Bioadsorption of Pb^{2+} and Cu^{2+} on Eucalyptus Camaldulensis Leaves

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Abstract— Herein, the efficiency of Eucalyptus camaldulensis leaves as biosorbent for lead and copper was investigated. The particle size distribution was determined by Granulometric analysis and the functional groups were identified by FT-IR spectroscopy. The effects of contact time, pH and initial metal ions concentration were investigated. The experimental kinetic data were well fitted by the pseudo-second order kinetic model and Langmuir isotherm with a maximum adsorption capacity up to 71 mg g^{-1} and 37 mg g^{-1} for Cu^{2+} and Pb^{2+} respectively. The selectivity was examined in a binary ions solution where the adsorbent showed preference for lead over copper.

Keywords— Biosorption, Eucalyptus leaves, copper, lead.

I. INTRODUCTION

Access to clean water is essential for the development of any country. Currently, many water resources are contaminated due to the direct discharge of domestic and industrial wastewater [1]. Contrary to organic pollutants, heavy metals are more dangerous since they are not biodegradable and thus persist in nature. The latter cause heavy metals transformation to the food chain through their accumulation by plants and animals which leads to several toxic health effects [2]. The ingestion of copper, zinc, cadmium, lead, mercury, iron and nickel in amounts exceeding guidelines damages severely human physiology [3]. Several treatment techniques for heavy metals removal from wastewater have been reported in literature [4]. Chemical precipitation, ion exchange and adsorption are among these methods are. For low metal ions concentrations in wastewater, adsorption is recommended for their removal. It is advisable that the adsorbent is available in large quantities, easily regenerable, and cheap [5]. Biosorption of heavy metals from aqueous solutions has proven very promising. Materials derived from low-cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions [6]. The major advantages of biosorption over conventional treatment methods include: low-cost; high efficiency; minimization of chemical sludge; and the possibility of metal recovery [7]. The cost advantage of this technology would guarantee a strong penetration of the large market of heavy metal polluting industries. Several studies have shown that non-living plant biomass materials are effective for the removal of trace metals from the environment [8].

Eucalyptus tree is one of the most widely distributed trees in most of arid and semiarid areas. This kind of tree exists in Lebanon. Accordingly, the objective of this study is to investigate the adsorption potential of Eucalyptus leaves for the removal of Cu^{2+} and Pb^{2+} from wastewater within various experimental conditions.

II. MATERIALS AND METHODS

2.1. Adsorbent preparation

Eucalyptus camaldulensis leaves were collected from Bekaa-Lebanon. The leaves were thoroughly rinsed with water to remove impurities like soluble materials and dust then dried in the oven at 50 ⁰C for 48 hours. The dried Eucalyptus leaves were then grinded to fine powder.

2.2. Characterization of the Eucalyptus leaves

The granulometric analysis was done to the grinded leaves in order to determine size distribution before and after modification using Partica LA-950V2 Horiba. The functional groups were identified by Fourier Transform Infrared (FTIR) Spectroscopy in the range of 4000–400 cm-1. The samples were first mixed with KBr and then pressed into pellets and analyzed with FT-IR – 6300 JASCO.

2.3. Batch adsorption tests

Lead and copper solutions were prepared from the corresponding nitrate salts in distilled water to obtain solutions of different concentrations. The pH of the solution was adjusted using 0.1M HNO_3 and 0.1M NaOH solution. In typical batch studies, 0.5 g of eucalyptus leaves powder was placed in a flask containing 50 mL of a metal solution with the desired concentration. The flask was continuously stirred at room temperature (25 ± 2ºC),

except where the effect of temperature was being investigated, at 250 rpm for 180 min. At the end of each step the solution was filtered and the metal ion concentration was determined for each metal using Atomic Adsorption Spectrophotometer (RAYLEIGH WFX-210) equipped with Automatic hollow cathode lamp changeover and air–acetylene burner. The equilibrium time was determined as the contact time required for the metals in the solution to reach equilibrium. The lead adsorption percentage was calculated by equation (1):

$$R = \frac{C_0 - C_t}{C_0} \times 100$$

where R is the adsorption rate (%), C_0 is the initial concentration and C_t is the concentration at time t. The adsorption capacity of the adsorbent at equilibrium was calculated by equation (2):

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

Where qe is the equilibrium adsorption capacity in mg g^{-1}, C_0 is the initial concentration and C_e is the concentration at equilibrium, V is the volume in L of metal solution and m is the mass in g of the adsorbent. For obtaining the isotherms, the batch experiments the initial metal ions concentrations were varied between 50 mg L^{-1} and 500 mg L^{-1}. The solutions were then filtered by a 0.45 μm nylon syringe filter and the remaining metal ions were measured by AAS in order to calculate Ce and qe.

III. RESULTS AND DISCUSSION

3.1. Granulometric analysis

Fig. 1.a shows the size distribution of the grinded powder of Eucalyptus leaves. The obtained results showed two particle distribution populations with average diameter 14.5 and 115 μm.

3.2. FT-IR spectroscopy

The obtained spectra for Eucalyptus leaves are shown in Fig. 1.b. The peak between 3400–3200 cm^{-1} is due to OH stretch. At 2925 cm^{-1}, the peak could be assigned to C-H stretching vibration. The absorption peak at 1750 cm^{-1} is characteristic to -COOH group and that at 1647 cm^{-1} can be attributed to HN$_2$ bending vibration. The C-N stretching vibration is at 1318 cm^{-1}, while C-O stretch is at 1032 cm^{-1}. The peak at 886 cm-1 and 646 cm^{-1} may be caused by C-H –CH$_2$ bending. The peak at 500-473 cm^{-1} is attributed to polysulfide (S-S stretch).

3.3. Effect of pH on Pb^{2+} and Cu^{2+} adsorption

Fig. 2 shows the adsorption capacity of Eucalyptus leaves as a function of pH. The obtained adsorption capacities were high over the studied pH range (between 2 and 8);
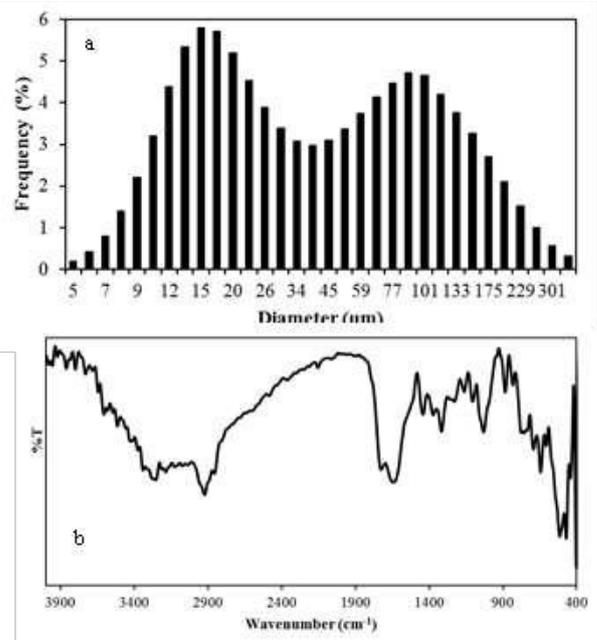

Fig. 1: Particle size distribution (a) and FT-IR spectrum (b) of Eucalyptus leaves.

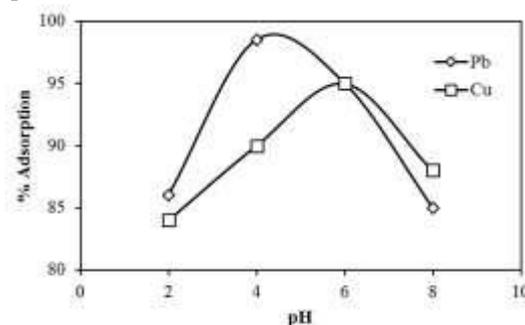However, the maximum adsorption capacity for Pb^{2+} was at pH = 4 and at 6 for Cu^{2+}.

Fig. 2: Effect of pH on metal ions biosorption ((m)/(V) = 0.5/50 mg mL^{-1}, at 25ºC, 300 rpm and [M^{2+}] = 50 ppm).

3.4. Adsorption Kinetic models

3.4.1. Pseudo-first order

The pseudo first-order kinetic model is expressed as follows:

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

Where q_t and q_e are the quantity of metal ions adsorbed (mg g^{-1}) at time t (min) and at equilibrium respectively, and k_1 is the rate constant of adsorption (min^{-1}). The plot of ln (q_e - q_t) versus t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively [9].

3.4.2. Pseudo-second order

The pseudo-second-order sorption rate is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where k_2 is the pseudo-second order rate constant (g mg^{-1} min^{-1}), q_t and q_e are the quantity of metal ions adsorbed at

t time and at equilibrium (mg g^{-1}) respectively. A plot of t/q_t versus t should yield a straight line from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively [10].

Lead and copper adsorption as a function of contact time is illustrated in Fig. 3.a. Equilibrium was reached within the first 30 min for both metal ions which indicates the high affinity of the adsorbents towards them. The kinetic parameters as well as the correlation coefficients (R²) and the experimental equilibrium capacities are reported in Table 1. The obtained results show that Pb^{2+} and Cu^{2+} adsorption on Eucalyptus leaves followed the pseudo-second order kinetic model (Fig. 3.b). This suggests that the adsorption rate depends mainly on the interaction between different functional groups present on the leaves and the metal ions.

Table.2: Comparison of Langmuir and Freundlich models for Me^{2+} adsorption on Eucalyptus leaves

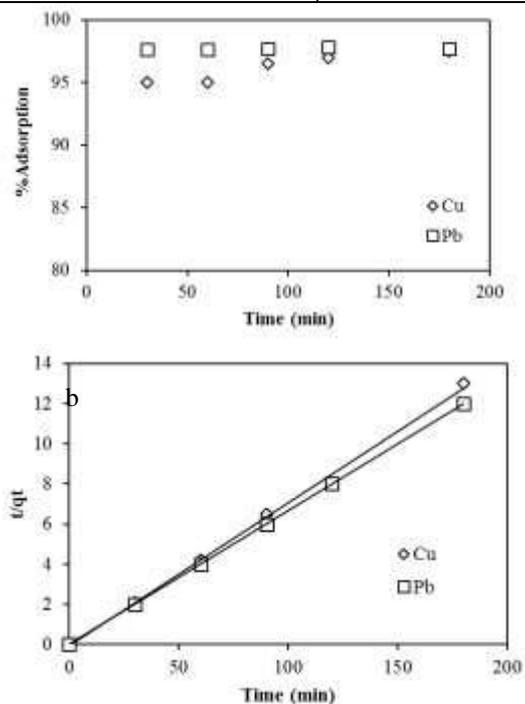| Me^{2+}	Langmuir model			Freundlich model		
	q^{exp}_{max}	K_L	R^2	n	K_f	R^2
Cu^{2+}	71	0.02	0.875	1.46	2.15	0.996
Pb^{2+}	37	0.06	0.988	2.3	4.5	0.983

Fig.3: biosorption of M^{2+} as a function of time (a) and pseudo-second-order model (b) ((m)/(V) = 0.5/50 mg mL^{-1}, at 25ºC, 300 rpm and [M^{2+}] = 50 ppm)

3.5. Adsorption Isotherms
Langmuir Isotherm:

Table.1: Comparison of the first and the second order kinetic models

Eucalyptus leaves						
	First order kinetic model			Second order kinetic model		
qe ^{exp}	k_1	qe^{cal}	R^2	k_2	qe^{cal}	R^2
Cu^{2+} 14.3	0.023	13	0.949	0.087	14.7	0.999
Pb^{2+} 15	0.009	15.6	0.948	0.514	14.7	0.999

Langmuir Isotherm is a model that assumes monolayer coverage of a finite number of identical sites present on the surface such that no further adsorption takes place.

Based on these assumptions, Langmuir represented the following equation [11]:

$$q_e = \frac{K_L \times q_{max}\ C_e}{1 + K_L C_e}$$

where q_{max} is the maximum adsorption capacity (monolayer coverage), i.e. mmol of the adsorbate per (g) of adsorbent and K_L is Langmuir isotherm constant. The adsorption parameters of Langmuir model can be determined from its linear form by sketching C_e/q_e versus C_e so that the values of q_{max} and K_L can be calculated from the slope and intercept of the linear plot respectively:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$$

Freundlich Isotherm:

This model describes the non-ideal and reversible adsorption, not limited to monolayer formation. It can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over a heterogeneous surface [12]. The equation is expressed as follows:

$$q_e = K_f C_e^{1/n}$$

Where K_f is Freundlich isotherm constant (mmol g^{-1}) and n is the adsorption intensity. The linear form:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e$$

The theoretical fittings for the experimental data are shown in Fig. 4 and the calculated parameters are shown in Table 2. The linear regression correlation coefficients R^2 show that the equilibrium data could be well interpreted by the Langmuir isotherm with maximum adsorption capacity q_{max} equals to 71 mg g^{-1} and 37 mg g^{-1} for Cu^{2+} and Pb^{2+} respectively.

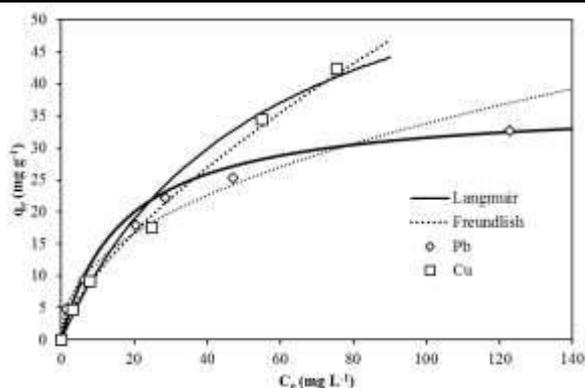*Fig. 4: Langmuir and Freundlish fit for the experimental points((m)/(V) = 0.5/50 mg mL^{-1}, at 25ºC, 300 rpm and [M^{2+}] = 50-500 ppm)*

3.6 Selectivity for Pb^{2+}/Cu^{2+} in binary ions solution

The competition in binary solutes was obtained by testing the adsorption capacity of the adsorbent in a mixed solution containing both lead and copper ions (both at 50 ppm). Figure 5 shows the adsorption percentages of these two metals. Eucalyptus leaves showed preference for lead over copper and this could be explained by the smaller size of hydrated lead ions.
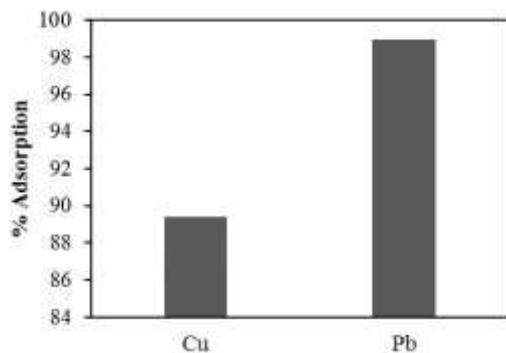

Fig. 5: Selectivity of Eucalyptus leaves in a binary metal ions solution ((m)/(V) = 0.5/50 mg mL^{-1}, at 25 ºC, 300 rpm and [M^{2+}] = 50-500 ppm).

IV.   CONCLUSION

In this study, the biosorption of lead and copper on Eucalyptus leaves was studied. The adsorption capacity was high at different pH values. The adsorption process followed the pseudo second order kinetic model. The maximum adsorption capacity was determined from Langmuir isotherm. The adsorbent was selective for lead in a binary metal solution containing both lead and copper.

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