



Chemically oxidized pineapple fruit peel for the biosorption of heavy metals from aqueous solutions

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ABSTRACT

Chemically oxidized pineapple fruit peel biomass has been used as a biosorbent for Cd(II) and Pb(II) removal from aqueous solutions. Fourier transform infrared spectroscopy and scanning electron microscopy techniques were used to characterize the treated pineapple fruit peel. The biosorption efficiency of pineapple fruit peel for Cd(II) and Pb(II) was greatly enhanced after chemical oxidation probably due to introduction of carboxylic and hydroxyl groups onto the biosorbent surface. Biosorption kinetics for both metals was well described by pseudo-second-order kinetic equation and intraparticle film diffusion. Langmuir, Freundlich, and Temkin isotherm models were applied to the biosorption equilibrium data and best results were obtained with Langmuir isotherm model. Maximum monolayer biosorption capacity was found to be 42.10 and 28.55 mg g⁻¹ for Cd(II) and Pb(II), respectively. Thermodynamic study indicates that the biosorption was exothermic and the spontaneity of the process decreases with the increase in solution temperature.

Keywords: Biosorption; Chemical modification; Isotherm; Kinetics; Thermodynamics

1. Introduction

Natural water contaminations due to heavy metals discharged by industrial and domestic activities are considered as a serious threat to the ecology and human health [1]. Heavy metals are non-biodegradable and have a tendency to accumulate in living tissues through food chain, causing various diseases and disorders [2]. Cadmium (II) and Lead (II) are

well-recognized pollutants with the permissible limit of 0.003 and 0.01 mg L⁻¹ in portable water, respectively. Pb(II) and Cd(II) are suspected carcinogens, may cause lung fibrosis, dyspnoea, anemia, muscle and joint pains, kidney problems, high blood pressure, etc. [3]. Therefore, wastewater laden with Pb(II) and Cd(II) must be treated before being discharged into the environment.

There are several advanced methods for the treatment of heavy metals-contaminated wastewaters such

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as filtration, membrane separation, electrochemical treatment, ion exchange, adsorption, etc. [4–8]. Among these methods, biosorption has been investigated as a cost-effective and highly efficient process, and the ability of the biosorbent was to bind and sequester the metal ions from wastewater [9]. Several agricultural-based biosorbents have been used for the removal of heavy metals such as *Portulaca oleracea* [10], Orange peel [11], *Annona squamosa* shell [12], rice husk, rice bran [13,14], tea wastes [15], Neem biomass [16], Ficus carica leaves [17], green alga biomass [18], tamarack bark, potato peel waste [19], *Peganum harmala* seeds [20], etc. The results show that the uses of agricultural waste materials as biosorbents are highly efficient for the treatment of heavy metals-laden wastewaters due to porous surface and presence of multifunctional groups on material surface.

Pineapple (*Ananas comosus*) is a herbaceous perennial plant with total production between 16 and 19 million tonnes worldwide. Pineapple can be consumed fresh, or as salads, fruit cocktail, jam, and juice combinations from food-processing industries [21]. Fresh pineapple fruit contains about 60% edible part and 35% peel as waste material which principally consists of cellulose, hemi-cellulose, lignin, and pectin [21,22]. Therefore, from the environmental and multipurpose utilization point of view, pineapple peel waste biomass can be used as an effective biosorbent for the removal of heavy metals from aqueous solutions.

The present work investigates the biosorption of divalent metal ions on binary oxidized pineapple fruit peel. Sulfuric acid and potassium permanganate were used as the oxidizing agents. The oxidation process introduces large quantities of oxygenous functional groups such as hydroxyl, epoxy, and carboxylic groups on the surface of the material which bind with the metal ions through sharing of electron pair [23]. In this work, kinetics and isotherms for Cd(II) and Pb(II) biosorption have been studied. The results show that the biosorption capacity of oxidized pineapple peels is much higher than the pristine pineapple peel.

2. Materials and methods

2.1. Materials

Cadmium nitrate, lead nitrate, H_2SO_4 , and KMnO_4 (AR grade) were obtained from QReC™ chemicals. A stock solution of lead nitrate and cadmium nitrate ($1,000 \text{ mg L}^{-1}$) was used as adsorbate and solutions of various concentrations were obtained by diluting the stock solution with distilled water (DW). Stock solutions of nitrate salts of Cd(II) and Pb(II) at the concentration of $1,000 \mu\text{g mL}^{-1}$ in 1% HNO_3 were

standardized by complexometric titration before use. Buffer solutions were used for pH adjustment. For this, solutions containing suitable amounts of KCl–HCl for pH 1–2, and acetic acid–ammonium acetate for pH 4.0–6.0 were prepared in DW. DW was used throughout the study.

2.2. Preparation of biosorbent

Pineapple fruit peel waste was collected from local market and thoroughly washed with DW to remove dirt. The washed material was dried in an oven at 80°C for 48 h. Thereafter, dried peel was grinded and sieved to the particle size ranges from 150 to $200 \mu\text{m}$. Twelve gram powered material was treated with 100 mL of 0.1 M H_2SO_4 and 100 mL of 0.1 M KMnO_4 solution and stirred at 60°C for 24 h. Finally, chemically activated pineapple peel was thoroughly washed with DW and dried in an oven at 80°C for 24 h for further use.

2.3. Characterization of biosorbent

Fourier transform infrared (FTIR) spectra of untreated and treated pineapple peel were recorded using a Thermo Scientific Nicolet 6700 apparatus in the region of $500\text{--}4,000 \text{ cm}^{-1}$ at a resolution of $\pm 4.0 \text{ cm}^{-1}$. Scanning electron microscope (SEM) images were recorded to find the change in the surface morphology of pineapple peel before and after acid treatment by Zeiss Supra 55 SEM. Zero point charge (pHzpc) of the treated pineapple fruit peel was determined by the previously reported method [24]. A series of flasks were prepared containing 50 mL of 0.1 M KCl and pH of solution was adjusted between 2 and 10 by adding 0.1 M HCl or 0.1 M NaOH solutions. After that 0.2 g of treated pineapple fruit peel was added in each flask and the resultant solutions were shaken for 24 h. The final pH of solution was measured and a plot between initial pH vs. final pH values was drawn to determine the pHzpc.

2.4. Batch biosorption studies

Biosorption studies were carried out by taking 0.2 g biosorbent in 50 mL metal ion solution with concentration ranges from 50 to 200 mg L^{-1} onto the water bath shaker at 200 rpm. The influence of pH on the retention of metal ions onto raw and treated biosorbents was investigated in the pH range of 1–7. The pH of the solutions was adjusted using the appropriate buffer solutions. Furthermore, the biosorption studies were also carried out by varying time interval

(5.0–180 min) at 100 mg L^{-1} concentration to optimize the equilibrium time for the removal of Cd(II) and Pb(II) from aqueous solutions. Atomic absorption spectrometer (Perkin–Elmer/Analyst 800) was used to determine the Cd(II) and Pb(II) concentration in the supernatants after the biosorption. The equilibrium biosorption capacity of treated and untreated pineapple waste material was estimated with the help of the following equation:

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (1)$$

where C_0 and C_e are the initial and final concentration of Cd(II) and Pb(II) in the solution, respectively. V is volume in (L) and M is the mass of biosorbent (g).

3. Results and discussion

3.1. Characterization

Surface morphology of pineapple fruit peel and chemically activated fruit peel is shown in Fig. 1. As

shown in Fig. 1(a), the surface of pristine pineapple fruit peel is coarse and has creases. After chemical treatment, the surface of biosorbent (Fig. 1(b)) appears to be highly cave like and porous due to the removal of tarry substances such as pigments, gum, other acid soluble oligosaccharides [25]. However, after adsorption with metal ion, the surface morphology of metal-loaded pineapple fruit peel (Fig. 1(c)) has been changed which was entirely different from the chemically oxidized pineapple fruit peel, authenticating the adsorption of metal ions on the surface of adsorbent.

The FTIR analysis was performed for the qualitative determination of the main functional groups present on the surface of pineapple fruit peel. The FTIR spectra of the pineapple fruit peel are shown in Fig. 2. The broad band that appeared around $3,200\text{--}3,600 \text{ cm}^{-1}$ was mainly ascribed to the free or hydrogen bond O–H and/or NH_2 (amino) symmetrical stretching variations, where as the peak that appeared at $2,917 \text{ cm}^{-1}$ was assigned to the aliphatic CH groups. However, after chemical treatment (Fig. 2(b)), new sharp band at $2,850 \text{ cm}^{-1}$ appears due to the C–H

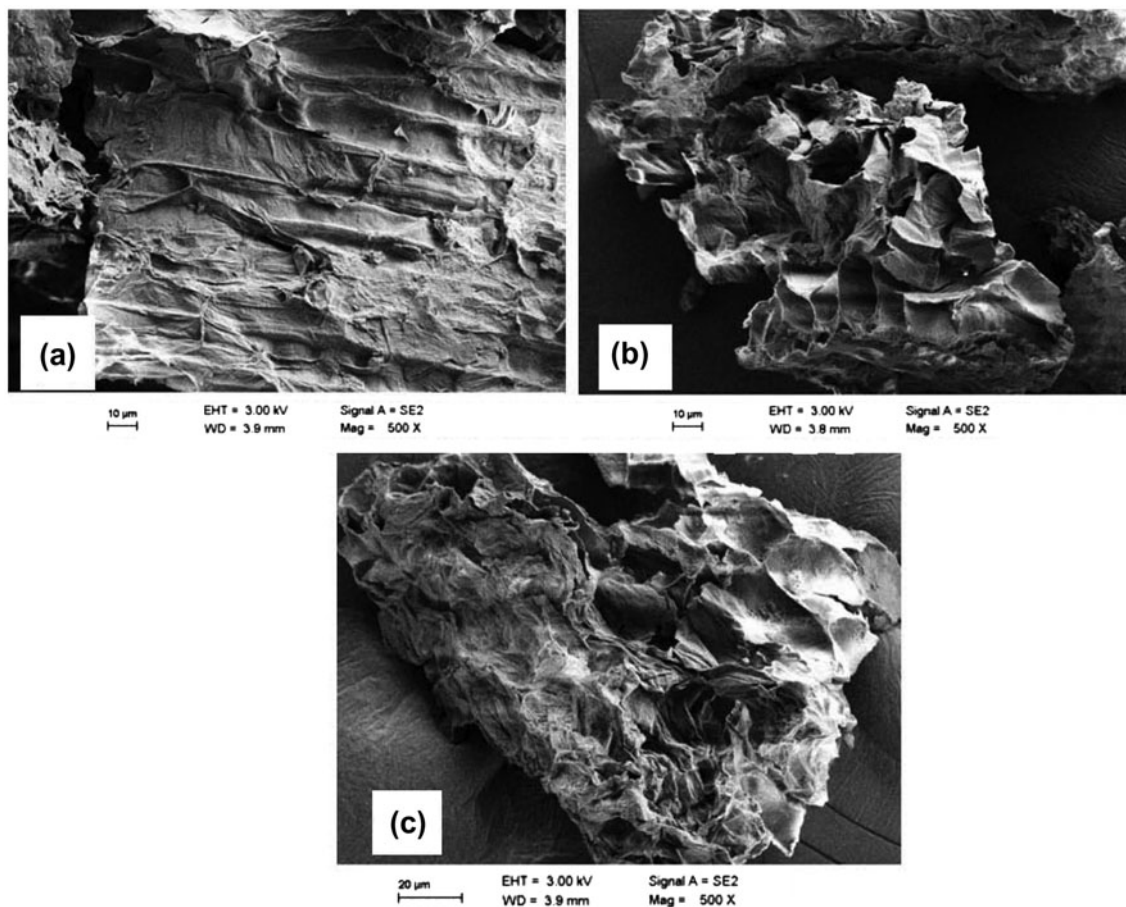


Fig. 1. SEM images (a) raw pineapple fruit peel, (b) chemically treated pineapple fruit peel, and (c) after adsorption.

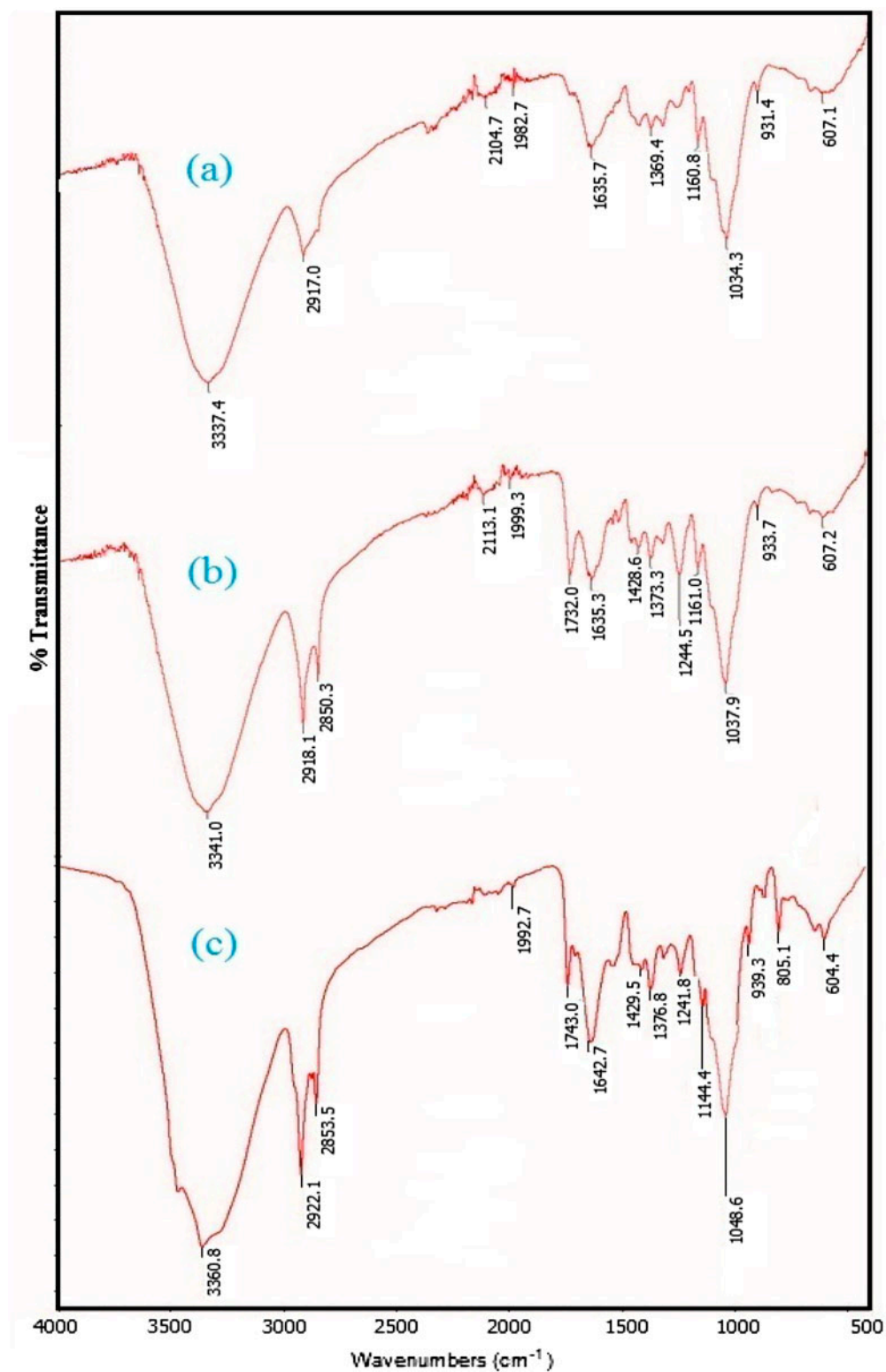


Fig. 2. FTIR spectra of (a) raw pineapple fruit peel, (b) chemically treated pineapple fruit peel, and (c) after adsorption.

stretching [26]. The strong peak at $1,635\text{ cm}^{-1}$ was mainly due to the C–O bond of the carboxylic group, and after chemical activation a new sharp peak appeared at $1,732\text{ cm}^{-1}$ which was also due to the carbonyl group of ester [27–29]. The peak at $1,428\text{ cm}^{-1}$ corresponds to the CH_2 bending vibration. The peaks in the region from $1,369$ to $1,244\text{ cm}^{-1}$ may be attributed to the O–H bending and O–H-stretching or C–H bending vibrations. The absorption band at $1,161\text{ cm}^{-1}$ corresponds to C–O antisymmetric bridge stretching of cellulosic moiety of pineapple fruit peel [28,29]. The strong band at $1,037\text{ cm}^{-1}$ is due to C–O of $-\text{OCH}_3$ group which belongs to lignin structure in pineapple fruit peel. Thus, the appearance of a new peak and shift in the absorption band of FTIR spectrum demonstrated that pineapple fruit peel was successfully modified with oxidizing agents. As shown in Fig. 2(c), functional groups of metal-loaded pineapple fruit peel are slightly affected in their position and intensity. A red shift has been observed in the range $(10\text{--}20)\text{ cm}^{-1}$ for COOH and OH/ NH_2 stretching frequencies indicating their role as active sites in electrostatic attraction/chelation with metal ions.

3.2. Effect of solution pH

The influence of pH on the removal of metal ions onto treated and untreated pineapple fruit peel was investigated in the pH range of 1–7 as shown in Fig. 3. The biosorption of Cd(II) and Pb(II) onto raw

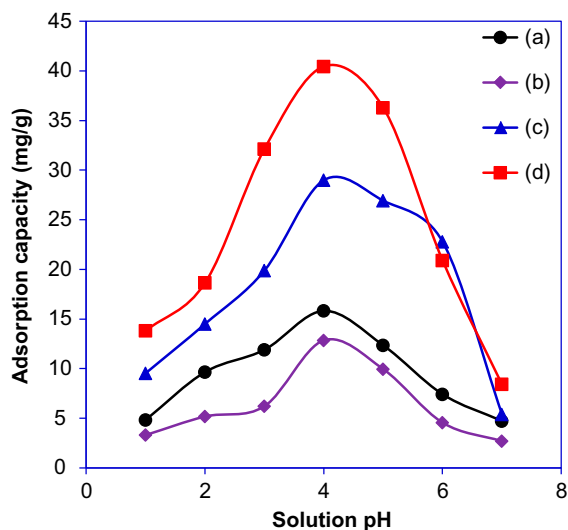


Fig. 3. Effect of solution pH, (a, b) biosorption of Cd(II) and Pb(II) onto raw pineapple fruit peel, (c, d) biosorption of Cd(II) and Pb(II) onto chemically treated pineapple fruit peel (biosorbent dose: 0.2 g , temp: 25°C , volume: 50 mL , and concentration: 100 mg L^{-1}).

and pretreated pineapple fruit peel increased with the increase in solution pH and maximum removal was found at pH 4. The results were more effective for pretreated pineapple fruit peel as compared to raw one for both metal ions; and maximum biosorption of Cd(II) and Pb(II) were found to be 40.46 , 29.40 g^{-1} and 15.73 , 12.84 g^{-1} for raw and pretreated pineapple fruit peel, respectively, at pH 4. This behavior can be explained on the basis of pH_{zpc} of the biosorbent which was found to be 4.2. At low pH values ($\text{pH}_{\text{zpc}} < 4.2$), protons compete with metallic cations for the same active sites of the biosorbent and H^+ occupies most of the active sites of biosorbent [27]. Reversibly, as the solution pH increases, the biosorption of both metal ions increases as biosorbent surface takes more negative charges due to the ionization of carboxyl and hydroxyl groups, as the ionization constants of various carboxyl groups have been reported to be around pH 3–4 [30]. As the solution pH increases ($\text{pH} > 4$), biosorption of both metal ions decreases due to the formation of hydroxylated complexes of Cd(II) and Pb(II) and lack of free metal ions for biosorption. Therefore, removal of metal ions decreases [31]. Several researchers have also studied the effect of pH on biosorption of heavy metals using various biosorbent. The optimum pH for heavy metals biosorption was found in the range of 4–5 [31–34].

The biosorption of Cd(II) onto pineapple fruit peel was observed much higher than the Pb(II). This behavior can be explained on the basis of the ionic radius of the metal ions. The ionic radii of the Cd(II) and Pb(II) are 0.97 and 1.20 \AA , respectively. The larger the ionic radii of Pb(II) may result in steric hindrance on the porous biosorbent surface and subsequently lower adsorption compared to the Cd(II) [35].

3.3. Biosorption kinetics

Biosorption kinetics was performed to find the mechanisms involved in heavy metals removal from aqueous solutions. Fig. 4 shows the effect of contact time on the biosorption of Cd(II) and Pb(II) onto pineapple fruit peel. From the Fig. 4, equilibrium was established within 30 min. The biosorption of both metal ions were observed to occur in two stages with respect to contact time. Initially, uptake of the metal ions was rapid probably due to the availability of vacant active sites and gradually the uptake becomes less efficient due to active sites being occupied, depicted by the equilibrium stage [36]. In order to elucidate the overall biosorption rate and migration mechanism of metal ions at solid–solution interface, pseudo-first-order [37], and pseudo-second-order kinetic [38] models were employed. The linear equations for pseudo-first-order

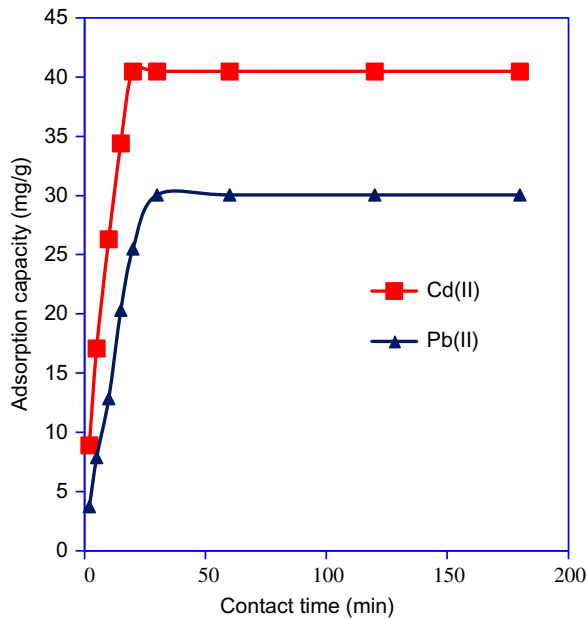


Fig. 4. Effect of contact time on biosorption of heavy metals by treated pineapple fruit peel (biosorbent dose: 0.2 g, temp: 25°C, volume: 50 mL, pH: 4, and concentration: 100 mg L⁻¹).

and pseudo-second-order kinetic models are as follows:

Pseudo-first-order model:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

Pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_e (mg g⁻¹) and q_t (mg g⁻¹) are the biosorption capacity at equilibrium and after time t (min), respectively. k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the pseudo-first- and pseudo-second-order rate constants, respectively. The values of the kinetic parameters were calculated from linear plots $\log(q_e - q_t)$ vs. t , for pseudo-first-order and (t/q_t) vs. t , for pseudo-second-order. The obtained values for kinetic parameters are tabulated in Table 1. For both metal ions, calculated biosorption capacity (q_e^{cal}) obtained from pseudo-second-order are much closer to the experimental biosorption capacity (q_e^{exp}) compared to the pseudo-first-order model. Furthermore, the values of correlation coefficient (R^2) for pseudo-second-order are higher than for

pseudo-first-order. These results demonstrate that biosorption of Cd(II) and Pb(II) onto pineapple fruit peel followed the pseudo-second-order kinetics. Similar results for the biosorption of Cd(II) and Pb(II) have been reported by Barkaa et al. [34] and Fan et al. [39].

In order to further elucidate the diffusion of Cd(II) and Pb(II) onto the pineapple fruit peel, Weber–Morris intraparticle diffusion model [40] was applied. The linear equation for intraparticle diffusion model is as follows:

$$q_t = k_{\text{id}} t^{1/2} + C \quad (4)$$

where k_{id} is the intraparticle diffusion rate constant (mg g⁻¹ min^{1/2}) and C is a constant (mg g⁻¹) related to the thickness of the boundary layer. Fig. 5 shows the multiple curved portions for both metals, implying more than one rate-limiting step was involved in biosorption process. First linear region is attributed to external diffusion (film diffusion) of metal ions onto the pineapple fruit peel surface and second linear portion belongs to the intraparticle diffusion of Cd(II) and Pb(II), as a delayed process. Furthermore, plot shown in Fig. 5 does not pass through the origin, indicating that film diffusion and intraparticle diffusion were involved in the biosorption process [41].

3.4. Biosorption isotherm

The biosorption of Cd(II) and Pb(II) was studied at the concentration ranges from 50–250 mg g⁻¹ as shown in Fig. 6. As seen from the Fig. 6, equilibrium uptake increases with the increase in metal ion concentration. The increase in the biosorption capacity in relation to the Cd(II) and Pb(II) concentration may be due to the high-driving forces for mass transfer [40]. For the better understanding of biosorption, Langmuir, Freundlich, and Temkin models were used to simulate the experimental data. The linearized form of Langmuir, Freundlich, and Temkin isotherms are represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (5)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

$$q_e = B \ln A + B \ln C \quad (7)$$

where C_e is the equilibrium concentration (mg L⁻¹), q_e is the amount biosorbed at equilibrium (mg g⁻¹), and

Table 1
Kinetics parameter for biosorption of Cd(II) and Pb(II) onto pineapple fruit peel

Metal ions	q_e^{exp} (mg g ⁻¹)	Pseudo-first-order model			Pseudo-second-order model			Intraparticle diffusion		
		q_e^{cal} (mg g ⁻¹)	k_1 (min ⁻¹)	R^2	q_e^{cal} (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	R^2	k_{id} (mg g ⁻¹ min ^{1/2})	C	R^2
Cd(II)	40.46	43.05	0.094	0.980	43.48	0.003	0.995	10.36	5.985	0.999
Pb(II)	30.05	36.30	0.124	0.950	33.34	0.005	0.993	6.868	6.908	0.983

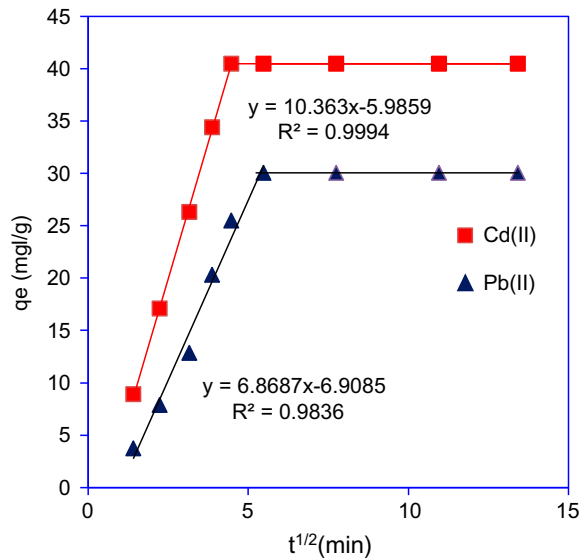


Fig. 5. Intraparticle diffusion model for heavy metal biosorption by pineapple fruit peel.

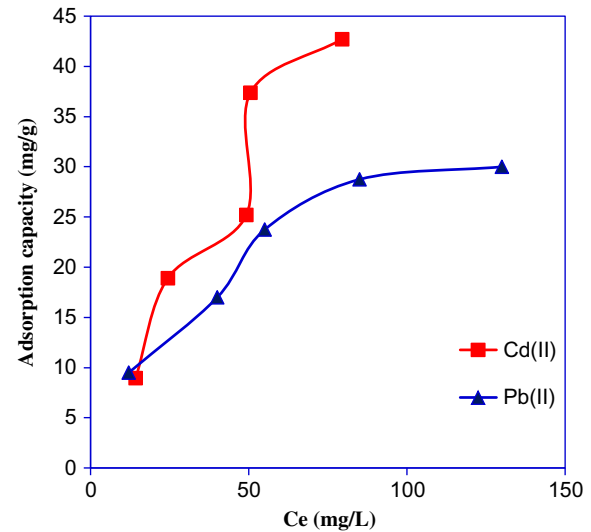


Fig. 6. Effect of initial concentration on biosorption of heavy metals by treated pineapple fruit peel (biosorbent dose: 0.2 g, temp: 25°C, volume: 50 mL, and pH: 4).

q_m and b is Langmuir constants related to biosorption efficiency and energy of biosorption, respectively. K_F and n are Freundlich constants. A is equilibrium binding constant (L mg⁻¹) and B is related to the heat of biosorption. The values of isotherm parameters were calculated from the slope and intercept of their respected plots. The isotherm parameters are shown in Table 2. The correlation coefficient of the Langmuir isotherm is relatively high [0.9839 for Cd(II) and 0.9916 for Pb(II)] than Freundlich [0.9489 for Cd(II) and 0.8956 for Pb(II)], and Temkin [0.9677 for Cd(II) and 0.7957 for Pb(II)] isotherm models. From the results, it can be concluded that both metal ions were homogeneously biosorbed with constant energy and no transmission of metal ions in the plane of pineapple fruit peel surface [34,39].

The biosorption of Cd(II) and Pb(II) was also characterized by Vermeulan criteria [42] associated with the Langmuir isotherm. The Vermeulan criteria are expressed by dimensionless separation factor " R_L ", represented by the following equation:

$$R_L = \frac{1}{(1 + bC_0)} \quad (8)$$

Table 2
Biosorption isotherm parameter for Cd(II) and Pb(II) biosorption onto pineapple fruit peel

Isotherm model	Cd(II)	Pb(II)
Langmuir isotherm		
q_m (mg g ⁻¹)	42.10	28.55
b (L mg ⁻¹)	1.15	2.10
R^2	0.9839	0.9916
Freundlich isotherm		
K_F (mg g ⁻¹ (L mg ⁻¹) ^{1/n})	16.17	11.33
n	01.60	01.97
R^2	0.9489	0.8956
Temkin isotherm		
A (L mg ⁻¹)	23.78	138.94
B	01.01	00.74
R^2	0.9677	0.7957

Table 3

Comparison of adsorption capacity of pineapple waste and other biosorbents for the removal of Cd(II) and Pb(II) from aqueous solutions

Adsorbents	q_e (mg g ⁻¹) for Cd(II)	q_e (mg g ⁻¹) for Pb(II)	References
Cactus (<i>Opuntia ficus indica</i>)	30.42	98.62	[31]
Green algae waste	22.48	43.51	[1]
<i>Penicillium simplicissimum</i>	52.5	76.9	[35]
NaOH chemically modified rice bran	–	147.78	[14]
Green alga (<i>Ulva lactuca</i>)	29.2	34.7	[18]
Orange peel	293.3	476.1	[11]
Ficus carcia leaves	30.31	34.36	[17]
<i>Portulaca oleracea</i>	–	43.48	[10]
<i>Peganum harmala</i> seeds	1.094	1.551	[18]
Chemically modified pineapple fruit peel	42.10	28.55	This work

where C_0 (mg L⁻¹) is the initial metal ion concentration and b (L mg⁻¹) is Langmuir constant. The value of R_L indicates the shape of isotherms to be either: $R_L > 1$ for unfavorable biosorption, $R_L = 1$ for linear biosorption, $0 < R_L < 1$ for favorable biosorption, and $R_L = 0$ for irreversible biosorption. The values of R_L are in the range of 0.0034–0.017 for Cd(II) and 0.0019–0.0094 for Pb(II) indicating that the biosorption for both metal ions was favorable. Comparison of adsorption capacity of pineapple waste and other biosorbents for the removal of Cd(II) and Pb(II) from aqueous solutions is tabulated in Table 3.

3.5. Biosorption thermodynamics

Thermodynamic parameters for Cd(II) and Pb(II) removal such as standard free energy change (ΔG°), entropy change (ΔS°), and enthalpy change (ΔH°) were calculated using following equations:

$$\Delta G^\circ = -RT \ln K_c \quad (9)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

where T (K) is the temperature and R (8.314 J mol⁻¹ K⁻¹) is gas constant, and K_c is the distribution coefficient. The values of entropy change and enthalpy change were calculated from the slope and intercept of Fig. 7. From Table 4, the value of ΔG° varies from -3.499 to -1.545 kJ mol⁻¹ and -0.857 to -4.297 kJ mol⁻¹ for Cd(II) and Pb(II), respectively, with temperature rising from 298 to 323 K indicating that biosorption process becomes more favorable at low temperature. For Pb(II) biosorption, the values of ΔG° at 298 K are negative and spontaneous. The negative values of ΔH° indicate the biosorption of Cd

(II) and Pb(II) onto pineapple fruit peel is exothermic in nature which causes the decrease in the uptake of Cd(II) and Pb(II) with increase in temperature. The negative ΔS° values demonstrate the decrease in randomness at solid/solution interface during biosorption process [43].

3.6. Biosorption mechanism

The FTIR analysis of pineapple fruit peel shows that carboxyl, hydroxyl, ester, ether, and amine groups are present on the surface. The biosorption of metal ions onto the pineapple fruit peel may be due to the electrostatic attraction/chelation between positively charged Pb(II) and Cd(II) and negatively charged carboxylate ($-\text{COO}^-$), and hydroxyl (OH^-) ligands as the

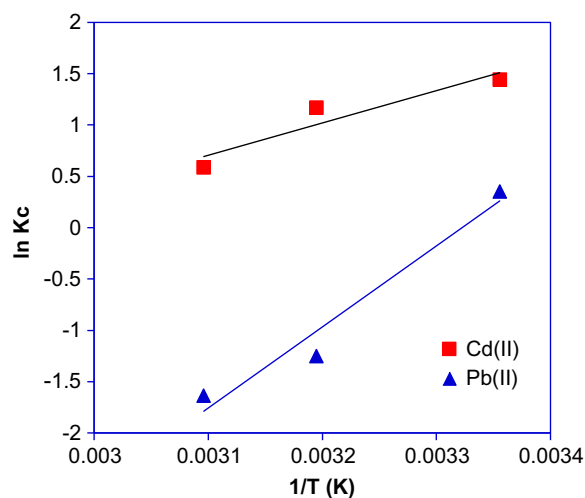


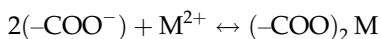
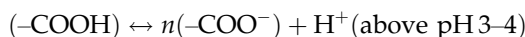
Fig. 7. van't Hoff plot for heavy metal biosorption by pineapple fruit peel.

Table 4

Thermodynamic parameters for heavy metal biosorption onto pineapple fruit peel

Metal	ΔG° (kJ mol ⁻¹)			ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
	25°C	40°C	50°C		
Cd(II)	-3.499	-2.980	-1.545	-26.089	-75.017
Pb(II)	-0.857	-3.182	-4.297	-63.530	-217.66

carboxylic/hydroxyl groups are deprotonated at pH over 3–4 [30,44]. The binding of metal ions onto pineapple fruit peel surface might be occurred as follows:



where $(-\text{COOH})$ and M^{2+} represent the functional groups on the surface of pineapple fruit peel and Pb(II) and Cd(II), respectively. Pb(II) and Cd(II) have a tendency for coordination bonding using vacant *d*-orbital by dative bond formation with nitrogen or oxygen containing lone pair electrons [45]. The proposed interaction/chelation between the functionalized pineapple waste and metal ions is shown in Fig. 8. According to Chen and Yang [46] and

Velazquez–Jimenez et al. [47], metal ions form the unidentate, bidentate, and bridge complexes with carboxylate ligands as follows:

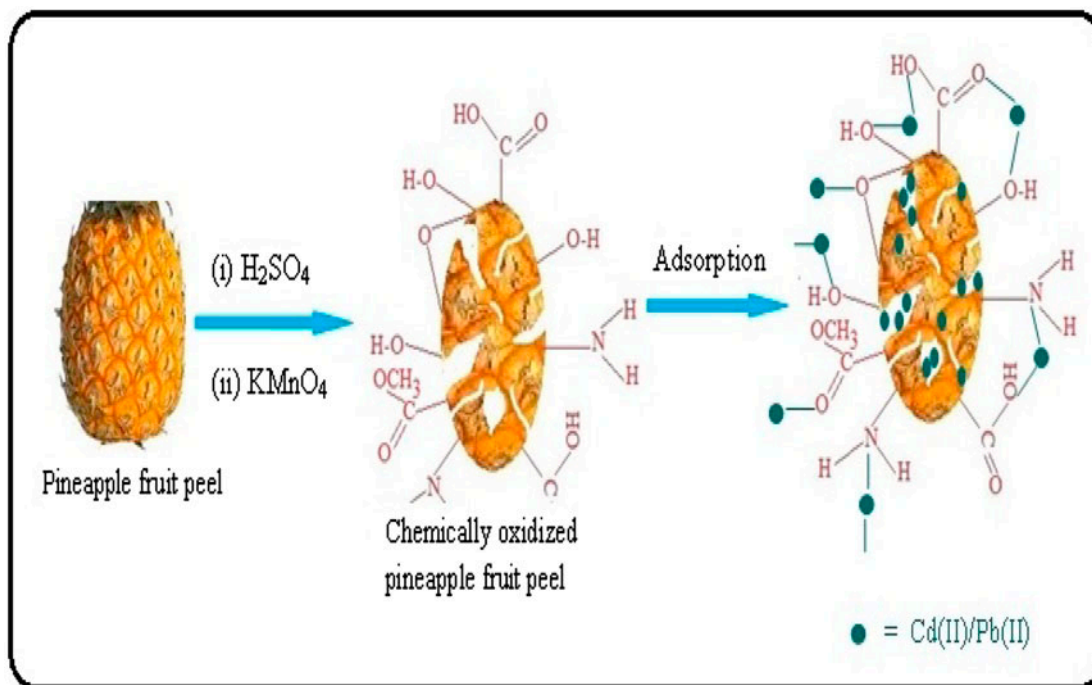
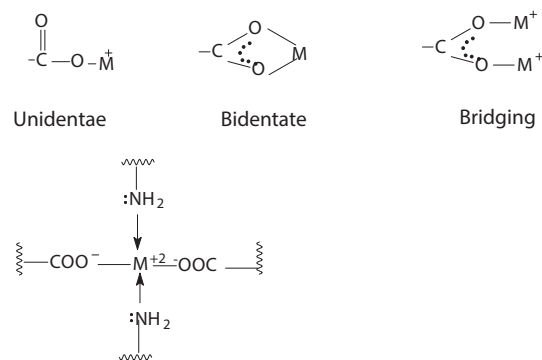


Fig. 8. The proposed interaction/chelation between the functionalized pineapple waste and metal ions.

3.7. Desorption studies

To make the process more economical, spent biosorbent was regenerated using HCl (0.1 M), H₂SO₄ (0.1 M), and HNO₃ (0.1 M). For the desorption studies, 0.2 g heavy metals saturated biosorbent was mixed with the 10 mL of each acid and shaken for 3 h. The percent recovery for Cd(II) and Pb(II) using 10 mL each of 0.1 M HCl, 0.1 M H₂SO₄, and 0.1 M HNO₃ were found to be 90, 86, 88 and 87, 83, 84, respectively. It was found that 90% of Cd(II) and 87% of Pb(II) were desorbed by 10 mL of 0.1 M HCl, which gives best regeneration among all the mineral acids used.

4. Conclusion

The pineapple fruit peel waste was successfully modified to facilitate the biosorption of Cd(II) and Pb(II) from aqueous solutions. Chemically oxidized pineapple fruit peel showed higher removal of both metal ions than the raw one. The maximum biosorption was observed at pH 4 within 30 min. A pseudo-second-order model and intraparticle diffusion model adequately describe the kinetics of biosorption process. The equilibrium biosorption data fit better with Langmuir equation than Freundlich and Temkin model. The pineapple fruit peel waste will be a promising, alternative, economical, and effective biosorbent for the removal of heavy metals from wastewater.

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References

- [1] D. Bulgariu, L. Bulgariu, Equilibrium and kinetics studies of heavy metal ions biosorption on green algae waste biomass, *Bioresour. Technol.* 103 (2012) 489–493.
- [2] A. Witek-Krowiak, R.G. Szafran, S. Modelski, Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent, *Desalination* 265 (2011) 126–134.
- [3] M. Ahmaruzzaman, Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals, *Adv. Colloid Interface Sci.* 166 (2011) 36–59.
- [4] B.E. Rittmann, Environmental biotechnology in water and wastewater treatment, *J. Environ. Eng.* 136 (2010) 348–353.
- [5] H. Daraei, A. Mittal, J. Mittal, H. Kamali, Optimization of Cr(VI) removal onto biosorbent eggshell membrane: Experimental and theoretical approaches, *Desalin. Water Treat.* 52 (2014) 1307–1315.
- [6] Cemal Cifci, Omur Durmaz, Removal of heavy metal ions from aqueous solutions by poly(methyl methacrylate-co-ethyl acrylate) and poly(methyl methacrylate-co-butyl-m-ethylacrylate) membranes, *Desalin. Water Treat.* 28 (2011) 255–259.
- [7] Ö. Arar, Removal of lead(II) from water by di (2-ethylhexyl) phosphate containing ion exchange resin, *Desalin. Water Treat.* 52 (2014) 3197–3205.
- [8] M. Shahadat, M. Rafatullah, T.T. Teng, Characterization and sorption behavior of natural adsorbent for exclusion of chromium ions from industrial effluents, *Desalin. Water Treat.* 51 (2013) 1–9.
- [9] H. Serencam, D. Ozdes, C. Duran, H.B. Senturk, Assessment of kinetics, thermodynamics, and equilibrium parameters of Cu(II) adsorption onto *Rosa canina* seeds, *Desalin. Water Treat.* 52 (2014) 3226–3236.
- [10] A. Dubey, A. Mishra, S. Singhal, Application of dried plant biomass as novel low-cost adsorbent for removal of cadmium from aqueous solution, *Int. J. Environ. Sci. Technol.* 11 (2014) 1043–1050.
- [11] N. Feng, X. Guo, S. Liang, Y. Zhu, J. Liu, Biosorption of heavy metals from aqueous solutions by chemically modified orange peel, *J. Hazard. Mater.* 185 (2011) 49–54.
- [12] C.P.J. Isaac, A. Sivakumar, Removal of lead and cadmium ions from water using *Annona squamosa* shell: Kinetic and equilibrium studies, *Desalin. Water Treat.* 51 (2013) 7700–7709.
- [13] M. Ghorbani, H. Eisazadeh, A.A. Ghoreyshi, Removal of zinc ions from aqueous solution using polyaniline nanocomposite coated on rice husk, *Iranica J. Energy Environ.* 3 (2012) 83–88.
- [14] T. Fatima, R. Nadeem, A. Masood, R. Saeed, M. Ashraf, Sorption of lead by chemically modified rice bran, *Int. J. Environ. Sci. Technol.* 10 (2013) 1255–1264.
- [15] S. Cay, A. Uyanik, A. Ozasik, Single and binary component adsorption of copper(II) and cadmium(II) from aqueous solutions using tea-industry waste, *Sep. Purif. Technol.* 38 (2004) 273–280.
- [16] M. Arshad, M.N. Zafar, S. Younis, R. Nadeem, The use of Neem biomass for the biosorption of zinc from aqueous solutions, *J. Hazard. Mater.* 157 (2008) 534–540.
- [17] A.M. Farhan, A.H. Al-Dujaili, A.M. Awwad, Equilibrium and kinetic studies of cadmium(II) and lead(II) ions biosorption onto *Ficus carcia* leaves, *Int. J. Ind. Chem.* 4 (2013) 2–8.
- [18] A. Sari, M. Tuzen, Biosorption of Pb(II) and Cd(II) from aqueous solution using green alga (*Ulva lactuca*) biomass, *J. Hazard. Mater.* 152 (2008) 302–308.
- [19] A.G.D. Prasad, M.A. Abdulsalam, Biosorption of Fe(II) from aqueous solution using tamarind bark and potato peel waste: Equilibrium and kinetic studies, *J. Appl. Sci. Environ. Sanit.* 4 (2009) 273–282.
- [20] A.A. Zamani, R. Shokri, M.R. Yaftian, A.H. Parizanganeh, Adsorption of lead, zinc and cadmium ions from contaminated water onto *Peganum harmala* seeds as biosorbent, *Int. J. Environ. Sci. Technol.* 10 (2013) 93–102.
- [21] D.I.S. da Silva, G.D.R. Nogueira, A.G. Duzzioni, M.A.S. Barrozo, Changes of antioxidant constituents

- in pineapple (*Ananas comosus*) residue during drying process, *Ind. Crops Prod.* 50 (2013) 557–562.
- [22] X. Hu, K. Hu, L. Zeng, M. Zhao, H. Huang, Hydrogels prepared from pineapple peel cellulose using ionic liquid and their characterization and primary sodium salicylate release study, *Carbohydr. Polym.* 82 (2010) 62–68.
- [23] R. Sitko, E. Turek, B. Zawisza, E. Malicka, E. Talik, J. Heimann, A. Gabor, B.F.R. Feist, Adsorption of divalent metal ions from aqueous solutions using graphene oxide, *Dalton Trans.* 42 (2013) 5682–5689.
- [24] R. Kumar, M.O. Ansari, M.A. Barakat, DBSA doped polyaniline/multi-walled carbon nanotubes composite for high efficiency removal of Cr(VI) from aqueous solution, *Chem. Eng. J.* 228 (2013) 748–755.
- [25] K.Y. Foo, B.H. Hameed, Porous structure and adsorptive properties of pineapple peel based activated carbons prepared via microwave assisted KOH and K_2CO_3 activation, *Microporous Mesoporous Mater.* 148 (2012) 191–195.
- [26] Y. Qi, J. Li, L. Wang, Removal of Remazol Turquoise Blue G-133 from aqueous medium using functionalized cellulose from recycled newspaper fiber, *Ind. Crops Prod.* 50 (2013) 15–22.
- [27] C.W. Oo, M.J. Kassim, A. Pizzi, Characterization and performance of *Rhizophora apiculata* mangrove polyflavonoid tannins in the adsorption of copper (II) and lead (II), *Ind. Crops Prod.* 30 (2009) 152–161.
- [28] X. Yu, S. Tong, M. Ge, L. Wu, J. Zuo, C. Cao, W. Song, Adsorption of heavy metal ions from aqueous solution by carboxylated cellulose nanocrystals, *J. Environ. Sci.* 25 (2013) 933–943.
- [29] S. Hokkanen, E. Repo, M. Sillanpää, Removal of heavy metals from aqueous solutions by succinic anhydride modified mercerized nanocellulose, *Chem. Eng. J.* 223 (2013) 40–47.
- [30] H. Eccles, S. Hunt, Immobilization of Ions by Biosorption, Ellis Horwood Limited, Chichester, England, 1986.
- [31] 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.
- [32] S. Özdemir, E. Kilinc, A. Poli, B. Nicolaus, K. Güven, 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.
- [33] M. Ianis, K. Tsekova, S. Vasileva, Copper biosorption by *Penicillium cyclopium*: Equilibrium and modelling study, *Biotechnol. Equip.* 20 (2006) 195–201.
- [34] N. Barka, M. Abdennouri, M. El Makhfouk, S. Qourzal, Biosorption characteristics of cadmium and lead onto eco-friendly dried cactus (*Opuntia ficus indica*) cladodes, *J. Environ. Chem. Eng.* 1 (2013) 144–149.
- [35] R. Kumar, M.A. Khan, N. Haq, Application of carbon nanotubes in heavy metals remediation, *Crit. Rev. Env. Sci. Technol.* 44 (2014) 1000–1035.
- [36] A. Idris, N.S.M. Ismail, N. Hassan, E. Misran, A.F. Ngomsik, Synthesis of magnetic alginate beads based on maghemite nanoparticles for Pb(II) removal in aqueous solution, *J. Ind. Eng. Chem.* 18 (2012) 1582–1589.
- [37] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe (For the theory of so-called adsorption of dissolved substances), *Kungliga Svenska, Vetenskapsakad. Handl.* 24 (1898) 1–39.
- [38] G. McKay, Y.S. Ho, Pseudo-second order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.
- [39] T. Fan, Y. Liu, B. Feng, G. Zeng, C. Yang, M. Zhou, H. Zhou, Z. Tan, X. Wang, Biosorption of cadmium(II), zinc(II) and lead(II) by *Penicillium simplicissimum*: Isotherms, kinetics and thermodynamics, *J. Hazard. Mater.* 160 (2008) 655–661.
- [40] W.J. Weber Jr., J.C. Morris, Kinetics of adsorption on carbon from solution, *J. Sanit. Eng. Div. ASCE* 89 (1963) 31–59.
- [41] Y. Wang, X.J. Wang, M. Liu, X. Wang, Z. Wu, L.Z. Yang, S.Q. Xia, J.F. Zhao, Cr(VI) removal from water using cobalt-coated bamboo charcoal prepared with microwave heating, *Ind. Crops Prod.* 39 (2012) 81–88.
- [42] R. Wang, Z.P. Dong, R.Q. Wang, X. Tian, C.Y. Li, R. Li, Efficient removal of Cd^{2+} by dialdehyde phenylhydrazine starch from aqueous solution, *RSC Adv.* 3 (2013) 20480–20487.
- [43] L. Wang, J. Li, Adsorption of C.I. Reactive Red 228 dye from aqueous solution by modified cellulose from flax shive: Kinetics, equilibrium, and thermodynamics, *Ind. Crops Prod.* 42 (2013) 153–158.
- [44] M. Torab-Mostaedi, M. Asadollahzadeh, A. Hemmati, A. Khosravi, Equilibrium, kinetic, and thermodynamic studies for biosorption of cadmium and nickel on grapefruit peel, *J. Taiwan Inst. Chem. Eng.* 44 (2013) 295–302.
- [45] P. Chand, A.K. Shil, M. Sharma, Y.B. Pakade, Improved adsorption of cadmium ions from aqueous solution using chemically modified apple pomace: Mechanism, kinetics, and thermodynamics, *Int. Biodegrad. Biodegrad.* 90 (2014) 8–16.
- [46] J.P. Chen, L. Yang, Study of a heavy metal biosorption onto raw and chemically modified *Sargassum* sp. via spectroscopic and modeling analysis, *Langmuir* 22 (2006) 8906–8914.
- [47] L.H. Velazquez-Jimenez, A. Pavlick, J.R. Rangel-Mendez, Chemical characterization of raw and treated agave bagasse and its potential as adsorbent of metal cations from water, *Ind. Crops Prod.* 43 (2013) 200–206.