Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22788

129 (2018) 216–226
October

Efficacy of *Sargassum filipendula* for the removal of Pb^{2+}, Cd^{2+} and Ni^{2+} ions from aqueous solution: a comparative study

Ayushi Verma*, Shashi Kumar, Chandrajit Balomajumder, Surendra Kumar

Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee – 247 667, Uttarakhand, India, Tel. +91 9634844960; emails: ayushi.mtech@gmail.com (A. Verma), shashi.iitroorkee@gmail.com (S. Kumar), chandfch@iitr.ac.in (C. Balomajumder), skumar.iitroorkee@gmail.com (S. Kumar)

Received 13 November 2017; Accepted 12 July 2018

ABSTRACT

The efficacy of *Sargassum filipendula* was evaluated for removal of Pb^{2+}, Cd^{2+} and Ni^{2+} ions. All experiments were performed in a batch system to study the effects of contact time, pH, biosorbent dose, initial metal ion concentration and temperature on the biosorption process. The optimum pH for Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption was found to be 5.0, 6.0 and 5.0, respectively. The equilibrium time for Pb^{2+} ions was 40 min and for Cd^{2+} and Ni^{2+} ions was 60 min. The equilibrium experimental data were analyzed using the six isotherm models and six kinetic models. The results were best fitted by the Bangham, pseudo-second order and pseudo-first order kinetic models for Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption, respectively. The biosorption isotherm was better explained by Fritz isotherm for Pb^{2+} ions and Redlich–Peterson isotherm for Cd^{2+} and Ni^{2+} ions biosorption. The uptake capacities of *S. filipendula* for Pb^{2+}, Cd^{2+} and Ni^{2+} ions were obtained as 367.94, 103.5 and 34.3 mg/g, respectively. According to the thermodynamic parameters, the biosorption process was spontaneous, feasible and endothermic in nature. The result obtained has shown that the order of metal ion binding affinity for *S. filipendula* was $Pb^{2+} > Cd^{2+} > Ni^{2+}$ ions.

Keywords: Biosorption; Kinetics; Isotherm; Lead; Cadmium; Nickel; *Sargassum filipendula*

1. Introduction

The rapid industrialization has increased the environmental pollution problems causing catastrophic effects on the ecosystem due to accumulation of many toxic pollutants such as heavy metals [1]. Water pollution due to heavy metals leads to severe global problems. Heavy metals are chemically stable, ubiquitous, persistent and non-biodegradable in nature. The bioaccumulation of heavy metals via food chain creates a significant danger to human health. Heavy metals are released in various industrial effluents such as pigment, fertilizer, storage batteries, plastic, textile, glass manufacturing, ceramic, metallurgical processes, and electroplating [2,3,4]. According to the guidelines of World Health Organization, the drinking water having heavy metals such as lead, cadmium, aluminum, chromium, nickel, manganese, iron, copper, zinc, mercury and cobalt is main concern due to its toxicity. Therefore, the removal and recovery of heavy metals are necessary regarding economic and environmental considerations [5]. Several conventional physicochemical technologies such as chemical precipitation, reverse osmosis, ion exchange, electrolysis, membrane filtration, precipitation, oxidation/reduction and evaporation were used for removal of heavy metal from wastewater [6]. These methods are costly, not eco-friendly, generate hazardous by-products and not able to remove metal ions from dilute solutions ranging from 1 to 100 mg/L of dissolved metal [5,7]. Adsorption has been proven to be an excellent way to treat industrial waste effluents, with several advantages such as low operating cost, easy handling, efficient removal of very low levels of

---

* Corresponding author.

heavy metals from dilute solutions, less sludge production and regeneration of the sorbents. Some of the reported sorbents of metal ions include activated alumina, activated carbon, ion exchangers, industrial and agricultural waste, natural materials and microorganism. However, these sorbents usually trap heavy metals through non-specific electrostatic interaction and thus display little or insufficient specific adsorption affinity toward metal ions. Recently, chemisorbents such as organic-inorganic hybrid solvent and ion-imprinted materials have received increasing attention as a sorbent to remove heavy metal ions from wastewater due to the relatively large external specific surface areas, high adsorption capacity, high selectivity and regeneration [8–10]. While most of the chemisorbents fail to bring down the concentration level of metal ion to acceptable low level in a single-stage operation and operation cost is not very attractive for large-scale operation [11]. Biosorption is an economically feasible alternative method which can be used for the removal of heavy metals from wastewater. The dead or living form of microorganisms such as bacteria, algae, fungi and yeast can be effectively used as biosorbent for the removal of metal ion from aqueous solution [2,5]. These biosorbents possess metal-sequestering property and can be used to decrease the concentration of heavy metal ions in solution from ppm to ppb level [12].

Among several biological materials which were used as biosorbent, marine algae (brown algae) play a significant role for biosorption purpose due to their high uptake capacities without producing any secondary wastes and able to remove low concentration of metal. The brown algae are cost-effective and abundantly available at the seashore [5]. The main component of brown alga cell wall is alginate which has strong ion-exchange properties. The alginate is a linear polysaccharide, which consists of 1,4-linked α-L-guluronic and β-D-mannuronic acid residues set in a block wise and non-regular order along the chain. Besides, carboxyl groups of alginates are the major functional groups responsible for binding of metal ions [5,13]. The cell wall of brown algae is highly porous and easily permeable for metal ions [14,15]. The *Sargassum* species of brown alga consist of floating bubbles due to which their density is decreased, thus contributing for their presence in the marine environment [16]. Based on the review of reported literature, no research work has been done on comparative study for Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption using *Sargassum filipendula*. Thus, this brown alga has been selected as biosorbent for the removal of Pb^{2+}, Cd^{2+} and Ni^{2+} ions. In the present study, the efficacy of *S. filipendula* to remove the lead, cadmium and nickel ions was compared. The effect of different parameters such as pH, temperature, biosorbent dose and initial metal ion concentration were also studied. To optimize the biosorption process, the six different isotherm models (Langmuir, Freundlich, Radke–Prausnitz, Redlich–Peterson, Toth and Fritz) were fitted to experimental data. In order to examine the biosorption behavior and mechanism, six kinetic models (pseudo-first order, pseudo-second order, intraparticle diffusion, Elovich, modified Freundlich and Bangham) were studied. The thermodynamic study was carried out to find out the feasibility of biosorption process. The comparison of uptake capacity of Pb^{2+}, Cd^{2+} and Ni^{2+} ions using *S. filipendula* has not yet been done.

2. Materials and methods

2.1. Biomass

The dried sample of *S. filipendula* was purchased from Aushadh Agri Science Private Limited, Gujarat (India). It was washed several times with deionized distilled water to remove impurities and ions such as Na^+ or Ca^{2+} bound on surface of biosorbent that can influence the biosorption. After that, it was oven-dried at 80°C for 24 h and stored in the desiccator. The dried biomass was then crushed and sieved through 212 μm sieve. The sieved fraction was used as biosorbent for biosorption process.

2.2. Biosorbate preparation

The stock solution of 1,000 mg/L metal ions was prepared by dissolving nitrate salts of lead (1.56 g), cadmium (2.1 g) and nickel (4.95 g) in deionized distilled water. All the reagents were obtained from Merck (Germany). The pH of solution was adjusted with 0.1 M HNO_3 and 0.1 M NaOH.

2.3. Batch biosorption experiment

All the batch biosorption experiments were conducted in batch mode using 250 mL Erlenmeyer conical flasks. 100 mL solution of each metal ion was taken separately in different flasks and placed on rotary shaker at 150 rpm for 85 min. The effect of pH on the Pb^{2+}, Cd^{2+} and Ni^{2+} ions was investigated by varying pH range from 2.0 to 7.0. The initial pH of each metal ions solution was adjusted to the requisite pH value by adding 0.1 M HNO_3 or 0.1 M NaOH. All other process parameters were kept at constant value (0.5 g biosorbent dose, 25°C and 100 mg/L initial concentration). Similarly, the effect of initial metal ions concentration (50–150 mg/L), temperature (20°C–35°C) and biomass dosage (0.1–3 g/L) was investigated for Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption. After regular time intervals, the samples were collected and filtered by Whatman No. 1 filter paper. The remaining metal ion concentration of filtrates was examined by flame atomic absorption spectroscopy (Avanta AAS, GBC Scientific Equipment Ltd.). All the experiments were carried out in triplicate and the relative standard deviation was less than 5%. The results were explained as removal efficiency of metal ion by using the following Eq. (4):

$$\%\ \text{Removal} = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

The metal uptake capacity of biosorbent at equilibrium was examined by using the following Eq. (4):

$$q_e = \frac{\left(C_i - C_e\right)V}{m} \tag{2}$$

where q_e is amount of metal ions biosorbed at equilibrium (mg/g), V is volume of solution (L), m is mass of *S. filipendula* (g), C_i is initial concentration of metal ion and C_e is equilibrium concentration of metal ion (mg/L).

3. Results and discussion

3.1. Influence of solution pH

The solution pH is an important factor which governed the extent of metal ions biosorption. The optimal pH value may be different for different metal ions depending on solution chemistry of the species [17]. The pH of solution influences the degree of ionization, species distribution of metal ions in aqueous solution, and surface charge of biosorbent [1]. The biosorption characteristic of each metal ion was studied at different pH values varying from 2.0 to 7.0. For this study, the range of pH was selected based on the reported data in the literature [2]. At acidic pH, the surface of *S. filipendula* becomes positively charged with H^+ ions which cause electrostatic repulsion of metal ions for binding site of *S. filipendula*. While at higher pH, H^+ ions desorbs from binding sites which results in exposure of negatively charged ligands of *S. filipendula* for metal ion biosorption. Hence with increase in pH the percentage removal of metal ions was increased. While after a certain value of pH, precipitation of metal ions occurs in the form of metal hydroxides which results in decrease of removal efficiency [5]. It is cleared from Fig. 1 that the biosorption of these metals is extremely pH-dependent and the optimal pH value for biosorption of Pb^{2+}, Cd^{2+} and Ni^{2+} ions was found to be 5.0, 6.0 and 5.0, respectively.

3.2. Influence of biosorbent dose

The biosorption process is greatly influenced by biosorbent dose as it examined the biosorbent potential by the number of available binding sites for removal of metal ions at a fixed initial concentration. Fig. 2 shows that the percentage removal of Pb^{2+}, Cd^{2+} and Ni^{2+} ions was increased with increase in the *S. filipendula* dose. It can be explained as for fixed initial metal ion concentration an increase in biosorbent dose provides large number of active sites and available surface area [2,18]. Biosorption of Pb^{2+}, Cd^{2+}, and Ni^{2+} ions reached an equilibrium at 0.5, 1 and 2 g/L dose of *S. filipendula*, respectively. Further increase in biosorbent dose does not show any significant increase in removal efficiency of these metal ions which may be due to the saturation of the *S. filipendula* surface [2]. Similar results were reported in the literature [19–21].

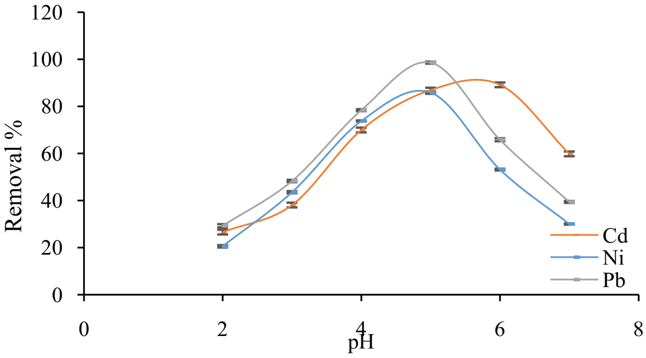

Fig. 1. Effect of pH on the removal of Pb^{2+}, Cd^{2+} and Ni^{2+} ions using *S. filipendula* (C_o = 100 mg/L, T = 25°C, m = 1 g/L). Error bars represent standard deviation of triplicate measurements.

3.3. Influence of initial metal concentration

The removal efficiency of *S. filipendula* as a function of the initial metal ions was studied for 50–150 mg/L range in batch experiments. Fig. 3 shows that the percentage removal of Pb^{2+}, Cd^{2+} and Ni^{2+} ions decreased with the increase in the initial metal ion concentration. It can be explained that all biosorbents have fixed number of binding sites which are available for binding of metal ions at low initial concentration but at high initial concentration the binding sites become saturated [22]. On the other hand, metal ions uptake capacity increased with increasing initial metal ion concentration. It may be due to the fact that increase in the initial ion concentration provides a larger driving force to overcome mass transfer resistances between the solid and the liquid phase. These results are in agreement with those reported in the literature [2,5].

3.4. Influence of temperature

The effect of temperature over the range of 20°C–35°C was examined to determine the exothermic or endothermic nature of the biosorption process. Fig. 4 shows that the removal percentage of Pb^{2+}, Cd^{2+} and Ni^{2+} ions increased with rise in temperature. It indicates the endothermic nature of Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption process. With increase in temperature, the boundary layer thickness of biosorbent

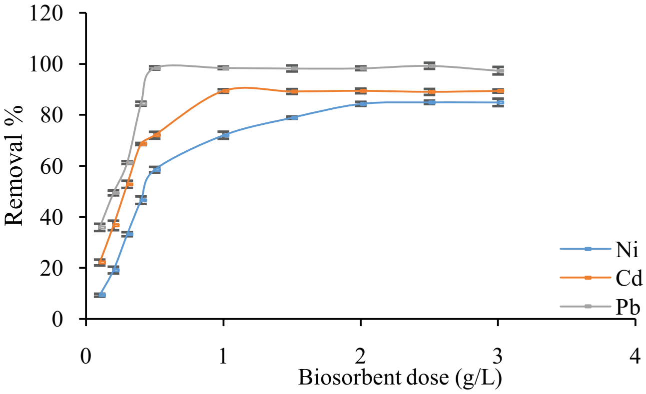

Fig. 2. Effect of biosorbent dose on removal of Pb^{2+}, Cd^{2+} and Ni^{2+} ions (C_o = 100 mg/L, T = 25°C, pH = 5). Error bars represent standard deviation of triplicate measurements.

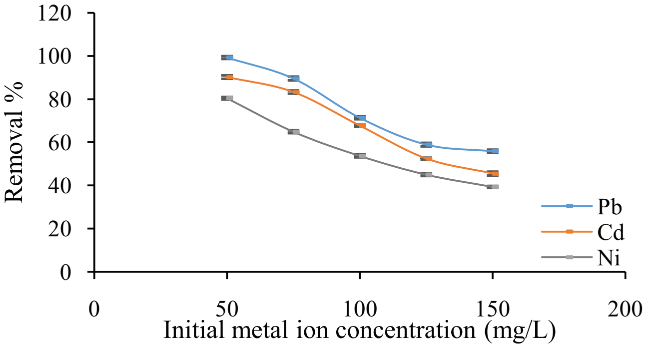

Fig. 3. Effect of initial metal ion concentration on removal of Pb^{2+}, Cd^{2+} and Ni^{2+} ions (m = 2 g/L, T = 25°C, pH = 5). Error bars represent standard deviation of triplicate measurements.

decreases which results in decrease of external layer resistance. More surface area for biosorption was available due to widening of micro-pores and the increased accessibility of binding sites [5].

3.5. Influence of contact time

Fig. 5 shows that the biosorption of the studied metal ions gradually increased with the increase in contact time until equilibrium condition was reached after which there was no change in removal percentage. Initially the removal rate of metal ions was very fast for first 10 min. In the initial stage, the biosorption of metal ions occurs generally on biosorbent surface instead of pores, whereas ion exchange processes occur between the ions available on the solid and liquid phase. Fast diffusion on outer surface is followed by slow pore diffusion [18]. The removal rate of Pb^{2+} ions was more than that of Cd^{2+} and Ni^{2+} ions. The equilibrium time for Pb^{2+} ions was 40 min while 60 min for Cd^{2+} and Ni^{2+} ions and beyond this time no further significant removal was noted. The fast biosorption rate at the initial stage may be due to the availability of a large number of vacant surface active sites while after a certain time period accessibility of active sites on biosorbent surface decreases which slows down the biosorption rate [5].

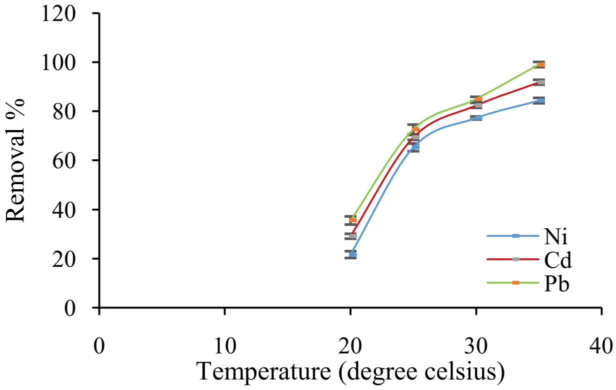

Fig. 4. Effect of temperature on removal of Pb^{2+}, Cd^{2+} and Ni^{2+} ions (C_o = 50 mg/L, m = 2 g/L, pH = 5). Error bars represent standard deviation of triplicate measurements.

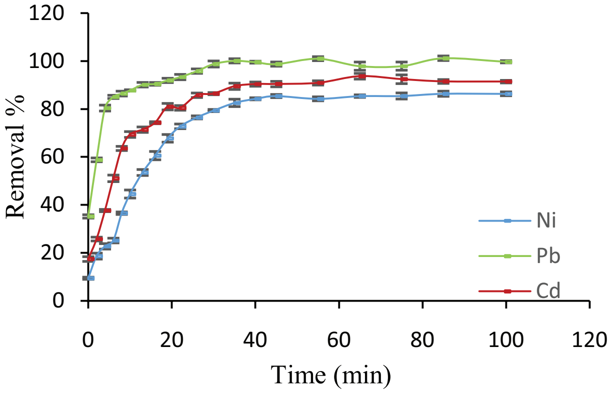

Fig. 5. Effect of contact time on removal efficiency of Pb^{2+}, Cd^{2+} and Ni^{2+} ions at T = 25°C, m = 2 g/L, C_o = 50 mg/L, pH = 5). Error bars represent standard deviation of triplicate measurements.

3.6. Biosorption isotherms

To optimize the biosorption process design, it is required to find the suitable correlation for the equilibrium curve. Here, the relationship between metal ion concentration and biosorption capacity at equilibrium was explained by fitting two two-parameter biosorption isotherm models: Langmuir and Freundlich; three three-parameter isotherm models: Redlich–Peterson, Radke–Prausnitz and Toth; and one four-parameter isotherm model: Fritz. The parameters, normalized standard deviation ($\Delta q\%$), and coefficient of determination (R^2) of all the models are given in Table 1. The parameters for all the models were determined by non-linear regression using the MATLAB 2013 software. Furthermore, normalized standard deviation was used to measure the goodness of fit. Normalized standard deviation is defined as follows [5]:

$$\text{Normalized standard deviation}(\Delta q\%) = 100\sqrt{\frac{\sum[(q_{e(\exp)} - q_{e(\text{pred})}) / q_{e(\exp)}]^2}{N}} \tag{3}$$

Table 1
Isotherm model parameters for Pb^{2+}, Cd^{2+} and Ni^{2+} ions at different temperatures

Isotherm	Parameters	Pb^{2+}	Ni^{2+}	Cd^{2+}
Langmuir	q_o	367.942	34.3	103.5
	b	1.024	0.343	0.593
	R^2	0.923	0.81	0.987
	$\Delta q\%$	5.89	39.27	7.691
Freundlich	k_f	215.342	23.04	26.82
	n	7.720	2.28	5.62
	R^2	0.96	0.994	0.964
	$\Delta q\%$	5.396	1.039	29.068
Radke–Prausnitz	q	3.139	26.27	0.339
	K_o	263.832	6.19×10^{-4}	72.03
	a_R	0.918	0.187	0.891
	R^2	0.988	0.994	0.988
	$\Delta q\%$	2.168	3.352	5.641
Redlich–Peterson	K_1	828.258	–0.0162	24.17
	K_2	3.139	26.27	0.339
	b_o	0.918	0.187	0.891
	R^2	0.988	0.994	0.998
	$\Delta q\%$	2.168	0.988	0.056
Toth	q_e^{∞}	473.129	61.33	60.44
	a	0.314	5.78	3.112
	n_1	0.321	40.1	1.171
	R^2	0.981	0.949	0.992
	$\Delta q\%$	2.89	39.27	5.612
Fritz	α_1	242.445	25.93	19.33
	α_2	0.2245	3.56×10^{-13}	7.144×10^{-6}
	β_1	0.100	0.1776	0.559
	β_2	–13.896	6.575	3.47
	R^2	0.994	0.957	0.984
	$\Delta q\%$	1.505	3.462	13.626

where $q_{e(\text{exp})}$ is the experimental q_e and $q_{e(\text{pred})}$ is the subsequent predicted q_e, N is the total number of measurements. Smaller value of $\Delta q\%$ signify better curve fitting of the predicted data to experimental data.

3.6.1. Two-parameter isotherms

The Langmuir isotherm model is based on monolayer biosorption process on a uniform surface. All the uniformly distributed binding sites of biosorbent are similar in biosorption affinity. There is no interaction between biosorbent vacant sites and the biosorbed molecules. The Langmuir isotherm model equation is given below [23,24]:

$$q_e = \frac{q_o b C_e}{1 + bC_e} \tag{4}$$

Here q_o (mg/g) is the maximum amount of metal ions biosorbed per gram of *S. filipendula* to form a complete monolayer over biosorbent surface and b (L/mg) is Langmuir constant. These constants are associated to monolayer biosorption capacity and biosorption energy, respectively The value of b indicates the affinity between the biosorbent and biosorbate [17,18]. The maximum uptake capacity for Pb^{2+}, Cd^{2+} and Ni^{2+} ions was obtained as 367.94, 103.5 and 34.3 mg/g, respectively. The b values of Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption were evaluated from isotherms to be 1.024, 0.193 and 0.343 L/mg, respectively. The *S. filipendula* obtained high q_e value for Pb^{2+}, followed by Cd^{2+} and Ni^{2+}. This sequence was followed according to the ionic radii of metals. Therefore, the relative affinity order of *S. filipendula* was $Pb^{2+} > Cd^{2+} > Ni^{2+}$ ions.

The Freundlich model is used to explain the multilayer biosorption on the heterogeneous biosorbent surface [2,25]. This model is expressed by an exponential equation which shows that increase in biosorbate concentration results in high uptake capacity. The equation for this model is given as [26]:

$$q_e = k_f C_e^{1/n} \tag{5}$$

where k_f and n both are Freundlich distribution coefficient which indicates the uptake capacity and strength of biosorption, respectively [27]. The affinity of metal ions biosorption on biosorbent surface can be estimated by the value of distribution coefficient. The high values of distribution coefficients show lower mobility and higher retention of metals on biosorbent while small value indicates that most of the metals remain in the solution which are available for transport and chemical processes [28]. The k_f values of Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption are 215.34, 26.82 and 23.04, respectively, which shows that *S. filipendula* has the higher affinity for Pb^{2+} ions. If $n = 1$, then the biosorption process is independent of the concentration, $n > 1$ shows a normal and favorable biosorption, and $n < 1$ shows cooperative biosorption [29,30]. Table 1 shows that the values of n are 7.72, 2.28 and 2.86 for Pb^{2+}, Cd^{2+} and Ni^{2+} ions, respectively, showing that the biosorption process was favorable.

3.6.2. Three-parameter isotherms

Toth is a modified Langmuir equation which reduces the error between experimental data and predicted values of equilibrium biosorption data. The use of this isotherm model is best suitable for multilayer biosorption. At low concentration of biosorbate, it obeys Henry's law. The equation for this model is given below [5]:

$$q_e = \frac{q_e^{\infty} C_e}{(a + C_e)^{1/n_1}} \tag{6}$$

where a (mg/L) is Toth isotherm constant and n_1 is dimensionless constant generally $n_1 < 1$. For $n_1 = 1$, this isotherm converts to the Langmuir equation.

Radke–Prausnitz isotherm is a modified form of Langmuir equation which can be expressed as follows [4,24]:

$$q_e = \frac{q_o K_o C_e}{1 + q_o C_e^{a_R}} \tag{7}$$

where q_o is maximum biosorption capacities (mg/g), a_R is Radke–Prausnitz model exponent and K_o is Radke–Prausnitz equilibrium constant. The Radke–Prausnitz isotherm model has some important properties due to which it is suitable for use in many biosorption systems. For high concentrations, it changes to the Freundlich isotherm and at low concentrations it becomes to a linear isotherm. This Radke–Prausnitz model fitted over a wide range of concentration.

Redlich–Peterson isotherm model is the combination of both Langmuir and Freundlich isotherm models [5,25]. The expression for this model is given as:

$$q_e = \frac{K_1 C_e}{1 + K_2 C_e^{b_o}} \tag{8}$$

where K_1 and K_2 are Redlich–Peterson isotherm constants and b_o is Redlich–Peterson isotherm exponent which lies between 0 and 1. For $b_o = 1$ this model reduces to Langmuir isotherm, for $K_2 C_e^{b_0} >> 1$, it becomes Freundlich isotherm, and for $K_2 C_e^{b_0} << 1$ it follows Henry's law. The ratio of $\frac{K_1 C_e}{K_2 C_e^{b_o}}$ indicates the adsorption capacity [31].

3.6.3. Four-parameter isotherms

Fritz isotherm model gives a good fit for wide range of experimental data because of large number of coefficients in their equation which is expressed as follows [5]:

$$q_e = \frac{\alpha_1 C_e^{\beta_1}}{1 + \alpha_2 C_e^{\beta_2}} \tag{9}$$

where β_1 and β_2 are Fritz equation exponents, α_1 and α_2 are Fritz parameters.

On the basis of R^2 value (>0.99) and small value of $\Delta q\%$, the best fitted models was Fritz model for Pb^{2+} ions and Redlich–Peterson model for Ni^{2+} and Cd^{2+} ions. Therefore, it can be concluded that Redlich–Peterson model is the best model for Ni^{2+} and Cd^{2+} ions and Fritz model for Pb^{2+} ions biosorption on *S. filipendula*.

3.7. Kinetic study

Kinetic study provides significant information regarding rate controlling step and the biosorption process controlling mechanism as either chemical reaction or mass transfer in order to find the optimum operating process parameters for industrial-scale batch processes [32]. In batch systems, biosorption kinetics is explained by fitting different kinetic models to experimental data based on biosorption equilibrium. For Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption six kinetic models were studied namely: Pseudo-first order, the Pseudo-second-order, Elovich, Bangham, intraparticle diffusion and modified Freundlich. The non-linearized form of these models was used to find the kinetic parameters which are given in Table 2.

3.7.1. Pseudo-first order

The pseudo-first order equation is expressed as follows [33,34]:

$$q_t = q_e(1 - e^{-k_0 t}) \tag{10}$$

where q_t is the amount of metal ions biosorbed at time t, k_o (min^{-1}) is biosorption rate constant of pseudo-first order kinetics.

Table 2
Kinetic model parameters calculated for Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption using *S. filipendula*

Kinetic model parameters	Pb^{2+}	Ni^{2+}	Cd^{2+}
$q_{e(\mathrm{exp})}$ (mg/g)	198	83.230	85.967
Pseudo-first order			
$q_{e(\mathrm{cal})}$ (mg/g)	130.03	88.25	81.48
k_o (min^{-1})	0.1069	0.057	0.346
R^2	0.86	0.989	0.957
Δq%	26.93	6.78	9.57
Pseudo-second order			
$q_{e(\mathrm{cal})}$ (mg/g)	138.67	108.7	87.15
K_2 (g/mg min)	5.7×10^{-3}	5.47×10^{-4}	6.33×10^{-3}
R^2	0.89	0.963	0.99
Δq%	12.14	12.13	2.06
Elovich			
α	1.628×10^5	13.81	594
β	0.067	0.042	0.09218
R^2	0.98	0.938	0.977
Δq%	1.94	20.12	2.73
Bangham			
α_o	0.355	0.842	0.316
k_b	89.32	6.97	59.52
R^2	0.94	0.957	0.964
Δq%	1.36	15.43	3.2
Intraparticle diffusion			
K_{id} (mg min$^{0.5}$/g)	6.73	9.58	5.153
C	147.81	9.612	51.81
R^2	0.90	0.826	0.84
Δq%	5.72	32.34	6.80
Modified Freundlich			
k_3 (L/g min)	1.403	0.173	0.50
m_1	11.862	2.612	6.99
R^2	0.98	0.857	0.927
Δq%	2.79	35.43	4.44

3.7.2. Pseudo-second order

The kinetic behavior of biosorption process with chemisorption being the rate-controlling step is more likely to be predicted by this model [35]. In chemisorption, the metal ions bind to the biosorbent surface which forms a chemical bond and tend to locate the sites that maximize their coordination number with the surface [36]. The pseudo-second order equation is given below [33,34]:

$$q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \tag{11}$$

where K_2 (g/mg.min) is pseudo-second order equilibrium rate constant.

3.7.3. Elovich model

This model is suitable for heterogenous biosorbing surface and chemisorption kinetics [37]:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta t) \tag{12}$$

where α (mg/g.min) represents initial rate of biosorption, β (g/mg) was related with the extent of surface coverage and activation energy for chemisorption.

3.7.4. Bangham model

This model is used to find whether the biosorption process is controlled by pore diffusion. The equation for this model is expressed as follows [38]:

$$q_t = \frac{C_o}{m}\left[1 - \exp\left(-\frac{m k_b t^{\alpha}}{V}\right)\right] \tag{13}$$

where a_o (<1) and k_b are constants.

3.7.5. Intraparticle diffusion model

Intraparticle diffusion is based on the movement of metal ions from aqueous phase to the solid phase. According to Weber and Morris theory, equation for this model is expressed as follows [5]:

$$q_t = K_{\mathrm{id}} t^{0.5} + C \tag{14}$$

where K_{id} is intraparticle diffusion rate constant (mg/g min$^{0.5}$) and C is constant. In this model, the metal ion uptake is directly proportional to $t^{0.5}$ instead of time t. The value of intercept C is proportional to thickness of boundary layer. It shows that higher the value of intercept more will be the boundary layer effect. The value of C equal to zero indicates that the intraparticle diffusion was the rate-controlling step.

3.7.6. Modified Freundlich model

Modified Freundlich model equation for kinetics of biosorption is developed by Kuo and Lotse [38]. This model is expressed as follows:

$$q_t = k_3 C_o t^{\left(\frac{1}{m_1}\right)} \tag{15}$$

where k_3 is uptake rate constant (L/g.min), m_1 is Kuo-Lotse constant and t is contact time (min). The values of m_1 and k_3 are used to examine the effect of ionic strength and surface loading on biosorption process.

The best fitted kinetic model was determined by the value of coefficient of determination (R^2) and normalized standard deviation (Δq%) which are given in Table 2. The higher R^2 and small Δq% value of Bangham, pseudo-first order and pseudo-second order show the best fitted models for Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption, respectively. It was obvious that different biosorption mechanisms were involved in the biosorption of Pb^{2+}, Cd^{2+} and Ni^{2+} ions. The Pb^{2+} ions biosorption followed Bangham kinetic model which indicates pore diffusion, Cd^{2+} ions biosorption followed pseudo-second order shows that it involves chemisorption and Ni^{2+} ions biosorption followed pseudo-first order which indicates that the reaction was more inclined toward physisorption.

3.8. Thermodynamic study

The thermodynamic parameters were determined to examine the thermodynamic feasibility of the process and to confirm the nature of the biosorption process. The Gibbs free energy, the enthalpy and entropy of the process was determined from experimental data using the given equation [39]:

$$\Delta G^\circ = -RT\ln K \tag{16}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{17}$$

where R is universal gas constant (8.314 × 10^{-3} kJ/mol K), K is equilibrium constant, determined as ratio of equilibrium metal concentration on the biosorbent surface C_a and in the solution C_e ($K = C_a/C_e$), and T is temperature in Kelvin. All the values of thermodynamic parameters are summarized in Table 3.

The value of biosorption capacity for Pb^{2+} and Cd^{2+} ions in this work is significantly greater than other reported biosorbents. The negative values of ΔG° show the spontaneous nature of the biosorption process and positive values of ΔH° indicate the endothermic nature of the biosorption. The positive values of entropy change ΔS° show the increase in randomness at the solid/liquid interface during metal ions biosorption onto *S. filipendula*.

3.9. Comparison of biosorption properties of S. filipendula with other biosorbents for Pb^{2+}, Ni^{2+} and Cd^{2+} ions biosorption

A comparative table (Table 4) on the basis of brief review of different biosorption properties and uptake capacity of different biosorbents for Pb^{2+}, Cd^{2+} and Ni^{2+} ions is presented. The removal efficiency of different biosorbents for Pb^{2+}, Cd^{2+} and Ni^{2+} ions varies due to different properties of adsorbents such as functional groups, structural and surface area. In addition to these properties, the degree of biosorption can also be affected by operating parameters such as temperature, pH, time, biosorbent dose and initial metal ion concentration. The amount of metal ions that binds on biomass surface depends on the number of active binding sites present [40].

3.10. Comparison of different biosorbent efficacy for Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption

The comparison of different biosorbents for Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption capacities with affinity order of $Pb^{2+} > Ni^{2+} > Cd^{2+}$ is shown in Table 5. The biosorption affinity of a biosorbent for metal ions correlates with physiochemical properties of metal ions [41]. The order of ionic radii: Pb^{2+} (133) > Cd^{2+} (109) >Ni^{2+} (83); electro negativity: Pb^{2+} (2.33) > Ni^{2+} (1.91) > Cd^{2+} (1.69); and atomic weight: Pb^{2+} (207.2) > Cd^{2+} (112.4) > Ni^{2+} (58.7). In the reported literature, similar order of affinity for Pb^{2+}, Cd^{2+} and Ni^{2+} ions was shown by different biosorbents. Hence it shows a clear correlation between the amount of metal ions biosorbed and metals ion properties (ionic radii and atomic weight).

Although electro negativity of Cd^{2+} has been found to be least in comparison with Ni^{2+}, the ionic radii and atomic weight favored Cd^{2+} was found to be biosorbed more than Ni^{2+}. The value of biosorption capacity for Pb^{2+} and Cd^{2+} ions in this work was much greater than other reported biosorbents. Therefore, *S. filipendula* can be used as effective biosorbent for these metal ions uptake.

Table 3
Thermodynamic parameters of Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption process using *S. filipendula*

Parameters Metal ion	T (K)	ΔG° (kJ/mol)	ΔH° (J/mol)	ΔS° (J/mol K)
Cd^{2+}	298	–0.0914	260.47	0.8743
	303	–3.822		
	308	–10.036		
	313	–12.592		
Pb^{2+}	298	–1.75	128	0.443
	303	–3.51		
	308	–5.35		
	313	–8.52		
Ni^{2+}	298	–0.097	79.175	0.270
	303	–1.533		
	308	–3.188		
	313	–4.060		

Table 4
Comparison of different biosorption properties of *Sargassum filipendula* with other biosorbents for Pb^{2+}, Ni^{2+} and Cd^{2+} ions biosorption

Metal ion	Biosorbent	Time (min)	pH	T (°C)	Initial Ni^{2+} ions concentration (mg/L)	Biosorbent dosage (g/L)	q_e (mg/g)	Reference
Ni^{2+}	*Yarrowia lipolytica*	60	6.0	40	100	2.0	30.12	[42]
	Baker's yeast	90	6.7	27	400	1.0	9.8	[43]
	Mucor hiemalis	150	8.0	40	50	0.5	15.83	[44]
	Sargassum ilicifolium	60	5.0	25	100	6.1	218.91	[45]
	Laminaria japonica	120	6.0	25	234.7	1	52.81	[46]
	Streptomonas maltophilia	30	6.0	30	45.6	2.0	54.3	[47]
	Bacillus subtilis	30	6.0	30	45.6	2.0	57.8	[47]
	Sargassum sp.		5.0	30	0–410	0.1	53.58	[48]
	Spirogyra neglecta	30	5.0	–	5-200	1	90.19	[49]
	Arthrospira platensis	120	5.0	20	29.34–176.0	2	20.77	[50]
	Codium vermilara	120	6.0	25	100–150	0.5	13.2	[40]
	Sargassum filipendula	60	5.0	35	50	2	34.3	This study
Cd^{2+}	*Deschampsia antarctica*	180	3.7	25	50–1,200	2.0	95.3	[51]
	Ulva lactuca	120	5.5	30	10	0.1	29.1	[52]
	D. antarctica	180	3.7	25	50–1,200	2.0	95.3	[51]
	Ulva latuca	120	5.5	30	10	0.1	29.1	[52]
	Scorpaenopsis neglecta	30	5.0	25	0–200	0.01	27.95	[49]
	Spirogyra hyalina	90	–	25	20–80	1.0	18.18	[53]
	Oedogonium sp.	30	5.0	25	5–200	0.01	13.07	[49]
	Codium vermilara	120	6.0	25	10–150	0.5	21.8	[54]
	Spirulina platensis	90	8.0	20	60	2.0	10.61	[55]
	Oedogonium sp.	30	5.0	25	5–200	0.01	13.07	[49]
	Ceramium virgatum	60	5.0	20	10	10	39.7	[56]
	Gelidium	20	5.3	20	6–91	0.2	18	[57]
	Sargassum filipendula	60	6.0	35	50	2	103.5	This study
Pb^{2+}	*Scorpaenopsis neglecta*	30	5.0	25	5.0	0.01	90.19	[49]
	Enterobacter sp.	100	2	25	100	–	50	[58]
	Pelvetia canaliculata	100	4.0	25	30–320	0.5	259	[59]
	Bacillus subtilis	30	5.0	30	8.4	1.0	166.7	[47]
	Aspergillus terreus	90	5.0	30	6,000	0.1	247.2	[59]
	A. platensis	120	–	25	–	2	113.13	[50]
	Chlorella vulgaris	120	–	25	–	2	138.27	[50]
	P. oedogonia	30	5.0	25	5–200	1.0	90.19	[60]
	Codium vermilara	120	5	–	–	0.5	21.8	[54]
	Spirogyra hyalina	120	–	–	80	0.25	31.25	[53]
	Spyridia filamentosa	30	5.0	25	414	2	178.19	[56]
	Aspergillus niger	30	5.0	30	50	0.91	2.47	[61]
	Spirogyra sp.	100	5.0	25	200	0.05	140	[58]
	Pleurotus florida	60	7.0	30	10	0.2	12.195	[62]
	Trichoderma viride	90	6.0	30	10	0.2	10.98	[62]
	Stenotrophomonas maltophilia	30	5.0	30	98.4	1.0	133.3	[47]
	Lactarius scrobiculatus	60	5.5	20	10	4	56.2	[15]
	Anabaena sphaerica	90	5.5	25	50–300	0.2	111.1	[63]
	Cladophora fascicularis	100	5.0	25	41–828	0.1	198.91	[64]
	Chlamydomonas reinhardtii	60	6.0	25	20-400	0.8	42.6	[65]
	Sargassum filipendula	40	5.0	35	50	2	367.942	This study

Table 5
Comparison of different biosorbents for biosorption capacities (mg/g) with affinity order of $Pb^{2+} > Ni^{2+} > Cd^{2+}$

S. No.	Biosorbent	Pb^{2+}	Cd^{2+}	Ni^{2+}	pH	Reference
1	*Penicillium chrysogenum*	91.08	26.88	18.16	-	[66]
2	*Nizamuddin zanardini*	29.3	3.15	2.11	4.0	[2]
3	*Padina australis*	21.53	3.07	2.44	4.0	[2]
4	*Sargassum gluacescens*	21.53	5.72	3.08	4.0	[2]
5	*Padina* sp.	258.75	84	36.3	5.5	[37]
6	*Sargassum* sp.	240	85.12	35.74	5.5	[37]
7	*Spirulina platensis*	75	54	31	6.0	[67]
8	Anaerobic biomass	255	60	26	5.5	[68]
9	Sugar beet pulp	74.52	24.64	11.72	5.5	[69]
10	Activated sludge	89.01	68.32	18.166	5.5	[70]
11	*Sargassum filipendula*	367.942	103.5	34.3	5.0	This study

4. Conclusions

This study was done to check the relative selectivity of *S. filipendula* for Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption from aqueous solution. The effect of various process parameters namely, biosorbent dose, pH, temperature and initial metal ions concentration was investigated. The optimum pH for Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption was found to be 5.0, 6.0 and 5.0, respectively. The equilibrium time for Pb^{2+} ions was 40 min and for Cd^{2+}, and Ni^{2+} ions was 60 min. Faster biosorption kinetics was noticed for Pb^{2+} ions as comparison with Cd^{2+} and Ni^{2+} ions. The optimum conditions for Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption were biosorbent dose: 2 g/L, initial metal ion concentration 50 g/L, temperature: 35°C. To examine the biosorption mechanism six kinetic models were fitted to the experimental data namely: pseudo-first order, pseudo-second order, Bangham, Elovich, intraparticle diffusion and modified Freundlich. The equilibrium data were analyzed by using six isotherm models namely: Langmuir, Freundlich, Redlich–Peterson, Radke–Prausnitz, Toth and Fritz. The maximum biosorption capacity achieved was 367.94, 103.5 and 34.3 mg/g for Pb^{2+}, Cd^{2+} and Ni^{2+} ions, respectively. The Bangham, pseudo-second order and pseudo-first order were found to be the best fitted kinetic models for Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption, respectively. It indicates that pore diffusion, chemisorption and physisorption mechanism were involved for Pb^{2+}, Cd^{2+} and Ni^{2+} ions, respectively. Thermodynamic study shows that Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption process was spontaneous, feasible and endothermic in nature. It may be concluded that *S. filipendula* can be used as a low cost and abundant source for removal of Pb^{2+}, Cd^{2+} and Ni^{2+} ions from aqueous solutions. The experimental results indicate that Pb^{2+} has the highest affinity for cell wall functional groups of *S. filipendula*.

Acknowledgments

The authors gratefully acknowledge the Ministry of Human Resource Development, Government of India, for the financial support (Scholarship to Ayushi Verma), and Institute Instrumentation Center, Indian Institute of Technology Roorkee, for providing its analytical instruments for the research work. The authors wish to state that Prof. (Mrs.) Shashi Kumar left to her heavenly abode in the recent past. The authors humbly dedicate this research paper to their loving and affectionate memory with profound regards.

References

[1] M.H. Jnr, A.I. Spiff, Studies on the effect of pH on the sorption of Pb^{2+} and Cd^{2+} ions from aqueous solutions by *Caladium bicolor* (Wild Cocoyam biomass), Electron. J. Biotechnol., 7 (2004) 313–323.

[2] M.M. Montazer-Rahmatia, P. Rabbani, A. Abdolali, A.R. Keshtkar, Kinetics and equilibrium studies on biosorption of cadmium, lead, and nickel ions from aqueous solutions by intact and chemically modified brown algae, J. Hazard. Mater., 185 (2011) 401–407.

[3] C. Cojocarua, M. Diaconua, I. Cretescua, J. Savic, V. Vasic, Biosorption of copper (II) ions from aqua solutions using dried yeast biomass, Colloids Surf., A, 335 (2009) 181–188.

[4] L.S. Ferreira, M.S. Rodriguesa, J.C.M. de Carvalho, A. Lodi, E. Finocchio, P. Perego, A. Converti, Adsorption of Ni^{2+}, Zn^{2+} and Pb^{2+} onto dry biomass of *Arthrospira (Spirulina) platensis* and *Chlorella vulgaris*. I. single metal systems, Chem. Eng. J., 173 (2011) 326–333.

[5] A. Verma, S. Kumar, S. Kumar, Biosorption of lead ions from the aqueous solution by *Sargassum filipendula*: equilibrium and kinetic studies, J. Environ. Chem. Eng., 4 (2016) 4587–4599.

[6] A.M.A. Aty, N.S. Ammar, H.H.A. Ghafar, R.K. Ali, Biosorption of cadmium and lead from aqueous solution by fresh water alga *Anabaena sphaerica* biomass, J. Adv. Res., 4 (2013) 367–374.

[7] N.H. Yarkandi, Removal of lead (II) from waste water by adsorption, Int. J. Curr. Microbiol. Appl. Sci., 3 (2014) 207–228.

[8] S. Schiewer, M.H. Wong, Ionic strength effects in biosorption of metals by marine algae, Chemosphere, 41 (2000) 271–282.

[9] J.D. Dodge, The Fine Structure of Algal Cells, Academic Press, London, UK, 1973, pp. 14–45.

[10] E. Percival, R.H. McDowell, Chemistry and Enzymology of Marine Algal Polysaccharides, Academic Press, London, 1967, pp. 99–126.

[11] W.M. Antunes, A.S. Luna, C.A. Henriques, A.C.A. da Costa, An evaluation of copper biosorption by a brown seaweed under optimized conditions, Electron. J. Biotechnol., 6 (2003) 208–222.

[12] V.K. Gupta, A. Rastogi, A. Nayak, Biosorption of nickel onto treated alga (*Oedogonium hatei*): application of isotherm and kinetic models, J. Colloid Interface Sci., 342 (2010) 533–539.

[13] H. Merrikhpour, M. Jalali, Comparative and competitive adsorption of cadmium, copper, nickel, and lead ions by Iranian natural zeolite, Clean Technol. Environ. Policy, 15 (2013) 303–316.

[14] S. Ozdemir, E. Kilinc, A. Poli, B. Nicolaus, K. Guven, Biosorption of Cd, Cu, Ni, Mn and Zn from aqueous solutions by thermophilic bacteria, *Geobacillus toebii* sub.sp. *decanicus* and *Geobacillus thermoleovorans* sub.sp. *stromboliensis*:

equilibrium, kinetic and thermodynamic studies, Chem. Eng. J., 152 (2009) 195–206.

[15] A. Sari, M. Tuzen, Biosorption of cadmium (II) from aqueous solution by red algae (*Ceramium virgatum*): equilibrium, kinetic and thermodynamic studies, J. Hazard. Mater., 157 (2008) 448–454.

[16] S. Sugashini, S. Gopalakrishnan, Studies on the performance of protonated cross linked chitosan beads (PCCB) for chromium removal, Res. J. Chem. Sci., 2 (2012) 55–59.

[17] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res., 34 (2000) 735–742.

[18] R.K. Singh, S. Kumar, S. Kumar, A. Kumar, Development of parthenium based activated carbon and its utilization for adsorptive removal of p-cresol from aqueous solution, J. Hazard. Mater., 155 (2008) 523–535.

[19] M.F. Carvalho, A.F. Duque, I.C. Goncalves, P.M.L. Castro, Adsorption of fluorobenzene onto granular activated carbon: isotherm and bioavailability studies, Bioresour. Technol., 98 (2007) 3424–3430.

[20] M.T. Morera, J.C. Echeverria, C. Mazkiaran, J.J. Garrido, Isotherms and sequential extraction procedures for evaluating sorption and distribution of heavy metals in soils, Environ. Pollut., 113 (2001) 135–144.

[21] S. Mohan, J. Karthikeyan, Removal of lignin and tannin color from aqueous solution by adsorption onto activated carbon solution by adsorption onto activated charcoal, Environ. Pollut., 97 (1997) 183–187.

[22] E. Cheraghi, E. Ameri, A. Moheb, Adsorption of cadmium ions from aqueous solutions using sesame as a low-cost biosorbent: kinetics and equilibrium studies, Int. J. Environ. Sci. Technol., 12 (2015) 2579–2592.

[23] M. Belhachemi, F. Addoun, Comparative adsorption isotherms and modeling of methylene blue onto activated carbons, Appl. Water Sci., 1 (2011) 111–117.

[24] L. Deng, Y. Su, H. Su, X. Wang, X. Zhu, Biosorption of copper (II) and lead (II) from aqueous solutions by nonliving green algae *Cladophora fascicularis*: equilibrium, kinetics and environmental effects, Adsorption, 12 (2006) 267–277.

[25] B. Alyuz, S. Veli, Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins, J. Hazard. Mater., 167 (2009) 482–488.

[26] I. Tuzun, G. Bayramoglu, E. Yalcin, G. Basaran, G. Celik, M.Y. Arica, Equilibrium and kinetic studies on biosorption of Hg (II), Cd (II) and Pb (II) ions onto microalgae *Chlamydomonas reinhardtii*, J. Environ. Manage., 77 (2005) 85–92.

[27] M.Z. Momcilovic, M.S. Randelovic, M. Purenovic, A.E. Onjia, B.M. Babic, B.Z. Matovic, Synthesis and characterization of resorcinol formaldehyde carbon cryogel as efficient sorbent for imidacloprid removal, Desal. Wat. Treat., 52 (2014) 7306–7316.

[28] B. Royer, N.F. Cardoso, E.C. Lima, J.C.P. Vaghetti, N.M. Simon, T. Calvete, R.C. Veses, Applications of Brazilian pine-fruit shell in natural and carbonized forms as adsorbents to removal of methylene blue from aqueous solutions-kinetic and equilibrium study, J. Hazard. Mater., 164 (2009) 1213–1222.

[29] Y.S. Ho, G. Mc Kay, Pseudo-second-order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[30] P.W. Atkins, Physical Chemistry, Oxford University Press, Oxford, 1995.

[31] Y.S. Ho, G. McKay, Application of kinetic models to the sorption of copper on to peat, Adsorpt. Sci. Technol., 20 (2002) 797–815.

[32] D. AmbogaAnzeze , J. MmariOnyari, P. Mwanza Shiundu, J. W. Gichuki, Equilibrium and kinetics studies for the biosorption of aqueous Cd (II) ions onto *Eichhorna crassipes* biomass, J. Appl. Chem., 7 (2014) 29–37.

[33] Y. Onal, Kinetics of adsorption of dyes from aqueous solution using activated carbon prepared from waste apricot, J. Hazard. Mater., 137 (2006) 1719–1728.

[34] I.A. Sengil, M. Ozacar, Competitive biosorption of Pb^{2+}, $Cu^{2+}$and Zn^{2+} ions from aqueous solutions onto valonia tannin resin, J. Hazard. Mater., 166 (2009) 1488–1494.

[35] B. Volesky, Z.R. Holan, Biosorption of heavy metals, Biotechnol. Prog., 11 (1995) 235–250.

[36] A.O. Dada, A.P. Olalekan, A.M. Olatunya, O. Dada, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk, J. Appl. Chem., 3 (2012) 38–45.

[37] P.X. Sheng, Y.P. Ting, J.P. Chen, L. Hong, Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms, J. Colloid Interface Sci., 275 (2004) 131–141.

[38] S. Kuo, E.G. Lotse, Kinetics of phosphate adsorption and desorption by hematite and gibbsite, Soil Sci., 116 (1973) 400–406.

[39] R.A. Anayurt, A. Sari, M. Tuzen, Equilibrium, thermodynamic and kinetic studies on biosorption of Pb (II) and Cd (II) from aqueous solution by macrofungus (*Lactarius scrobiculatus*) biomass, Chem. Eng. J., 151 (2009) 255–261.

[40] A.H. Hawari, C.N. Mulligan, Biosorption of lead (II), cadmium (II), copper (II) and nickel (II) by anaerobic granular biomass, Bioresour. Technol., 97 (2006) 692–700.

[41] Z. Reddad, C. Gerente, Y. Andres, P.L. Cloirec, Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies, Environ. Sci. Technol., 36 (2002) 2067–2073.

[42] A. Hammaini, A. Ballester, F. Gonzalez, M.L. Blazquez, J.A. Munoz, Activated Sludge as Biosorbent of Heavy Metals, Biohydrometallurgy and the Environment Toward the Mining of the 21st Century, International Biohydrometallurgy symposium IBS_99, 1999, pp. 185–192.

[43] R.A.K. Rao, M.A. Khan, Biosorption of bivalent metal ions from aqueous solution by an agricultural waste: kinetics, thermodynamics and environmental effects, Colloids Surf., A, 332 (2009) 121–128.

[44] H.T. Fan, W. Sun, B. Jiang, Q.J. Wang, D.W. Li, C.C. Huang, K.J. Wang, Z.G. Zhang, W.X. Li, Adsorption of antimony (III) from aqueous solution by mercapto functionalized silica-supported organic–inorganic hybrid sorbent: mechanism insights, Chem. Eng. J., 286 (2016) 128–138.

[45] C.A. Quirarte-Escalante, V. Soto, W. Cruz, G.R. Porras, R. Manriquez, S.G. Salazar, Synthesis of hybrid adsorbents combining sol-gel processing and molecular imprinting applied to lead removal from aqueous streams, Chem. Mater., 21 (2009) 1439–1450.

[46] H.T. Fan, X.T. Sun, Z.G. Zhang, W.X. Li, Selective Removal of lead (II) from aqueous solution by an ion-imprinted silica sorbent functionalized with chelating n-donor atoms, J. Chem. Eng. Data, 59 (2014) 2106–2114.

[47] E.K. Unnikrishnan, A.K. Basu, N. Chattopadhyay, B. Maiti, Removal of arsenic from water by ferrous sulphide, Indian J. Technol., 10 (2003) 281–286.

[48] J. Wang, C. Chen, Biosorbents for heavy metals removal and their future, Biotechnol. Adv., 27 (2009) 195–226.

[49] S. Wierzba, Biosorption of nickel (II) and zinc (II) from aqueous solutions by the biomass of yeast *Yarrowia lipolytica*, Pol. J. Chem. Technol., 19 (2017) 1–10.

[50] V. Padmavathy, Biosorption of nickel (II) ions by baker's yeast: kinetic, thermodynamic and desorption studies, Bioresour. Technol., 99 (2008) 3100–3109.

[51] K.A. Shroff, V.K. Vaidya, Kinetics and equilibrium studies on biosorption of nickel from aqueous solution by dead fungal biomass of *Mucor hiemalis*, Chem. Eng. J., 171 (2011) 1234–1245.

[52] R. Tabaraki A. Nategh, Multimetal biosorption modeling of Zn^{2+}, Cu^{2+} and Ni^{2+} by *Sargassum ilicifolium*, Ecol. Eng., 71 (2014) 197–205.

[53] Y. Liu, Q.C.F. Luo, J. Chen, Biosorption of Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} ions from aqueous solutions by pretreated biomass of brown algae, J. Hazard. Mater., 163 (2009) 931–938.

[54] S. Wierzba, Biosorption of lead (II) zinc (II) and nickel (II) from industrial wastewater by *Stenotrophomonas maltophilia* and *Bacillus subtilis*, Pol. J. Chem. Technol., 17 (2015) 7–87.

[55] C.E.R. Barquilha, E.S. Cossich, C.R.G. Tavares, E.A. Silva, Biosorption of nickel (II) and copper (II) ions in batch and fixed-bed columns by free and immobilized marine algae *Sargassum* sp, J. Cleaner Prod., 150 (2017) 58–64.

[56] A. Singh, S.K. Mehta, J. Gaur, Removal of heavy metals from aqueous solution by common freshwater filamentous algae, World J. Microbiol. Biotechnol., 23 (2007) 1115–1120.

[57] V.J.P. Vilar, C.M.S. Botelho, R.A.R. Boaventura, Equilibrium and kinetic modelling of Cd (II) biosorption by algae *Gelidium* and agar extraction algal waste, Water Res., 40 (2006) 291–302.

[58] E. Romera, F. Gonzalez, A. Ballester, M.L. Blazquez, J.A. Munoz, Comparative study of biosorption of heavy metals using different types of algae, Bioresour. Technol., 98 (2007) 3344–3353.

[59] C. Gutierrez, H.K. Hansen, P. Hernandez, C. Pinilla, Biosorption of cadmium with brown macroalgae, Chemosphere, 138 (2015) 164–169.

[60] M.M. Ghoneim, H.S. El-Desoky, K.M. El-Moselhy, A. Amer, E.H.A. El-Naga, L.I. Mohamedein, A.E. Al-Prol, Removal of cadmium from aqueous solution using marine green algae, *Ulva lactuca*, Egyptian. J. Aquat. Res., 40 (2014) 235–242.

[61] J.I.N. Kumar, C. Oommen, Removal of heavy metals by biosorption using freshwater alga *Spirogyra hyaline,* J. Environ. Biol., 33 (2012) 27–31.

[62] A.A.A. Homaidan, J.A. Alabdullatif, A.A.A. Hazzani, A.A.A. Ghanayem, A.F. Alabbad, Adsorptive removal of cadmium ions by *Spirulina platensis* dry biomass, Saudi J. Biol. Sci., 22 (2015) 795–800.

[63] V.J.P. Vilar, C.M.S. Botelho, R.A.R. Boaventura, Equilibrium and kinetic modelling of Cd (II) biosorption by algae *Gelidium* and agar extraction algal waste, Water Res., 40 (2006) 291–302.

[64] W.B. Lu, J.J. Shi, C.H. Wang, J.S. Chang, Biosorption of lead, copper and cadmium by an indigenous isolate *Enterobacter* sp. J1 possessing high heavy-metal resistance, J. Hazard. Mater., 134 (2006) 80–86.

[65] F.V. Hackbarth, F. Girardi, S.M.A.G.U. de Souza, A.A.U. de Souza, R.A.R. Boaventura, V.J.P. Vilar, Marine macroalgae *Pelvetia canaliculata* (Phaeophyceae) as a natural cation exchanger for cadmium and lead ions separation in aqueous solutions, Chem. Eng. J., 242 (2014) 294–305.

[66] Y.M. Sun, C.Y. Horng, F.L. Chang, L.C. Cheng, W.X. Tian, Biosorption of lead, mercury, and cadmium ions by *Aspergillus terreus* immobilized in a natural matrix, Pol. J. Microbiol., 59 (2010) 37–44.

[67] K. Kowanga, G.O. Mauti, E.M. Mauti, Biosorption for lead (II) ions from aqueous solutions by the biomass of *Spyridia filamentosa* algal species found in Indian Ocean, J. Innov. Sci. Res., 4 (2015) 218–220.

[68] T. Netpae, Removal of lead from aqueous solutions by *Aspergillus niger* from artificial vinegar factory, Electron. J. Biol., 8 (2012) 7–10.

[69] V.K. Gupta, A. Rastogi, Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: kinetics and equilibrium studies, J. Hazard. Mater., 152 (2008) 407–414.

[70] A.S.A. Prasad, G. Varatharaju, C. Anushri, S. Dhivyasree, Biosorption of lead by *Pleurotus florida* and *Trichoderma viride,* Br. Biotechnol. J., 3 (2013) 66–78.