Removal of Heavy Metals from Aqueous Solutions by *Cercis siliquastrum* L.

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This article is dedicated to Professor Habib Firouzabadi who actively participated in training of the new generation of scinetists in Iran on the occasion of his 65th birthday.

In this study the ability of *Cercis siliquastrum* L. leaves for the adsorption of Pb(II), Cu(II) and Ni(II) ions were studied. The effects of different parameters such as contact time of biosorbent and sorbents, pH of metal solution, and initial metal ion concentration on the biosorption were investigated. The maximum sorption of all metals were carried out in pH 4. Increasing the initial metal concentration in lower values caused a steep growth in biosorption, which was not observed in higher values. In the optimum sorption condition, the affinity of the leaves to metal ions was in the order of Pb(II)>Cu(II)>Ni(II). The biosorption of the metal ions were studied by Langmuir and Freundlich adsorption isotherm models. It was observed that the data were fitted very well to Langmuir adsorption isotherm model. According to the obtained correlation coefficient values, Freundlich model could predict Pb(II) and Cu(II) adsorption adequately but it was not suitable for Ni(II) sorption. Experimental data were exploited for kinetic evaluations related to the sorption process. According to our results, second-order kinetic provided a good description of biosorption for the tested metals with regression correlation coefficients more than 0.9998 for all the sorbate-sorbent systems.

INTRODUCTION

Heavy metals are one of the major factors of environmental contaminations. Physical and chemical methods have been proposed and applied to remove metal ions from effluents, but in general, these methods are commercially impractical, either because of high operating cost or the difficulty in treating. For example, the use of conventional technologies, such as ion exchange, chemical precipitation,

reverse osmosis, and evaporative recovery, for this purpose is often inefficient and/or very expensive [1-4]. Consequently, attempts have been made in order to find new simple and efficient techniques. For dilute concentrations, adsorption is one of the suitable methods for removal of heavy metal ions. Activated carbon is an example of efficient sorbents, that its application is limited by high cost of production and regeneration. Thus searching for new, low-cost and eco-freindly sorbents has been considered. Various types of biological materials such as non-living biomass of algae, aquatic ferns and seaweeds, waste biomass originated from plants, *etc*. have been cited as effeicient biosorbents [5-18].

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The biosorption mechanism of heavy metals is theorized to be an active or passive transport [19]. It needs to be mentioned that metal uptake by dead cells will take place by the passive mode and for living cells both active and passive modes may be involved [18]. The active method is a metabolism-dependent and slow process that can be due to a number of mechanisms, including covalent bonding, surface precipitation, diffusion into the cell interior and binding to proteins and intracellular sites [20]. The passive mode is a metabolism-independent mechasnism that essentially involves adsorption process such as ionic, chemical and physical adsorption. This stage is very rapid and occurs in a short time after the biomass comes into contact with the metal solution [21- 23].

In the present study, the ability of *Cercis siliquastrum* L. leaves biomass to eliminate Pb(II), Cu(II) and Ni(II) from waste water, and the effect of various parameters, such as contact time of biosorbent and sorbents, pH of metal solution, and initial metal ion concentration have been investigated. Equilibrium modeling was carried out using the Langmuir and Freundlich adsorption isotherms. The nature of the sorption process has been evaluated with respect to its kinetic aspect.

EXPERIMENTAL

Materials

C. siliquastrum is grown wild in northern and western parts of Iran [24]. The leaves of *C. siliquastrum* were collected in May 2006 from Tehran. The leaves were soaked in deionized water, then dried and powdered in a laboratory blender and sorted by sieving using the standard test sieves (35-60 mesh). Atomic absorption spectroscopy grade metal solutions were prepared by diluting 1000 mgl^{-1} stock solutions, which was obtained by dissolving a weighed quantity of metals nitrate salts (Merck). Diluted solutions were prepared at room temperature in ion-free doubeld distilled water to the desired concentrations. The pH of each solution was adjusted, with diluted or concentrated HCl and NaOH solutions.

Experimental Conditions

Batch biosorption assays were carried out in 100 ml flasks on a shaker at 100 rpm by transferring 50 ml of 10 ppm metal solutions and 0.5 gr of biosorbents. For determination of the best contact time between biosorbent and metal solutions, in which the amount of uptaked metal was maximum, the incubation time was varied between 5-360 min. The optimization of pH was performed at different values of 2-6 in optimized contact time with the same solution concentration as mentioned above. For the adsorption isotherm studies, initial metal concentrations used for biosorption ranged between 5-1000 ppm.

Initial and equilibrium metal ion concentrations in the aqueous solutions were assessed by using flame atomic absorption spectrophotometer (Shimadzu, AA-6800) equipped with Hallow Cathode Lamp and air acetylene burner.

RESULTS AND DISCUSSION

Effect of pH on Metal Ion Biosorption

The solution pH is one of the effective factors which influences the metal ions biosorption. In low pHs, occupation of the negative sites of the adsorbent by H$^+$ and H$_3$O$^+$ leads to reduction of the vacancies for metal ions and consequently causes decrease in metal ions biosorption [25].

It was observed that the biosorption was very low in pH 2 (42.1%, 31.5% and 23.2% for Pb(II), Cu(II) and Ni(II), respectively). As the pH was raised, the ability of metal ions for competition with H$^+$ ions was also increased. The optimum pH for the maximum biosorption of metal ions was 4 (Fig. 1). Although the sorption of metal ions raised by growing pH, further increment of pH caused declining in adsorption due to precipitation of metal hydroxides.

The Effect of Initial Metal Ion Concentrations

The mechanism of metal adsorption is in reliance with initial metal ion concentrations. At low concentrations, metals are adsorbed by particular sites, while by further increment of metal ion concentrations, the specific sites are saturated and the exchange sites are filled [26]. In order to obtain the maximum uptake capacity of *C. siliquastrum* leaves and necessary data for Langmuir and Freundlich isotherms, solutions with concentrations between 5-1000 ppm were prepared and biosorption process was studied for them. It was observed that the higher C_{eq} (equilibrium concentration), resulted in the more q_{eq} (equilibrium adsorption capacity) in
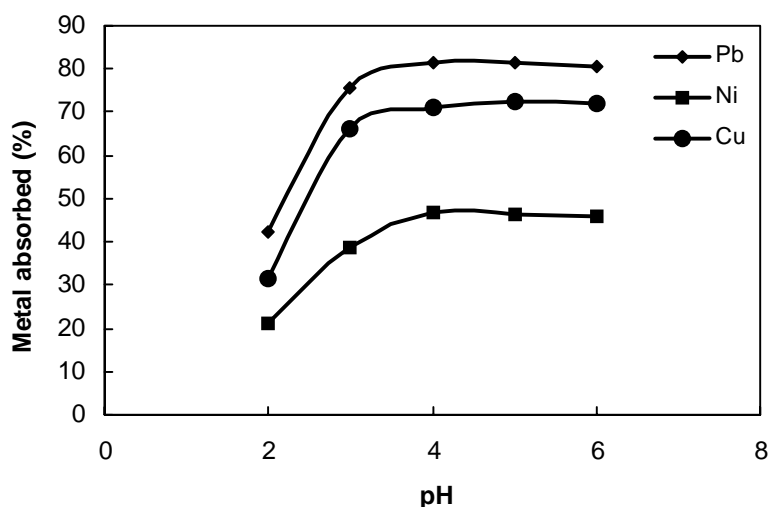
Fig 1. The effect of pH on the biosorption of Pb(II), Cu(II) and Ni(II) from 10 mgl^{-1} metal ion solution and 10 gl^{-1} *C. siliquastrum* under optimized contact times and shake flask at 100 rpm at room temperature.
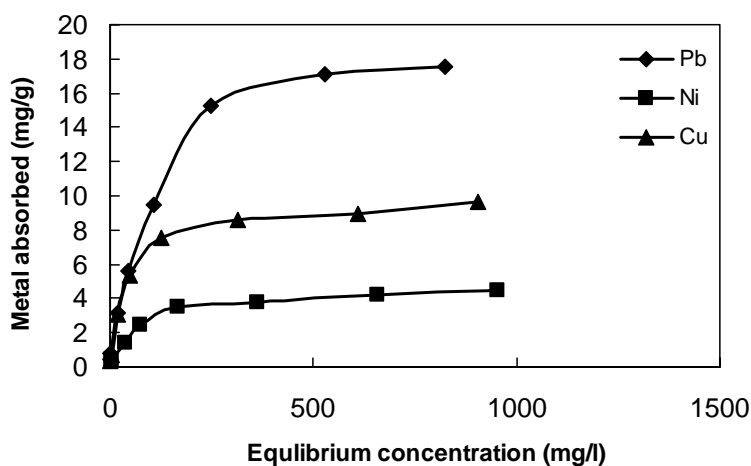
Fig 2. The effect of initial metal ion concentration (5–1000 mgl^{-1}), on the biosorption of Pb(II), Cu(II) and Ni(II), pH 4, 10 gl^{-1} *C. siliquastrum* under optimized contact times in shake flask at 100 rpm at room temperature.

low equilibrium concentrations [27]. As can be seen in Fig. 2, at higher concentrations of 400, 200 and 200 ppm for Pb(II), Cu(II) and Ni(II), a small variation on q_{eq} values was observed.

Adsorption Isotherms

In this study, the Langmuir and Freundlich isotherm models were used to interpret the efficiency of metal biosorption. Langmuir isotherm assumes that sorption occurs uniformly on the active sites of the sorbent, and once a sorbate occupies a site, no more sorption can take place at this site [28]. the Langmuir model is presented by the following equation:

$$q_{eq} = \frac{q_{max}bC_{eq}}{1 + bC_{eq}} \tag{1}$$

Where q_{eq} is equilibrium adsorption capacity, q_{max} is maximum adsorption capacity, b is adsorption efficiency and C_{eq} is equilibrium concentration [19, 26].

The Freundlich isotherm is an empirical model that is based on sorption on heterogeneous surface [28] and is presented below:

$$\ln q_{eq} = \ln k_F + \frac{1}{n} \ln C_{eq} \qquad (2)$$

where K_f and n are Freundlich constants which represent sorption capacity and sorption intensity, respectively [19, 26].

Both isotherms show the relationship between C_{eq} and q_{eq}. Different parameters namely q_{max}, b, r^2, K_f and $1/n$ for both models were calculated and are reflected in Table 1. The r^2 values are respected as a measure of fitness of experimental data on the isotherm models which for all the metals in the Langmuir model, being very close to 1 [29]. The experimental maximum adsorption values were 17.69, 9.65 and 4.50 mg/g for Pb(II), Cu(II) and Ni(II), respectively, which were similar to the theoretical values from the Langmuir equation. The relative order of metal uptake affinity of *C. siliquastrum* was Pb(II)> Cu(II)> Ni(II) based on q_{max}
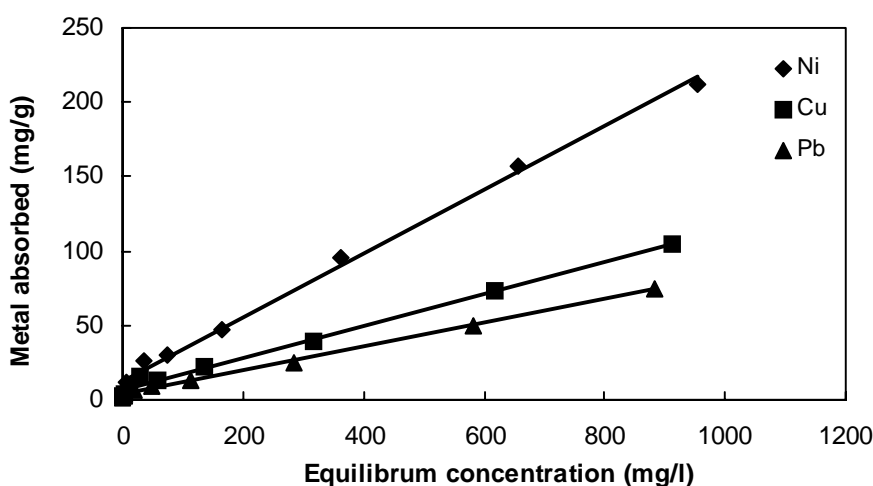
Fig 3. The Langmuir adsorption isotherms for Pb(II), Cu(II) and Ni(II) biosorption by *C. siliquastrum* (10 gl^{-1}). Conditions: initial metal concentration of 5–1000 mgl^{-1}, pH 4, flask shaking at 100 rpm at room temperature under optimized contact time for each metal.
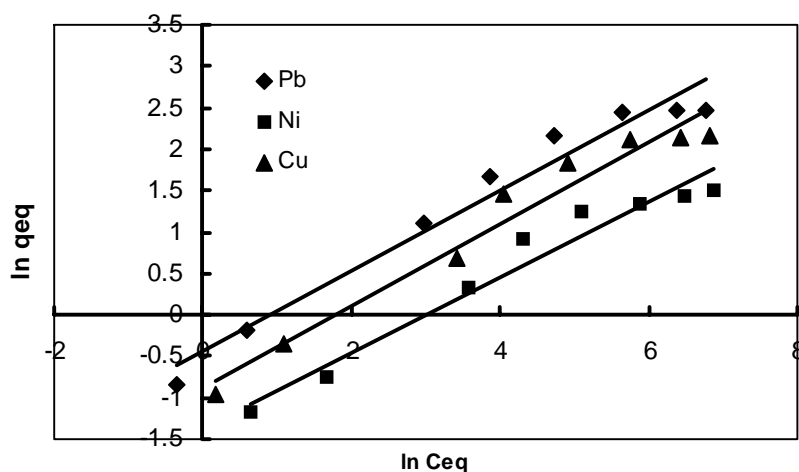
Fig 4. The Freundlich adsorption isotherm for Pb(II), Cu(II) and Ni(II) biosorption by *C. siliquastrum* (10 gl^{-1}). Conditions: initial metal concentration of 5–1000 mgl^{-1}, pH 4, flask shaking at 100 rpm at room temperature under optimized contact time for each metal.

Tablel 1. The Langmuir and Freundlich isotherms model constants, and their respective coefficients for the biosorption of Pb(II), Cu(II) and Ni(II) from their aqueous solutions.

| Metal ions	Experimental	Langmuir parameters			Freundlich parameters		
	q_{max}	q_{max}	b	r^2	K_F	$1/n$	r^2
Pb	11.829	12.44	0.025	0.9972	0.643	0.4842	0.9644
Cu	8.751	9.35	0.017	0.994	0.415	0.4936	0.9634
Ni	4.5	4.68	0.016	0.9964	0.257	0.4547	0.9591

amounts. The r^2 values in the case of Freundlich isotherm expressed low accordance of experimental data to this model. According to the correlation coefficient of 0.93 for Pb adsorption by the fungal biomass of *Aspergillus niger* [30], and a similar trend in other reports [26, 31] we concluded that Pb(II) and Cu(II) adsorptions are relatively conform to the Freundlich model, though not as perfect as to the Langmuir isotherm equation. The Langmuir and Freundlich plots for studied heavy metal ions adsorption on *C. siliquastrum* biomass are shown in Fig. 3 and 4, respectively.

Time-Course Relationship

The time-course studies on the biosorption of metals showed a fast rate of heavy metals removal initially due to plentiful unoccupied sites on the biosorbent [32]. The equilibrium contact time for Pb(II), Cu(II) and Ni(II) were 60, 120 and 30 min, respectively (Fig. 5). The percent of heavy metal removal on the mentioned contact times were 79.8%, 68.5% and 43.3%. The differences between biosorption values after equilibrium times were unconsiderable. For example, Pb(II) indicated a rapid rate of sorption during the first 30 minutes (Fig. 5), whereas the removal percentages after this time were 70.8%, 71%, 71.3% and 71.3% for 60, 120, 240 and 360 min, respectively.

In order to investigate the repeatability of metal sorption by leaves of *C. siliquastrum*, the experiments were carried out
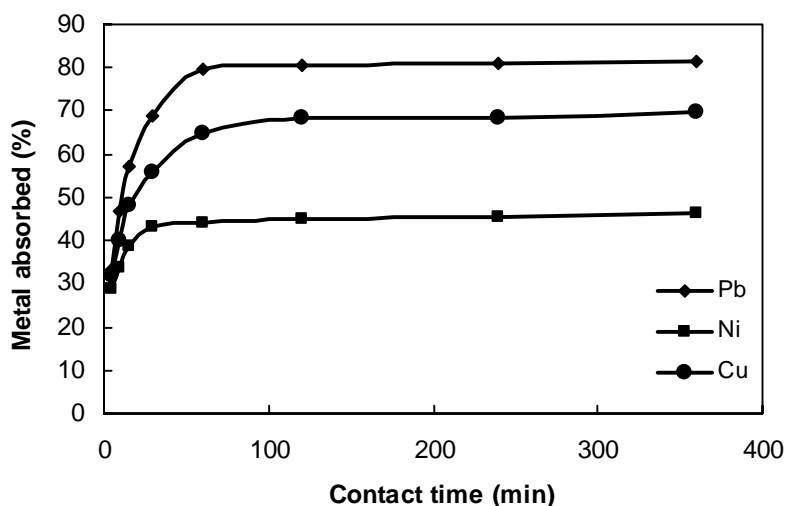
Fig 5. The time-course relationship of the biosorption of Pb(II), Cu(II) and Ni(II) from 10 mgl^{-1} metal ion solution, pH 4, 10 gl^{-1} *C. siliquastrum* in shake flask at 100 rpm at room temperature.
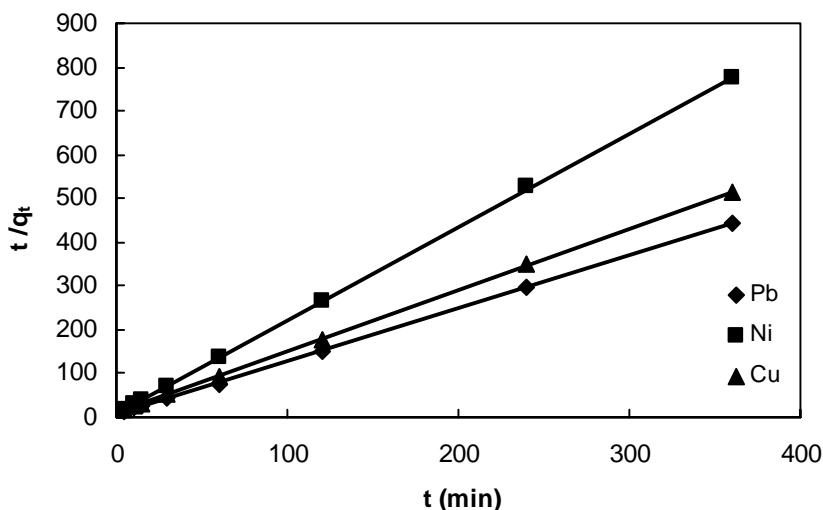
Fig 6. Biosorption of Pb(II), Cu(II) and Ni(II) by *C. siliquastrum* on the second-order reaction kinetic model, as related to time (*t*) and the quantity of metal adsorbed at *t* (q_t).

five times under optimum conditions for each metal. The mean values of adsorbed metals and related standard deviations for Pb(II), Cu(II) and Ni(II) were 113.47±4.91, 89.02±3.17 and 34.44±3.32 mg/g, respectively.

Metal Sorption Kinetics

The kinetic characteristics of heavy metal ions biosorption, can be investigated by the pseudo-first-order and second-order kinetic models. The first order rate equation of the Lagergren is one of the most commonly used for the uptake of a solute from liquid solution [30] and is represented as:

$$\ln(q_{eq} - q_t) = \ln q_{eq} - K_1 t$$

The second-order kinetic is in the form of [33]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_{eq}^2} + \frac{t}{q_{eq}}$$

in both mentioned equations, q_{eq} is the mass of metal adsorbed at equilibrium, q_t is the mass of metal adsorbed at time t, K_1 and K_2 are the first-order and second-order reaction rate equilibrium constants, respectively.

The plots of $\ln(q_{eq} - q_t)$ versus t gives a straight line. The rate constants (k_1) and theoretical equilibrium sorption capacities q_{eq} (theoric), can be calculated from the slopes and intercepts. As can be seen from Table 2, linear correlation coefficients of the plots for all studied metals are not good. Also q_{eq} (theoric) and q_{eq} (experimental) values are not in agreement with each other. So it could be suggested that the adsorption of Pb(II), Cu(II) and Ni(II) metal ions onto *C. siliquastrum* leaves is not a first-order process [34].

Straight lines obtained from second-order kinetic model (Fig. 6) and good accordance of experimental and theoretical q_{eq} values has been proved that this kinetic model can exhibit a better discription of heavy metals adsorption kinetic by *C. siliquastrum* leaves. As can be seen in Table 2, the correlation coefficient values of all the three metals were equal or higher than 0.9998 and experimental and theoretical q_{eq} values were in reasonable agreement with each other.

CONCLUSIONS

The potential of *Cercis siliquastrum* L. leaves has been investigated for removing heavy metals, such as Pb(II), Cu(II) and Ni(II) from aqueous solution. The maximum uptake for all

Table 2. Theoretically determined constants of second-order reaction kinetic based on the sorption of metals from 10 mgl^{-1} solutions, pH 4, 10 gl^{-1} *C. siliquastrum* during shake flask at 100 rpm in optimized contact times.

Metal ions	Experimental	Second-order constants		
	q_{eq}	q_{eq}	K_2	r^2
Pb	0.833	0.829	0.208	0.9998
Cu	0.706	0.71	0.207	0.9999
Ni	0.47	0.467	0.614	0.9999

metal ions was obtained in pH 4. The results obtained in this study indicated the highest adsorption ability of *C. siliquastrum* for Pb(II), among the tested metal ions. The study of metals biosorption by *C. siliquastrum* leaves proved that the process conform Langmuir better than Freundlich isotherm model. The overall adsorption rate of the Pb(II), Cu(II) and Ni(II) can be best described by the second-order kinetic.

ACKNOWLEDGEMENT

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