

Surface modification of *Nizimuddinina zanardini* and *Stoechospermum marginatum* using 4-phenyl-3-thiosemicarbazide to improve heavy metals biosorption from water

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Abstract Surface modification of two algal biomasses, *Nizimuddinina zanardini* and *Stoechospermum marginatum*, using 4-phenyl-3-thiosemicarbazide ligand was performed to investigate the consequences on the adsorption of heavy metals from aqueous solution. Stabilization of amino group of 4-phenyl-3-thiosemicarbazide on the surface of biomasses was confirmed using Fourier transform infrared spectroscopy. Chemical modification was found to exert significant positive effects on biosorption. Adsorption capacities for Pb(II), Cd(II) and Cr(VI) using modified *N. zanardini* were observed to be 19.3, 16.75 and 15.75 mg/g, respectively, compared to 17.48, 14.18 and 11.85 mg/g for raw *N. zanardini* biomass. Also, adsorption of Pb(II), Cd(II) and Cr(VI) by the modified *S. Marginatum* was found to be 17.54, 15.62 and 14.77 mg/g, respectively, in comparison with that of the raw biomass which were 16.86, 12.9 and 11.2 mg/g. The obtained results of the equilibrium adsorption were studied through different isotherm models of Langmuir, Freundlich and Temkin, where the Langmuir model was observed to agree well with the results. Prevalent kinetic models including pseudo-second order and intra-particle diffusion were applied, and the pseudo-second order was found to describe the adsorption kinetics data adequately. Intra-particle model was also utilized in order to show penetration of metal ions, where it was

realized that the biosorption took place in two or three steps including film diffusion, molecular diffusion and chemical reaction.

Keywords 4-Phenyl-3-thiosemicarbazide · Algal biomass · Biosorption · Heavy metals · Surface modification

Introduction

The escalating human population and industrial activities such as mining, electroplating and oil refining have led to increasing water resources pollution by heavy metal ions and urged the demand for development of novel methods for pollutant removal from water resources (Lopez-Mesas et al. 2011). Heavy metals are considered as one of the most toxic groups, which endure in the environment and accumulate in food chain through the disposal of wastes to water receptors or land. Heavy metals impose toxic effects, cancer and diseases because they cannot be degraded (Farooq et al. 2010; Barakat 2011). Among different heavy metals, lead, cadmium and chromium are frequently encountered in industrial activities. Pb(II) usually enters into wastewaters within plastics, batteries, petrochemical, pigments, alloys and glass manufacturing industries. Cd(II) is known as an important metal in batteries, electroplating and alloy industry (Sar and Tuzen 2008b). Cr(VI) is used in metallurgical, leather tanning, dye, wood preservation and battery industries. Maximum acceptable limits of Pb(II), Cd(II) and Cr(VI) ions in drinking water are 10, 3 and 50 µg/L, respectively (Barakat 2011).

Different techniques have been used to decrease the concentrations of such heavy metals. Some of these methods are only effective when there is high

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concentration of the heavy metals like ion exchange, and other ones like membrane methods are not economically justified having high operational cost (Kumar Giri et al. 2012). Among prevalent methods, biosorption is considered as a low-cost route of enhanced performance for low metal concentrations (Elwakeel et al. 2017; Elwakeel and Ahmed 2010). Biosorption, also recognized as passive metal uptake, is metabolism-independent uptake of metals by non-living biomass. Mechanisms of cell surface sorption are based on physicochemical interactions between metal ions and functional groups of the cell surface (Flouty and Estephane 2012).

Many biosorbents like bacteria, fungi, algae and raw materials such as agricultural waste, sawdust and native grapefruit have been employed for the removal of heavy metals (Elwakeel et al. 2012). Algae offer higher amount of metal uptake than bacteria and fungi. Among different types of alga, brown algae are more effective than green and red algae (Mata et al. 2008). Different types of red, green and brown algae have been used for biosorption process. Algae bear several functional groups such as carboxyl, hydroxyl, phosphate, amino and sulfhydryl (thiol). Green and red algae are mainly composed of cellulose. Biosorption capability of red algae is due to the presence of sulfated polysaccharides made of galactans, while in green algae, high percentage of the cell wall is proteins bonded to polysaccharides (Romera et al. 2007). In brown algae, alginate and fucoidan can play an important role in the removal of heavy metals. Alginate is the main constituent of brown algae (approximately 10–40% of dry weight), which is composed of mannuronic and guluronic acids. Fucoidan is a branched polysaccharide whose major component is sulfate ester with L-fucose 4-sulfate building blocks (Bhatnagar et al. 2012).

Nizimuddin zanardini and *Stoechospermum marginatum* are two common species of brown algae existing in Oman Sea. Abundance, availability and existence of efficient functional groups, which provide suitable sites for biosorption, are features of such algae. Carboxyl and hydroxyl groups provide specific sites for biosorption, which have an important role in different mechanisms of biosorption such as ion exchange, chelation and precipitation (Hu et al. 2012).

Chemical modification and pretreatment of biosorbent like algae are successful strategies to increase sorption capacity through providing more active sites available for grabbing heavy metal ions, which enhance the removal efficiency. However, a literature survey reveals different effects of pretreatments on biosorption. For instance, acid pretreatment using HCl of *Oedogonium hatei* biomass leads to degradation of cellular compounds such as cell wall, proteins and complex organic components of biomass (Gupta et al. 2010), while formaldehyde, glutaraldehyde and CaCl₂ increase the stability of the biosorbent material, where polyethyleneimine has been used for its metal-chelating characteristics to increase the

adsorption capacity (Montazer-Rahmati et al. 2011). The effects of pretreatments are indeed associated with many parameters such as the number of the adsorbing sites in the biosorbent, the accessibility of the sites, the affinity between the sites and metal and the chemical state of the sites (Vieira and Volesky 2000). It has been shown that cationic exchange mechanism is predominant for cationic metals adsorption using algae and the carboxyl group on the surface of brown algae is responsible for binding cationic heavy metals such as Pb²⁺ and Cd²⁺ (Park et al. 2005). Luo et al. (2006) used epichlorohydrin to improve the surface characteristics of algae *Laminaria japonica*. They used 4-phenyl-3-thiosemicarbazide for biomass pretreatment in order to add the amine groups to the biosorbent and increase the availability of active sites for biosorption.

The aim of this study is to use, for the first time, 4-phenyl-3-thiosemicarbazide to chemically modify the surface of algae *N. zanardini* and *S. marginatum* and compare the sorption capacity for Pb(II), Cd(II) and Cr(VI) between the raw and modified biomasses. These two biomasses have not yet been used as the biosorbent of the heavy metal contaminant removal. This is the novelty of the current work. To characterize the modifications, besides doing a qualitative test, the quantitative evaluations are also performed, that is, studying influential parameters (biomass dosage, initial metal concentration and pH), isotherms and kinetics of adsorption. This research was carried out from November 2014 to November 2015 in the Department of Chemical Engineering, Isfahan University of Technology, Iran.

Materials and methods

Raw biomass

Biomasses of *N. zanardini* and *S. Marginatum* were provided from Chabahar (Oman Sea). They were collected and washed twice with distilled water and were placed at room temperature to dry for 24 h and then dried in an oven at 70 °C for 24 h. The dried biomasses were pestled in a mortar and subsequently sieved to obtain the particles with characteristic size of less than 600 µm to be used for adsorption experiments.

Chemical modification of biomass

An amount of 0.5 g of each dry biomass was dispersed by ultrasonicator in 10 mL of solution buffer A containing 0.003 M phosphate solution and 0.1 M NaCl at pH 6. Simultaneously, 2.5 mL of 1,1-carbonyldiimidazole solution (0.03 g/mL in buffer A) and 50 mL of 0.05 M solution of 4-phenyl-3-thiosemicarbazide were added to the mixture. This mixture was mixed for 12 h by blender. At the

end, the functionalized biomasses were separated through filter paper and then washed using ethanol. The particles were finally dried in vacuum oven.

Metals preparation

The stock solutions (1000 mg/L) of Pb(II), Cd(II) and Cr(VI) were prepared by dissolving appropriate amounts of Pb(NO₃)₂, CdSO₄·8H₂O and K₂Cr₂O₇ in distilled water, separately. Working solutions ranging from 5 to 25 mg/L were prepared by diluting the stock solutions in distilled water. pH of the metals solution was adjusted to the desired value with 0.1 M NaOH and 0.1 M HCl using pH meter (Metrohm, 620, Switzerland).

Adsorption experiments

Batch experiments were performed in 100-mL Erlenmeyer flasks with working volume of 75 mL. Then, flasks were shaken at 120 rpm using rotary shaker (Labcon, FSIM-SPO16) for the required time period at 25 ± 2 °C. Finally, 10 mL sample from each experiment was taken and centrifuged at 6000 rpm for 15 min. The metal uptake was calculated as:

$$q = \frac{V(C_0 - C_{eq})}{M} \quad (1)$$

where q is the metal uptake (mg/g), C_0 and C_{eq} are the initial and final concentrations of metal in solution (mg/L), respectively, V is volume of solution (L), and M is mass of biosorbent based on dry weight (g).

To obtain the optimum conditions of the influential parameters of adsorption (that is maximum capacity of metal removal), the experiments were performed under various initial pH values (3–8), for various reaction durations (0–150 min), biomass dosage (0.26–2.6 g/L) and initial metal concentration (5–25 mg/L). All experiments were performed in duplicate in the presence of blank sample, and the average of duplicate results was presented as the final values.

Adsorption isotherms

Batch tests were performed to investigate the isotherms of adsorption. Equilibrium experiments were carried out by taking 1.06 g/L of biomass in 100-mL conical flasks containing 75 mL of the metal solution. Initial concentrations in the range of 5–25 mg/L at initial pH 5.5 for Pb(II) and Cd(II) and pH 3 for Cr(VI) were used. The mixture was shaken in a rotary shaker at 120 rpm at 25 ± 2 °C. After 150 min, the samples were centrifuged and analyzed quantitatively. Then, the common isotherms such as Langmuir, Freundlich and Temkin models were fitted to the empirical data.

Adsorption kinetics

Batch experiments were performed to determine kinetic adsorption properties of the biosorbents. The experiments of adsorption kinetics were carried out in 100-mL flasks containing 75 mL of the solutions by using 1.06 g/L of biosorbents at initial pH 5.5 for Pb(II) and Cd(II) and pH 3 for Cr(VI). The flasks were rotated on a rotary shaker at 120 rpm at 25 ± 2 °C. A flask was removed at each intended time periods, and sample was taken, centrifuged and analyzed to determine the concentration of metal. The results were studied using pseudo-second-order and intra-particle diffusion kinetic models (Mata et al. 2008).

Fourier transform infrared spectra study

Fourier transform infrared (FTIR) spectra of raw and modified algal biomasses in the range of 400–4000 cm⁻¹ were obtained with a Jasco-680 (Japan). This technique was used to obtain information about the functional groups on the surface of samples and consider accuracy of coating biomasses. Raw and modified algae were dried at 50 °C for 24 h. The biomasses were mixed with KBr beforehand and then pulverized at approximately defined ratio for the preparation of pellets.

Results and discussion

FTIR analysis of biosorbents

Fourier transform infrared analysis is principally used to evaluate the surface modification of algal biomasses and also to assess qualitatively the stabilization of amino group of 4-phenyl-3-thiosemicarbazide on biomass surface. The FTIR spectra of the raw and modified biomasses are presented in Fig. 1. Surface modification was performed to add amino groups to biomass in order to increase sorption capacity via enhancement of effective functional groups. In order for 4-phenyl-3-thiosemicarbazide to react with biomass, reactive functional groups like aldehyde, ketone and carboxyl are required. The strong and broad band at 3450 cm⁻¹ is indicative of hydroxyl group for both raw algae. The next noticeable peak in raw algae appears around 1630 cm⁻¹, which is related to stretching vibration of C=O. There is a peak near 1050 cm⁻¹, which is ascribed to the stretching vibration of C–O in *S. marginatum* (Ren et al. 2011). Amino group in 4-phenyl-3-thiosemicarbazide is identified by two peaks close to each other at wave number of 3303 cm⁻¹. The modified algae show distinguished peaks. Four strong bands at 1310, 1485, 1608 and 3303 cm⁻¹ are ascribed to the C=S (stretching vibration), N–H (bending vibration), benzene (stretching vibration) and N–H (stretching vibration) groups, respectively. The results from



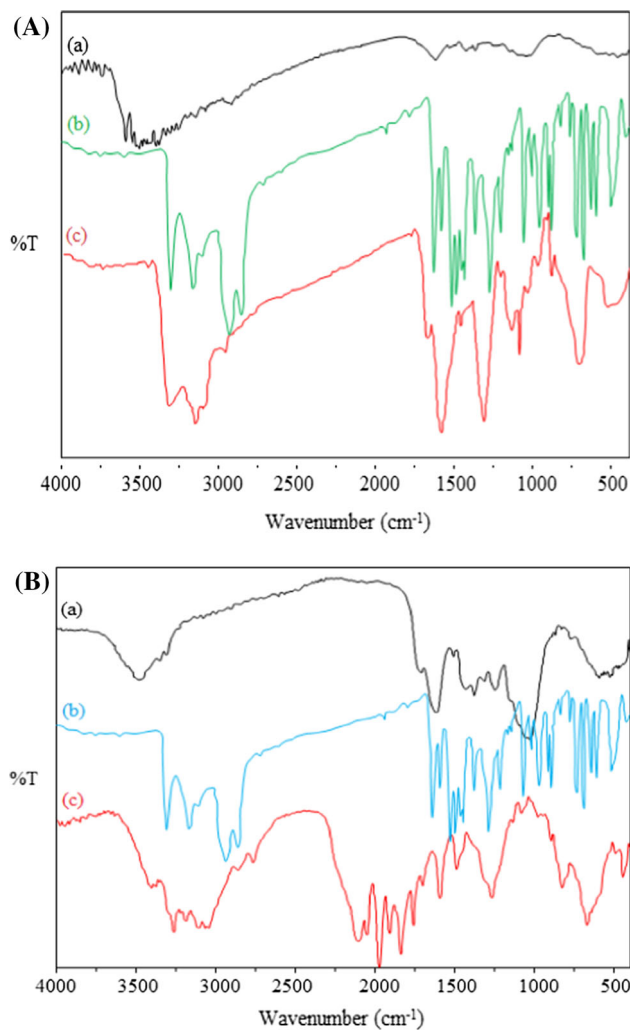


Fig. 1 FTIR spectra of raw biomass (a), 4-phenyl-3-thiosemicarbazide (b), modified biomass (c), *N. zanardini* (A) and *S. marginatum* (B)

FTIR spectra confirm the fulfillment of surface modification of algal biomasses.

Influence of sorption variables

To reach maximum removal of heavy metal ions, the most important parameters to study are pH, initial concentration of metal and biomass dosage. The strong influence of pH of solution on metal adsorption has been reported by many authors through alteration of the surface charge of the biosorbent. The effect of pH on the removal efficiency of metal ions is examined by varying within 3–8 range, where the results are presented in Fig. 2. It can be seen that the maximum percentage of biosorption for lead and cadmium occurs in pH 5.5, while for chromium takes place at pH 3. The observed decrease in the removal efficiency of Pb(II) and

Cd(II) in low pH is because of competing sorption between H⁺ and positive metal ions. At lower pH, the acidity of solution and therefore the probability of dominant H⁺ ions are increased. Chromium exists in the anionic form as Cr₂O₇²⁻ (Wu et al. 2012); therefore, in acidic media, the maximum percentage of biosorption takes place for this metal.

At high pH values, the concentration of free metal ions is decreased because of formation of anionic hydroxide complexes (Pahlavanzadeh et al. 2010). Low percentage of metal biosorption is a result of hydroxide formation. The pH of solution affects the functional groups of biomass, which causes to participate in metal ion binding (Sar and Tuzen 2008a). Wu et al. (2012) used cross-linked chitosan for Cr(VI) biosorption involving positively charged amino groups and negatively charged dichromate ions. Lopez-Mesas et al. (2011) utilized cork waste to remove Pb(II) and Cd(II) and showed that carboxylic and phenolic groups at low pH are protonated, resulting in a low interaction between biosorbent and heavy metals.

The biosorption yield for Pb(II), Cd(II) and Cr(VI) ions as a function of biomass dosage is depicted in Fig. 3. It is observed that on increasing the biomass concentration, the metal removal efficiency is enhanced. Maximum percentage of biosorption occurs when the biomass dosage of

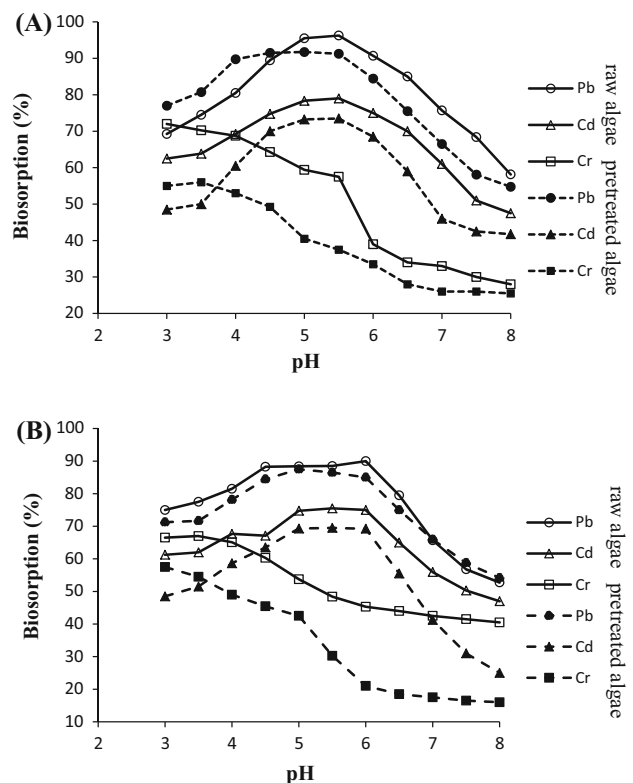


Fig. 2 Effect of initial pH of solution on biosorption of Pb(II), Cd(II) and Cr(VI) by modified *N. zanardini* (a) and *S. marginatum* (b) compared to raw biomass ($T = 25 \pm 2$ °C, initial concentration = 20 mg/L, biomass dosage = 1.066 g/L)



1.06 g/L is applied. This performance is explained through providing more accessible exchangeable sites for metal ions by increasing the dosage of adsorbent in the solution (Karthikeyan et al. 2007). However, constant biosorption percentages at high concentrations can be explained by ions which are not adsorbed and the adverse effect of interfering sites. Therefore, an increase in biosorption is limited. Increasing the site of sorption has negative effect in some cases. This behavior could be justified as an effect of partial aggregation of biomass at higher biomass doses, where effective surface area and sites for the biosorption are reduced. Gupta et al. used treated *O. hatei* for the removal of nickel in the range of 0.1–1 g biomass/L using biomass of up to 0.7 g biomass/L and reported that the percentage of biosorption is increased, while increasing biomass dosage beyond 0.7 g/L imposes negative effects on the biosorption yield (Gupta et al. 2010). In another study, using gum kara for biosorption of Hg(II) ions in the range of 0.1–4 g/L biomass dosage, 1 g biomass/L was found for maximum removal of mercury(II) (Vinod et al. 2011).

Initial metal concentration is adjusted in the ranges of 5–25 mg/L for adsorption on the modified algae under pH 5.5 for Pb(II) and Cd(II) and pH 3 for Cr(VI) at

25 ± 2 °C for 2 h as shown in Fig. 4. When the initial concentrations of metal ions are increased in the solution, the sorption capacity is increased. By increasing the initial concentrations of Pb(II), Cd(II) and Cr(II) from 5 to 25 mg/L, the percentage of biosorption is altered from 98 to 71.6, 95 to 57.6 and 90 to 47.2% for *N. zanardini* and from 97.6 to 68.4, 94 to 52 and 88 to 44% for *S. marginatum*, respectively. Mao et al. investigated the biosorption of Cr(VI) onto magnetic PS-EDTA resin for the initial concentration of 5–1000 mg/L. Adsorption capacity of Cr(VI) by resins was increased rapidly with increasing the Cr(VI) concentration (Mao et al. 2012). In similar works on treated *Undaria pinnatifida* biomass, initial concentrations in the range of 5–50 mg/L were used for the removal of nickel ions, where sorption capacity of the treated algae was increased from 0.88 to 38.82 mg/g (Chen et al. 2008).

Adsorption isotherms for raw and modified algae

Adsorption isotherm is useful to design adsorption systems and can explain the interactions between biosorbent and adsorbate. Batch experiments have been performed with initial concentration in the range of 5–25 mg/L. Two-parameter models such as Langmuir, Freundlich and Temkin

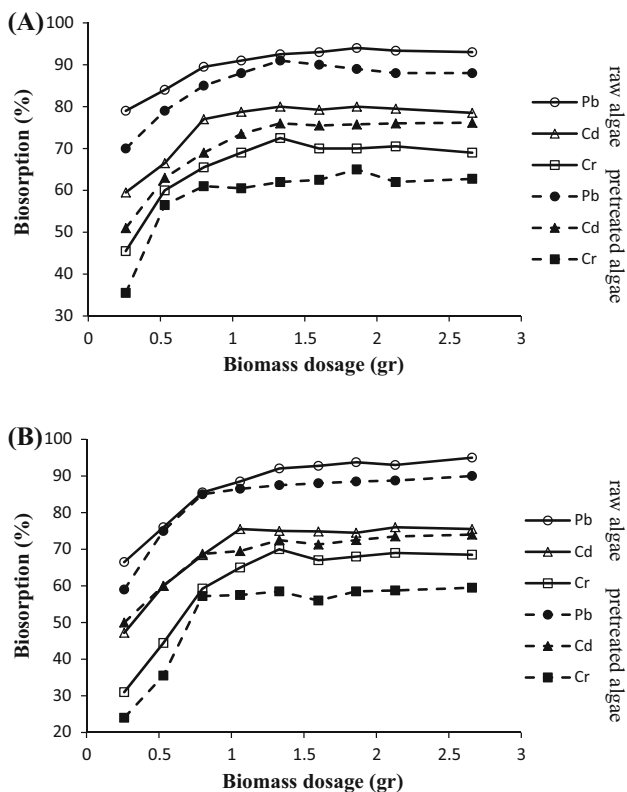


Fig. 3 Effect of dosage of modified *N. zanardini* (a) and *S. marginatum* (b) on Pb(II), Cd(II) and Cr(VI) biosorption ($T = 25 \pm 2 \text{ }^\circ\text{C}$, initial concentration = 20 mg/L)

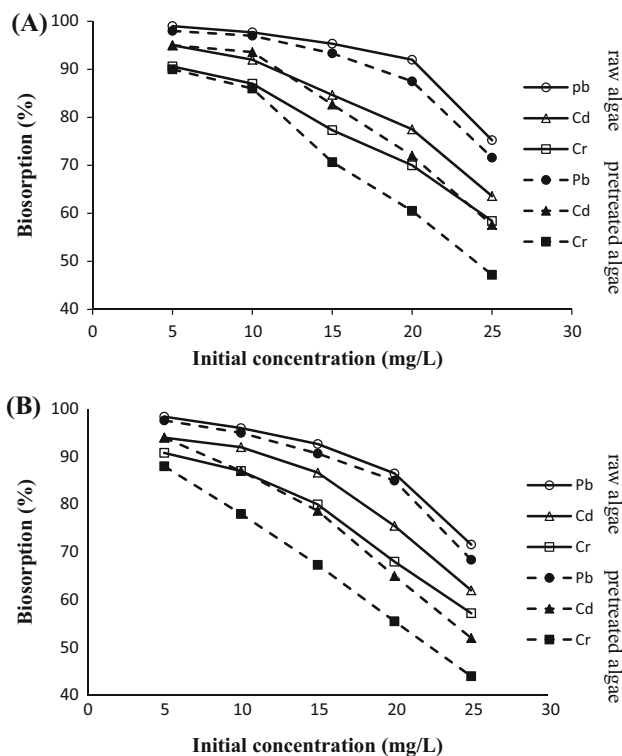


Fig. 4 Effect of initial ions concentration on biosorption by raw and modified algae *N. zanardini* (a) and *S. marginatum* (b) ($T = 25 \pm 2 \text{ }^\circ\text{C}$, biomass dosage = 1.066 g/L)

isotherms have been used, and their constants have been calculated by linear regression method.

Assumptions in Langmuir adsorption model are homogeneity of binding site distribution on the surface, equivalency of the sorption energy on active sites and absence of interactions between molecules of biosorbent. It has produced good conformity with experimental data and in mathematical form, written as (Langmuir 1918):

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}b} + \frac{C_e}{q_{\max}} \quad (2)$$

where q_{\max} (mg/g) is the maximum adsorption capacity and b (L/mg) is the affinity of the binding sites. Comparison between raw and modified biomasses (summarized in Table 1) shows that q_{\max} for modified versus raw forms is enhanced as much as 3.6, 12 and 29% for *N. zanardini* and 3.5, 20, 32% for *S. marginatum* for Pb(II), Cd(II), Cr(VI), respectively.

In Freundlich isotherm, an exponential distribution between sorption sites and energy of sorption is assumed. In addition, this model refers to the point that the ratio of metal ions on the surface of biosorbent and in solution is changed in different initial concentrations and is given by:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

where K_F is a constant related to the biosorption capacity and n is an empirical parameter, which refers to an affinity constant varying with the heterogeneity of the material (Mao et al. 2012). This model shows an inadequate overlap with experimental data being clear from R^2 values in given Table 1.

The equilibrium data are also fitted by Temkin isotherm. The assumption, which is used in this isotherm, is that the interactions between biomasses and metal ions to be adsorbed are associated with free energy of sorption as a function of the surface coverage given by:

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \quad (4)$$

where A_T is equilibrium binding constant being related to the maximum binding energy, b_T is Temkin isotherm constant, T is temperature, and R is ideal gas constant (equal to 8.315 J/mol/K) (Chen et al. 2008). This isotherm shows moderate agreement with experimental data presented in Table 1. The maximum binding energy for sorption of Pb(II) using modified *N. zanardini* and *S. Marginatum* is enhanced as much as 2.3 and 1.7%, respectively, compared to that of the raw forms. For Cd(II) and Cr(VI), the maximum binding energy values decrease in modified form by 21.1 and 32% for *N. zanardini* and 25.6 and 29.4% for *S. marginatum*, respectively. Reduction of b_T values for modified compared to that of the raw algae indicates the less amount of energy required for interaction between metal ions and binding sites; hence, more ions are adsorbed on the surface of biosorbent, which promote the sorption capacity (Javanbakht et al. 2014).

Kinetic modeling of metal adsorption for raw and modified algae

The data, obtained from the batch experiments, have been fitted with pseudo-second-order and intra-particle

Table 1 Isotherm constants of adsorption using raw and modified biomasses of *N. zanardini* and *S. marginatum* ($T = 25 \pm 2$ °C, biomass dosage = 1.066 g/L)

Type of biomass	Metal ions	Isotherm model								
		Langmuir			Freundlich			Temkin		
		q_{\max} (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n	R^2	b_T	A_T (L/mg)	R^2
Raw	Pb	17.48	3.69	1.000	11.28	3.32	0.992	828.34	62.5	0.950
<i>N. zanardini</i>	Cd	14.18	2.14	0.999	8.03	3.57	0.971	1030.5	39.27	0.937
	Cr	11.85	1.35	0.998	6.04	3.48	0.963	1166.4	21.05	0.927
Modified	Pb	19.31	4.39	0.991	12.9	3.48	0.992	848.19	116	0.990
<i>N. zanardini</i>	Cd	16.75	1.30	0.996	8.16	2.94	0.971	812.58	19.74	0.998
	Cr	15.75	0.77	0.996	6.4	2.66	0.963	792.06	9.29	0.995
Raw	Pb	16.86	2.77	0.999	10.13	3.2	0.920	835.88	44.2	0.954
<i>S. marginatum</i>	Cd	12.90	1.38	0.999	6.9	3.52	0.920	1111	28.7	0.956
	Cr	11.20	1.01	0.998	5.27	3.32	0.928	1184.8	14.05	0.959
Modified	Pb	17.54	3.28	0.999	11.06	3.44	0.936	850.52	64.7	0.969
<i>S. marginatum</i>	Cd	15.63	1.56	0.999	8.02	2.96	0.877	825.85	19.53	0.945
	Cr	14.77	0.95	1.000	6.52	2.77	0.912	1204.4	1.25	0.970



diffusion models. The pseudo-second-order equation is more capable than intra-particle model in describing the dynamic metal sorption process by the raw and modified algae (see Fig. 5). The pseudo-second-order kinetic model is based on the notion that the sorption rate is controlled by chemical sorption (Lodeiro et al. 2006). At the start of the process, adsorbing sites of biomass are unoccupied and therefore the rate of adsorption is high. After passing a period of time, the sorption sites become saturated and between solid–liquid interfaces, the ion concentration gradient decreases giving rise to reduce the sorption rates. Second-order equation is written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where $K_2 q_e^2$ is described as the initial adsorption rate at the beginning of process and K_2 is the rate constant of sorption (g/mg min) (Bhattacharyya and Gupta 2011). Sorption capacities for modified form in comparison with the raw form, for Pb(II), Cd(II) and Cr(VI), are enhanced by 10.5, 18.4 and 38% for *N. zanardini* and by 10.2, 17.6 and 39.7% for *S. marginatum*, respectively. The R^2 values are presented in Table 2.

Another model that considers the kinetics of metal ions adsorption onto biomass is intra-particle diffusion. In this model, diffusion consists of one or more than one step. The first step is film diffusion, whereby metal ions diffuse through the solution to reach the surface of biosorbent. The second step is molecular diffusion identified by transport of metal ions from outer surface to the inner surface, and the third step includes interactions between metal ions and active sites by chemical reaction (Jellali et al. 2011). The intra-particle diffusion rate is estimated by the following relation:

$$q_t = k_i t^{0.5} + c \tag{6}$$

where k_i (g/mg min^{0.5}) is the intra-particle diffusion rate constant and C is the adsorption constant. The result of this model is presented in Fig. 5. It is observed that as the variations in the slope of diagram increase, the extent of sorption capacity variations enhances. It is also shown that many of biomass sites are vacant and tend to react with free metal ions in solution related to the beginning of process.

Conclusion

It is concluded from this study that the biomasses of *N. zanardini* and *S. marginatum*, surface modified by 4-phenyl-3-thiosemicarbazide ligand, seem to be

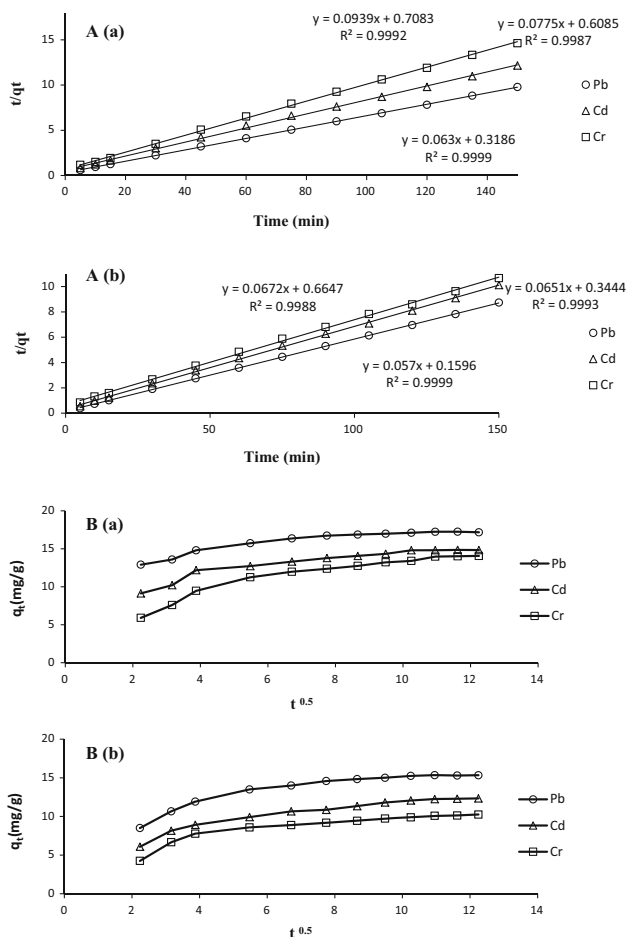


Fig. 5 Pseudo-second-order (A) and intra-particle diffusion (B) kinetic plots for the adsorption of metal ions by raw (a) and modified (b) biomass of *N. zanardini* ($T = 25 \pm 2 \text{ }^\circ\text{C}$, initial concentration = 20 mg/L, biomass dosage = 1.066 g/L)

Table 2 Kinetic parameters obtained from pseudo-second order of metal ions using raw and modified biomasses of *N. zanardini* and *S. marginatum* ($T = 25 \pm 2 \text{ }^\circ\text{C}$, initial concentration = 20 mg/L, biomass dosage = 1.066 g/L)

Type of biomass	Metal ions	q_e (mg/g)	k_2 (g/mg min)	R^2
Raw <i>N. zanardini</i>	Pb	15.87	0.0124	0.999
	Cd	12.98	0.0097	0.998
	Cr	10.75	0.012	0.999
Modified <i>N. zanardini</i>	Pb	17.54	0.02	0.999
	Cd	15.38	0.012	0.999
	Cr	14.92	0.0049	0.998
Raw <i>S. marginatum</i>	Pb	15.38	0.01	0.999
	Cd	12.5	0.0077	0.998
	Cr	10.52	0.0068	0.997
Modified <i>S. marginatum</i>	Pb	16.95	0.0112	0.999
	Cd	14.7	0.0055	0.998
	Cr	14.6	0.0055	0.999

promising biosorbents for the removal of toxic metal ions of Pb(II), Cd(II) and Cr(VI) from wastewater. Stabilization of amino group of 4-phenyl-3-thiosemicarbazide on the surface of biomasses is confirmed using Fourier transform infrared spectroscopy. The maximum percent of biosorption occurs at 1.06 g/L biomass dosage and pH 5.5 for lead and cadmium while pH 3 for chromium. By increasing the initial concentrations of Pb(II), Cd(II) and Cr(II) from 5 to 25 mg/L, the percentage of biosorption is decreased. Among tested isotherm and kinetic models, Langmuir and pseudo-second order are found to well describe the experimental data. It is shown that for both algal biomasses, the surface modification using amino group of 4-phenyl-3-thiosemicarbazide shows the highest improvement for adsorption of Cr(II) (32–33%) and then for adsorption of Cd(II) (18 and 21%), while shows the least improvement (4 and 10.5%) for adsorption of Pb(II).

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