Comparison of biosorption of cadmium ions from aqueous solutions by the lichens Acarospora strigata, Lecanora muralis and Caloplaca aurantia

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Abstract

Introduction: Biosorption of heavy metals can be an effective process for the removal of heavy metal ions from aqueous solutions. Also, living lichens are known to accumulate metals across their surface.

Materials and methods: In this study, the biosorption of cadmium ions Cd (II) by the lichens *Acarospora strigata*, *Lecanora muralis* and *Caloplaca aurantia* was investigated in aqueous solution in a batch system with respect to pH, biomass dosage, temperature initial cadmium ion concentration and contact time.

Results: The biosorption capacity of the biomass was found to be 6.9 mg/g at pH 7 for *L. muralis*, 7.6 mg/g at pH 6 for *A. strigata* and 8.6 mg/g at pH 7 for *C. aurantia*. The experimental adsorption data were fitted to the Freundlich adsorption model. Experimental data were also tested in terms of kinetic characteristics and it was found that biosorption processes of Cd (II) ions followed well pseudo-second-order kinetics.

Conclusion: The results indicated that the biomass of *L. muralis*, *A. strigata* and *C. aurantia* are suitable biosorbents for removing Cd (II) from aqueous solutions and among these three species, *C. aurantia* has greater ability to remove cadmium from aqueous solutions.

Keywords: Heavy metal, Isotherm, Kinetics, Lichen

Introduction

In late years, heavy metal pollution has become one of the most serious environmental problems (1). Heavy metals have been entered into the environment over long periods of time by natural processes and manmade activities produce uncommon concentrations of metals. Once the metals have been entered into the environment, they are hard to be removed by physical or chemical methods and most of them expose toxic effects on organism (2). Considerable attention has been paid to the removal of heavy metals from industrial wastewaters because of their hazardous to living organisms (3). Among the heavy metal, copper, lead, cadmium, mercury, nickel and zinc have high precedence for removal from aqueous environments (4). Cadmium is one of the most toxic metals (5, 6). The main sources of cadmium released into the environment are water flows from electroplating, smelting, alloy manufacturing pigments, plastic, battery, mining, and refining process. Cadmium desires to accumulate in living organisms causing important threats to both, the environment public health (6).

The usual methods used for removing heavy metal from wastewater comprise chemical precipitation, lime coagulation, ion exchange, reverse osmosis, electrochemical treatment, evaporation and solvent extraction. Application of this

treatment method has been found to be sometimes restricted, because of costly investment, operational costs and potential generation of secondary pollution. Therefore, the search for new cost-effective technologies for the elimination heavy metal from wastewater has been directed toward biosorption, which is known for the last few decades (7, 8).

Biosorption processes show one of the possible interactions of toxic metals with biological systems in contaminated environment. Bioremoval of single species of metal ions is affected by several factors such as the special surface properties of biosorbent, temperature, pH, initial metal ion and biomass concentrations. Biosorption of metals is not based on only one mechanism. It consists of various mechanisms that quantitatively and qualitatively differ according to the kind of biomass (9). The main advantages of biosorption over usual treatment methods include low cost, high performance of metal removal from dilute solution, minimization of chemical and/or biological sludge, no additional nutrient requirement, and regeneration of biosorbent and the possibility of metal resumption. Biosorption for the removal of heavy metal ions may provide an attractive alternative to physico-chemical ways (10, 11).

Lichens are a symbiotic relationship between algae and fungi and employed as biomonitors for the heavy metal evidence in terrestrial ecosystems because of their good metal accumulation properties. Today more than 20,000 lichen species distributed throughout the world are known and about 8% of the terrestrial ecosystems consist of them (12). They have been frequency used as air pollution monitors because of their ability to strongly bind and accumulate many metals. These organisms have also bind and accumulate many metals. They have also been found to bind metals in a strongly pH dependent manner. Generally optimum binding is observed at a pH of around 5.0. Little binding is seen below pH values of 2.0 for most metal ions, the metal ion-binding properties of lichens have been pointed out that nonliving lichen biomass is able to bond metal-ions to a greater degree than living lichens. This strong metal binding ability of lichen biomass from aqueous solutions would seem to make this material an ideal biosorbent for removal of heavy metals (13, 14).

The objective of the present work is to investigate the biosorption potential of *Acarospora strigata*, *Lecanora muralis* and *Caloplaca aurantia* biomass in the removal of Cd (II) ions from aqueous solution. The effects of different parameters such as pH, biomass dosage, temperature, initial concentration of cadmium ion and contact time on the adsorption capacity were studied.

Materials and methods

Lichens biomass of *Acarospora strigata*, *Lecanora muralis* and *Caloplaca aurantia* was used as a biosorbent for the biosprption of Cd (II) ions. Samples of the lichens were collected from Ilam province, Dareh Arghavan. They were washed with deionized water and inactivated by heating in an oven at 80ºC for 48 hours. The inactivated dried lichen biomass was ground and sieved through different size and used in all experiments.

Preparation of stock solution: The stock solution of Cd (II) (500 mg/L) was prepared by dissolving 1.0515 g of Cd (NO$_3$) by deionized water. The required concentrations were prepared from the stock solution by dilution (15).

Biosorption studies: The effect of the factors of temperature, biosorbent concentration, pH, connection time and initial Cd (II) concentration on the uptake of cadmium ions by lichens was studied. Biosorption experiments were optimized out at the desired pH value, contact time and biomass dosage level, temperature and initial Cd (II) concentration using the necessary biomass in a 100 ml Erlenmeyer

flask containing 50 mL of test solution. Initial solutions with different concentration of Cd (II) were prepared by proper dilution from stock 500 mg/L Cd (II) standard. Necessary amount of the biomass was then added and contents in the flask were shaken for the desired contact time in an electrically thermostatic reciprocating shaker at 150 rpm. The contents of the flask were filtered through filter paper and the filtrate was analyzed for metal concentration by using flame AAS. The percent biosorption of metal ion was calculated as follows:

$$\text{Bhosorption (\%)} = \frac{c_i - c_f}{c_i} \times 100 \qquad (1)$$

Where, C_i and C_f are the initial and final metal ion concentrations, respectively (16). Amount of adsorbed metal ions per gram of biomass was obtained by using the general equation:

$$q_e = \frac{(c_i - c_f) \times v}{m} \qquad (2)$$

Where q_e is the amount of metal adsorbed on the biomass (mg/g), C_i is the initial metal ion concentration in solution (mg/L), C_f is the equilibrium metal ion concentration in solution (mg/L), v is the volume of the medium (L) and m is the amount of the biomass used in the reaction mixture (17).

The pH of each solution was adjusted to the required value (3.0, 5.0, 6.0, 7.0 and 8) by using HCl and NaOH solutions (0.1 and 0.01 N). The biosorbent concentrations was set between 1 to 9 mg/L, the contact time was varied from 5 to120 min, the initial metal concentration from 30 to 150 mg/L and The experiments were repeated at 20, 30, 40 and 50ºC (18, 19).

Results

Effect of pH: The effect of pH on the biosorption of Cd (II) ions onto the tree species of lichens was studied by changing pH values in range of 3–8 and the results were presented in figure 1A. The maximum biosotption was found to be 69% for *L. muralis*, 76% for *A. strigata* and 86% for *C. aurantia* at pH 7, 6 and 7, respectively. Biosprption efficiency (%) reduced with pH reduction in all three species.

Effect of biosorbent concentrate: The effect of biomass dosage on the biosorption of Cd (II) ions was studied using the biomass in the range of 1-9 g/L (Figure 1B). Results showed that in all three species the biosorption of the metal ion increased with increasing biomass dosage because of the availability of more binding sites for complexation of Cd (II) ions and almost constant at higher than 5 g/L in *L. muralis* and *C. aurantia* and higher than 7 g/L in *A. strigata*.

Effects of contact time: Figure 1C shows the effect of contact time on the biosorption of Cd (II) ions onto biosorbents. This figure shows that biosorption of Cd (II) increases with rise in contact time up to 90 min for three species. Maximum biosorption was 69%, 76% and 86% for *L. muralis*, *A. strigata* and *C. aurantia* biomass, respectively, in 90 min. After this time there was no considerable increase. Therefore the optimum contact time was selected as 90 min for further experiments.

Effect of temperature: The biosorption percentage decreased for Cd (II) ion as temperature was increased from 20 to 50°C for the equilibrium time (90 min) (Figure 1D).
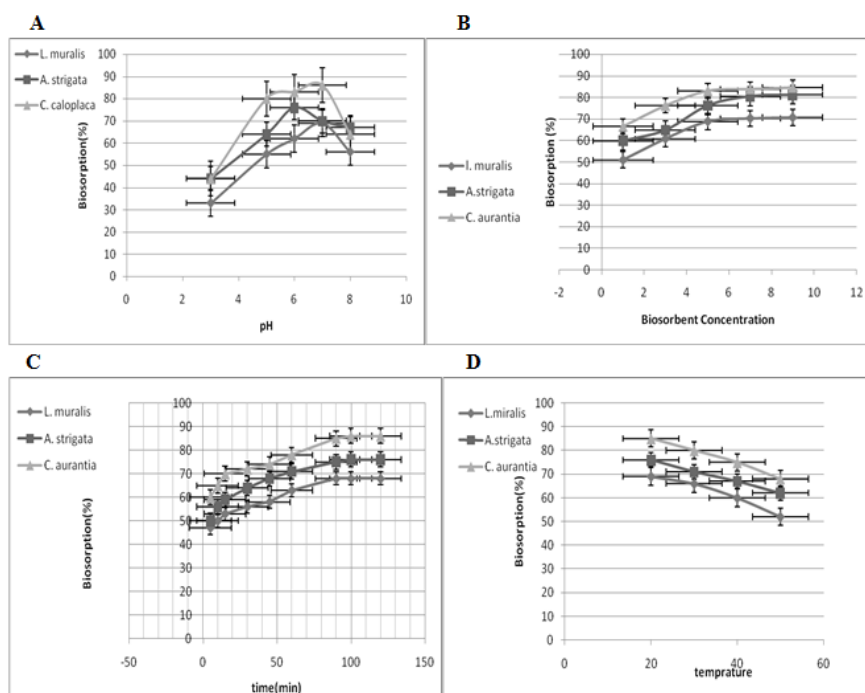
Figure 1. Effects of (A): pH (metal concentration: 50 mg/L; biomass dosage: 5 g/L; temperature: 20°C), (B): biomass dosage (metal concentration: 50 mg/L; pH 6 and 7; temperature: 20ºC), (C): contact time (metal concentration: 50 mg/L; biomass dosage: 5 g/L; temperature: 20ºC) and (D): temperature (metal concentration: 50 mg/L; biomass dosage: 5 g/L: time contact: 90 min) on the biosorption of Cd (II) ions.

Effect of initial cadmium ion concentration: Biosorption experiments were carried out at different initial Cd (II) concentrations ranging from 30 to 150 mg/L. The biosorption efficiency decreased with increasing of initial Cd (II) ion concentration, however, the amount of Cd (II) adsorbed on the biomass (mg Cd (II)/g biomass) increased as seen from Table 1.

Table 1. Effect of initial Cd (II) concentration on biosorption (T=15°C, m= 5 g/L, t = 90 min).

Lichen	*C_i(mg/L)	**C_e(mg/L)	Adsorbed Cd(II)	***q_e	Biosorption(%)
	30	8/64	21.36	4.27	71.2
L. muralis	50	15.35	34.65	6.93	69.3
(pH: 7)	70	25.06	44.4	8.98	64.2
	110	44.63	65.64	13.12	59.4
	150	73.9	76.1	15.22	50.7
	30	3.9	26.1	5.22	87
A. strigata	50	11.65	38.35	7.67	76.7
(pH:6)	70	20.28	49.72	9.9	71
	110	41.4	68.6	13.7	62.3
	150	67.3	82.7	16.54	55
	30	4.7	25.3	5.06	84.3
	50	9.4	40.6	8.1	81.2
C. aurantia	70	17.2	52.8	10.56	75.4
(pH: 7)	110	31.8	78.2	15.64	71.09
	150	60.8	89.2	17.84	59.4

*C_i: the initial metal ion concentration, **C_e: the final concentration at the equilibrium (mg/L), ***q_e: the metal uptake at the equilibrium (mg/g).

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Adsorption isotherms: The Langmuir isotherm was represented by the following equation:

$$q_e = \frac{bq_{max}c_e}{1+bc_e} \qquad (3)$$

The linear form of this equation can be given as:

$$\frac{1}{q_e} = \frac{1}{bq_{max}c_e} + \frac{1}{q_{max}} \qquad (4)$$

Where q_e is the metal uptake at the equilibrium (mg/g), q_{max} is the maximum Langmuir uptake (mg/g), c_e is the final concentration at the equilibrium (mg/L) and b is the Langmuir affinity constant (mg/ L). From the slope and intercept of a plot of c_e/q_e versus C_e, q_{max} and b can be determined. Figure 2 gives the plot of the Langmuir adsorption isotherm for Cd (II) ion biosorption onto the lichen biomass.
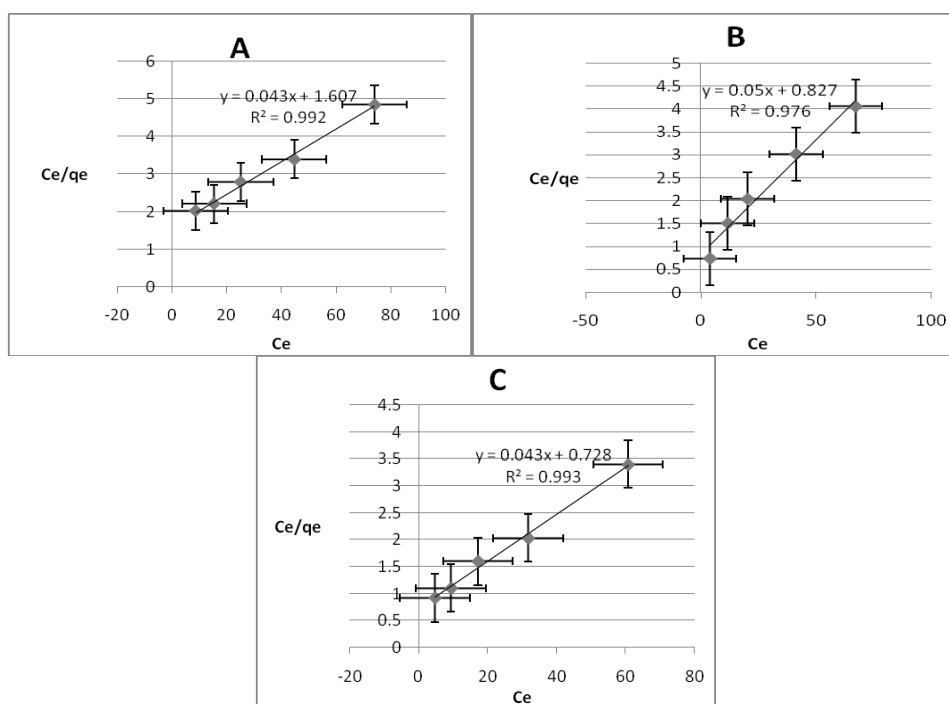

Figure 2. Langmuir adsorption isotherm for Cd (II) ion biosorption onto (A): *L. muralis*, (B): *A. strigata* and (C): *C. aurantia* [(*Ce/qe= 1/Qob + Ce/Qb*), *Ce*: equilibrium concentration, *qe*: amount adsorbed of CD (II) at equilibrium, *Qo*: Langmuir constants related to adsorption capacity, *Qb*: Langmuir constants related to energy of adsorption].

The Freundlich isotherm model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. The Freundlich model is:

$$\text{Log } q_e = \log k_f + 1/n \log C_e \qquad (5)$$

Where K_f is a constant relating the biosorption capacity and 1/n is an empirical parameter relating the biosorption intensity, which varies with

the heterogeneity of the material. The slope 1/n, ranging between 0 and 1, is a measure for the adsorption intensity or surface heterogeneity. A value for 1/n below 1 indicates a normal Langmuir isotherm while 1/n above 1 is indicative of cooperative adsorption. The plot of log qe versus log Ce for the adsorption of Cd^{2+} ions onto the lichen biomass is given in Figure 3. Comparison of isotherm models show that, R^2 obtained from the Langmuir model for *L. muralis*, *A. strigata* and *C. aurantia* is 0.99, 0.97 and 0.99 respectively. R^2 obtained from the

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Freunlich model is 0.97, 0.99 and 0.97, respectively (Table 2). Since the qe obtained from the Langmuir equation is very different from the qe experimental capacity can be said Langmuir model is

not a good model to describe the adsorption characteristics of Cd by this three species of lichen and the Freundlich model is a more appropriate model.
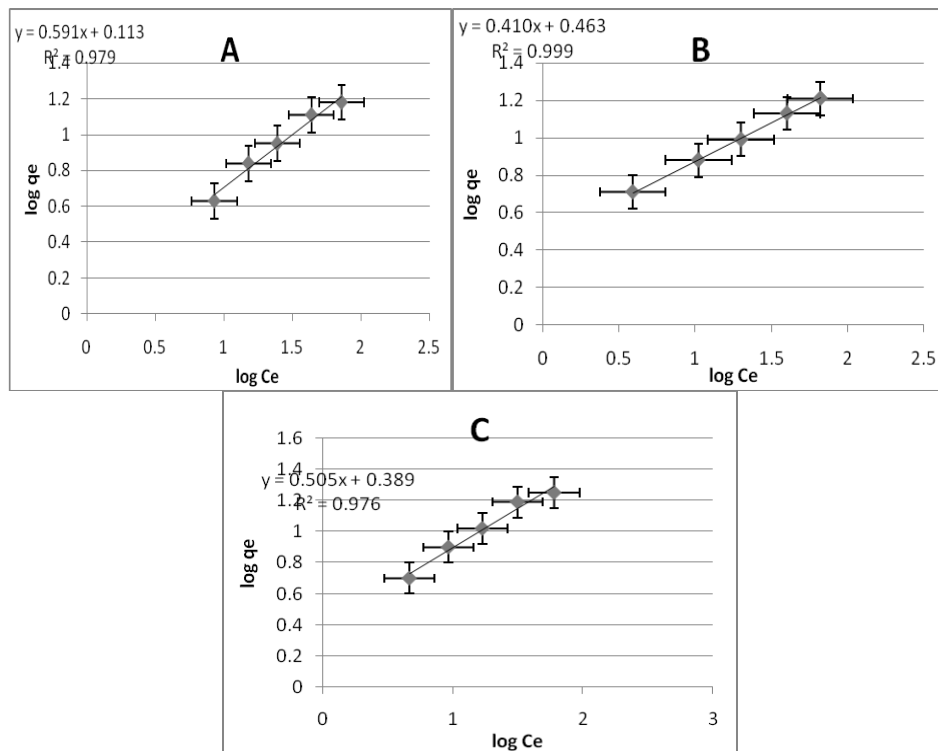

Figure 3. Freunlich adsorption isotherm for Cd (II) ion biosorption onto (A): *L. muralis*, (B): *A. strigata* and (C): *C. aurantia* [(*log qₑ=log kf+1/n log Cₑ*), *kf*: constant relating the biosorption capacity, *1/n*: empirical parameter relating the biosorption intensity, C_e: final concentration at the equilibrium (mg/L), q_e: metal uptake at the equilibrium (mg/g)].

Kinetics of the Biosorption: In order to clarify the biosorption kinetics of Cd (II) two kinetic models, which are Lagergren's pseudo-first-order and pseudo-second-order model were applied to the experimental data. The linearized form of the pseudo-first-order rate equation is given as:

$$Ln\ (q_e - q_t) = \ln q_e - k_1 t \qquad (6)$$

Where qt and qe (mg/g) are the amounts of the metal ions biosorbed at equilibrium (mg/g) and t (min), respectively and k1 is

the rate constant of the equation (min-1). The biosorption rate constants (k1) can be determined experimentally by plotting of ln (qe − qt) vs. t. The plots of ln (qe − qt) vs. t for the pseudo-first-order model were not shown as figure because the coefficients of determination for this model at studied temperatures is low (as see in Table 2). It can be concluded from the R^2 values that the biosorption mechanism of Cd (II) ions onto *L. muralis*, *A. strigata* and *C. aurantia* does not follow the pseudo-first-order kinetic model.

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Table 2. Pseudo-first-order and pseudo-second-order parameters and Langmuir and Freundlich model equation parameters estimated from the fitting of experimental points of Cd (II) biosorption.

Lichen		Langmuir equation			Freundlich equation		
	pH	*Q_{max}(mg/g)	**KL (L/mg)	R^2	[a]KF (L/mg)	[b]1/n	R^2
L. muralis	7	23.2	1.6	0.9925	1.25	0.591	0.9793
A. strigata	6	20	0.82	0.976	2.51	0.410	0.999
C. aurantia	7	22.27	0.75	0.9939	1.99	0.505	0.9768
		Pseudo-first-order			Pseudo-second-order		
	pH	[c]q_e	[d]K1	R^2	q_e	[e]K2	[f]R^2
L. muralis	7	2.25	2.3×10^{-2}	0.9455	7.14	0.013	0.9938
A. strigata	6	3	2.8×10^{-2}	0.9931	8.3	0.007	0.9981
C. aurantia	7	2.64	1.8×10^{-2}	0.9356	9.09	0.004	0.9942

*Q_{max}: the maximum Langmuir uptake, **KL: the rate constant of the equation, [a] KF: constant relating the biosorption capacity, [b] 1/n: empirical parameter relating the biosorption intensity, [c] q_e: the amount of the metal ions biosorbed at equilibrium (mg/g), [d] K1: the rate constant of the first-order equation, [e] K_2: the rate constant of the second-order equation, [f] R^2: correlation coefficient.

Experimental data were also tested by pseudo-second order kinetic model which is given in the following form:

$$\frac{t}{qt} = \frac{1}{k_2\, q_e^2} + \left(\frac{1}{q_e}\right) \qquad (7)$$

Where k_2 (g/mg min) is the rate constant of the second-order equation, qt (mg/g) is the amount of biosorption time t (min) and q_e is the amount of biosorption equilibrium (mg/g). This model is more likely to predict kinetic behavior of biosorption with chemical sorption being the rate-controlling step. The linear plots of t/qt vs t for the pseudo-second-order model for the biosorption of Cd (II) were shown in Figure 4. It is clear that the R^2 values are very high. These results indicated that the biosorption of Cd (II) ions onto *L. muralis*, *A. strigata* and *C. aurantia* follows well the pseudo-second-order kinetic model.
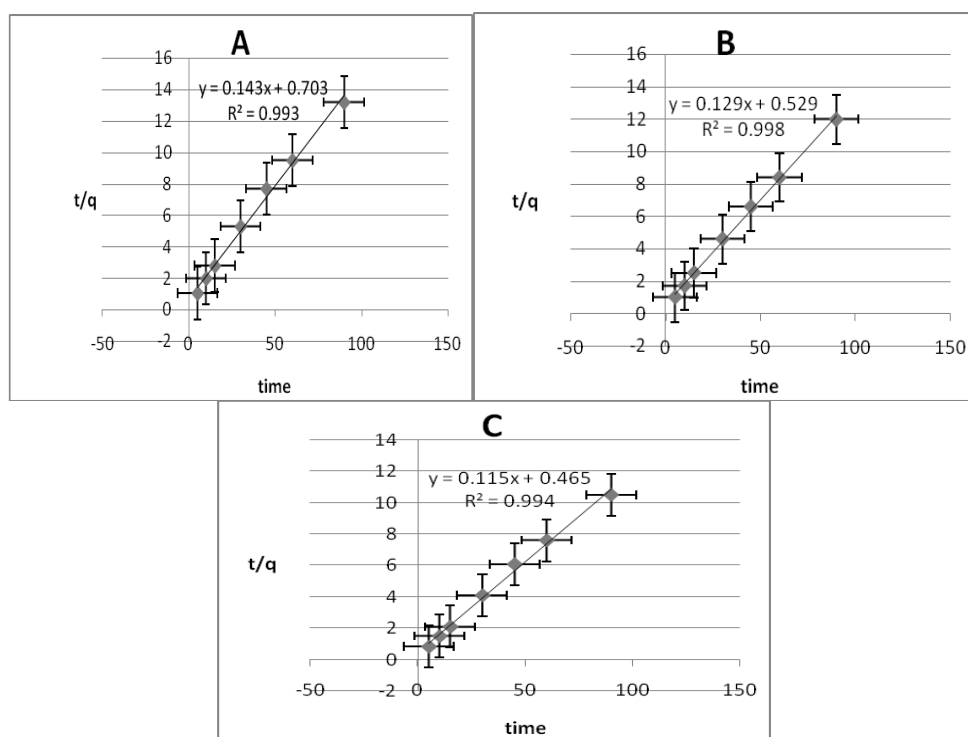

Figure 4. Pseudo-second-order kinetic plot for the biosorption of Cd (II) ions onto (A): *L. muralis*, (B): *A. strigata* and (C): *C. aurantia* [(*t/q = 1/Kqe² + 1/qe * t*), *t*: contact time (min), *qe* (mg/g) and *qe²* (mg/g): amount of solute adsorbed at equilibrium, *K*: the rate constant].

Discussion

One of the most important affecting biosorption of metal ions is acidity of solution. The acidity of the medium affects the competition ability of hydrogen ions with metal ions to active sites on the biosorbent surface (20-22). Our results can be explained by the pH effect on both metal binding sites on the biomass surface and metal chemistry in aqueous solutions. Increased positive charge (protons) density on the sites of biomass surface at low pH value (pH= 2) restricted the approach of metal cations as a result of repulsive force. In contrast, when the pH values increased, adsorbent surfaces were more negatively charged and the biosorption of the metal ions with positive charge (Cd^{2+}) process was reached maximum around pH 6–7. Decrease in biosorption at higher pH (>7) is due to the formation of soluble hydroxylated complexes of the metal ions and their competition with the active sites, and as a consequence, the retention would decrease again (14, 20, 23). The almost same contact time was reported in several earlier works which related with the biosorption of same metal ions on various biomasses (14, 24).

Our result can be explained as a consequence of a partial aggregation, which occurs at higher biomass dosage giving rise in a decrease of active sites on the biomass (13, 25, 26). The researchers implied that a partial cell aggregation taking place at high biomass concentrations caused a decrease of active sites. Various reasons including pH, ionic strength temperature, and metal ion in solution and biomass concentration have been suggested to explain the decreased adsorption capacity at increasing biomass (13, 27). Therefore, the amount of biomass was selected as 5 g/L for further experiments.

The result of this research indicated the exothermic nature of Cd (II) biosorption onto lichens biomass. A decrease in the biosorption of Cd (II) ions with the rise in temperature may be due to either the damage of active binding sites in the biomass or increasing tendency to desorb metal ions from the interface to the solution (28, 29). The optimum solution temperature was selected as 20°C for further biosorption experiments.

In this study the biosorption efficiency decreased with increasing of initial Cd (II) ion concentration, however, the amount of Cd (II) adsorbed on the biomass increased. This trend suggests that most of the available sorption sites become occupied at high initial metal ion concentrations. Therefore, more Cd (II) ions were left unadsorbed in solution at higher concentration levels (30-34).

Analysis of equilibrium data on a specific mathematical equation is of significance for comparing different sorbents under different experimental conditions. The two well-known adsorption isotherm models Langmuir and Freundlich were applied for the analysis of the experimental data in single sorption systems (9). The Langmuir isotherm considers sorption as a chemical phenomenon. This model suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate (30).

Conclusions

The purpose of this study was to investigate cadmium uptake by *L. muralis*, *A. strigata* and *C. aurantia* and compare the absorption of Cd by this three species. It was found that cadmium uptake by the effect of various parameters such as pH, temperature, time of connection, the concentration of adsorbent and initial concentration of cadmium. PH suitable for adsorption obtained 7, 6 and 7 for *L. muralis*, *A. strigata* and *C. aurantia*, respectively. Also, it was found that the optimum temperature absorption 20ºC and

the optimum time 90 minutes, for all three species. The adsorption capacity biosorption of the lichen for cadmium ions increased with increasing initial concentration of cadmium ions. The pseudo-second-order equation for the kinetics of the adsorption appears to be the better-fitting model compared to the pseudo-first-order equation. The experimental results were well modeled according to the Freundlich adsorption isotherms. Comparison of biosorption present shows that *C. aurantia* have greater ability for cadmium uptake (*L. muralis*: 69.6%, *A. strigata*: 72% and *C. aurantia*: 86%).

Acknowledgements

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