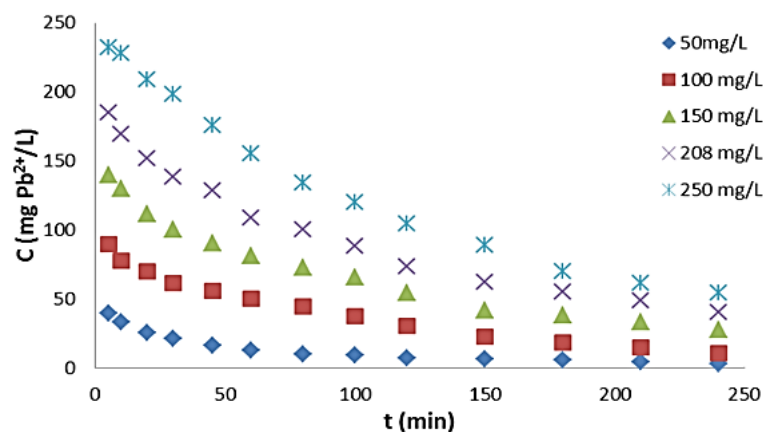


Figure 2. The effect of contact time and initial concentration on the biosorption of Pb^{2+} on FCAC; pH = 5.0, $d = 150 - 300 \mu m$, 296 K, 0.5 g biomass, 200 rpm.

The effect of initial Pb^{2+} concentration on the adsorption capacity was analyzed within the range of 50-250 mg/L. Fig. 3 shows that the adsorption capacity increases with an increase of lead concentration. The increase in adsorption capacity occurs due to the higher biosorption rate and the utilization of all the available active sites for biosorption at higher heavy metal concentration. Moreover, higher initial concentration provides increased driving force to overcome all mass transfer resistance of lead ions between aqueous and solid phase. It was noted that initial concentration increased the sorption of Pb^{2+} as is generally expected due to the equilibrium process. A further increase in the initial metal ion concentration does not lead to any other modifications in the adsorption capacity.

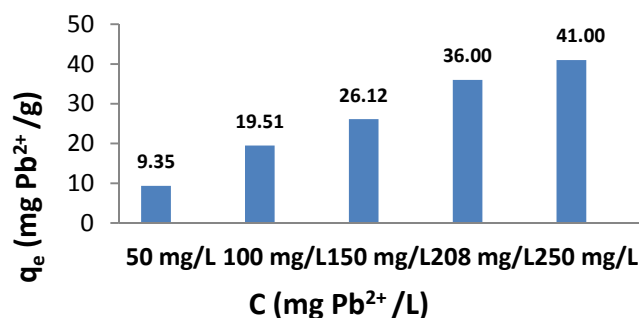


Figure 3. Influence of the initial Pb²⁺ concentration over the adsorption capacity of FCAC; 0.5 g biomass, $d = 150 - 300 \mu\text{m}$, 296 K, pH 5.0, 200 rpm.

The effects of biomass quantity

The amount of the FCAC added to the metal solutions varied between 0.1 and 0.5 g, while the total volume, initial concentration of the metal solution, temperature and the pH value were kept constant. The result of variation of biosorption removal with quantity of FCAC is shown in (Fig. 4). The amount of Pb²⁺ biosorption increased with an increase in bioadsorbent quantity. This result can be explained by the fact that for optimum biosorption, extra sites must be available for biosorption reaction, whereas by increasing the biomass of the already available sites for biosorption, the site increased. However, a further increase of the bioadsorbent quantity did not lead to better results in the removal efficiency values at these experimental conditions; therefore, the optimum biomass was taken as 0.5 g for further batch experiments.

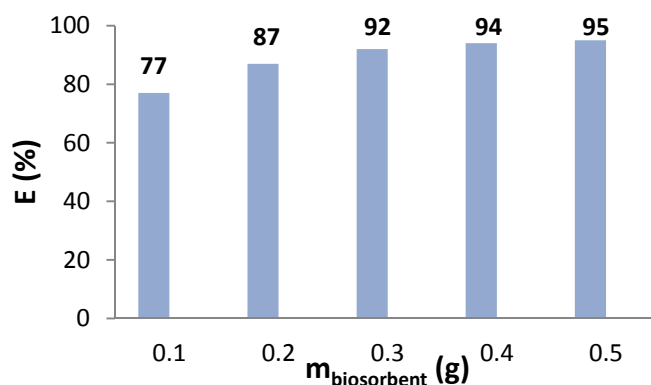


Figure 4. The effect of the FCAC quantity on Pb²⁺ biosorption over the removal efficiency; C_i = 50 mg Pb²⁺/L, 296 K, $d = 150 - 300 \mu\text{m}$, 5.0 pH, 296 K and 200 rpm.

The effect of initial pH of solution

The effect of initial pH of solution is an important factors in biosorption studies, which controls the biosorption process, particularly, the adsorption capacity and removal efficiency [35]. The effect of the pH on the amount of lead removed from the solution was assessed by performing experiments in acid/base pH scale and the results are shown in Fig. 5. The results point out that lead removal was 90.73% at initial pH of 2.0, which increased to 94.56% at initial pH 5.0. An appreciable decrease in percentage removal of Pb^{2+} was observed after pH 5.0. At lower pH values, the removal of Pb^{2+} was inhibited as a result of competition between hydrogen and metal ions on the sorption sites. Thus, the electrostatic repulsive forces between positively charged H_3O^+ and Pb^{2+} ions inhibited the Pb^{2+} removal at lower pH. As pH is increased, the active sites on the adsorbents are exposed to increasing negative charge density on the surface and the resultant is an increasing attraction of metal cation onto the surface. Consequently, an initial pH value of 5.0 was used as the optimum pH throughout the experimental work to avoid the formation of metal hydroxides.

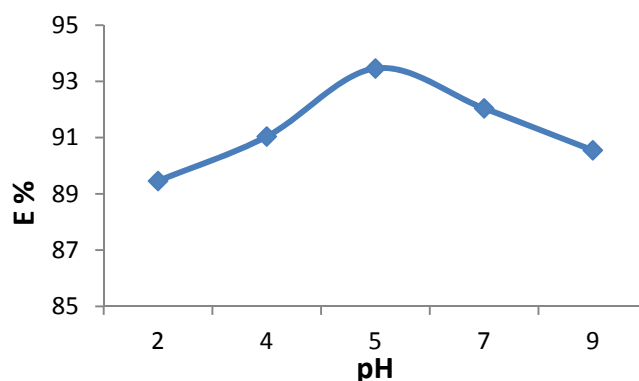


Figure 5. The effect of initial pH values on Pb^{2+} biosorption using FCAC; $C_i = 50 \text{ mg } Pb^{2+}/L$, 0.5 g biomass, $d = 150 - 300 \text{ }\mu\text{m}$, 296 K and 200 rpm.

The effects of temperature

The amount of Pb^{2+} adsorbed on FCAC as function of solution temperature is shown in Fig. 6. As the figure shows, the removal efficiency decreased as the temperature increased from 23 to 53°C, showing that low temperature favors the Pb^{2+} removal from aqueous solutions. It was observed that the maximum biosorption was found at 23°C with a maximum removal percentage of 94%. The observed increase in biosorption of Pb^{2+} with decrease

in temperature is indicative of the fact that the biosorption process is exothermic in nature. The general trend in decrease of biosorption for FCAC with an increase in temperature may be attributed to the Pb²⁺ escaping from the solid phase with a rise in temperature. The optimum temperature of 23°C was used for all further experiments.

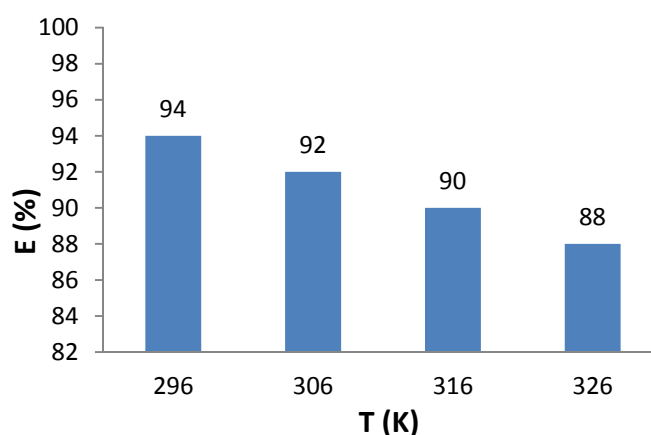


Figure 6. Temperature influence over the removal efficiency of Pb²⁺ on FCAC $C_i=50$ mg Pb²⁺/L, $d=150 - 300$ μ m, 0.5 g biomass, 5.0 pH, 296 K and 200 rpm.

Adsorption isotherms

Isotherm equations have been used for the equilibrium modeling of adsorption systems. The adsorption data have been subjected to different adsorption isotherms, namely; Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Temkin required for Pb²⁺ biosorption from simulated wastewaters onto FCAC.

The Freundlich isotherm assumes that adsorption takes place on a heterogeneous surface which involves a multilayer adsorption of metal ions. The Freundlich isotherm linear equation can be expressed as [36]:

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

where, K_F is related to the adsorption capacity and n is related to the intensity of adsorption. The $\log q_e$ versus $\log C_e$ plot allows the determination of the Freundlich constants.

The Langmuir isotherm model describes the monolayer adsorption onto the surface of an adsorbent with finite number of identical sites and is the most widely used isotherm for adsorption studies in recent years. The linear form of the Langmuir isotherm model [37] can be represented by:

$$\frac{1}{q_e} = \frac{1}{q_m b} \times \frac{1}{C_e} + \frac{1}{q_m} \quad (2)$$

where, C_e (mg/L) is the equilibrium concentration, q_e is the amount of metal ion adsorbed at equilibrium, q_m is the maximum adsorption capacity and b is the equilibrium Langmuir constant.

The Freundlich constants n and K_F , Langmuir constants b and q_m , and their corresponding correlation coefficients, R^2 are given in Table 1.

The adsorption constants were calculated for concentration ranges between 50 and 250 mg/L the results are presented in Table 1. Based on the correlation coefficients (R^2), it is clear that the biosorption of lead ions onto FCAC is best fitted to the Freundlich adsorption isotherm for the entire range of concentrations. The fact that the Freundlich isotherm fits the experimental data very well may be due to heterogeneous distribution of active sites on the carbon surface, since the Freundlich equation assumes that the surface is heterogeneous.

The n value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if $n = 1$, then adsorption is linear; if $n < 1$, then adsorption is a chemical process; if $n > 1$, then adsorption is a physical process. The values of n for Freundlich isotherm were found to be greater than 1, which indicates that the adsorption system is a favorable one and suggesting physical adsorption.

The Temkin isotherm equation assumes that the fall in the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy [38]. The Temkin isotherm has been applied in the following form:

$$Q_e = B \ln A_T + B \ln C_e \quad (3)$$

$$B = \frac{RT}{b_T} \quad (4)$$

where, b_T is the Temkin isotherm constant, T is the absolute temperature in Kelvin and R is the universal gas constant (8.314 J/mol K). The model constants A_T and B are determined by the linear plot of q_e versus $\ln C_e$. The Temkin isotherm assumes that the heat of adsorption of the molecules in a layer decreases linearly due to adsorbent-adsorbate interaction and that the binding energies are uniformly distributed. The Temkin constants are presented in Table 1.

The Dubinin–Radushkevich (D–R) model is given by [39]:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{5}$$

where, q_e is the whole amount of metal ions adsorbed on per unit weight of biomass (mol/g), q_m is the maximum adsorption capacity (mol/g), β is the activity coefficient related to biosorption mean free energy (mol²/J²) and ε is the Polanyi potential. This energy E is determined by the following equation [40]:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{6}$$

The isotherm constants q_m and β were obtained from the intercept and the slope of the plot $\ln q_e$ vs. ε^2 . It is known that the magnitude of apparent adsorption energy E is useful for estimating the type of adsorption and, if this value is below 8 kJ/mol, the adsorption type can be explained by physical adsorption, between 8 and 16 kJ/mol, the adsorption type can be explained by ion exchange, and, over 16 kJ/mol, the adsorption type can be explained by a stronger chemical adsorption than ion exchange [41, 42]. The values of E are found to be below 8 kJ/mol (Table 1) which correspond to physical adsorption [43].

Table 1. Langmuir, Freundlich, Dubinin-Radushkevich and Temkin calculated coefficients using linear regression analysis for Pb²⁺ removal using FCAC; C_i = 50-250 mg/L, 0.5 g biomass, d = 150 – 300 μm, 296 K, pH 5.0, 200 rpm.

Langmuir			Freundlich		Dubinin-Radushkevich			Temkin			
K _L (L/mg)	q _{max} (mg/g)	R ²	n	K _F (mg ^(1-1/n) L ^{1/n} /g)	R ²	β (mol ² /kJ)	E (kJ/mol)	R ²	A _T (L/g)	B (J/mol)	R ²
10.01	48.54	0.981	1.70	4.76	0.997	2×10 ⁻⁵	5	0.885	2.89	2×10 ⁻⁶	0.807

Adsorption kinetics

The adsorption kinetics is one of the most important data in understanding the mechanism of the adsorption and in assessing the performance of the adsorbents. Different kinetic models including pseudo-first-order [44] and pseudo-second-order [45] were applied for the experimental

data to predict the adsorption kinetics of Pb^{2+} . The linear form of the pseudo-first-order and pseudo-second-order rate equation is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (8)$$

where, q_t and q_e (mg/g) are the amounts of the adsorbed lead ions at equilibrium time (mg/g) and t (min), respectively and the values of k_1 (min^{-1}) and k_2 (g/mg min) are the adsorption rate constants of the pseudo-first-order and pseudo-second-order models.

The experimental value of solid phase concentration of adsorbate at equilibrium ($q_{e,exp}$) and the calculated value of solid phase concentration of adsorbate at equilibrium ($q_{e,calc}$) for the pseudo-first-order and pseudo-second-order models are also presented in Table 2. The $q_{e,exp}$ and the $q_{e,calc}$ values from the pseudo-second-order kinetic model are very close to each other, and also the calculated coefficients of determination, R^2 are also closer to unity for pseudo-second-order kinetics than that for the pseudo-first-order kinetics. Therefore, the adsorption kinetic could be approximated more favorably by pseudo-second-order kinetic model for the biosorption of Pb^{2+} by FCAC.

Table 2. Pseudo-first-order and pseudo-second-order rate constants, calculated and experimental q_e values for Pb^{2+} removal by FCAC biomass using different initial concentrations; $C_i = 50\text{-}250$ mg/L, $d = 150 - 300$ μm , 0.5 g biomass, 296 K, pH 5.0, 200 rpm.

C (mg/L)	q_e (exp) (mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1 (1/min)	q_e (calc) (mg/g)	R^2	k_2 (g/mg·min)	q_e (calc) (mg/g)	R^2
Fir cone activated carbon							
50	9.35	1.01×10^{-2}	0.002	0.6625	1.98×10^{-2}	9.40	0.999
100	19.51	1.75×10^{-2}	0.066	0.9356	5.4×10^{-3}	19.54	0.994
150	26.12	1.96×10^{-2}	1.216	0.9048	1.9×10^{-3}	26.22	0.994
200	36.00	1.82×10^{-2}	1.343	0.8788	3.8×10^{-3}	37.00	0.997
250	41.00	1.94×10^{-2}	1.576	0.8994	1.5×10^{-3}	40.87	0.998

Desorption experiments

In wastewater treatment, the regeneration and reusability of the bioadsorbent material is very important from an economic point of view, and it also helps to protect the environment and recycling of adsorbate (Pb^{2+} ions) and bioadsorbent (fir cone activated carbon). The biosorption-desorption

processes were repeated consecutively to designate the reusability of the fir cone. The biosorption process was performed under the optimal batch conditions previously determined. Also, desorption studies help in process design systems by giving information on the mechanism and recovery process of the adsorbates from industrial wastewater and the bioadsorbent. In the present work, different concentrations of HCl (0.1, 0.2, 0.3 and 0.4 M) as stripping agents were used for the desorption studies. The experiments were performed in order to determine the optimum concentration of the HCl solution and to attained the maximum desorption efficiency. The desorption process were repeated three times consecutively and the biosorption-desorption efficiencies of FCAC after each cycle were determined separately (Fig. 6). It can be observed that the desorption rate decreases with the increase in HCl concentration, where at concentration of 0.1 M, more than 80% were desorbed from FCAC. This can be explained by the fact that low concentration acidic treatment activates and opens the pore spaces in the surface of the bioadsorbent [46, 47]. Further biosorption-desorption cycle experiments can be performed in order to show the reusability by saturation of FCAC with Pb²⁺ ions at each cycle.

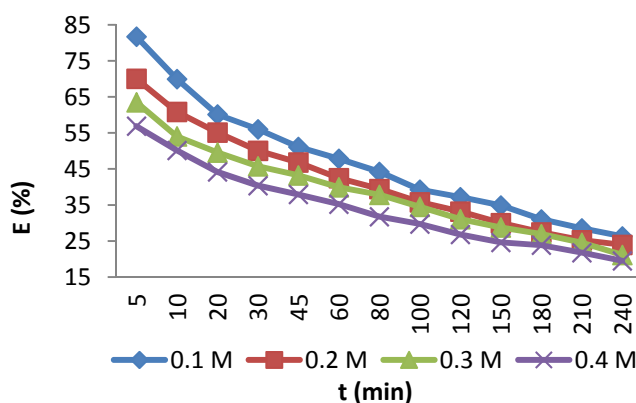


Figure 6. Desorption of Pb²⁺ ions from FCAC; C_i=50 mg Pb²⁺/L, d =150 – 300 μm, 0.5 g biomass, 5.0 pH, 296 K and 200 rpm.

CONCLUSIONS

This study presented the results obtained at Pb²⁺ ions biosorption where the fir cone biomass was used as a precursor for the preparation of fir cone activated carbon (FCAC) by sulfuric acid treatment and activation. The biosorption of Pb²⁺ on FCAC was found to be depending on factors such as initial pH, bioadsorbent quantity, initial lead concentration and temperature.

The following important results can be mentioned:

- pH 5.0 was deduced as optimum for the removal of Pb²⁺ for the FCAC biomass.
- Following the biosorption process, a contact time of 240 min was necessary to reach equilibrium, depending on lead ions initial concentration.
- The biosorption rate increased with increasing bioadsorbent quantity and decreased with increasing of Pb²⁺ ion concentration.
- Equilibrium was best described by Freundlich isotherm model (R²= 0.9971).
- The maximum adsorption capacity obtained from Langmuir model was 48.54 mg/g.
- From the values of activation energy of the process calculated according to Dubinin-Radushkevich and Temkin models, it is suggested that biosorption of Pb²⁺ by FCAC biomass is physical in nature.
- Kinetic study showed that the biosorption follows pseudo-second-order kinetic model.
- The biosorption is favorably influenced by a decrease in temperature of the operation.
- Desorption experiments showed that more than 80% can be desorbed at 0.1 M concentration of HCl.

In conclusion, the experimental results entail that the FCAC is a reasonably good, low cost and promising bioadsorbent for the efficient removal of Pb²⁺ from contaminated aqueous media.

EXPERIMENTAL SECTION

Preparation of biomass

Fir tree (*Abies alba*) cones were obtained from a botanical garden in Cluj-Napoca, Romania. The cones were washed to remove impurity such as sand and leaves, and then the washed cones were dried at 105°C for 24 h. The scales on the cones were then removed and crushed using a bead mill. Prior to being used, the fir cone biomass was washed with distilled water several times until it yielded colorless filtered water. The dried fir cone biomass were then soaked in concentrated sulphuric acid (98%) at 1:1 (W:V) ratio for 48 h at normal temperature and pressure. After treatment, the reaction product was soaked in 1% sodium bicarbonate solution overnight

(for neutralization) and washed with distilled water again until a neutral pH. The samples were then carbonized in a Muffle furnace at 600°C and at a heating rate of 10°C and held at this temperature for 1 h. The prepared FCAC material was sieved (150 – 300 µm) and used as bioadsorbent for the removal of Pb²⁺ from aqueous solutions.

Preparation of Pb²⁺ solutions

The stock solution of 1000 mg/L was prepared by dissolving Pb(NO₃)₂ in deionized water. Pb²⁺ solutions of different concentrations in range between 50-250 mg/L were prepared by serial dilution of the stock solution using deionized water. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with 0.1 M KOH or 0.1 M HCl. All chemicals used during the experiments were of analytical grade.

Biosorption experiments

Batch biosorption experiments were carried out in conical Erlenmeyer flasks containing 100 mL of Pb²⁺ solutions. The flasks with bioadsorbent quantity of 0.5 g were stirred at 200 rpm, 23°C and pH 5.0. In order to establish the evolution of the removal process, samples of 500 µL were collected at different time intervals (0-240 min). The collected samples at predetermined time intervals were filtered (ME cellulose 0.45 µm microfilter) and the remaining concentration in aqueous phase was determined using an Atomic Absorption Spectrometer (SensAA Dual GBS Scientific Equipment, Australia).

In order to evaluate the amount of lead ions retained per unit mass of biomass, the adsorption capacity and efficiency was calculated using the following equations:

$$E, (\%) = \frac{C_i - C_f}{C_i} \cdot 100 \quad (9)$$

$$q_t (\text{mg/g}) = \frac{(C_i - C_f) \cdot V}{m} \quad (10)$$

where E , (%) represents the efficiency, C_i and C_f the initial and final concentration of lead (mg/L) in the aqueous solution, the q_t (mg/g) represents the amount of lead ions adsorbed onto unit weight of biomass, V (L) means the volume of lead ions in aqueous solution and m (g) the bioadsorbent quantity.

In order to study the pH influence over the biosorption process, the initial pH was adjusted using 0.1 M HCl and 0.1 M KOH solutions. The relationship between temperature and removal efficiency values for Pb²⁺ biosorption were established and performed at different temperatures (296, 306, 316 and 326 K) using a thermostat water bath. All the experiments were repeated three times, the values presented were calculated using averaged concentration values.

Desorption experiments

In order to consider the practical use fullness of the bioadsorbent, desorption experiments were performed. For the desorption study 0.5 g biomass was contacted with 100 mL of Pb²⁺ solution (50 mg/L). After the biosorption test, the biomass was collected by filtration and washed with deionized water two times to remove excess Pb²⁺ residual on the surface. Then, it was treated with 100 mL of 0.1, 0.2 0.3 and 0.4 M HCl each and stirred at 200 rpm for 240 min and 23°C. Supernatants were collected and Pb²⁺ analysis were done. For the best eluent, the biosorption and desorption steps were repeated three times. All of the experiments were carried out in duplicate and the average values were used in the calculations.

Scanning electron microscopy (SEM) analysis

Scanning electron microscopy is utilized for characterizing surface microstructures, porosity and fundamental physical properties of different adsorbents. The surface morphology of FCAC was determined using a scanning electron microscope JEOL JSM 5510 LV (Japan). Prior to the analysis, the bioadsorbent samples were mounted on a stainless stab with a double stick tape. Then they were coated with a thin layer of gold under vacuum to improve electron conductivity and image quality.

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