RESEARCH ARTICLE Am. J. PharmTech Res. 2014; 4(5) ISSN: 2249-3387

AMERICAN JOURNAL OF
PHARMTECH RESEARCH
Journal home page: http://www.ajptr.com/

Removal of Lead (II) ions from waste water using Lebanese *scabiosaprolifera* (Carmel Daisy) as adsorbent

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ABSTRACT

Lebanese *scabiosaprolifera*(Carmel Daisy) was used to remove Pb (II) free ions from aqueous solutions. The adsorption process was found to be dependent on pH, Temperature, contact time, adsorbent dose and concentration. The maximum adsorption capacity was obtained at pH 5 after 1 hour at 25°C. Langmuir and Freundlich isotherms were employed to interpret the adsorption behavior, with a better fit to Langmuir. This adsorption is a spontaneous process with applicability to pseudo second order kinetic model. It was concluded that *scabiosaprolifera* is an effective, low cost and environmentally friendly adsorbent.

Keywords: *scabiosaprolifera*, Adsorption, Isotherms, Kinetics

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Received 27 July 2014, Accepted 13 August 2014

Please cite this article in press as: Hijazi A *et al.*, Removal of Lead (II) ions from waste water using Lebanese *scabiosaprolifera* (Carmel Daisy) as adsorbent American Journal of PharmTech Research 2014.

INTRODUCTION

The term heavy metals refers to metals and metalloids having densities greater than 5 g.cm^{-3} and is usually associated with pollution and toxicity although some of these elements (essential metals) are required by organisms at low concentrations[1].Heavy metals are toxic for the environment and belong to the most important groups of water pollutants. The potential harmful effects associated with the accumulation of heavy metals in the environment are well known. The toxic effects on human populations and potential health hazard have been extensively studied[2]. Heavy metal toxicity and the danger of their bioaccumulation in the food chain represent one of the major environmental and health problems of our modern society. Primary sources of pollution is from the burning of fossil fuels, mining and melting of metallic ferous ores, municipal wastes, fertilizers, pesticides, and sewage sludge. The most common heavy metal contaminants are: Cadmium (Cd), Chromium (Cr), Copper (Cu), Mercury (Hg), Lead (Pb), Nickel (Ni) and Zinc (Zn)[1]. New line Lead : New line Lead is one such heavy metal with specific toxicity and cumulative effects. The chief sources of lead in water are the effluents of lead and lead processing industries. Lead is also used in storage batteries, insecticides, plastic water pipes, food, beverages, ointments and medicinal concoctions for flavoring and sweetening[3].Lead poisoning causes damage to liver, kidney and reduction in hemoglobin formation, mental retardation, infertility and abnormalities in pregnancy. Chronic lead poisoning may cause three general disease syndromes:(a) Gastro intestinal disorders, constipation, abdominal pain, etc.(b) Neuromuscular effects (lead lapsy) weakness, fatigue muscular atrophy.(c) Central nervous system effects or CNS syndrome that may result to coma and death[4].The conventional methods used to remove toxic cations and anions from wastewaters are membrane techniques (reverse osmosis, nanofiltration, etc.), oxidation/precipitation (hydroxides, sulfides, etc.), coagulation and flocculation, ion-exchange, adsorption by activated carbon.[5] However, these methods have certain disadvantages such as incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal[5].Adsorption has proved to be a promising technique because of the ease of operation and comparable low cost of application in treatment process. Even though the most promising adsorbent for adsorption is activated carbon due to a high surface area, it has high operation costs[6]. Therefore, there is a growing need to find an efficient, low cost and locally available material for the removal of lead ions due to their high toxicity. *Scabiosaprolifera* (Carmel Daisy) has been utilized as an adsorbent for the removal of Pb (II) from aqueous solutions. The sorption data have also been correlated with adsorption isotherms and kinetics of adsorption.

MATERIALS AND METHODS

Preparation of Lead (II) Solution

Pb(II) solution, was prepared from $Pb(NO_3)_2$ supplied by Aldrich and used as an adsorbate. Stock solution of 1000 ppm was prepared by dissolving an accurately measured weight in 1 L deionized water. The solutions for use in experiments were obtained by diluting the stock solution to the desired concentration.

Preparation and Characterization of Adsorbent

Carmel Daisy (CD) utilized in this work was collected from Houla valley South Lebanon. The collected plants were carefully washed with running water to remove impurities, and then they were washed with distilled water. The clean plant was dried at room temperature for 10 days then in an oven at 70 ^oC for 6 hours. The dried CD was grinded to a fine powder in a grinding mill to get a size of 0.25 mm. Fourier transformation infrared (FTIR) analysis using JASCO FT/IR-6300 spectrometer was applied to determine the surface functional groups interfering in the adsorption of pb, where the spectra was recorded in the range of 4000 to 400 cm^{-1}.

Experimental Methods

Batch experiments were carried out using a series of Erlenmeyer flasks of 50 ml capacity where 25 ml of Pb (II) were mixed with 0.25 g of the *scabiosaprolifera*. The experiments were prepared to study the effect of initial metal ion concentration, pH, contact time, adsorbent dose and temperature on adsorption of Pb (II) from its solution. All the adsorption experiments were carried out at room temperature except where the effect of temperature was being investigated. The pH of the solution was adjusted with (0.1 M) HNO_3 or (0.1 M) NaOH solutions. At the end of each adsorption experiment, the adsorbent was removed by Buchner filtration, and a second filtration using a (0.45 µm) syringe micro-filters. Concentration remaining was measured using Atomic Absorption Spectroscopy (AAS) at 217 nm. The dye removal efficiency (R) and the amount of dye adsorbed per unit mass of adsorbent at time t (q_t, $mg.g^{-1}$) and at equilibrium (q_e, $mg.g^{-1}$), were calculated using the following equations:

$R (\%) = [(C_0 - C_e)/C_0]*100$

$q_t = [(C_0 - C_t)/m]*V$

$q_e = [(C_0 - C_e)/m]*V$

C_0 ($mg.L^{-1}$): initial dye concentration

C_t (mg.L^{-1}): dye concentration at time t

C_e (mg.L^{-1}): equilibrium dye concentration

q_e(mg.g^{-1}): amount of dye adsorbed onto the adsorbent at equilibrium

q_t(mg.g^{-1}): amount of dye adsorbed onto the adsorbent at time t

V (L): volume of the dye solution

m(g): mass of the adsorbent

Adsorption Isotherms

Adsorption isotherms are essential for understanding 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[7]. Two models have been tested:

Langmuir Isotherm

It is based on the assumption that it 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 sorbed molecules[8]. Linear form of Langmuir isotherm is:

$1/q_e=1/bq_mC_e + 1/q_m$

C_e (mg.L^{-1}): equilibrium dye concentration

q_e(mg.g^{-1}): amount of dye adsorbed onto adsorbent at equilibrium

q_m (mg.g^{-1}): maximum monolayer capacity of the adsorbent

b (L.mg^{-1}): 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[7], R_L expressed as in the following equation:

$R_L = 1/(1+bC_0)$

There are four possible values for R_L: to be irreversible (R_L=0), favorable ($0<R_L<1$), linear (R_L=1) or unfavorable ($R_L>1$)

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[7]; its linear form is expressed by:

$\ln q_e = \ln K_F + (1/n)\ln C_e$

K_F(L.mg^{-1}): Freundlich constant indicating adsorption capacity

n adsorption intensity

Where the n value indicates the degree of non-linearity between solution concentration and adsorption as follows: if n=1, the adsorption is linear; if n<1, the adsorption is a chemical process; if n>1, the adsorption is a physical process.

RESULTS AND DISCUSSION

IR Spectroscopy

Figure 1 represents the IR spectra of CD before and after the adsorption of Pb (II) ions. The intense broad peak at 3100 ~3600 cm^{-1} corresponds to the stretching vibration of amino and hydroxyl groups. The decrease in the chemical shift of these groups to around 3100 cm^{-1} can be referred to the change in their environment due to the adsorption of Pb (II).The peak at ~2900 cm^{-1}refers to C-H stretching vibrations. The peaks at 1740, 1600 and 1500 cm^{-1} are attributed to carboxyl group, C=C stretching vibration and N-H bending mode. The intense peak at 1100 cm^{-1} reveals the stretching vibration of C-O.

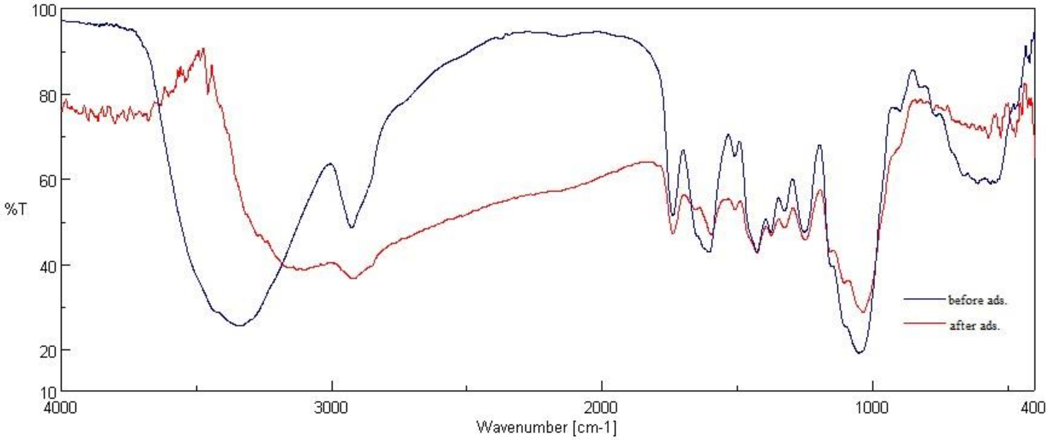

Figure 1: IR spectra of CD before and after adsorption of Pb (II)

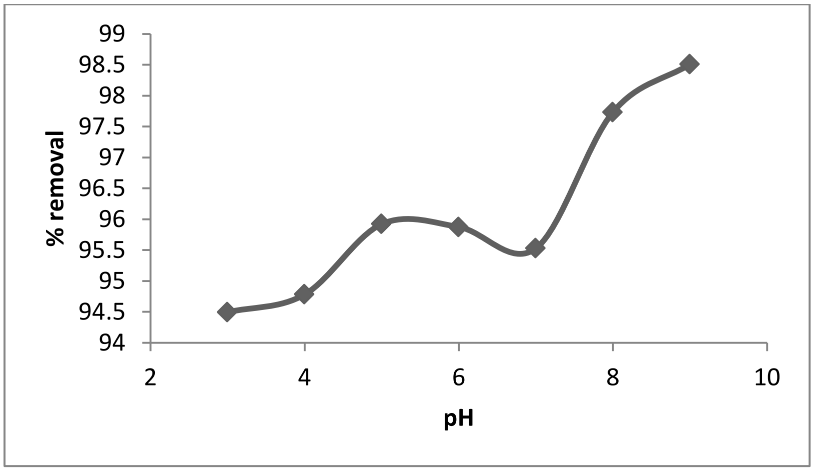

Figure 2: Percentage removal of Pb(II) as function of pH

Effect of pH

The pH of the aqueous solution is an important parameter which controls the Pb (II) adsorption process[9]. Figure 2 shows clearly that *scabiosaprolifera* exhibit maximum Pb (II) removal at pH 5, which were rather acidic. The solution pH affects the adsorbate surface charge and the degree of ionization of the bio-sorbent speciation, consequently affects the adsorption process of Pb (II) from water[10]. According to Qiu et al.[11], lead exists predominantly as a free ion in acidic solution (pH<6.01). Moreover, at pH>6 the species : $Pb(OH)_2$, $Pb(OH)_3^-$, $Pb_2(OH)^{3+}$, $Pb_3(OH)_4^{2+}$ and $Pb_4(OH)_4^{4+}$ may form, the formation of these species decreases the concentration of Pb(II) free ions, therefore decreasing the removal of Pb(II) by sorption, and enhancing its removal by other means as precipitation.

Effect of temperature

Temperature is an important factor that affects the adsorption of Pb (II) from its solution too. To study the effect of temperature, a series of experiments at temperature ranging from 25 to 55°C have been done. As shown in Figure 3, as temperature increases from 25 to 55°C, adsorption efficiency decreases to reach a minimum of 93.2 % at 55°C, this can be explained by: the adsorbed species might gain enough energy from temperature of the system and get desorbed at even a faster rate than adsorption rate[12].

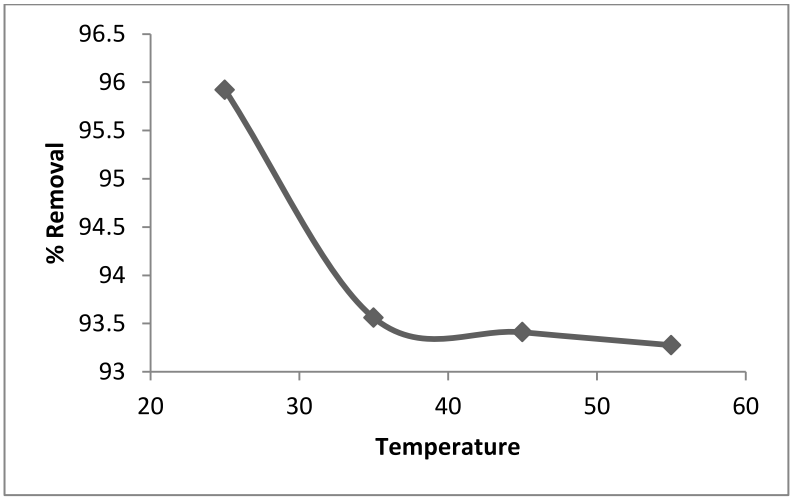

Figure 3: Percentage removal of Pb(II) as function of Temperature

Effect of Adsorbent Dose

The effect of the quantity of adsorbent used in the removal of Pb(II) from its solution was studied using mass ranging between 0.1 and 0.7 g. Figure 4 shows that with increasing the mass, the capacity of adsorption decreases from 32.32 $mg.g^{-1}$ at 0.1 g to 5.16 $mg.g^{-1}$ at 0.7 g. But the % removal of the ion increased from 86.27 to 96.45 %. This increase can be attributed to the limited availability of the number of adsorbing species for a relatively larger number of surface sites on the adsorbent at higher dosage of adsorbent. Therefore more metal ions are removed at higher dose since of the availability of more surface area[13].

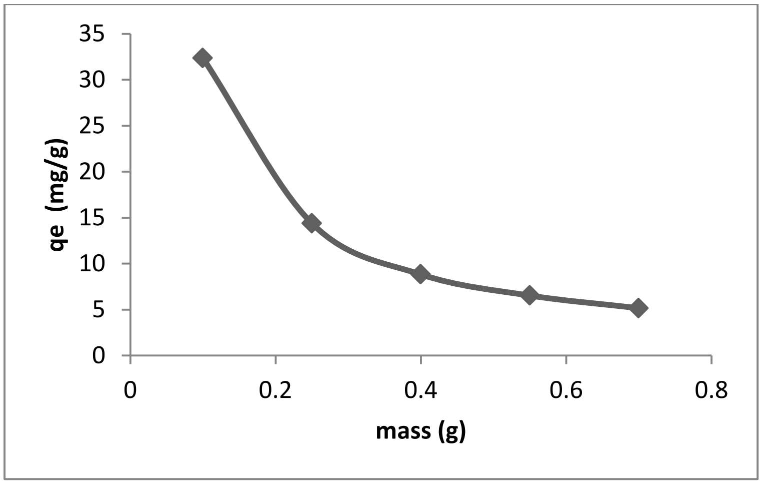

Figure 4: Adsorption capacity as function of adsorbent dose

Effect of Contact Time

Contact time is another factor that affects the adsorption. As can be seen from Figure 5, the rate of adsorption was high within the first 5 minutes, and then it started to decrease when equilibrium was attained after 20 minutes. After that a slight increase from 94.9 to 95.9% in the removal of Pb(II) was detected as time passes from 20 to 60 minutes. After reaching the equilibrium at 60 min, the % removal remained constant as the time increase. Generally, equilibrium is established at the surface of adsorbent after some time or it can be instantaneous. This probably resulted from saturation of adsorbent surfaces with heavy metals followed by adsorption and desorption processes that occur after saturation[14].

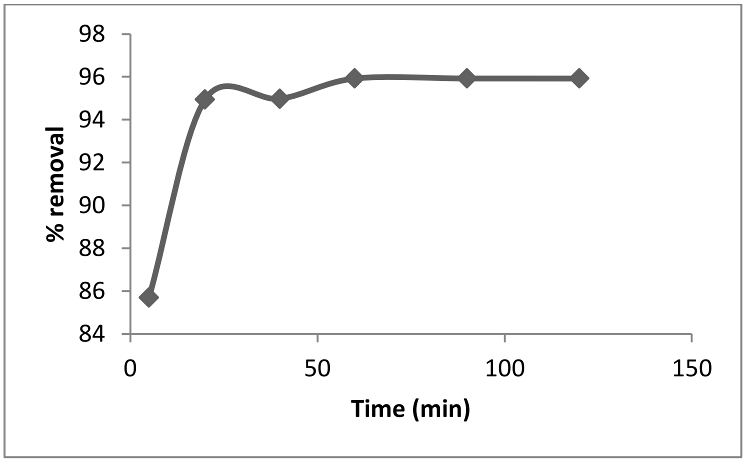

Figure 5: Percentage removal of Pb(II) as function of contact time

Effect of Concentration

To investigate the effects of the Pb (II) concentration on the adsorption capacity, the process was carried out with initial Pb(II) concentration between 150 and 600 mg.L^{-1} while keeping the other four parameters constant. As can be seen from Figure 6, as the ion concentration increases from 150 to 600 mg.L^{-1}, the adsorption capacity of the adsorbent increases as well from 14.38 to 56.51 mg.g^{-1} respectively, and this can be attributed to an increase in the driving force for the mass transfer between the aqueous phases and the solid phase[15].

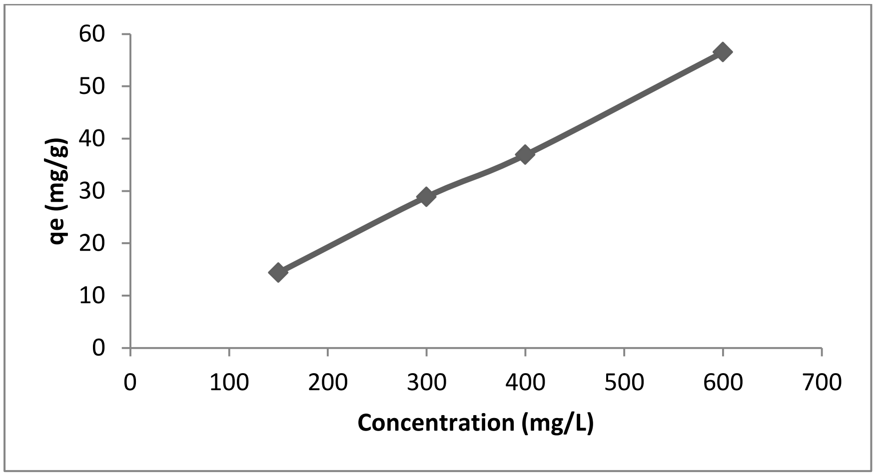

Figure 6: Adsorption capacity as function of Pb(II) concentration

Adsorption Isotherms

The linear plot of $1/q_e$ versus $1/C_e$has a correlation coefficient $R^2 = 0.94$ for Langmuir isotherm. On the other hand, Freundlich isotherm represented by the plot of ln q_e versus ln C_e shows linearity of $R^2 = 0.884$. The maximum monolayer capacity q_m and Langmuir isotherm constant b can be calculated from the intercept and slope of Figure 7.a, respectively. The adsorption capacity n and Freundlich constant K_F can be calculated from the slope and intercept of Figure 7.b. And the values are listed in Table 1. R_L was found to be 0.188 indicating the favorable sorption of Pb(II) on the surface of CD, and n>1 revealing that this process is of a physical nature.

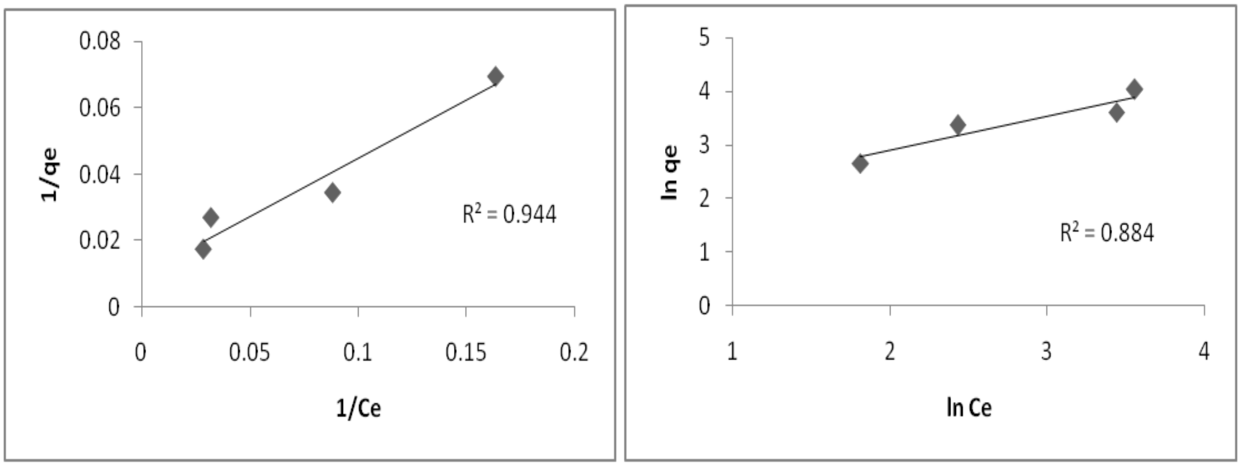

Figure 7: (a) Langmuir Isotherm (b) Freundlich Isotherm

Table 1: Equilibrium constants for Pb(II) adsorption on CD

Langmuir	q_{max} (L.mg^{-1})	*b* (L.mg^{-1})	**R^2**
	100	0.028	0.944
Freundlich	*n*	K_F (mg.g^{-1})	**R^2**
	1.55	40.27	0.884

Kinetic studies

The time data up to 120 min was tested for the following two kinetic models:

Pseudo-first-order rate equation of Lagergren

$log\ (q_e\text{-}q_t) = log q_e - k1/2.303 * t$

Pseudo-second-order rate equation

$t/q_t = 1/k_2 q_e^2 + 1/q_e * t$

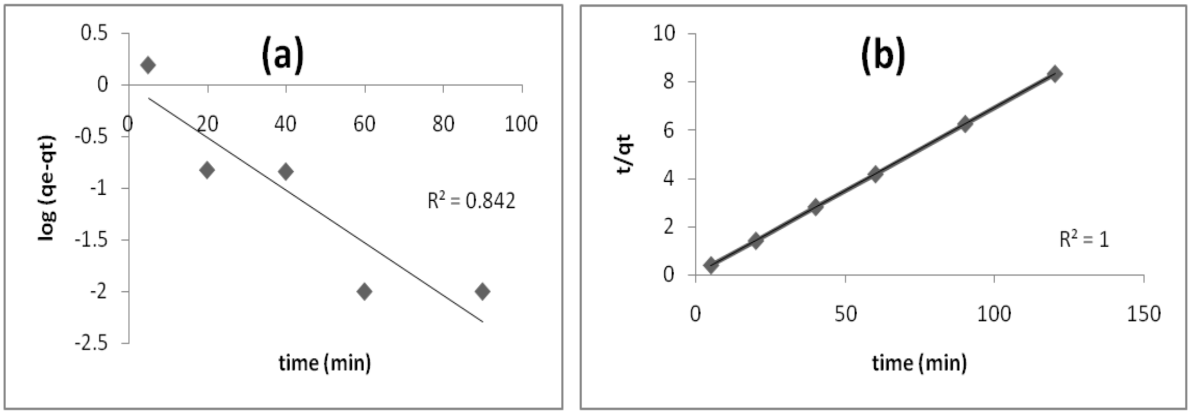

Figure 8: Kinetic plot of Pb(II) adsorption on CD, (a) pseudo first order, (b) pseudo second order

Table 2: Kinetic parameters for adsorption of Pb(II) on CD

Pseudo 1storder	**k_1 (L.min^{-1})**	**qe**	**R^2**
	0.057	0.986	0.842
Pseudo 2ndorder	**k_2 (g.mg^{-1}.min)**	**qe**	**R^2**
	0.148	14.49	1

From Figure 8.a it is observed that for the first order kinetic model $R^2 = 0.842$ and the adsorption capacity is much lower than that obtained experimentally. On the other hand, R^2 for the second model is 1 showed in Figure 8.b, and the values obtained are comparable with the experimental values. This observation shown in Table 2 suggests the applicability of the second kinetic model on the adsorption of Pb(II) on the surface of CD.

CONCLUSION

This study investigated the applicability of *scabiosaprolifera* (Carmel Daisy) a natural occurring plant in Lebanese valleys as a Bio-sorbent for the removal of Pb (II) ions from waste water and to study its adsorption behavior. The adsorption process follows the pseudo-second-order kinetic model. Freundlich and Langmuir isotherms were demonstrated. The adsorption process was found to be spontaneous and of exothermic nature under the studied conditions. This study provided a natural occurring, low cost, and environmentally friendly adsorbent for the removal of Pb (II) free ions.

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