Removal and recovery of heavy metals from aqueous solution using *Ulmus carpinifolia* and *Fraxinus excelsior* tree leaves

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Abstract

Ulmus carpinifolia and *Fraxinus excelsior* tree leaves, which are in great supply in Iran, were evaluated for removal of Pb(II), Cd(II) and Cu(II) from aqueous solution. Maximum biosorption capacities for *U. carpinifolia* and *F. excelsior* were measured as 201.1, 172.0 mg/g for Pb(II), 80.0, 67.2 mg/g for Cd(II) and 69.5, 33.1 mg/g for Cu(II), respectively. For both sorbents the most effective pH range was found to be 2–5 for Pb(II), 3–5 for Cd(II) and 4–5 for Cu(II). Metal ion biosorption increased as the ratio of metal solution to the biomass quantity decreased. Conversely, biosorption/g biosorbent decreased as the quantity of biomass increased. The biosorption of metal ions increased as the initial metal concentration increased. Biosorption capacities of metal ions were in the following order: Pb(II) > Cd(II) > Cu(II). The equilibrium data for Pb(II) and Cu(II) best fit the Langmuir adsorption isotherm model. Kinetic studies showed that the biosorption rates could be described by a second-order expression. Both the sorbents could be regenerated using 0.2 M HCl during repeated biosorption–desorption cycles with no loss in the efficiency of the Cu(II) removal observed. Biosorption of Pb(II), Cd(II) and Cu(II) was investigated in the presence of Na, K, Mg and Ca ions. The results from these studies show a novel way of using *U. carpinifolia* and *F. excelsior* tree leaves to remove Pb(II), Cd(II) and Cu(II) from metal-polluted waters.
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1. Introduction

Heavy metals are not biodegradable and tend to accumulate in biological systems, posing health hazards if their concentrations exceed allowable limits [1]. Industries, such as metal plating, mining, painting, car manufacturing, smelters and metal refineries are major sources of heavy metal pollution [2–4]. Traditional methods such as ion-exchange, chemical precipitation, ultrafiltration and chemical deposition do not seem to be economically feasible because of relative high costs, particularly when used for the removal of heavy metals at low concentrations (<100 mg/l) [5]. Furthermore, most of these methods generate toxic sludge [6], the disposal of which is an additional burden on the techno-economic feasibility of treatment procedures. Therefore, there is a need to find alternative methods which are environmentally friendly, effective and economic. Biological methods to adsorb metal ions may provide the answer. Successful metal biosorption

has been reported using a variety of biological materials including micro-algae and seaweed, bacteria, fungi and crop residues [7–9], pine bark and needles [10], modified chitosan [11], petiolar felt-sheath of palm [12], papaya wood [13], loofa sponge and plant-immobilized biomass [14,15].

The objective of this study was to investigate the potential of *Ulmus carpinifolia* and *Fraxinus excelsior* tree leaves to treat wastewaters contaminated with heavy metals. The *U. carpinifolia* and *F. excelsior* tree leaves are in great supply, inexpensive and easily found around Arak, a city in the centre of Iran. There are no special commercial uses for them and because they are not a food source for livestock there is no risk of livestock poisoning. These attributes provided the incentive for investigating these two tree leaves as potential novel natural biosorbents.

2. Materials and methods

2.1. Biosorbent materials

The *U. carpinifolia* and *F. excelsior* tree leaves were gathered from twigs into clean plastic bags, washed with ion-free distilled

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water and laid flat on a clean table to dry. The dried leaves were ground and sieved to 40–50 mesh, then stored in plastic bags ready for use.

2.2. Metal ion solutions

The stock solutions of Pb(II), Cd(II) and Cu(II) were prepared by dissolving appropriate quantities of Pb(NO$_3$)$_2$, Cd(NO$_3$)$_2$ and Cu(NO$_3$)$_2$ salts in 5% HNO$_3$. All the chemicals used were AR grade and ion-free distilled water was used throughout. The solutions were adjusted to pH 5, or as otherwise stated, with 0.1 M HCl or 0.1 M NaOH. Fresh dilutions were made for each study.

2.3. Metal analysis

The concentration of each metal ion remaining in solution after biosorption was determined using a flame atomic absorption spectrophotometer (PerkinElmer 2380). Unless indicated, the data shown are the mean of three separate experiments. Two different controls were also performed. The control without sorbents showed whether metal ions were adsorbed onto the walls of the flask. The control without metal ions (ion-free distilled water instead of metal solution) was used to estimate any leaching from sorbents during the study period. All experiments were performed in triplicate.

Analysis of variance (ANOVA) and consequently Duncan's multiple range test ($p = 0.05$) [16] on the data were carried out to find out whether there are statistically significant differences between observed values and the expected ones.

2.4. FT-IR studies

FT-IR spectra of raw (before metal treatment) and treated (after metal biosorption) samples of solid tree leaves were obtained using a FT-IR spectrophotometer (Shimadzu IR Prestige, Japan). The mixture of dry tree leaves (about 0.1 g) with KBr (0.5 g) was grounded into fine particles and pressed into a tablet from. The FT-IR spectrum was then recorded.

2.5. Shake flask biosorption

Batch biosorption experiments were carried out in 250 ml Erlenmeyer flasks by transferring 100 ml of 50, 25 and 15.5 mg/l Pb(II), Cd(II) and Cu(II) solutions, respectively (to maintain similar molar concentrations for all the three metal ions) and 1 g (10 g/l) 40–50 mesh tree leaves. The mixtures were shaken on an orbital shaker at 200 rpm in tightly stoppered flasks at $25 \pm 5\,^{\circ}$C for 60 min. The suspensions were filtered through Whatman filter paper (No. 42) and the concentration of metal ions in the filtrate was measured, from which the amount of metal ion biosorbed per unit mass of biosorbent (mg metal/g dry biosorbent) was determined. The time dependency of batch experiments was examined by varying the contact time of sorbents from 5 to 150 min. The influence of pH on metal ion biosorption was determined by equilibrating the suspensions in solutions of differing pH ranging from 1 to 6. For the adsorption

isotherm studies, the initial metal ion concentration was varied over the range of 5–5000 mg/l. The concentration of *Ulmus* and *Fraxinus* tree leaves was varied between 1 and 100 g/l to determine the ratio required for optimum biosorption. For the determination of any interference caused by the presence of other cations, monovalent Na and K, and divalent Mg and Ca (as the nitrate) were added to the Pb(II), Cd (II) and Cu(II) solutions ranging from 0 to 0.1 M.

2.6. Desorption and regeneration

The metal loaded *Ulmus* and *Fraxinus* leaves (1 g) were desorbed with 100 ml of 0.2 M HCl, which has been reported to be an efficient metal desorbent [17–19], for 60 min. The desorbed tree leaves were washed and the regenerated sorbents were used in three biosorption–desorption cycles to determine reusability of the leaves.

3. Results and discussion

3.1. Metal ion biosorption mechanism by plants

Various metal-binding mechanisms are thought to be involved in the biosorption process including ion exchange, surface adsorption, chemisorption and adsorption–complexation [20]. Plant cell walls, mainly consisting of polysaccharides, proteins and lipids, offer many functional groups such as carboxyl, carbonyl, hydroxyl and amino which can be involved in metal binding [21].

The FT-IR spectra before and after adsorption of metal ions by *Ulmus* and *Fraxinus* tree leaves in the range of 400–4000 cm^{-1} were taken to obtain information on the nature of possible cell–metal ions interactions and presented in Fig. 1. Since a high similarity between *Ulmus* and *Fraxinus* FT-IR spectra was observed and in order to save space, this study limits the demonstration to the *Fraxinus* spectrum.

The FT-IR spectroscopic analysis of metal-loaded biosorbent of *Fraxinus* tree leaf indicated intensity decrease and shifted strong asymmetrical stretching bands at 3321 (indicative of –OH and –NH groups) and 2927 cm^{-1} (indicative of C–H groups) when compared with that of unloaded biomass which showed the same absorption at 3338 and 2920 cm^{-1}, respectively. The similar band shift was observed for one of the double band of the carboxylate ion (at 1636 and 1431 cm^{-1}) moving from 1431 to 1390 cm^{-1}. These observations indicated the involvement of these functional groups in the biosorption process.

The order of affinity in metal ion removal by both sorbents may be explained by the Hard Soft Acid Base theory of Pearson (HSAB) [22]. This theory classifies different species as acids or bases arranged in a specific order of softness assuming that soft bases react preferentially with soft acids. The supposed active sites on the adsorbents, namely carboxylic and hydroxylic groups are soft bases that will react preferentially with soft acids (the metal ions in the solution). The softness order as acids of the investigated heavy metals is Pb(II) (3.58) > Cd(II) (3.04) > Cu(II) (2.89), in agreement with the affinity series observed from experimental tests [23].
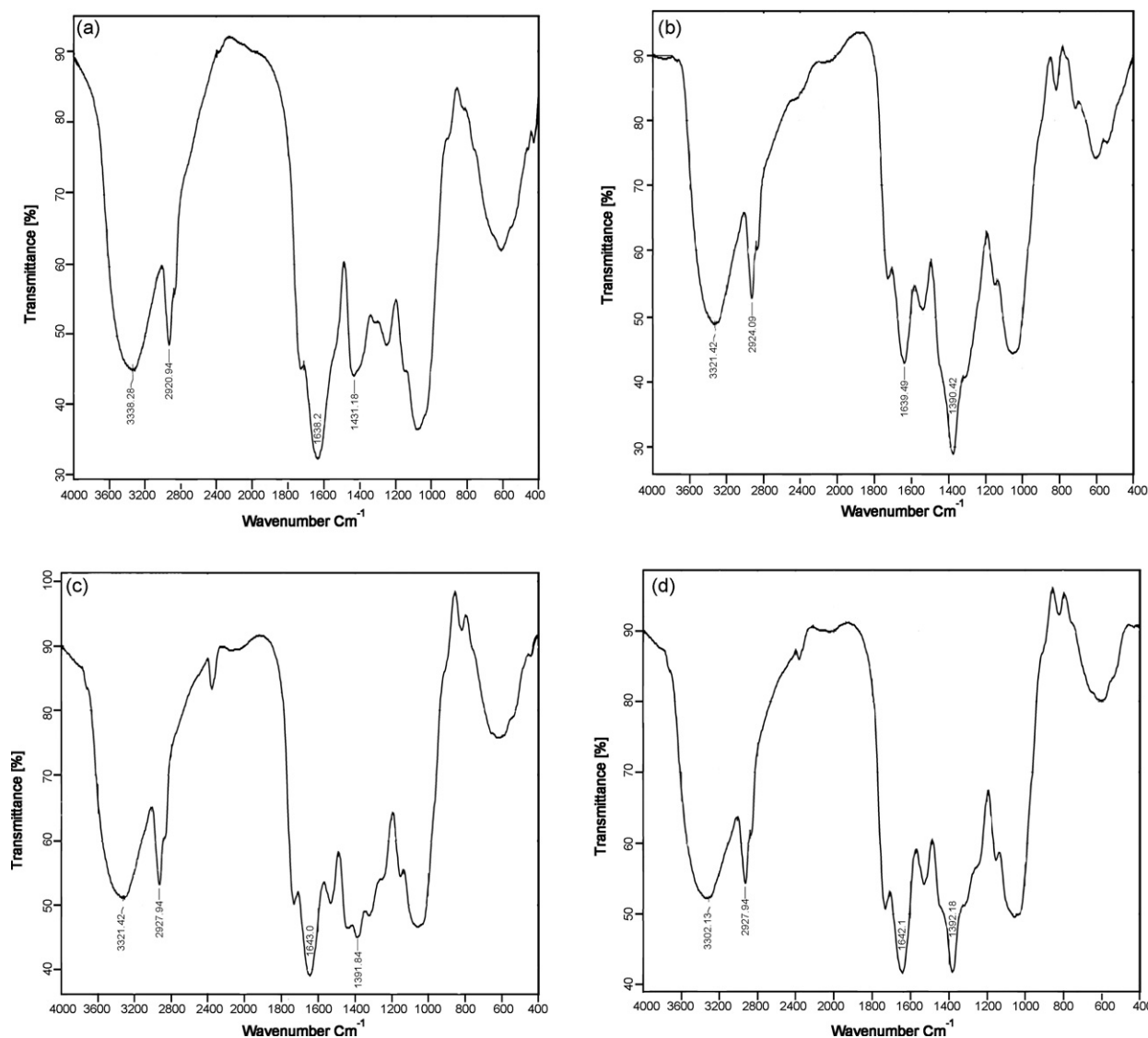
Fig. 1. The FT-IR spectra of *Fraxinus* tree leaf: (a) unloaded; (b) Pb(II)-loaded biomass; (c) Cd(II)-loaded biomass; and (d) Cu(II)-loaded biomass.

3.2. Effect of biosorbent–biosorbate contact time

The duration of the batch experiments was varied from 5 to 150 min. All other parameters such as ion concentration (50, 25 and 15.5 mg/l for lead, cadmium and copper, respectively), the volume of the metal ion solution (100 ml), sorbent quantity (1 g) and pH (5) were kept constant. All three metal ions show a fast rate of adsorption during the first 10 min (Fig. 2), during which period the fraction removed were Pb(II) 89.5%, Cd(II) 79.1% and Cu(II) 77.5% for the *Ulmus* tree leaves, and Pb(II) 89.3%, Cd(II) 78.1% and Cu(II) 60.2% for *Fraxinus* tree leaves. After the initial rapid uptake there was an ongoing slow adsorption appearing to reach equilibrium after about an hour which the fractions removed were Pb(II) 98.8%, Cd(II) 91.0% and Cu(II) 88.0% for the *Ulmus* tree leaves and Pb(II) 96.6%, Cd(II) 83.8% and Cu(II) 74.0% for the *Fraxinus* tree leaves. At the contact time of 60 min the amount of biosorbed metal ions did not change significantly with contact time ($p > 0.05$) and it is thus fixed as the optimum contact time.

This two-stage biosorption, the first rapid initial uptake followed by a slow stage reaching equilibrium, is similar to previous reports on the biosorption of heavy metals with different sorbents [9,13,14,18,24].

The rapid stage is probably due to the abundant availability of active sites on the biomass, and with the gradual occupancy of these sites, the sorption becomes less efficient in the slower stage. The fast metal uptake by the sorbents may be attributed to its highly porous and mesh structure, which provides ready access and large surface area for the sorption of metals on the binding sites [13].

3.3. Effect of pH on biosorption

The initial solution pH has been reported to be an important parameter affecting the uptake of heavy metal ions from aqueous solutions by biosorbents [19,25,26]. The biosorption experiments were conducted at six solution pH values ranging from 1.0 to 6.0. The results presented in Fig. 3 show that the
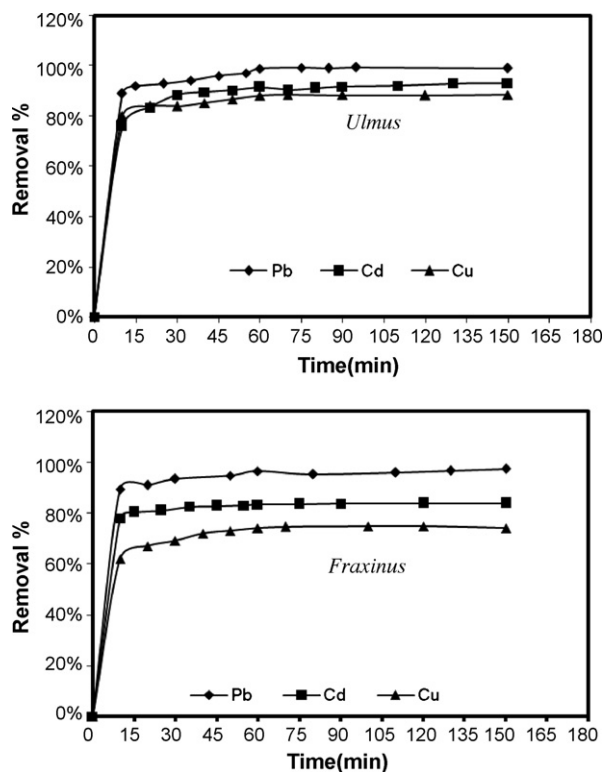
Fig. 2. The time course relationship of the biosorption of Pb(II), Cd(II) and Cu(II) from 50, 25 and 15.5 mg/l metal solutions, respectively, pH 5, 10 g/l *Ulmus* and *Fraxinus* tree leaves in shake flask at 200 rpm at room temperature.
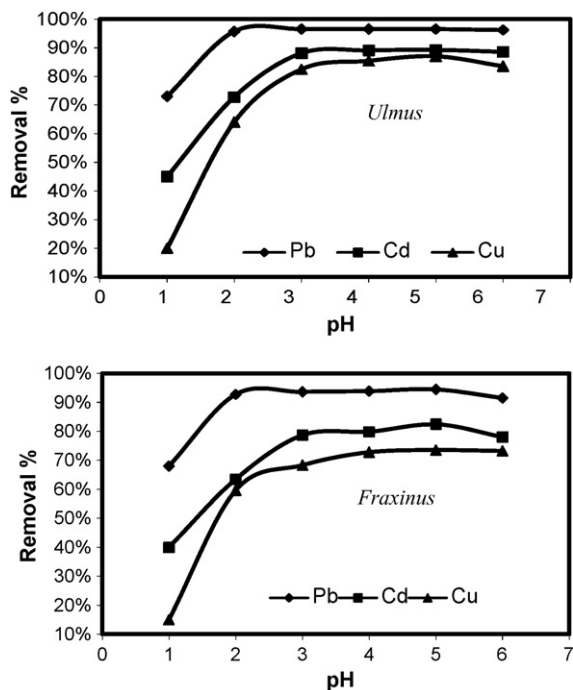

Fig. 3. The effect of pH on the biosorption of Pb(II), Cd(II) and Cu(II) from 50, 25 and 15.5 mg/l metal solutions, respectively, 10 g/l *Ulmus* and *Fraxinus* tree leaves in shake flask at 200 rpm at room temperature during 60-min contact time.

optimum uptake of metal ions was observable by both *Ulmus* and *Fraxinus* tree leaves at pH 2–5 for Pb(II), 3–5 for Cd(II) and 4–5 for Cu(II). In the ranges of pH mentioned for different metal ions no significant difference in biosorption capacity of sorbents was observed ($p > 0.05$). Increasing pH from 6 to 7 resulted in lower biosorption with both sorbents for all three metal ions. This may be attributed to the decreased solubility of metals at high pH. For this reason, the experiments were not conducted beyond pH 6.0.

The dependence of metal uptake on pH is related to both the surface functional groups present on the biomass and the metal chemistry in solution. At low pH, the surface ligands are closely associated with the hydronium ions (H_3O^+) and restricted the approach of metal cations as a result of the repulsive force [27,28].

Furthermore, the pH dependency on the metal ions uptake by biomasses can also be justified by the association–dissociation of certain functional groups, such as the carboxyl and hydroxyl groups present on the biomass. In fact, it is known that at low pH, most of the carboxylic groups are not dissociated and cannot bind the metal ions in solution, although they take part in complexation reactions [29]. Based on these results, the following experiments were performed at pH 5.

3.4. Relationship of the sorbents quantity with metal biosorption

With the metal ion concentration and all other parameters fixed, the quantity of *Ulmus* and *Fraxinus* tree leaves was varied between 0.1 and 10 g (1–100 g/l) to find the optimum concentration of biomass needed for maximum biosorption. The percentage of metal ion adsorbed increased with increasing sorbent concentration (Fig. 4). The maximum metal ion uptake was observed at about 10 g/l for both sorbents for all three metal ions. Further increase in the sorbents concentration showed no significant increase in the percentage of metal ion adsorbed ($p > 0.05$). An increase in fraction removed, by increasing biomass concentration, is expected as there is greater surface area available. Saeed et al. [13] obtained similar results. The values of metal concentration at equilibrium (C_{eq}) also showed that increase in the tree leaves biomass strongly affected the removal of lead(II), cadmium(II) and copper(II) from their aqueous solutions. This was reflected by lower C_{eq} values indicating that as the tree leaves biomass was increased, the unoccupied sorption sites became more surplus with every increment of the biomass.

3.5. Effect of initial metal ion concentration

The metal ion biosorption capacities of *Ulmus* and *Fraxinus* tree leaves are presented as a function of equilibrium concentration (5–3500 mg/l) in aqueous solution in Fig. 5. To prevent precipitation of metal ions as hydroxides at high concentrations, the solution pH was adjusted to 4.0 in this experiment. All other parameters such as contact time (60 min), volume of solution (100 ml) and quantity of sorbents (1 g) were kept constant. The metal uptake mechanism is particularly dependent on the initial heavy metal concentration (C_i): at low concentrations metals are
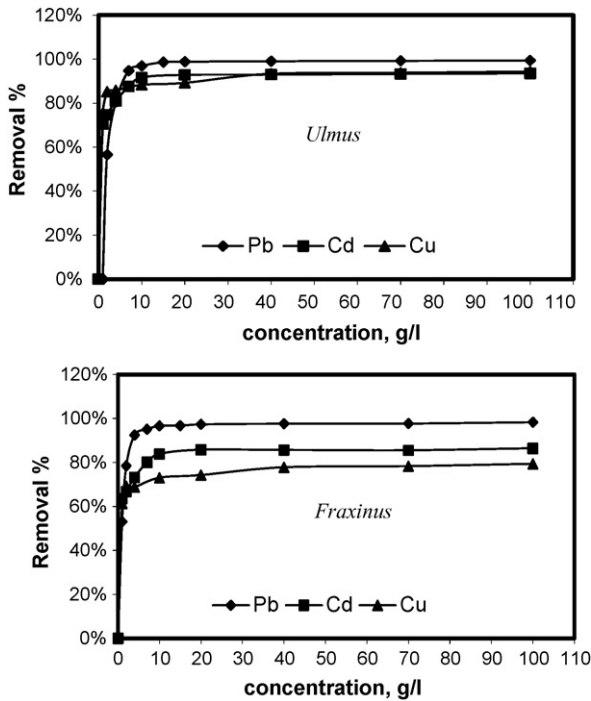
Fig. 4. The effect of increasing *Ulmus* and *Fraxinus* tree leaves quantity (g/l) on the biosorption of Pb(II), Cd(II) and Cu(II) from 50, 25 and 15.5 mg/l metal solutions, respectively, pH 5 in shake flask at 200 rpm at room temperature during 60-min contact time.
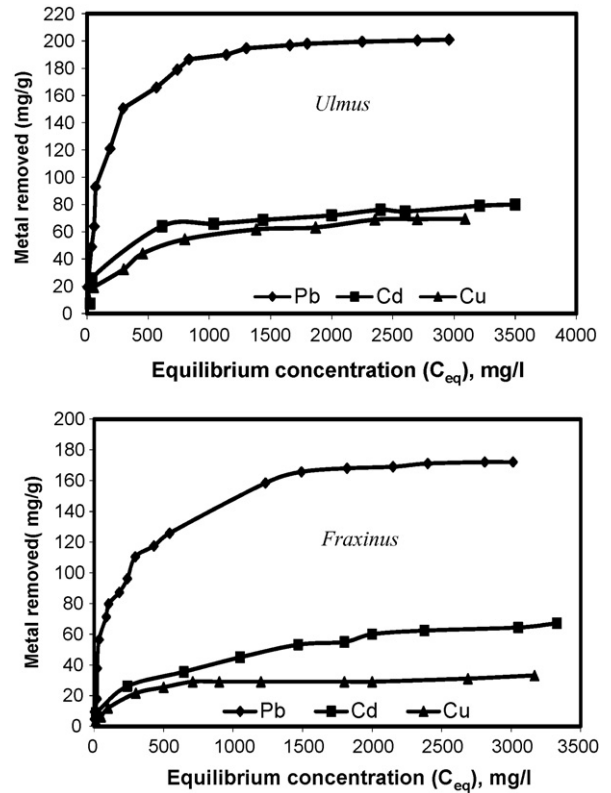

Fig. 5. Effect of initial metal ion concentration (5–5000 mg/l), solution pH 4, using 10 g/l *Ulmus* and *Fraxinus* tree leaves during 60 min biosorbent–metal contact in shake flask at 200 rpm at room temperature.

Table 1
Biosorption results of Pb(II), Cd(II) and Cu(II) ions from literature by various biosorbents and operating conditions

Metal ions	Biosorbents material	Biosorption capacity (mg/g)	Operating conditions				
			pH	T (°C)	Initial concentration (mg/l)	Biomass (g/l)	Reference
	Saccharomyces cerevisiae	2.7	5	25	10.4	2	[31]
	Sago waste	46.6	4–5.5	25	100	4	[32]
Pb(II)	*Cicer arientinum*	50.2	5	25	10	10	[9]
	Botrytis cinerea	107.1	4	25	350	2	[26]
	Streptomyces rimosus (NaOH treated)	135	2–12	n.a.	10	3	[33]
	Fraxinus tree leaf	172.0	5	25	50	1	This study
	Ulmus tree leaf	201	5	25	50	1	This study
	Olive pomace	7	5	25	n.a.	10	[34]
	Papaya wood	17.35	5	n.a.	10	5	[13]
	Chlorella sorkiniana	33.5	5	25	10	1	[35]
Cd(II)	*Cicer arientinum*	42.56	5	25	10	10	[9]
	Fraxinus tree leaf	67.2	5	25	25	1	This study
	Ulmus tree leaf	80.0	5	25	25	1	This study
	Green coconut shell	285.7	7	27	20	5	[36]
	Olive pomace	4.3	5	25	n.a.	10	[34]
	Sago waste	12.4	4–5.5	25	50	4	[32]
Cu(II)	Papaya wood	19.99	5	n.a.	10	5	[13]
	Cicer arientinum	27.97	5	25	10	10	[9]
	Fraxinus tree leaf	33.1	5	25	15.5	1	This study
	Ulmus tree leaf	69.5	5	25	15.5	1	This study

n.a.: not available.

adsorbed by specific sites, while with increasing metal concentrations the specific sites are saturated and the exchange sites are filled [13]. Biosorption capacities of both sorbents increased with increasing metal ion concentration in the medium. This effect maybe due to an increase in electrostatic interactions (relative to covalent interactions) which involve sites of progressively lower affinity for metal ions [30]. Both sorbents exhibited very high metal loading capacities for all three metal ions 201.1, 172.0 mg/g for Pb(II), 80.0, 67.2 mg/g for Cd(II) and 69.5, 33.1 mg/g for Cu(II) for *Ulmus* and *Fraxinus* tree leaves, respectively. These values were higher than many corresponding biosorbents reported in the literature (Table 1).

3.6. Adsorption isotherms model

Adsorption isotherm models were used to characterize the interactions of metal ions with the sorbents. The Langmuir model is based on the assumption that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane [37,38]. This is represented by the following equation:

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

where q_{eq} and q_{max} are the equilibrium and maximum uptake capacities (mg/g biosorbent); C_{eq} the equilibrium concentration (mg/l), b the equilibrium constant. It can be rearranged to its linear form

$$\frac{c_{eq}}{q_{eq}} = \frac{1}{b q_{max}} + \frac{c_{eq}}{q_{max}} \tag{2}$$

The Freundlich equation is the empirical relationship whereby it is assumed that the adsorption energy of a metal ion binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied [38,39] and is represented below

$$q_{eq} = K_F c_{eq}^{1/n} \tag{3}$$

where K_F and n are the Freundlich constants characteristic of the system. A linear form of this equation is

$$\ln q_{eq} = \frac{1}{n} \ln c_{eq} + \ln K_F \tag{4}$$

The linearized Langmuir and Freundlich isotherms obtained for Pb(II), Cd(II) and Cu(II) for both sorbents are presented in Figs. 6 and 7. The Langmuir and Freundlich adsorption constants calculated from the corresponding isotherms and their respective coefficients are presented in Table 2. Both isotherms consider q_{eq} as a function of C_{eq}, corresponding to the equilibrium distribution of ions between aqueous and solid phases as the initial metal ion concentration increases. The values of r^2 are regarded as a measure of goodness-of-fit of experimental data to the isotherm models [40]. As seen from Table 2 Langmuir modelling exhibited a better fit to the data for the all metals therefore, biosorption process in this study may be interpreted as monolayer adsorption. According to Langmuir model, sorption
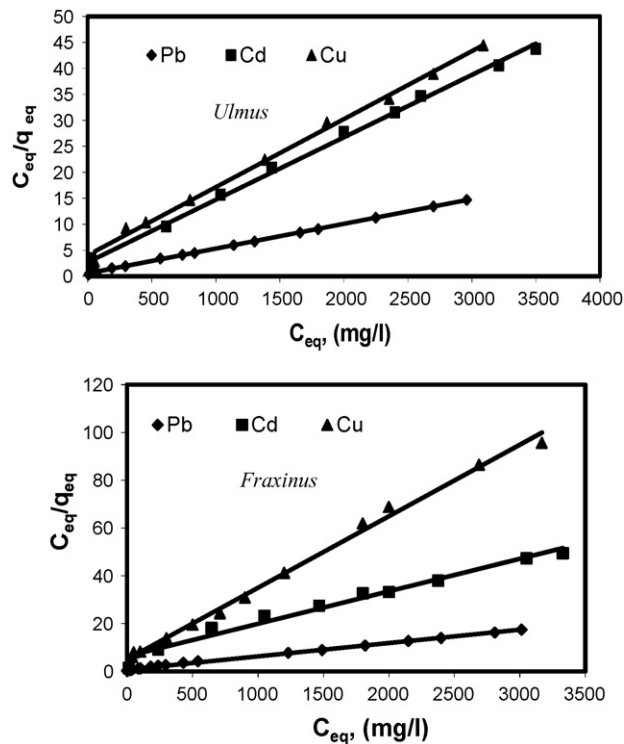

Fig. 6. The Langmuir adsorption isotherms for Pb(II), Cd(II) and Cu(II) biosorption by *Ulmus* and *Fraxinus* tree leaves (10 g/l). Conditions: initial metal concentration of 5–5000 mg/l, pH 4, flask shaking at 200 rpm at room temperature during 60-min contact time.
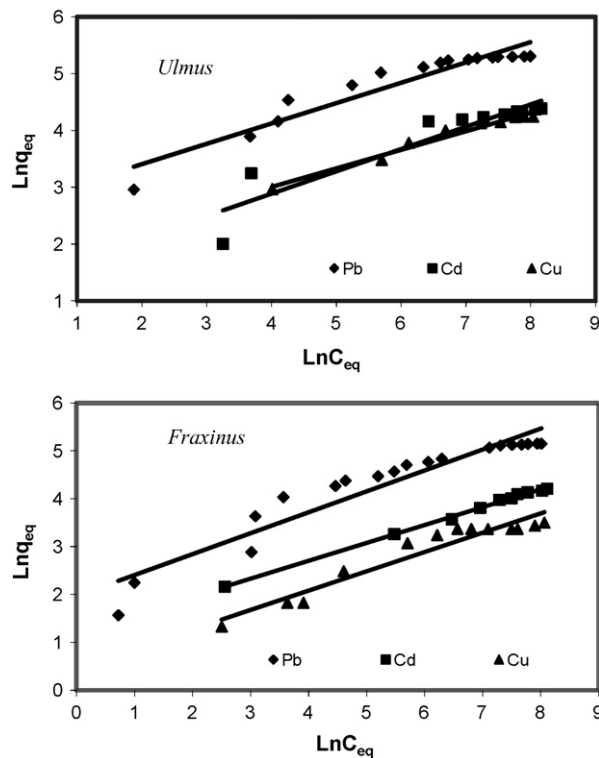

Fig. 7. The Freundlich adsorption isotherms for Pb(II), Cd(II) and Cu(II) biosorption by *Ulmus* and *Fraxinus* tree leaves (10 g/l). Conditions: initial metal concentration of 5–5000 mg/l, pH 4, flask shaking at 200 rpm at room temperature during 60-min contact time.

Table 2
The Langmuir and Freundlich isotherms model constants, and their respective coefficients for the biosorption of Pb(II), Cd(II) and Cu(II) from their aqueous solutions

Metal ion	Sorbent						
	Experimental (mg/g)	Langmuir			Freundlich		
		q_{max} (mg/g)	b	r^2	K_F	$1/n$	r^2
Ulmus tree leaf							
Pb(II)	201	208.3	0.0088	0.999	14.780	0.376	0.908
Cd(II)	80	83.3	0.0044	0.996	3.713	0.394	0.855
Cu(II)	69.5	76.3	0.0026	0.996	5.467	0.327	0.973
Fraxinus tree leaf							
Pb(II)	172	178.60	0.0069	0.998	7.140	0.437	0.980
Cd(II)	67.17	73.53	0.0021	0.976	3.352	0.373	0.997
Cu(II)	33.14	33.44	0.0059	0.996	1.597	0.403	0.927

occurs uniformly on the active sites of the sorbent, and once a sorbate occupies a site, no further sorption can take place at this site [26].

3.7. Metal biosorption kinetics

In order to analyze the biosorption kinetics of heavy metal ions, the pseudo-first- and second-order kinetic models were applied to the data. The first-order rate equation of the Lagergren is one of the most widely used for the biosorption of a solute

from liquid solution [41] and is represented as

$$\ln(q_{eq} - q_t) = \ln q_{eq} - K_{1,ad}t \tag{5}$$

where $K_{1,ad}$ is the rate constant of first-order biosorption (min^{-1}), and q_{eq} and q_t denote the amounts of biosorption at equilibrium and at time t (mg/g), respectively. The pseudo-first-order considers the rate of occupation of adsorption sites to be in proportion to the number of unoccupied sites. A plot of $\ln(q_{eq} - q_t)$ versus t should give a straight line to confirm the applicability of the first-order kinetic model. In a true
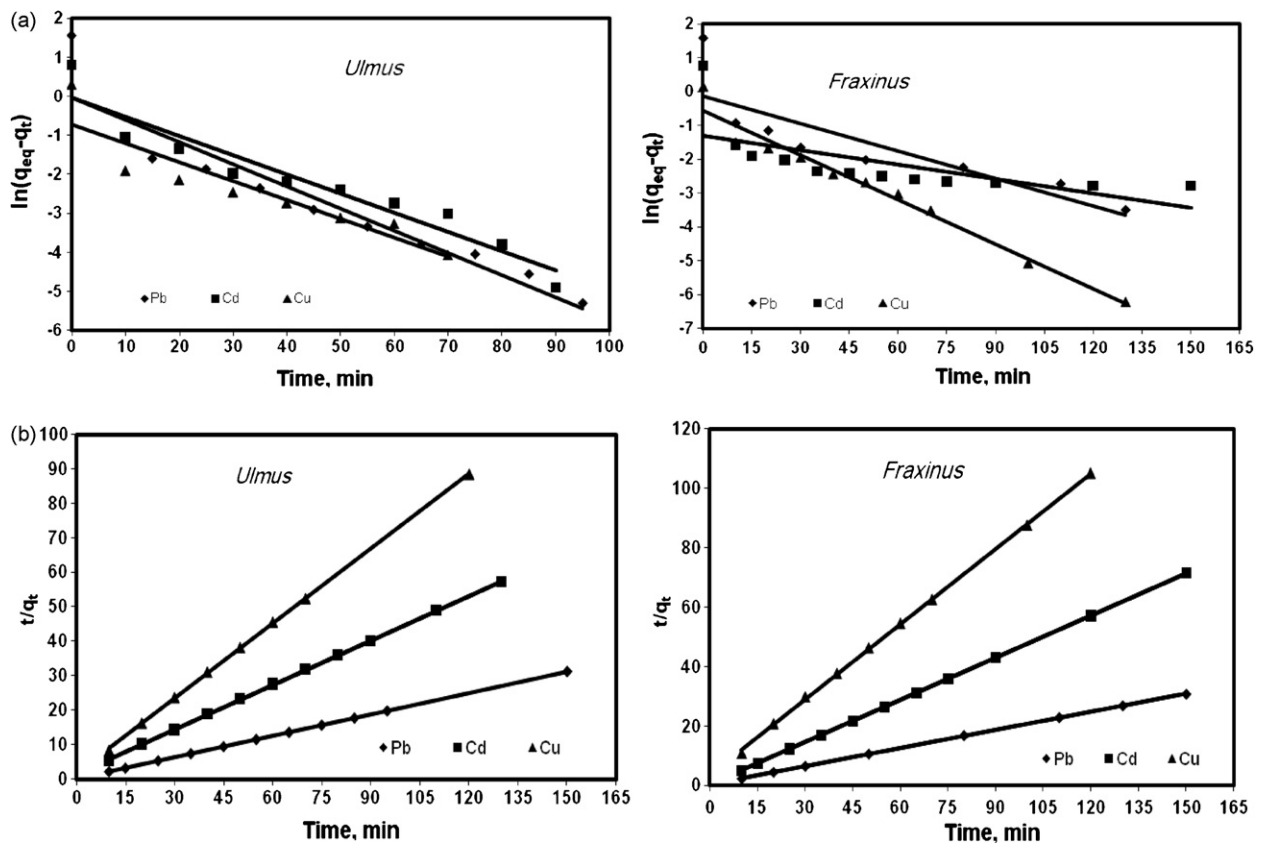

Fig. 8. (a) Biosorption of Pb(II), Cd(II) and Cu(II) by *Ulmus* and *Fraxinus* tree leaves on the first-order reaction kinetics model, as related to time (t), the quantity of metal adsorbed at equilibrium (q_{eq}) and the quantity of metal adsorbed at t (q_t); (b) biosorption of Pb(II), Cd(II) and Cu(II) by *Ulmus* and *Fraxinus* tree leaves on the second-order reaction kinetics model, as related to time (t), and the quantity of metal adsorbed at t (q_t).

Table 3
Theoretically determined constants of first- and second-order reaction kinetics based on the biosorption of the Pb(II), Cd(II) and Cu(II) from 50, 25 and 15.5 mg/l solutions, respectively, pH 5 by 10 g/l *Ulmus* and *Fraxinus* tree leaves during shake flask at 200 rpm

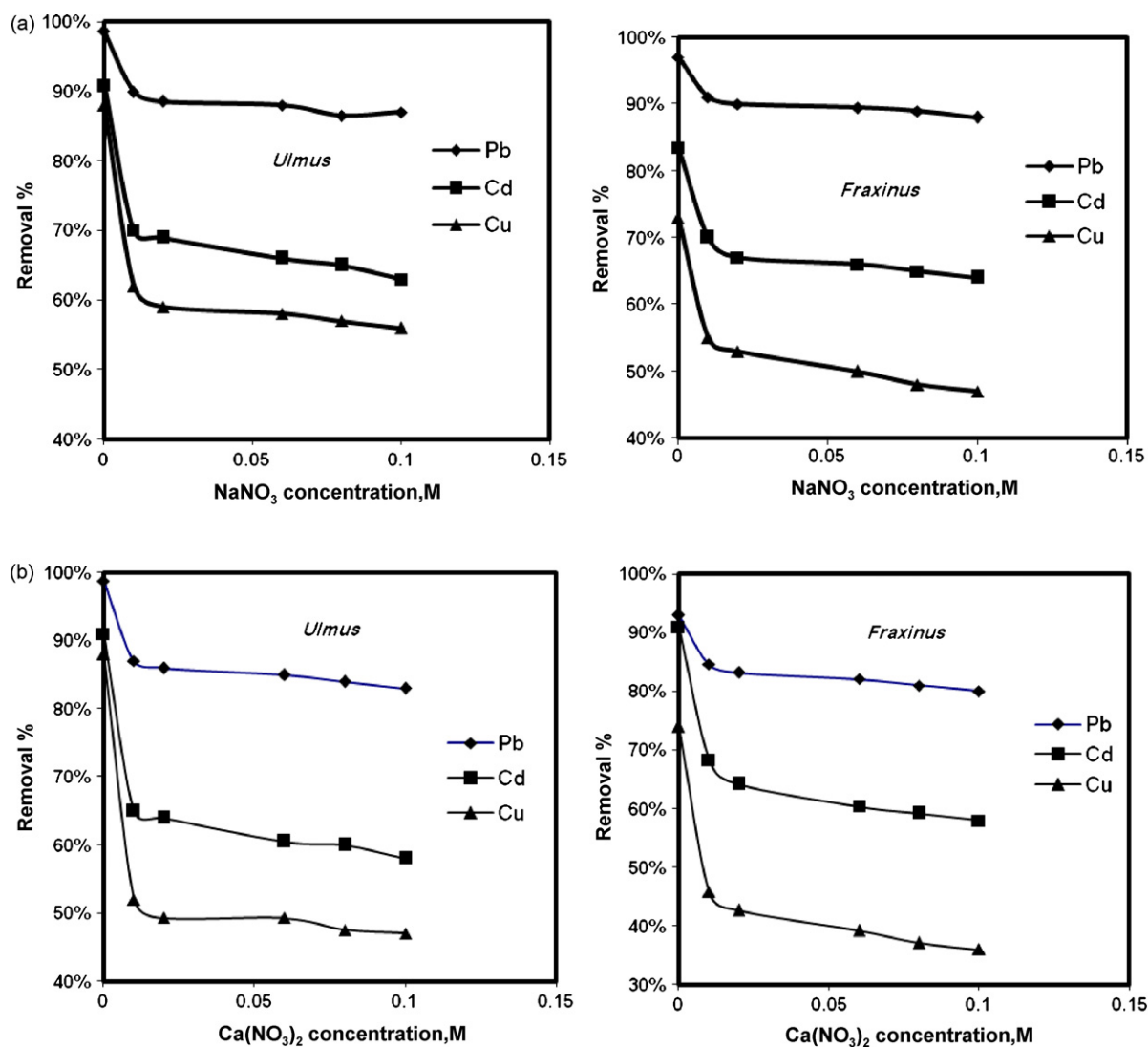| Metal ion	Sorbent						
	Experimental q_{eq} (mg/g)	First-order constants			Second-order constants		
		q_{eq} (mg/g)	K_1	r^2	q_{eq} (mg/g)	K_2	r^2
Ulmus							
Pb(II)	4.800	0.956	0.057	0.895	4.833	0.249	1
Cd(II)	2.251	0.969	0.049	0.916	2.320	0.135	0.999
Cu(II)	1.356	0.481	0.048	0.833	1.377	0.321	0.999
Fraxinus							
Pb(II)	4.865	0.847	0.027	0.729	4.888	0.013	0.999
Cd(II)	2.111	0.271	0.014	0.439	2.110	0.570	1
Cu(II)	1.149	0.577	0.044	0.970	1.184	0.196	0.999

Fig. 9. (a) The effect of NaNO$_3$ concentration on biosorption of Pb(II), Cd(II) and Cu(II) by *Ulmus* and *Fraxinus* tree leaves from 50, 25 and 15.5 mg/l metal solution, respectively, pH 5 in shake flask at 200 rpm at room temperature during 60-min contact time; (b) the effect of Ca(NO$_3$)$_2$ concentration on biosorption of Pb(II), Cd(II) and Cu(II) by *Ulmus* and *Fraxinus* tree leaves from 50, 25 and 15.5 mg/l metal solution, respectively, pH 5 in shake flask at 200 rpm at room temperature during 60-min contact time.

first-order process $\ln q_{eq}$ should be equal to the intercept of a plot of $\ln(q_{eq} - q_t)$ versus t. In addition, a pseudo-second-order equation based on adsorption equilibrium capacity may be expressed in the form:

$$\frac{t}{q_t} = \frac{1}{K_{2,ad}q_{eq}^2} + \frac{t}{q_{eq}} \tag{6}$$

where $K_{2,ad}$ (g mg^{-1} min^{-1}) is the rate equilibrium constant of pseudo-second-order reaction. A plot of t/q_t versus t should give a linear relationship for the applicability of the second-order kinetic model. The results show that the second-order equation fitted well with the experimental data (Fig. 8). The theoretical q_{eq} values for the biosorbents were very close and significantly different to the experimental q_{eq} values in the case of second- and first-order kinetic models, respectively (Table 3).

Therefore the second-order kinetics best describe the data, which relies on the assumption that biosorption may be the rate limiting step involving valence forces through sharing or exchange of electrons between biosorbent and sorbate [13].

3.8. Desorption and reuse

The regeneration of the biosorbents is of crucial importance in assessing their potential for commercial application. Desorption of Pb(II), Cd(II) and Cu(II) from the metal loaded *Ulmus* and *Fraxinus* tree leaves using 0.2 M HCl, one of the most effective desorbents [18], resulted in 35.21 ± 0.11, 60.46 ± 1.62 and $85.36 \pm 1.16\%$ recovery of these metal ions, respectively for *Ulmus* and 40.11 ± 1.67, 66.82 ± 0.36 and $91.24 \pm 0.76\%$ recovery of these metal ions, respectively for *Fraxinus*. In order to show the reusability of the sorbents, adsorption–desorption cycle of Cu(II) was repeated three times using the same preparations. The adsorption efficiency of both sorbents did not noticeably change and only a maximum 5% decrease was observed after three cycles. This may be due to the small amount of biomass lost during the repeated adsorption–desorption operations. The regeneration of both biomasses shows that biosorption–desorption is a reversible process.

3.9. Effect of the salt concentration

To investigate any interference caused by the presence of other cations, Na, K, Mg and Ca ions, were added to the Pb(II), Cd(II) and Cu(II) solution in a batch system, all parameters such as pH (5), contact time (60 min), volume of solution (100 ml) and quantity of sorbents (1 g) were kept constant.

These elements are likely to be encountered in most industrial effluents [18], from which toxic metals are intended to be removed by biosorption.

The results indicated that the presence of Na or Mg ions, even at much higher concentration (0.1 M) than heavy metals, reduced the Pb(II) removal by 10%, the Cd(II) removal by 20% and the Cu(II) removal by 30% (Fig. 9a) and also the presence of K or Ca ions reduced the Pb(II) removal by 15%, the Cd(II) removal by 30% and the Cu(II) removal by 40% (Fig. 9b). It should be added that the effect of the presence of Na and Mg

on one hand and Ca and K on the other hand on the adsorption of heavy metal ions by sorbents were very similar so the figures depict the first counterpart of each group, i.e., Na and Ca.

This drop in the biosorption of Pb(II), Cd(II) and Cu(II), respectively by both sorbents may be attributed to greater adsorption at the binding sites by the larger ion size of Pb(II), Cd(II) and Cu(II). Ionic radius (Å) of the metals are 1.33, 1.09 and 0.87 and also hydrated ionic radius (Å) of the metals are 2.74, 2.28 and 2.07 for Pb(II), Cd(II) and Cu(II), respectively [42].

Also the different drop in the biosorption of heavy metals by sorbents in the presence of Na or Mg ions and K or Ca ions could be related to both ionic size; ionic radius (Å): 1.16, 0.86, 1.14 and 1.52 for Na, Mg, Ca and K ions [43], and ionic charge.

From a practical point of view however, these results imply that *Ulmus* and *Fraxinus* tree leaves can be used for removal of Pb(II) from salt containing wastewaters.

4. Conclusion

The biosorption capacities of *Ulmus* and *Fraxinus* tree leaves used in this study compared with those found in the literature show that these sorbents are very effective for the removal of Pb(II), Cd(II) and Cu(II) from aqueous solutions. Among the advantages of these new sorbents are their high capacity for removal of heavy metals from contaminated waters even in the presence of high concentrations of Na, K, Ca and Mg typically found in wastewaters [44]. Another advantage of using these new sorbents is their high capacity for removal of heavy metals from medium acidic aqueous solutions. Furthermore, the *Ulmus* and *Fraxinus* trees are grown widely in Iran, the leaves have no commercial value and are a good, inexpensive source of readily available biomaterial.

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