Valorization of Adenanthera pavonina seeds as a potential biosorbent for lead and cadmium removal from single and binary contaminated system

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ABSTRACT
This study investigated the biosorption of Pb (II) and Cd (II) on powdered seeds of Adenanthera pavonina from single and binary heavy metal solutions. The adsorption capacity of the metal ions was studied as a function of pH, adsorbent dose, initial metal ion concentration, and contact time. In the single heavy metal system, maximum removal of Pb (II) and Cd (II) were achieved at pH 4 and 6, respectively, while the equilibrium was attained at a contact duration of 35 min at a constant dose of 5 g L\(^{-1}\) was maintained for both Pb (II) and Cd (II). Further, the kinetic study revealed that the biosorption process was best described by the second-order kinetic model. In the competitive biosorption of binary mixtures of Pb (II) and Cd (II) were studied in terms of percentage removal of metal ions, adsorption capacity and equilibrium sorption isotherm. The percentage removal of metal ions in binary solutions was suppressed in presence of the other competitive metal ion. Field emission scanning electron microscopy integrated with energy dispersive X-ray spectroscopy of the biomass before (control) and after (metal loaded biomass) the biosorption process, confirmed the presence of respective heavy metal on to the biomass. Fourier transmission infrared spectroscopy spectra supported the activity of hydroxyl, amines, amides, and carboxyl groups in uptake of both heavy metal ions.

1. Introduction

Heavy metal discharge due to industrial operations has increased evidently; thereby posing deleterious effects on to the ecosystem and disrupting the environmental balances (Goswami, Manikandan, et al., 2017). Wastewater generated from the industries such as electroplating, mining operations, metal finishing, and metallurgical industries having low pH have been reported to cause the lethal effect on the living organisms (Arul Manikandan, Alemu, Goswami, Pakshirajan, & Pugazhenthi, 2016). Heavy metals viz., lead (Pb), cadmium (Cd), copper (Cu), iron (Fe), chromium (Cr), cobalt (Co) can be classified as toxic, non-degradable, inorganic pollutants and is being utilized extensively in industrial processes (Bind, Goswami, & Prakash, 2018; U.S. HHS, 1999). Heavy metal tends to bioaccumulate into the food chain and gets absorbed by the living organisms (Sathe, Mahanta, & Mishra, 2018). Simultaneously, it affects their health severely and also influences the aesthetic quality of potable water.

Lead (Pb (II)) is utilized extensively in various industrial processes and is commonly found in the industrial wastewaters (Davydova, 2005). Bioaccumulation of Pb (II) in living tissues even at low concentrations can generate toxicity and have detrimental effects on the nervous system, kidney and reproductive system (Volesky, 1990). Thus, it is essential that Pb (II) must be removed from waste streams. Activities like mining, electroplating, smelting, battery manufacturing and burning of coal and household wastes also lead to the release of cadmium (Cd (II)) into the environment. Cd (II) can be transmitted over large distances through the air before its particles settle on the ground or on the water (ATSDR, 1999). Exposure of heavy metals in human beings takes place by breathing contaminated air, drinking contaminated water and eating foods containing low levels of heavy metals (Sharma & Bhattacharyya, 2005). The chronic and acute disorders caused by Cd (II) exposure include itai-itai disease, renal disorder, emphysema, hypertension, and testicular atrophy (Bind et al., 2018).

The pervasive and toxic nature of heavy metals and their propensity to bio accumulate in the food chain have made it imperative to develop technologies to remove heavy metal ions from wastewater effectively (Bind et al., 2018). Methods like chemical precipitation, chemical oxidation and reduction, electrochemical treatment, membrane filtration, ion-exchange, and adsorption on activated carbon, have been conventionally applied for removal of heavy metals from industrial wastewater (Tobin & Roux, 1998). Exorbitant costs and inadequate
efficiencies at low metal concentrations along with technical constraints have restricted the applicability of these traditional processes, thereby leading to the search of alternative methods that will enable metal sequestration at low concentrations and is at the same time cost-effective in treating industrial wastewater (Hussein et al., 2005).

Recently, the focus has been shifted towards the use of novel materials, particularly bio-materials, to be used as adsorbents for bioremediation of wastewater contaminated with heavy metals. Biosorbents are cheap, effective, and recyclable and can effectively treat large volumes of wastewater with low concentrations of heavy metals, thereby offering distinct advantages over the conventional methods (Puranik & Paknikar, 1997). In the present study, seeds of *Adenanthera pavonina* L. (Red Sandalwood), utilized as a non-conventional biosorbent with an objective of removing Pb (II) and Cd (II) from aqueous solutions. *Adenanthera pavonina* (Family Fabaceae) is endemic to the tropical and sub-tropical regions of the world. The leaves, barks and seeds of the tree are well known for their medicinal and nutritive values. The seeds are known to be effective in treating cardiovascular diseases, boils and inflammatory reactions, gout and rheumatism (Adedapo et al., 2009). The powdered seeds of *Adenanthera pavonina* were found to contain around 7.4% moisture, 31% crude proteins, 11% fats, 52% carbohydrates, and 7.8% total dietary fibre (Senga et al., 2013).

Hence, the present study examined the valorization of *Adenanthera pavonina* seeds as a potential biosorbent for Pb (II) and cadmium Cd (II) removal in an individual and mixture systems. Initially, the biosorbent was characterized by various physical, chemical, thermal, and morphological parameters by employing field emission scanning electron microscopy (FESEM) equipped with energy dispersive spectroscopy (EDX) and fourier transform infrared spectroscopy (FTIR) analyses. Further, the effect of different process parameters, viz. initial pH of the solution, contact time, initial heavy metal concentration and biosorbent dose were also examined in the batch system (Table 1). Adsorption isotherms and kinetics were also examined for both the heavy metals.

### 2. Materials and methods

#### 2.1. Preparation of biosorbent

Seeds of *Adenanthera pavonina* were collected from Dolaigaon village area (26.5039° N, 90.5376° E) of Bongaigaon district, Assam, India and washed thoroughly with distilled water. The seeds were then air dried and crushed mechanically. To get rid of any colour, the crushed seeds were washed again with distilled water and were further dried in a hot air oven at 105°C for 5 h. The dried seeds were then sieved to 250 µm and stored in a desiccator without any pre-treatment until further use.

#### 2.2. Preparation of metal ion solution

All the chemical salts (analytical grade) used for the experiment were procured from Merck (Mumbai, India). Stock solution of 1000 mg L⁻¹ for Pb (II) and Cd (II) were prepared individually from Pb (NO₃)₂ and Cd (NO₃)₂·4H₂O respectively. Adequate dilution of the stock solution with distilled water was performed to prepare working solutions of different concentrations for biosorption experiments.

#### 2.3. Characterization of the adsorbent

The prepared biosorbent was further characterized chemically, physically, and morphologically. For determining the ash content of the biosorbent, 1 g of biosorbent was incinerated at 650°C in presence of air for 12 h in a muffle furnace (LabTech, India) according to the ASTM D1762-84 standard. The elemental compositions of biosorbent were analysed using an elemental analyzer (Eurovector EA3000, Germany). Brunauer–Emmett–Teller (BET) analysis of the biosorbent was performed for determining the surface area by N₂ multilayer adsorption at ambient temperature using Autosorb-IQ MPinstrument (Nova 1000E, Quantachrome, U.S.A.). The examination of the functional groups present on the surface of biosorbent was further recorded using a Fourier transform infrared (FTIR) spectrophotometer (IR Affinity, Shimadzu, U.S.A.) in the range 400–4000 cm⁻¹ for the analysis (Goswami, Kumar, et al., 2017a). The surface morphology of the biosorbent was analysed by utilizing field emission scanning electron microscope at ultra-high resolution (FESEM, ((Zeiss, Sigma VP, Germany) equipped EDX, operated at operated at 3.0 kV) (Goswami, Kumar, et al., 2017b).

#### 2.4. Biosorption experiments

All the batch biosorption experiments were performed in the 250 mL of Erlenmeyer flasks with a working volume of 100 mL. For determining the effect of process parameters on to the biosorption phenomena, experiments were carried out considering all the parameters individually. Batch adsorption experiments were performed by taking a pre-weighed amount of adsorbent with 100 mL of metal ion solution in a series of Erlenmeyer flasks and agitating for a pre-determined duration at a constant speed of 120 rpm at room temperature 35°C. pH of the aqueous solutions was adjusted using 0.1 N HNO₃ or
0.1N NaOH. After agitation, the concentration of heavy metal ions in the solution was measured using Atomic Absorption Spectrophotometer (Varian SpectrAA220, The Netherlands). The percentage removal of Pb (II) and Cd (II) was calculated using the following expression:

$$\text{Removal of metal ion(\%)} = \frac{(C_o - C_f)}{C_o} \times 100$$

where, $C_i$ and $C_f$ denotes the initial and final concentrations of Pb (II) and Cd (II) in mg L$^{-1}$. Further, the metal uptake ($q_e$) at equilibrium was calculated from the Equation (2):

$$\text{Heavy metal uptake (q_e)} = \frac{C_o - C_e}{V} \times W \quad (2)$$

where $q_e$ is the adsorption capacity in mg g$^{-1}$, $C_o$ and $C_e$ are the initial and equilibrium concentrations of the heavy metal ions (mg L$^{-1}$), respectively, $V$ volume of metal ion solution (mL) and $W$: total amount of biosorbent (g).

### 2.5. Biosorption of Pb (II) and Cd (II) in the binary system

The competitive biosorption of Pb (II) and Cd (II) ions were elucidated from the simultaneous combinations of these two metals in the solution. The initial concentration of competing metal was maintained within the range 20–60 mg L$^{-1}$, while the concentration of dominant metal ion was maintained at constant concentrations of 20, 40, and 60 mg L$^{-1}$, pH value of the biosorption system was calibrated to the optimum pH of the dominant metal ion.

### 2.6. Kinetics of the sorption

The kinetic models were further investigated at different agitation time to determine the mechanism of biosorption and the potential rate controlling step in the experiments. These include the pseudo-first order model (Lagrgren & Svenska, 1898) and pseudo-second order kinetic model (Ho & McKay, 1999) illustrated in the expressions (3) and (4) respectively.

$$\log(q_e - q_f) = \log q_e - \frac{k_1}{2.303}t \quad (3)$$

$$\frac{t}{q_f} = \frac{1}{h} + \left(\frac{1}{q_e}\right)t \quad (4)$$

where $q_f$ and $q_e$ are the amount of metal ions adsorbed in time (t) and at equilibrium respectively, $k_1$ is the pseudo-first order rate constant, $h = k_2q_f^2$, where, $k_2$ is the second order rate constant, which is evaluated by plotting $(t/q_f)$ versus $t$. The intra-particle diffusion model (Weber & Morris, 1963) given by Equation (5):

$$q_t = k_d t^{0.5} + I \quad (5)$$

where $\alpha$ is the constant for initial sorption rate, $\beta$ is the desorption rate constant, $k_d$ is the intra-particle diffusion rate constant and I is the intercept of the intra-particle diffusion plot.

### 2.7. Adsorption isotherm

The adsorption data were further fitted to Langmuir (Langmuir, 1916) and Freundlich isotherm models (Freundlich, 1906) to determine the maximum uptake of Pb (II) and Cd (II) by the biosorbent. Dubinin–Radushkevich isotherm model (Dubinin, 1960) was also studied to determine whether physical or chemical process was prevalent during the adsorption of metal ions from aqueous solution. Langmuir isotherm is applicable for monolayer adsorption and is represented by the Equation (6):

$$\frac{C_e}{q_e} = \frac{C_m}{Q_m} + \frac{1}{bQ_m} \quad (6)$$

where $b$ is $(K_d/K_p)$ ($K_d$ and $K_p$) are the rate constants for adsorption and desorption, respectively) (L mg$^{-1}$), $q_e$ (mg g$^{-1}$) is the amount adsorbed on unit mass of the adsorbent, $Q_m$ (mg g$^{-1}$) is the quantity of adsorbate required to form a single monolayer on the unit mass of the adsorbent and $C_e$ (mg L$^{-1}$) is the equilibrium concentration. The values of $Q_m$ and $b$ were calculated from the slope and intercept of the plot of $(C/q_e)$ versus $C_e$.

The separation factor ($R_L$) (Hall, Eagleton, Acrivos and Vermeulen, 1966) is a dimensionless equilibrium parameter, developed as an extension of the Langmuir equation, given by:

$$R_L = \frac{1}{1 + b C_o} \quad (7)$$

where $C_o$ is the initial concentration of respective metal ions in the aqueous medium. The value of $R_L$ should be $0 < R_L < 1$ for favourable adsorption. The linearized form of Freundlich isotherm is given by Equation (8):

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \quad (8)$$

where $K_f$ is Freundlich constant representing the relative adsorption capacity of the adsorbent and n is the Freundlich coefficient representing the deviation from linearity of adsorption. $K_f$ and n values were obtained from the plot of log $q_e$ versus log $C_e$.

Dubinin–Raduskevich (D–R) model is represented by the Equation (9):

$$\ln q_e = \ln q_D - B_D \epsilon^2 \quad (9)$$

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \quad (10)$$
and Cd (II) were 119 and 95 pm, respectively (Pauling, 1960), which agrees with the pore size of the biosorbent. Surface area provides the measure for the availability of surface for heavy metal adsorption. In the current study, the average surface area was found to be 8.565 m$^2$ g$^{-1}$, which is higher than that of several biosorbent reported in literature. Further, the pore volume of the biosorbent is found to be 0.267 cc g$^{-1}$ and total ash content was found to be 62.7%.

3.2. FTIR analysis

FTIR spectra of the prepared biosorbent samples shows various vibrational frequencies due to various functional groups present in the biosorbent and is presented in Figure 2 (a and b) for Cd (II) and Pb (II), respectively.
heterogeneous surface which facilitates the biosorption of Pb (II) and Cd (II) ions on the different parts of the biosorbent. FESEM micrograph of the metal loaded biosorbent (Figure 4 (b and c) for Pb (II) and Cd (II), respectively, and 4 (d) for the binary solution) clearly shows the presence of shiny particles the presence of which are absent in the fresh biosorbent (Bansal, Singh, Garg, & Rose, 2009). EDX spectrum obtained from the fresh biomass (Figure 5 (a)) shows the presence of elements like, N, K, Na, Ca, Mg, Cl, S, Fe, Zn along with O and C. Appearance of new peaks for Pb (II) and Cd (II) in EDX spectra of the metal loaded biosorbent confirmed the biosorption of heavy metals (Figure 5 (b and c)). Figure 5 (d) authenticates the simultaneous uptake of both Pb (II) and Cd (II) on the surface of biosorbent.

3.4. Effect of different process parameters

3.4.1. Effect of pH

pH plays a significant role in the adsorption processes. It influences the binding of metal ions by determining the surface charge of the adsorbent, degree of ionization and speciation of the adsorbate (El-Ashtoukhy et al., 2008). Here, in order to determine the effect of pH on the biosorption of Pb (II) and Cd (II), batch adsorption studies were carried out within pH range of 1–7 for both the metals with an adsorbent dose of 0.5 g and contact time of 30 min. The initial concentrations of the metal ions were maintained within the range of 10–70 mg L⁻¹. The effect of pH on the adsorption of Pb (II) and Cd (II) were shown in Figure 5 (a and b), respectively. Figure 6(a) revealed that 98% removal of Pb (II) ions was achieved at pH 4, whereas in Figure 6(b), 96% removal of Cd (II) ions was attained at pH 6 with an initial concentration of...
Figure 4. Scanning electron micrographs of powdered *Adenanthera pavonina* seeds, (a) before metal biosorption, (b) after Pb (II) biosorption, (c) after Cd (II) biosorption, (d) after Pb (II), and Cd (II) uptake from binary mixture.

Figure 5. EDX spectra of powdered *Adenanthera pavonina* seeds, (a) before metal biosorption, (b) after Pb (II) biosorption (c) after Cd (II) biosorption (d) after Pb (II) and Cd (II) uptake from binary mixture.
capacities decreased from 6.61 mg g\(^{-1}\) to 1.23 mg g\(^{-1}\) for Pb (II) and 5.61–1.20 mg g\(^{-1}\) for Cd (II). At lower biosorbent dose, less surface area is available which in turn relates to lower number of binding sites for metal ion adsorption. With the increase in adsorbent dose, the availability of binding sites increases, which leads to increased percentage removal. However, with the initial metal ion concentration remaining constant, any further addition of biosorbent does not have any impact on percentage removal as the available metal ions in the system do not suffice to cover all the exchangeable sites on the biosorbent (El-Ashtoukhy, Amin, & Abdelwahab, 2008).

Thus, any surplus biosorption sites remain unsaturated resulting to a decline in the amount of metal adsorbed per unit mass of the biosorbent (mg g\(^{-1}\)).

3.4.2. Effect of adsorbent dose
Adsorbent dose is also an important parameter that influences the sorption capacity of the adsorbent. In case of both Pb (II) and Cd (II), at fixed initial concentration of 10 mg L\(^{-1}\), the percentage removal increased from 66 to 99% for Pb (II) and 56–96% for Cd (II) as the biosorbent dose was increased from 1 g L\(^{-1}\) to 5 g L\(^{-1}\). No significant deviation in the percentage removal was recorded beyond a dose of 5 g L\(^{-1}\). However, there was a decrease in adsorbent capacities (mg g\(^{-1}\)) with every increment in adsorbent dose. (Figure 7 (a and b)). The biosorbent capacities decreased from 6.61 mg g\(^{-1}\) to 1.23 mg g\(^{-1}\) for Pb (II) and 5.61–1.20 mg g\(^{-1}\) for Cd (II). At lower biosorbent dose, less surface area is available which in turn relates to lower number of binding sites for metal ion adsorption. With the increase in adsorbent dose, the availability of binding sites increases, which leads to increased percentage removal. However, with the initial metal ion concentration remaining constant, any further addition of biosorbent does not have any impact on percentage removal as the available metal ions in the system do not suffice to cover all the exchangeable sites on the biosorbent (El-Ashtoukhy, Amin, & Abdelwahab, 2008). Thus, any surplus biosorption sites remain unsaturated resulting to a decline in the amount of metal adsorbed per unit mass of the biosorbent (mg g\(^{-1}\)).

3.4.3. Effect of initial metal ion concentration
The effect of initial metal ion concentrations was studied at optimum pH 4 and pH 6 for the removal of Pb (II) and Cd (II), respectively, and contact time of 30 min over a concentration range of 10–70 mg L\(^{-1}\) (Figure 7 (a and b)). The percentage removal of Pb (II) decreases from 99 to 87% where as the adsorption capacity increases from 1.98 to 12.14 mg g\(^{-1}\) with an increase in initial Pb (II) concentration from 10 to 70 mg L\(^{-1}\). For Cd...
(II), the percentage removal decreases from 96 to 55%. However, the metal uptake capacity increases with the increase in initial concentration and attains a saturation value. At 10 mg L\(^{-1}\) initial concentration, the biosorption capacity of Adenanthera pavonina seeds for Cd (II) was found to be 1.92 mg g\(^{-1}\), where as it was calculated to be 7.67 mg g\(^{-1}\) at an initial concentration of 70 mg L\(^{-1}\) (Figure 8). At low adsorbate concentrations and fixed biosorbent dose, greater numbers of exchangeable sites were available in comparison to the number of moles of metal ions in the system. With the increase in number of moles of metal ions in the biosorption system, these exchangeable sites were saturated which further leads to decreased percentage removal (Nasir, Nadeem, Akhtar, Hanif, & Khalid, 2007).

### 3.4.4. Effect of contact time
In case of both Pb (II) and Cd (II), initially the rate of adsorption was rapid and attains the saturation point within 30 min. Thus, the equilibrium time for powdered Adenanthera pavonina seeds was considered to be 30 min for both the heavy metals (Figure 9 (a and b)). The biosorption of the metal ions takes place in two stages: rapid stage followed by the slower stage. The rate of adsorption was higher due to the availability of larger surface area. As adsorption proceeds towards the equilibrium, the rate of uptake was governed by the rate of diffusion of adsorbate from the exterior to the interior sites of the adsorbent and consequently becomes quantitatively negligible (Verma, Chakraborty, & Basu, 2006). With the exhaustion of sorption sites, the rate of removal of sorbate also decreases. Such mechanism involving a rapid rate of biosorption initially followed by an insignificant slower stage is extensively reported in literature (Saeed, Akhter, & Iqbal, 2005).

### 3.5. Adsorption isotherms
The representation of the results by developing an equation for designing purposes demands the analysis of the adsorption isotherms. In the present study, Langmuir, Freundlich and D-R isotherm models were analysed. The values of regression coefficients along with the constants are shown in Table 3. Langmuir constants (\(Q_m\) and \(b\)) were calculated to be 12.94 mg g\(^{-1}\) and 0.57 L g\(^{-1}\) for Pb (II) and 8.10 mg g\(^{-1}\) and 0.67 L g\(^{-1}\) for Cd (II), respectively. The values for the separation factor (\(R_L\)) satisfies
the condition of $0 < R_l < 1$, in case of both Pb (II) and Cd (II), thereby indicating that the sorption is favourable (Namane, Mekarzia, Benrachedi, Belhanechebensemra, & Hellal, 2005). A comparison of biosorption capacities ($Q_a$) of various adsorbents in uptake of Pb (II) and Cd (II) is summarized in Table 4. It could be perceived in general that the biosorption capacity of the powdered *Adenanthera pavonina* seeds is comparable to those of other adsorbents and even shows promising values obtained in some cases.

Values of $K_f$ and $n$ obtained from the plot of Freundlich isotherm model were found to be 5.05 and 2.59 for Pb (II), whereas 3.09 and 3.15 for Cd (II), respectively. Ibrahim et al. stated that the value of $n$ between 1 and 10 suggests beneficial adsorption. Thus, the magnitude of $n$ calculated in the present study indicates the favourable conditions for adsorption of the metal ions on powdered *Adenanthera pavonina* seeds.

D–R isotherm gives the value of the mean energy of adsorption and also furnishes information on whether adsorption was due to chemical or physical phenomena. $E_D$ values within the range of 1–8 kJ mol$^{-1}$ indicate physisorption and those within the range of 8–16 kJ mol$^{-1}$ indicate chemisorption (Jain, Garg, & Kadirvelu, 2009). The calculated $E_D$ value for the present study is found to be 3.55 and 3.16 kJ mol$^{-1}$ for Pb (II) and Cd (II), respectively, which clearly refers to physical adsorption.

The comparison of the correlation coefficients ($R^2$) (Table 3) obtained for the three isotherm model analysed shows that biosorption of the metal ions from the aqueous solution was described better by Langmuir isotherm model than Freundlich or D–R isotherm models. This indicates that biosorption has taken place through monolayer adsorption. A comparison of maximum biosorption capacities ($Q_a$) of various biosorbents including *Adenanthera pavonina* is summarized in Table 4.

### Table 3. Isotherm models and their calculated constants for biosorption of Pb (II) and Cd (II) on powdered *Adenanthera pavonina* seed.

| Metals | Langmuir | Freundlich | Dubinin-Radushkevich |
|--------|----------|------------|-----------------------|
|        | $Q_m$ (mg g$^{-1}$) | $b$ (L mg$^{-1}$) | $R^2$ | $K_f$ (mg g$^{-1}$) | $n$ | $R^2$ | $q_L$ (mg g$^{-1}$) | $E_D$ (mol$^2$ J$^{-1}$) | $E_E$ (kJ mol$^{-1}$) | $R^2$ |
| Pb (II) | 12.94 | 0.57 | 0.96 | 5.05 | 2.59 | 0.96 | 8.49 | 4×10$^{-8}$ | 3.55 | 0.79 |
| Cd (II) | 8.10 | 0.67 | 0.99 | 3.09 | 3.15 | 0.92 | 2.26 | 5×10$^{-8}$ | 3.16 | 0.85 |

### Table 4. Biosorption capacity of Pb (II) and Cd (II) from literature by various adsorbents.

| Metal type | Biosorbent | Biosorbent capacity, $Q_a$ (mg/g) | pH | References |
|------------|------------|---------------------------------|----|------------|
| Pb (II)    | Sargassum natans | 1.22 | 3.5 | Holan & Volesky, 1994 |
|            | Calotropis procera | 22.8 | 4.0 | Lodeiro et al. 2006 |
|            | Rhizophus nigricans | 80.8 | 5.5 | Hassan & El-Kassas, 2012 |
|            | Aspergillus niger | – | 5.5 | Barros et al. 2003 |
|            | Cork wastes | 13.46 | 5.0 | López-Mesas et al., 2011 |
|            | Bacillus pumilus | 28.06 | 6.0 | Colak, Atil, Yazıcıoğlu, & Olğun, 2011 |
|            | Sugar beet pulp | 43.97 | 5.0 | Pehlivan et al. 2008 |
|            | Phosphorylated orange waste | 1.15 (mol/kg) | 4.4 | Ghimire, Inoue, Inoue, Kawakita, & Ohto, 2008 |
|            | Pinus sylvestris | 11.38 | 4.0 | Ucun, Bayhana, Kaya, Cakici, & Algur, 2003 |
|            | Bacillus sp. (ATS-1) | 92.27 | 3 | Tunali et al., 2006 |
|            | Saccharomyces cerevisiae | 2.7 | 5 | Huang, Huang, & Morehart, 1990 |
|            | Pomegranate peel | – | 5.6 | El-Ashoukhy et al. 2008 |
|            | Cystosera bacata | 186 | 4.5 | Lodeiro et al., 2006 |
|            | Orzya sativa husk | 8.6 | 5.0 | Zulkal, Ahmad, & Norulakmal, 2006 |
|            | Waste tea leaves | 8.6 | 5.0 | Abluvalia and Goyal, 2005 |
|            | *Adenanthera pavonina* seeds | 12.94 | 4 | This study |
| Cd (II)    | Sawdust of Pinus sylvestris | 19.08 | – | Taty-Costodes et al. 2003 |
|            | Bone char | 0.004 | – | Ko et al., 2004 |
|            | Neem leaf powder | 157.80 | 9.5 | Sharma & Bhattacharya, 2005 |
|            | Activated biocarbon | 2.88 | 4.8 | Singanan, 2011 |
|            | Ceiba pentandra hulls | 19.59 | 6.0 | Rao et al., 2006 |
|            | Coconut copra meal | 4.92 | 6.0 | Ho & Ofomaja, 2006 |
|            | Caulerpa lentillifera | 4.69 | 5.0 | Pavanant et al., 2006 |
|            | Bacillus jeotgali | 37.30 | 7.0 | Green-Ruiz, Rodríguez-Tirado, & Gomez-Gil, 2008 |
|            | Agabani clay | 1.427 | 5.0 | Dawodu, Alkornie, & Ogbu, 2012 |
|            | Heartwood powder of Areca catechu | 10.660 | 6.0 | Chakrvartty et al. 2010 |
|            | Sugar beet pulp | 46.10 | 5.3 | Pehlivan, Yanik, Ahmetli, & Pehlivan, 2008 |
|            | Pomelo peel | 21.83 | 5.0 | Saikaew, Kaewsarn, & Saikaew, 2009 |
|            | Olive stone | 6.97 | 7.0 | Blázquez, Hernández, Calero, & Ruiz-Núñez, 2005 |
|            | Papaya wood | 17.22 | 5.0 | Saeed et al., 2005 |
|            | Sugarcane bagasse | 6.97 | 7.0 | Ibrahim, Hanafiah, & Yahya, 2006 |

3.6. Adsorption kinetics

In order to analyse the controlling mechanisms in the present biosorption system, the pseudo-first and pseudo-second order kinetic models (Equations 3 and 4) were examined by fitting the experimental values
obtained in the study. The kinetic parameters obtained for all initial concentrations are shown in Table 5 (a and b). Non-occurrence of sorption of one ion per adsorption site exclusively was exhibited by the low correlation values obtained for the pseudo-first order kinetic model (Oliveira, Franca, Oliveira, & Rocha, 2008). By comparing the correlation coefficients, it can be considered that the pseudo-second order kinetic model is a better fit for the experimental data. Thus, the formation of chemisorptive bond between the metal ions and the adsorption sites by valence forces or covalent forces can be assumed as the rate-limiting step in the present study (Sharma & Bhattacharyya, 2005). The variations in the values of the constants can be attributed to the heterogeneous surface characteristics of the biosorbent (Al-Degs, El-Barghouthi, Issa, Khraisheh, & Walker, 2006).

The intra-particle diffusion model (figure not shown) helps in defining the mechanism of adsorption. Film diffusion, pore diffusion and intra-particle transport constitute the mechanism of adsorption. The rate-limiting steps in the batch system were constituted by pore diffusion and intra-particle diffusion, where as in a continuous system, film diffusion was considered to be the rate-limiting step (Goswami & Ghosh, 2005). In the present experiment, the plot of $q_t$ versus $t^{0.5}$ (figure not shown) constitutes a linear portion and a curved portion that gradually becomes constant.

### 3.7. Competitive biosorption

The uptake capacities of the biomass for initial Pb (II) concentrations at 20, 40, and 60 mg L$^{-1}$ were found to be 3.90, 7.46, and 10.58 mg g$^{-1}$, respectively, while in the presence of Cd (II) ions in binary metal solutions, the uptake capacities were slightly reduced (Figure 9(a)). The effects of Pb (II) on removal of Cd (II) were examined in a similar procedure (Figure 9 (b)) and it

### Table 5a. Parameters for estimated kinetic models for biosorption of Pb (II).

| $C_0$ (mg/L) | Pseudo-first order | Pseudo-second order | Intra-particle diffusion |
|--------------|--------------------|---------------------|--------------------------|
|              | $k_1$ | $q_e$ (exp) (mg/L) | $R^2$ | $k_2$ | $q_e$ (exp) (mg/L) | $R^2$ | $K_{id}$ | $I$ | $R^2$ |
| 10           | 0.12  | 0.76 | 0.9792 | 0.33 | 2.06 | 0.9997 | 0.078 | 1.501 | 0.793 |
| 20           | 0.095 | 1.42 | 0.9601 | 0.126 | 4.12 | 0.9994 | 0.168 | 2.885 | 0.900 |
| 30           | 0.12  | 2.43 | 0.9603 | 0.095 | 5.98 | 0.9993 | 0.227 | 4.332 | 0.876 |
| 40           | 0.14  | 3.77 | 0.9041 | 0.074 | 7.69 | 0.9993 | 0.299 | 5.322 | 0.856 |
| 50           | 0.12  | 4.74 | 0.9127 | 0.045 | 9.62 | 0.9987 | 0.448 | 6.310 | 0.862 |
| 60           | 0.095 | 4.58 | 0.9535 | 0.045 | 11.25 | 0.9990 | 0.540 | 7.222 | 0.895 |
| 70           | 0.133 | 8.51 | 0.8343 | 0.028 | 12.94 | 0.9976 | 0.683 | 7.872 | 0.862 |

### Table 5b. Parameters for estimated kinetic models for biosorption of Cd (II).

| $C_0$ (mg/L) | Pseudo-first order | Pseudo-second order | Intra-particle diffusion |
|--------------|--------------------|---------------------|--------------------------|
|              | $k_1$ | $q_e$ (exp) (mg/L) | $R^2$ | $k_2$ | $q_e$ (exp) (mg/L) | $R^2$ | $K_{id}$ | $I$ | $R^2$ |
| 10           | 0.079 | 1.256 | 0.8892 | 0.096 | 2.124 | 0.9959 | 0.1427 | 0.9644 | 0.8606 |
| 20           | 0.080 | 2.436 | 0.8912 | 0.050 | 4.054 | 0.9955 | 0.2712 | 1.8480 | 0.8563 |
| 30           | 0.082 | 3.891 | 0.8662 | 0.030 | 5.960 | 0.9941 | 0.4273 | 2.4526 | 0.8560 |
| 40           | 0.079 | 4.734 | 0.8769 | 0.024 | 7.410 | 0.9946 | 0.5333 | 3.0387 | 0.8584 |
| 50           | 0.086 | 5.966 | 0.8356 | 0.015 | 8.772 | 0.9916 | 0.6200 | 3.3388 | 0.8479 |
| 60           | 0.120 | 6.217 | 0.8498 | 0.029 | 8.340 | 0.9963 | 0.5149 | 4.2244 | 0.8270 |
| 70           | 0.061 | 3.139 | 0.8438 | 0.035 | 8.157 | 0.9974 | 0.4249 | 4.7284 | 0.8710 |

Figure 10. (a) Comparison of percentage removal of (a) Pb (II) and (b) Cd (II) on powdered Adenanthera pavonina seed with Pb (II) ions present as single metal and with the presence of increasing concentration of Cd (II); and (b) Cd (II) on powdered Adenanthera pavonina seeds with Cd (II) ions present as single metal and with the presence of increasing concentration of Pb (II).
Table 6. Langmuir isotherm constants for Pb (II) and Cd (II) biosorption in binary mixtures.

| Constants   | Pb (II) | Cd (II) |
|-------------|---------|---------|
| Q_max (mg/g) | 20 mg/L Cd (II) | 40 mg/L Cd (II) | 60 mg/L Cd (II) | 20 mg/L Pb (II) | 40 mg/L Pb (II) | 60 mg/L Pb (II) |
| Q_max (mg/g) | 13.69   | 14.71   | 13.51   | 7.52   | 7.57   | 3.18   |
| b (L/g)     | 0.37    | 0.22    | 0.22    | 0.53    | 0.41    | 1.26    |
| R²          | 0.994   | 0.986   | 0.997   | 0.997   | 0.998   | 0.997   |

was found that the biosorption capacities for Cd (II) were also decreased. For initial Cd (II) concentration of 20 mg L⁻¹ in a single ion solution, the adsorption capacity was calculated to be 3.69 mg g⁻¹, whereas for the same initial concentration of Cd (II), the uptake values were found to be 3.57, 3.51, and 3.46 mg g⁻¹ when Pb (II) concentrations were maintained at 20, 40, and 60 mg L⁻¹, respectively (Figure 10 (b)). Thus, it was observed that with the increase in concentration of Pb (II), uptake of Cd (II) was decreased. The suppression of uptake of metal ions in competitive biosorption can be attributed to the non-selective nature of the functional groups on the surface of the biosorbent. In presence of another different metal ion, chemical interactions take place between the metal ions which results in competition for adsorption sites (Al-Rub, El-Naas, Ashour, & Al-Marzouqi, 2006). The differences in the electro-negativity of the metals can be considered as a prime reason for the differences in the biosorption capacities (Şengil & Özçar, 2009). Pb (II) is more electronegative than Cd (II) and thus it has higher affinity towards the binding sites, thereby resulting in remarkable suppression of uptake of Cd (II) ions. Langmuir isotherm model was investigated to evaluate the results obtained in the binary mixture of metal ions and is presented in Table 6.

4. Conclusions

The results demonstrated that seeds of Adenanthera pavonina that is copiously available at low cost could be effectively and economically utilized for the removal of heavy metals viz., Pb (II) and Cd (II) from wastewater. FTIR, FESEM and EDX studies validated the interactions between heavy metals and the functional groups on the surface of the adsorbent. The experimental conditions were also found to influence the biosorption of the metal ions to a great extent. For both Pb (II) and Cd (II), biosorption data fits well to the Langmuir isotherm model. In addition, the kinetic studies demonstrated that both bulk and intra-particle diffusion governed biosorption mechanisms. The competitive biosorption studies show that the percentage removal and hence the biosorption capacities of the biomass for one metal species reduced with the increasing concentrations of the other. The results provided a valid basis for the designing of heavy metal contaminated wastewater treatment plants in future.

Further, the regeneration and techno-economic assessment of the biosorbent for the heavy metal removal from the wastewater is needed for determining the practical feasibility of the biosorbent. Also, the surface modification could be performed for the biosorbent for making it more feasible for the heavy metal removal. Upscaling of the experimental process should be also performed.

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Disclosure statement

The authors of this work declare that they have no conflict of interest.

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