Sustainable use of biomass for cleaning-up aqueous effluents contaminated with heavy metals

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Abstract.
The utilization of no economical value biomass as low-cost biosorbent for the removal of heavy metals from aqueous effluents is a relatively new concept, which began to be increasingly used in the wastewater treatment processes, mainly because it is in agreement with the principles of sustainable development. In this study, mustard biomass obtained from mustard husk and low quality seeds, was investigated as suitable biosorbent for the removal of heavy metals (Pb(II) and Cd(II)) from aqueous effluents, through batch biosorption experiments. The biosorbent was characterized by EDX spectrometry, IR spectrometry and SEM microscopy. The effect of initial solution pH, biosorbent dose, initial heavy metals concentration, contact time and temperature on the biosorption of Pb(II) and Cd(II) ions were analyzed. The mustard biomass has a good biosorption potential fro Pb(II) and Cd(II) at pH 5.5, 5 g/L biomass dose and a contact time higher than 60 min. The experimental kinetic data were better fitted with pseudo-second order kinetic model than pseudo-first order model. The Langmuir isotherm model was found to be more adequate for the mathematical description of equilibrium data. The maximum biosorption capacity calculated under mentioned conditions was 0.39 mmol/g for Pb(II) and 0.53 mmol/g for Cd(II), respectively.

Key words: mustard biomass, biosorption, heavy metals, aqueous effluents.

1. Introduction

Heavy metals are considered persistent pollutants in environment, because they have a considerable toxic effect even at lower concentration, have an accumulating tendency and cannot be destroyed or degraded (Hlihor R.M. and Gavrilescu M., 2009). Among all heavy metals, Pb(II) and Cd(II) are the most hazardous, because they cannot be biologically metabolized and are toxic for most life forms (Londrigan P.J. et al., 1990). From this reason, the permissible limits of Pb(II) and Cd(II) in drinking water are very low (0.5 mg/L for Pb(II) and 0.3 mg/L for Cd(II), respectively) (NTPA 001/2005). Beyond the permissible limits, both Pb(II) and Cd(II) causes acute and chronic diseases in human body, such as anemia, hypertension, learning disabilities, kidney damage and mental retardation (Gogate P.R. and Pandit A.B., 2004; Yuan G. et al. 2014).

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Unfortunately, due to their numerous industrial applications in electroplating industries, battery manufacturing, fertilizers production, painting, printing, etc. (Han R. et al., 2006; Hlihor R.M. and Gavrilescu M., 2009), important quantities of aqueous effluents that contains these heavy metals in considerable concentrations are discharged into environment, causing the degradation of ecosystems quality and also of human health. Therefore, it is desirable to eliminate heavy metals from industrial wastewaters prior discharged, and this could be also important from economical consideration, due to high value of these.

Until now is not an efficient technology for the removal of heavy metals from aqueous effluents that to achieve a level lower enough for the safe release into environment. The most frequently used methods applied in practice, such as chemical precipitation, membrane filtration, flocculation, reverse osmosis, ion-exchange etc. (Dabrowski et al., 2004; Gavrilescu, 2004; Demirbas, 2008; Febrianto et al., 2009; Llanos et al. 2010), have several important disadvantages, like high cost of operation, low selectivity, incomplete removal of heavy metals pollutants, generation of large quantities of secondary wastes that required further treatments, etc. These entire disadvantages make that mentioned methods to not be economically feasible in the treatment of aqueous effluents, even for small scale industries, and in present efforts are being made to develop more efficient and cost-effective treatment possibilities.

Biosorption of heavy metals onto various biological materials has attracted a great deal of attention during of the last years, for its potential application in heavy metals removal from aqueous effluents. In this context, the optimization of biosorption methods should be carried out, first of all, by choosing inexpensive biosorbents that to have a relative high selectivity for the heavy metals that should be removed. Therefore, different types of biomasses (natural materials, wastes or by-products obtained from various industrial activities) such as peat, algae, bacteria, cereal husk, plant leavers, fruit peel etc. (Brown et al., 2000; Kandah, 2004; Ajmal et al., 2005; Nagpal et al., 2011; Gautam et al., 2014) have been tested for their metal biosorptive potential, in various experimental conditions. These biosorbent materials have in their structure various types of functional groups (carboxylic, carbonilic, hydroxylic, sulfates, phosphates, etc.) that can bind heavy metals from aqueous media through ion exchange of superficial complexation processes.

Many agricultural wastes or by-products (tea, tobacco and coffee waste, pines bark, coconut husk, rice hulls, sawdust, wheat straw, corn cobs, and many others (Khan Ajmal et al., 2005; Qi and Aldrich C., 2008; Rao and Khan, 2009; Farooq et al., 2010; Khan et al. 2012) that are abundantly available are considered low-cost (or of no economical value) materials, and instead being thrown away or incinerated, they have been used as biosorbents for the removal and recovery of heavy metals from aqueous effluents. In this way is ensured a more sustainable use of such biomasses, minimizing the negative impact on environment, both by a superior valorization of an important category of biomass, and by reducing the heavy metals pollution degree of aqueous effluents.

In this study, mustard biomass (obtained from mustard husk and low quality seeds) was used as a suitable biosorbent for the removal of some heavy metals (Pb(II) and Cd(II)) from aqueous effluents. The effects of some process parameters (initial solution pH, biomass dose, initial heavy metals concentration, contact time and temperature) on Pb(II) and Cd(II) biosorption efficiency has been studied in batch experiments. The equilibrium and kinetic data obtained from biosorption studies were modeled using Langmuir and Freundlich isotherm models, and pseudo-first order and pseudo-second order kinetic models, respectively. Also a detailed characterization of mustard biomass is provided in order to highlight the porosity of biomass surface and main functional groups that can be involved in the heavy metals uptake process.

2. Experimental

Materials

All chemical reagents were of analytical degree and were used without further purifications. Sock solution of heavy metals (Pb(II) and Cd(II)), containing 10^{-2} mol M(II)/l were prepared by dissolving metal nitrate salts in doubly distilled water. The working solutions were obtained by diluting the stock solutions with doubly distilled water. Fresh dilution were prepared and used for each experiment. The initial pH of working solutions was adjusted at required value with 0.1 N HCl or NaOH solutions. The mustard biomass used in this study as biosorbent was obtained from mustard husk and low quality seeds, purchased from Faculty of Agriculture, USAMV Iasi, Romania. After washing several times with doubly distilled water, the biomass material was dried in air at 70 °C for 8 hours, crush 3000N) coupled with energy dispersive X-ray diffraction spectrometer (Bruker EDX spectrometer). The samples for SEM-EDX analysis were coated with tin carbon film, to prevent the influence of charge effect during of analysis. The main functional groups of mustard biomass were identified using IR spectra recorded with a Bio-Rad IR spectrometer, in 400 – 4000 cm^{-1}, with a resolution of 4 cm^{-1} and 32 scans, by KBr pellet technique.

Biosorption experiments

Biosorption experiments were carried out for a single component in 100 ml conical flasks. 25 ml of each heavy metal solution of desired concentration were contacted with 0.125 g of biosorbent, in a temperature controlled regime, with intermittent stirring. At equilibration, the samples were filtered and the heavy metals concentration from obtained solutions were analyzed spectrophotometrically (Digital Spectrophotometer S 104 D, 1 cm glass cell) using an adequate method (Dean, 1995). The biosorption capacity (*q*, mmol/g) and removal percent (*R*, %) were calculated using the following expressions:

$$q = \frac{(c_0 - c) \cdot V}{m} \tag{1}$$

$$R,\% = \frac{c_0 - c}{c_0} \cdot 100 \tag{2}$$

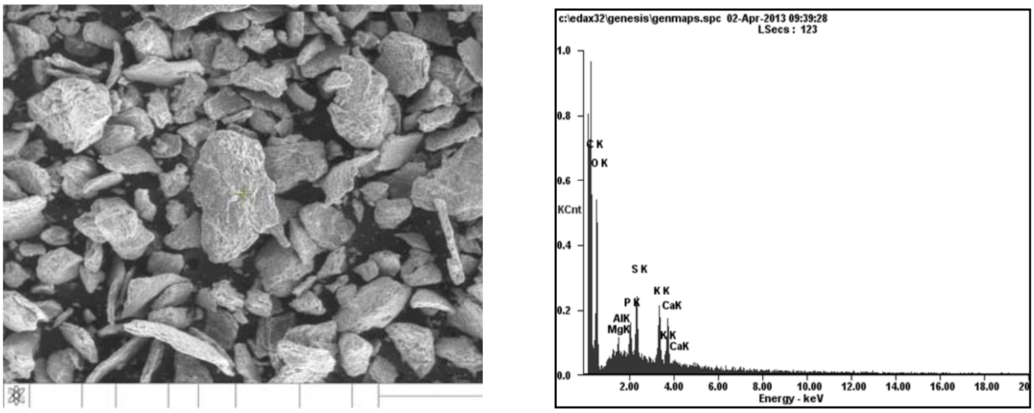
where: c_0 and c are initial and equilibrium concentrations of heavy metals (mmol/l), V is volume of solution (l) and m is mass of biosorbent (g).

The initial solution pH experiments were carried out at constant temperature (25 °C), biosorbent dose of 5 g/l and a constant initial concentration of heavy metals (0.40 mmol M(II)/l), adjusting the pH from 1.0 to 6.5 by adding 0.1 N HCl or NaOH solutions. The biosorbent dose studies were performed by varying the biosorbent amount between 4 and 40 g/l, under similar experimental conditions. The influence of initial heavy metals concentration was examined within 0.20 – 2.00 mmol/l concentration range, and different three temperatures (10, 25 and 55 °C), for 3 hours contact time. In the kinetic experiments, the same amount of biosorbent (0.125 g) was mixed with 25 ml of aqueous solution containing 0.40 mmol M(II)/l at various time intervals between 5 and 180 min.

3. Results and discussion

3.1. Characterization of biosorbent.

In order to characterize the mustard biomass used as biosorbent in this study, scanning electron microscopy (SEM), EDX spectrometry and IR spectrometry were used. SEM image (Fig. 1a) obtained by applying 30 kV at 100 magnification time, demonstrates that the biosorbent surface is wrinkled, porous and has crackers, which can facilitate the retention of heavy metal ions.



(a) (b)

Fig. 1. SEM image (a) and EDX spectra (b) of mustard biomass.

In addition, the EDX analysis (Fig. 1b) indicate that the mustard biomass contains in its structure various elements (C, O, P, S) that can be included in different functional groups, which may be binding size for heavy metals ions from aqueous solution. The presence of different functional groups on the surface of mustard biomass was highlight by using IR spectra (Fig. 2), recorded for dry material, where several important peaks can be observed. The identification of absorption bands from IR spectra has show that in the structure of biosorbent various functional groups (such as: hydroxyl, carbonyl, carboxyl, phosphate, etc.) are present, and these can interact with heavy metal ions from aqueous solution, during of biosorption process.

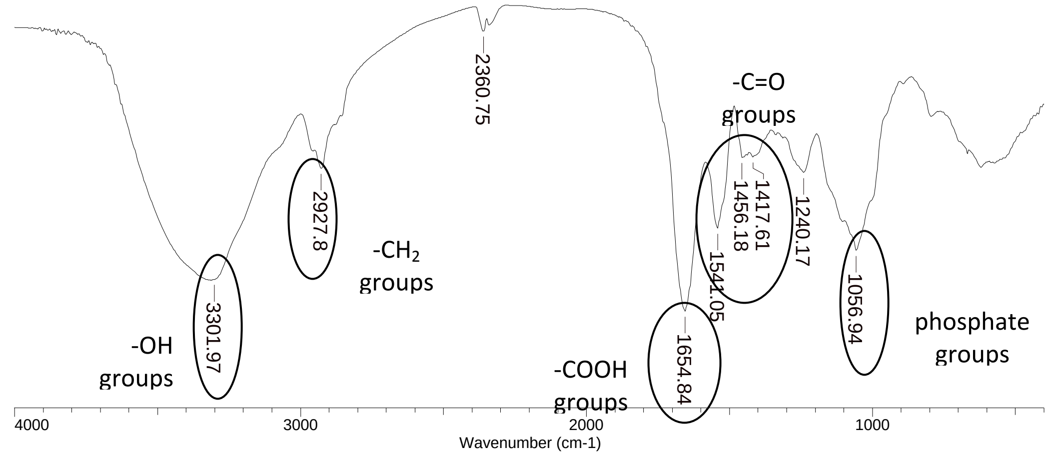


Fig. 2. IR spectra of mustard biomass.

Optimization of experimental parameters

It is well known that the biosorption of heavy metals take place with maximum efficiency only in well-defined experimental conditions (Gupta S. et al., 2009; Bulgariu L. et al., 2012). From this reason, batch biosorption experiments were performed to establish the optimum value of initial solution pH, biosorbent dose, initial heavy metals concentration, contact time and temperature.

Effect of initial solution pH. The initial solution pH has a considerable influence on heavy metals biosorption process. The change of heavy metals speciation and protonation / deprotonation of biosorbent surface are the most possible effects caused by the variation of initial solution pH (Yipmantin A. et al., 2011). The biosorption of Pb(II) and Cd(II) on mustard biomass was studied at room temperature (25 °C), by varying initial solution pH from 1.0 to 6.5, and the obtained results are illustrated in Fig. 3.

In strong acid media (pH = 1.0), the heavy metals biosorption was lower (43.14 % for Pb(II) and 41.08 % for Cd(II)). This indicates that at lower pH protons dominate the competition for binding sites from biosorbent surface. The increasing of initial solution pH determined a progressive increase of heavy metals biosorption, maximum being obtained at pH 5.5. After this value a slowly decrease of biosorption capacity is observed, both for Pb(II) and Cd(II) ions, respectively. When the initial solution pH is increased, the dissociation degree of functional groups from biosorbent surface also increase, and this will facilitate the interactions of these with heavy metal ions from aqueous solution.

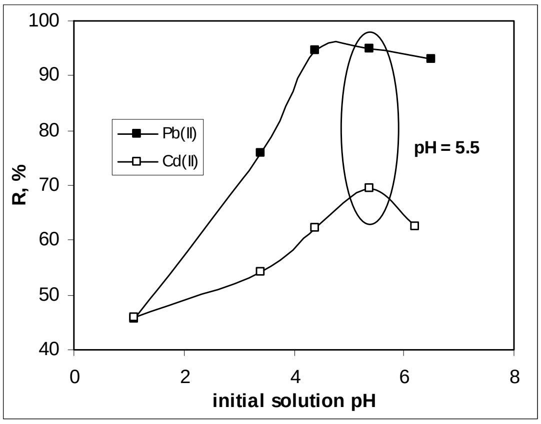


Fig. 3. Effect of initial solution pH on Pb(II) and Cd(II) biosorption onto mustard biomass

The decreasing of the biosorption capacity at initial solution pH higher than 5.5 is probably determined by the secondary hydrolysis processes that can change the speciation of considered heavy metal ion in aqueous solution. Therefore, and initial solution pH of 5.5 was considered as optimum value and was used for further experiments.

Effect of biosorbent dose. The biosorbent dose is a significant parameter used to determine the capacity of biosorbent for a given initial concentration of heavy metal ions in aqueous solution (Meena A.K.et al., 2008). It can be observed from Fig. 4 that the biosorption capacity of mustard biomass decreases from 0.09 to 0.01 mmol/g in case of Pb(II), and from 0.05 to 0.007 mmol/g in case of Cd(II) respectively, as biosorbent dose increase from 4 to 40 g/l.

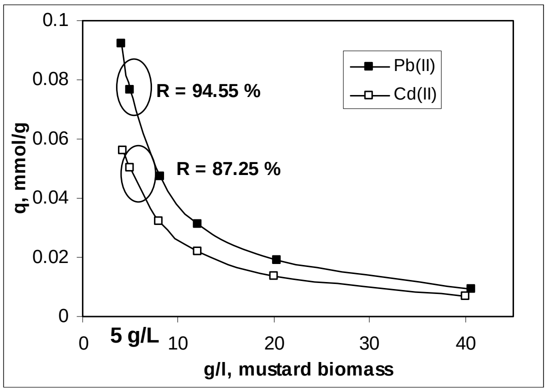


Fig. 4. Effect of biosorbent dose on Pb(II) and Cd(II) biosorption onto mustard biomass

This variation is mainly determined by the fact that even if the increase in biosorbent dose leads to the increase in the binding sites number, at high biosorbent dose some of these remains unsaturated, resulting thus the decrease of biosorption capacity. Basis of experimental results and from economical considerations a biosorbent dose of 5 g/l was selected as optimum value for the biosorption experiments.

Effect of initial heavy metals concentration. In order to investigate the influence of initial heavy metals concentration (c_0, mmol/l) on the biosorption onto mustard biomass, batch experiments were performed at room temperature (25 °C) by varying the initial heavy metals concentration from 0.20 to 2.00 mmol/l, under optimum establish experimental conditions (initial solution pH of 5.5, 5 g/l biosorbent dose). The obtained results (Fig. 5) indicate that the biosorption capacity of mustard biomass gradually increase with the increasing of initial concentration of heavy metals from aqueous solution. This variation can be mainly attributed to the fact that the increases of heavy metals concentration provide higher driving force to overcome all mass transfer resistances between solid and solution phase.

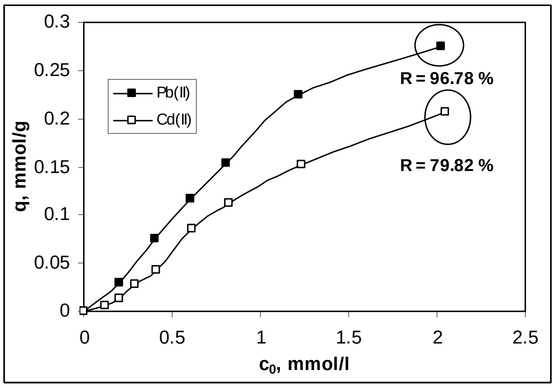


Fig. 5. Effect of initial heavy metals concentration on Pb(II) and Cd(II) biosorption onto mustard biomass

Nevertheless, the best removal of Pb(II) and Cd(II) ions by biosorption onto mustard biomass is obtained at low initial concentrations of heavy metals (lower than 20 mg/l in case of Pb(II) and 10 mg/l in case of Cd(II), respectively). Under these conditions, the heavy metals concentration in effluent solutions is lower that the maximum permissible limits (NTPA 002/2005), and the mustard biomass can be considered an effective biosorbent for wastewater treatment processes. When the initial concentration of considered heavy metals is higher, they concentration in effluent solution also increase, and in consequence two or more biosorption steps are necessary to reduce the metal ions content below the permissible limits.

Effect of contact time. The contact time studies (Fig. 6) showed an increase of biosorption capacity of mustard biomass with increasing of contact time, for both studied heavy metals. Initially, the biosorption was fast, in the first 30 min about 81 % of Pb(II) and 63 % of Cd(II) being retained.

After this fast step, the rate of biosorption process becomes more slowly, near to equilibrium which is practically attained after 60 min, for both studied heavy metals. Once the equilibrium was reached, the biosorption of Pb(II) and Cd(II) onto mustard biomass did not significantly change. These experimental data indicate that for efficient removal of Pb(II) and Cd(II) ions from aqueous solution by biosorption onto mustard biomass in mentioned experimental conditions, a contact time of minimum 60 min is required.

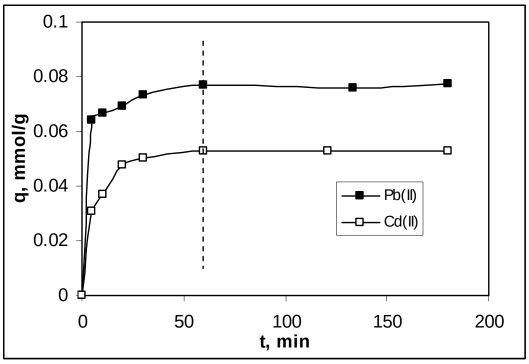


Fig. 6. Effect of contact time on Pb(II) and Cd(II) biosorption onto mustard biomass

Effect of temperature. The equilibrium biosorption capacity of Pb(II) and Cd(II) ions onto mustard biomass is favored by the increase of temperature (Fig. 7).

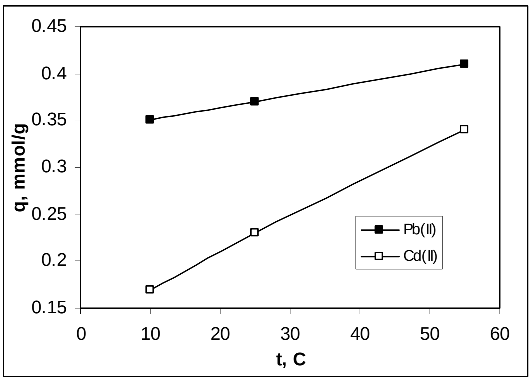


Fig. 7. Effect of temperature ob Pb(II) and Cd(II) biosorption onto mustard biomass

The experimental results show that when temperature increase from 10 to 55 °C, the biosorption capacity increase from 0.35 to 0.41 mmol/g in case of Pb(II), and from 0.17 to 0.34 mmol/g in case of Cd(II) respectively, at a contact time of three hours.

An explanation of such variation is that with increasing of temperature more binding sites from biosorbent surface becomes available to interact with metal ions from aqueous solution. However, because the increasing of temperature from 25 to 55 °C determined a relatively low increase of biosorption capacity (10.81 % for Pb(II) and 27.82 % for Cd(II), respectively), the performing of biosorption process at ambient temperature (25 °C) is more economical advantageous.

Biosorption isotherm modeling

Two linear isotherm models, Langmuir and Freundlich, were employed to evaluate the biosorption properties of this low-cost biomass. The mathematical equations of these models can be written as (Bulgariu L. et al., 2007; Rangabhashiyam S. et al., 2014):

Langmuir model: $$\frac{c}{q} = \frac{1}{q_{\max} \cdot K_L} + \frac{c}{q_{\max}} \qquad (3)$$

Freundlich model: $$\log q = \log K_F + \frac{1}{n} \log c \qquad (4)$$

where: q_{max} is maximum biosorption capacity (mmol/g) and represent a practical limiting of biosorption capacity when the surface is fully covered with metal ions; c is the concentration of heavy metals at equilibrium (mmol/l); K_L is the Langmuir constant (l/g); K_F is Freundlich constant and represent an indicator of the biosorption capacity; and n is an empirical parameter which reflects the intensity of biosorption that varies with the heterogeneity degree of biosorbent surface.

The parameters of Langmuir and Freundlich isotherm models have been evaluated from the slopes and intercepts of corresponding linear plots c/q vs. c, and log q vs. log c, respectively), and the obtained values for both studied heavy metals at each temperature are summarized in Table 1.

Table 1. Langmuir and Freundlich isotherm parameters for Pb(II) and Cd(II) biosorption onto mustard biomass

Isotherm model	Model parameters	Pb(II)			Cd(II)		
		10 °C	25 °C	55 °C	10 °C	25 °C	55 °C
Langmuir	***R^2***	***0.9989***	***0.9986***	***0.9993***	***0.9920***	***0.9829***	***0.9965***
	q_{max}, mmol/g	***0.3831***	***0.3913***	***0.4223***	***0.2812***	***0.5324***	***0.6391***
	K_L, l/g	***0.0384***	***0.0792***	***0.0122***	***0.0232***	***0.0146***	***0.0105***
Freundlich	R^2	0.8880	0.9681	0.9782	0.8979	0.8607	0.8971
	K_F	20.2512	17.3646	11.0937	13.5447	9.2972	7.6823
	n	0.3051	0.2933	0.3573	0.5560	0.6101	0.7075

The values of correlation coefficients (R^2) indicate that the biosorption isotherm data are very well represented by the Langmuir isotherm model, both for Pb(II) and Cd(II) biosorption onto considered biosorbent. This means that the mustard biomass surface is made up of homogeneous biosorption patches, and demonstrates the formation of monolayer coverage of Pb(II) and Cd(II) ions on the other surface of biosorbent. The maximum biosorption capacity (q_{max}, mmol/g), calculated from Langmuir isotherm model, increase with the increasing of temperature, for both studied heavy metals. The highest values of q_{max} obtained at 55 °C are 0.42 mmol/g for Pb(II) and 0.64 mmol/g for Cd(II), respectively. On the other hand, the high values of K_L suggest that between functional groups of biosorbent and metal ions from aqueous solution strong interactions occurs.

Biosorption kinetics modeling

In order to analyze the kinetics of biosorption process of Pb(II) and Cd(II) ions onto mustard biomass, the pseudo-first order and pseudo-second order kinetics models were used. The mathematical equations of these two models can be expressed by the following relations (Ho, Y.S., McKay, G., 2000; Gerente C. et al., 2007):

pseudo-first order kinetic model: $\log(q_e - q_t) = \log q_e - k_1 \cdot t \quad (5)$

pseudo-second order kinetic model: $\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad (6)$

where: q_e and q_t are the biosorption capacity at equilibrium and at time t respectively, (mmol/g); t is biosorption time (min), k_1 is the rate constant of pseudo-first order kinetic model (1/min) and k_2 is the rate constant of pseudo-second kinetic model (g/mmol min).

The straight lines in the graphical representation of log $(q_e\text{-}q_t)$ vs. t for the pseudo-first order kinetic model, and t/q_t vs. t for the pseudo-second order kinetic model, indicate the applicability of these, and will permit the calculation of the characteristic kinetic parameters (q_e, k_1 and k_2) from the slopes and intercepts of linear plots. In Table 2 are summarized the kinetics parameters of these two models, together with the corresponding correlation coefficients (R^2) for the biosorption of Pb(II) and Cd(II) ions onto mustard biomass.

Table 2. Kinetics parameters for Pb(II) and Cd(II) biosorption onto mustard biomass

Kinetic model	***Kinetic parameter***	***Pb(II)***	***Cd(II)***
	q_e^{exp}, mmol/g	*0.0774*	*0.0529*
Pseudo-first order	R^2	0.9554	0.9552
	q_e, mmol/g	0.0163	0.0322
	k_1, 1/min	0.0205	0.0361
Pseudo-second order	***R^2***	***0.9998***	***0.9997***
	q_e, mmol/g	***0.0777***	***0.0541***
	k_2, g/mmol min	***$1.8534\ 10^{-3}$***	***$4.7860\ 10^{-3}$***

The rate constant k_1 obtained from the slope of pseudo-first order representation correspond to a calculated biosorption capacities at equilibrium of 0.0163 mmol/g for Pb(II) and 0.0322 mmol/g for Cd(II), respectively. These values are very different from those obtained experimentally (q_e^{exp}, mmol/g), which indicate that the pseudo-first order kinetic model is not suitable to describe the biosorption process of Pb(II) and Cd(II) onto mustard biomass. In comparison with these, the rate constant k_2 obtained from the slopes of t/q_t vs. t plots, correspond to a calculated biosorption capacities at equilibrium of 0.0777 mmol/g for Pb(II) and 0.0541 mmol/g for Cd(II) respectively. The very good correspondence between experimentally values of q_e and those calculated from the pseudo-second order kinetic model suggest that the biosorption of Pb(II) and Cd(II) ions onto mustard biomass comply with this model. The pseudo-second order kinetic model is based on the assumption that the rate limiting process is chemical interactions between heavy metal ions from aqueous solution and functional groups from biosorbent surface (Gerente C. et al., 2007). In addition, the higher values of rate constant obtained both for Pb(II) and Cd(II) biosorption indicate that in the biosorption process are involved strong interactions, most probably ion-exchange.

4. Conclusions

In this study, the biosorption of Pb(II) and Cd(II) from aqueous solution onto mustard biomass was investigate in batch experiments in order to pointed out the applicability of this low-cost biosorbent in the clean up processes of aqueous effluents. The biosorbent characterization indicate that beside this material is low-cost, has a rough surface and contains in its structure various elements (C, O, S, P) that can be included in different functional groups, ensuring the binding sites fro heavy metals from aqueous effluents. The higher biosorption capacity of mustard biomass was obtained at pH of 5.5 and 5 g biosorbent/l, but under these conditions the removal percents of Pb(II) and Cd(II) not exceed 92 % and 80 %, respectively. The Langmuir and Freundlich isotherm models were used for the mathematical description of studied heavy metals biosorption onto mustard biomass, and the maximum biosorption capacities were 0.3913 mmol/g in case of Pb(II) and 0.5324 mmol/g in case of Cd(II), respectively. The analysis of kinetic data showed that the biosorption of Pb(II) and Cd(II) ions onto mustard biomass followed well the pseudo-second order kinetic model, which means that the rate controlling step is the chemical interactions (probably ion exchange type) between functional groups from biosorbent surface and heavy metals from aqueous solution. The results presented in this study demonstrates that the mustard biomass can be an efficient alternative biosorbent for the removal of Pb(II) and Cd(II) ions from aqueous effluents.

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