A breakthrough biosorbent in removing heavy metals: Equilibrium, kinetic, thermodynamic and mechanism analyses in a lab-scale study

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Highlights

- A novel multi-metal binding biosorbent (MMBB) was studied.
- The biosorption of Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} on MMBB was evaluated.
- Hydroxyl, carbonyl and amine groups are involved in metal binding of MMBB.
- Equilibrium data were presented and the best fitting models were identified.
- The obtained results recommend this MMBB as potentially low-cost biosorbent.

Abstract

A breakthrough biosorbent namely multi-metal binding biosorbent (MMBB) made from a combination of tea wastes, maple leaves and mandarin peels, was prepared to evaluate their biosorptive potential for removal of Cd(II), Cu(II), Pb(II) and Zn(II) from multi-metal aqueous solutions. FTIR and SEM were conducted, before and after biosorption, to explore the intensity and position of the available functional groups and changes in adsorbent surface morphology. Carboxylic, hydroxyl and amine groups were found to be the principal functional groups for the sorption of metals. MMBB exhibited best performance at pH 5.5 with maximum sorption capacities of 31.73, 41.06, 76.25 and 26.63 mg/g for Cd(II), Cu(II), Pb(II) and Zn(II), respectively. Pseudo-first and pseudo-second-order models represented the kinetic experimental data in different initial metal concentrations very well. Among two-

parameter adsorption isotherm models, the Langmuir equation gave a better fit of the equilibrium data. For Cu(II) and Zn(II), the Khan isotherm describes better biosorption conditions while for Cd(II) and Pb(II), the Sips model was found to provide the best correlation of the biosorption equilibrium data. The calculated thermodynamic parameters indicated feasible, spontaneous and exothermic biosorption process. Overall, this novel MMBB can effectively be utilized as an adsorbent to remove heavy metal ions from aqueous solutions.

Keywords: Heavy metal; Biosorption; Isotherm; Kinetic; Thermodynamics; Lignocellulosic waste

1. Introduction

Heavy metals are discharged to aquatic environments from various industries such as paper, textile, plastic, ceramic and cement manufacturing, mining and electronics plating. These poorly biodegradable pollutants are harmful for all plants, animals and human life due to high environmental mobility in soil and water and also a strong tendency for bioaccumulation in the living tissues along the food chain (Vargas-García et al., 2012, Akar et al., 2012 and Bulut and Tez, 2007). In order to remediate polluted water and wastewater streams, a wide range of treatment technologies are employed in industry (e.g. chemical precipitation, extraction, ion exchange, filtration, reverse osmosis, membrane bioreactor and electrochemical techniques) (Santos et al., 2015,Abdolali et al., 2014a, Montazer-Rahmati et al., 2011 and Fu and Wang, 2011). Nonetheless, these methods are not effective enough in low concentrations and might be very expensive as a result of high chemical reagent and energy requirements, as well as the disposal problem of toxic secondary sludge (Bulut and Tez, 2007 and Sud et al., 2008).

Therefore, introducing a properly eco-friendly and cost effective technology for wastewater treatment has provoked many researchers into this matter in recent decades (Abdolali et al., 2014b, Tang et al., 2013, Fu et al., 2013, Kumar et al., 2012, Hossain et al., 2012, Witek-Krowiak et al., 2011, Gadd, 2009, Volesky, 2007 and Šćiban et al., 2007) to use cheap agro-industrial wastes and by-products as biosorbents. Some of these materials include sawdust and wood waste (Wahab et al., 2010, Bulut and Tez, 2007 and Šćiban et al., 2007), sugarcane bagasse (Homagai et al., 2010, Martín-Lara et al., 2010 and Khoramzadeh et al., 2013),fruit rind, pulp and seeds (Martín-Lara et al., 2010; Liu et al., 2012, Pehlivan et al., 2012 and Schiewer and Patil, 2008), wheat or barley straw, rice husk, hull and straw (Asadi et al., 2008), and olive pomace and stone (Blázquez et al., 2010, Blázquez et al., 2009 and Fiol et al., 2006).

All of the previous attempts have been made to study the agro-industrial wastes and by-products individually. The novelty of the present work is using combination of selected agro-industrial multi-metal binding biosorbents for removal of cadmium, copper, lead and zinc ions from synthetic aqueous multi-metal solutions. The significant difference between previous studies and current work is gaining the advantages and also using the biosorptive

potentials of various biosorbents in a combination. The purpose of blending different lignocellulosic materials is having all potentials of biosorbents for heavy metal uptake (Abdolali et al., 2014a, Martín-Lara et al., 2010 and Martín-Lara et al., 2010). Also these wastes were selected because of the good results reported in other literatures for heavy metal removal (Abdolali et al., 2014a, Feng et al., 2011 and Amarasinghe and Williams, 2007). Additionally, they are properly available in Australia and also all over the world.

Firstly, the adsorption studies were carried out to select the best combination of different biosorbents, as mentioned hereinabove. Then the experiments were continued to compare the effect of different contact times, pH, initial metal concentration, temperature, and biosorbent dose and particle size on biosorptive potential of selected combination. The results were mainly evaluated by two popular kinetic models of pseudo-first-order and pseudo-second-order correlations and three two-parameter and three three-parameter adsorption models (Langmuir, Freundlich, Dubinin–Radushkevich, Khan, Sips and Redlich–Peterson). In addition, thermodynamic parameters were determined for the sorption of all metal ions to explain the process feasibility.

2. Material and methods

2.1. Preparation of adsorbents and heavy metal-containing effluent

The stock solutions containing Cd, Cu, Pb and Zn were prepared by dissolving cadmium, copper, lead and zinc nitrate salt, $Cd(NO_3)_2 \cdot 4H_2O$, $Cu_3(NO)_2 \cdot 3H_2O$, $Pb(NO_3)_2$ and $Zn(NO_3)_2 \cdot 6H_2O$ in Milli-Q water. All the reagents used for analysis were of analytical reagent grade from Scharlau (Spain) and Chem-Supply Pty Ltd. (Australia). The metal concentration was analyzed by Microwave Plasma-Atomic Emission Spectrometer, MP-AES, (Agilent Technologies, USA).

The biosorbents were applied in metal removal process for selecting the best ones in term of biosorption capacity sawdust (SD), sugarcane (SC), corncob (CC), tea waste (TW), apple peel (AP), grape stalk (GS), palm tree skin (PS), eucalyptus leaves (EU), mandarin peel (MP), maple leaves (ML) and garden grass (GG). All biosorbents were collected from Sydney area or local markets. After using or removing their useable parts, they were washed by tap and distilled water to remove any dirt, color or impurity and then dried in the oven (Labec Laboratory Equipment Pty Ltd., Australia) at 105 °C overnight. Having ground and sieved (RETSCH AS-200, Germany) to different sizes (< 75 μm, 75–150 μm, 150–300 μm and > 300 μm), the natural biosorbents were kept in a desiccator prior to use in future experiments.

2.2. Biosorption studies in batch system

The tests were performed with synthetic multi-metal stock solution with concentration of 3000 mg/L for each metal, prepared by dilution in Milli-Q water. Solution pH was adjusted with 1 M HCl and NaOH solutions.

A known weight of adsorbent (5 g/L) was added to a series of 200 mL Erlenmeyer flasks containing 50 mL of metal solution on a shaker (Ratek, Australia) at room temperature and the flasks were shaken at 150 rpm for 3 h. After equilibration, to separate the biomasses from solutions, the solutions were filtered by Whatman™ GF/C-47 mm/circle (GE Healthcare, Buckinghamshire, UK) filter paper and final concentration of metal was measured using MP-AES. All the experiments were carried out in duplicates. The statistical analysis was performed by analysis of variance (ANOVA).

The amount of heavy metal ion adsorbed, q (mg/g) was calculated from the following Eq.(1):

$$q = \frac{v(C_i - C_f)}{m} \quad (1)$$

where, C_i and C_f (mg/L) are the initial and equilibrium metal concentrations in the solution, respectively. v (L) the solution volume and m (g) is the mass of biosorbent.

2.3. Characterization of adsorbents by FTIR and SEM

To determine the functional groups involved in biosorption of Cd(II), Cu(II), Pb(II) and Zn(II) onto MMBB, a comparison between the Fourier Transform Infrared Spectroscopy (FTIR) before and after meal loading was done using Shimadzu FTIR 8400S (Kyoto, Japan). Metal-loaded biosorbent were filtered and dried in the oven. The small amount of samples was placed in the FTIR chamber on the KBr plates for analyzing the functional groups involving in biosorbent process by comparing with unused multi-metal biosorbent.

Scanning Electron Microscopy (SEM) of the free and loaded MMBB was performed on ZEISS EVO | LS15 (Germany) at an accelerating voltage of 10 kV and with the working distance of 10 μm for MMBB to observe the porous properties of the biosorbents.

2.4. Influence of pH

In order to study the effect of pH on heavy metal adsorption, the initial pH of the solutions varied from 2 to 5.5, by adding appropriate amounts of NaOH or HCl solutions. The batch procedure at each pH was followed as above described using an initial concentration of 50 mg/L.

2.5. Influence of contact time

The contact time varied from 15 min to 5 h for the biosorption of Cd(II), Cu(II), Pb(II) and Zn(II) adsorption on MMBB at different initial concentrations of 50 mg/L and room temperature with similar procedures explained above.

2.6. Influence of adsorbent dose

The dependence of Cd(II), Cu(II), Pb(II) and Zn(II) adsorption on biosorbent dose was studied at room temperature and optimum pH by varying biosorbent doses (0.2, 1, 2, 5, 10 and 20 g/L).

2.7. Influence of particle size

In order to study the effect of particle size on adsorption, batch experiments as above described were carried out using the biosorbent with different particle sizes of < 75 μm, 75–150 μm, 150–300 μm and > 300 μm and an initial metal concentration of 50 mg/L, at room temperature.

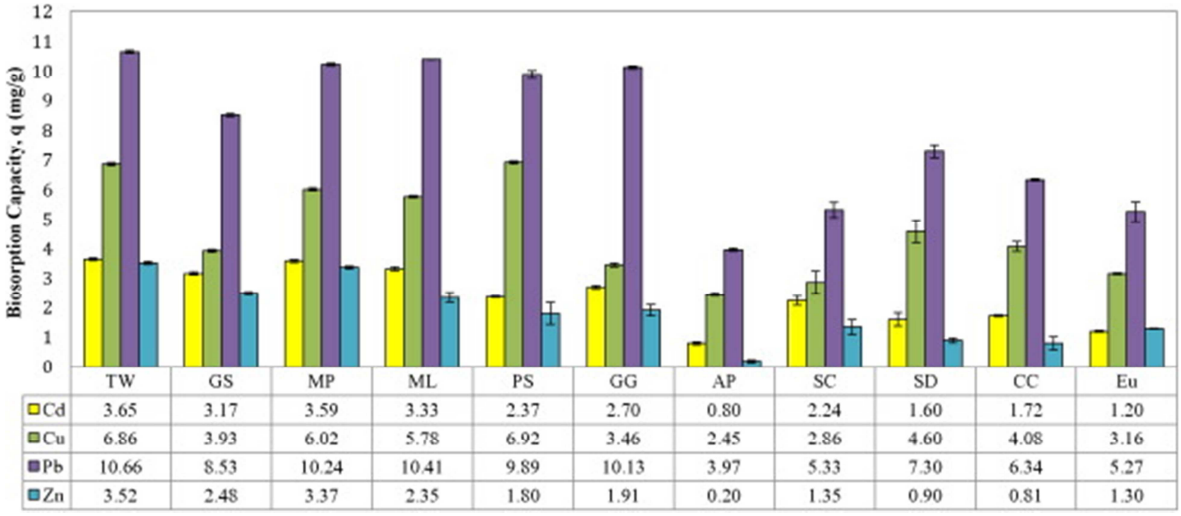
2.8. Influence of temperature

The effect of temperature on the Cd, Cu, Pb, and Zn adsorption was investigated in the range 298–323 K (25–50 °C) in batch experiments already described and initial concentration of 1–50 mg/L.

3. Results and discussion

3.1. Selection of adsorbents

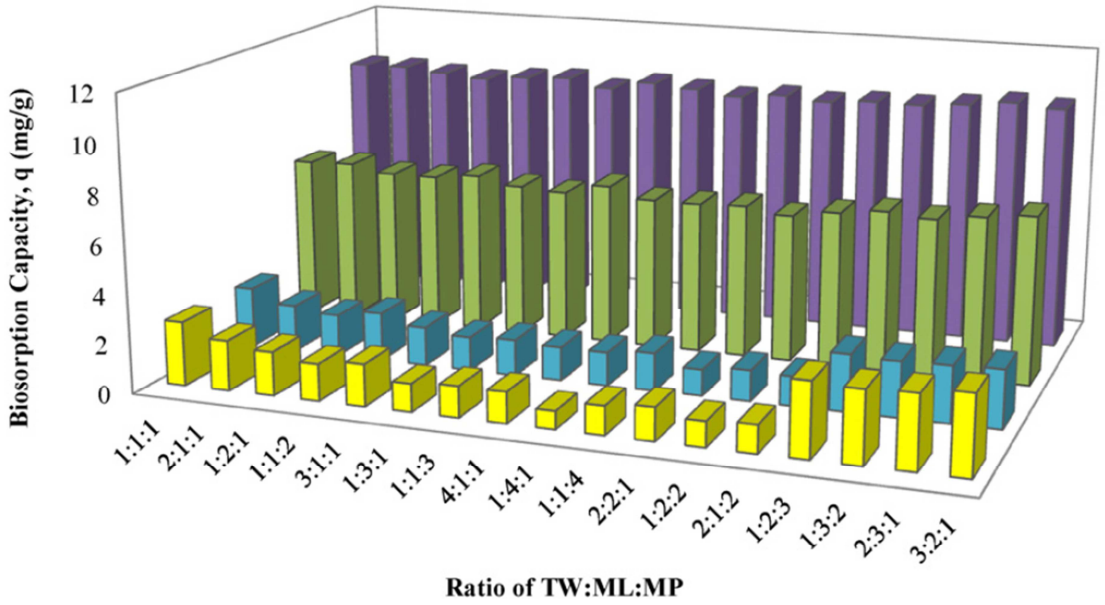
Eleven different natural biosorbents, namely sawdust, sugarcane, corncob, tea waste, apple peel, grape stalk, palm tree skin, eucalyptus leaves, mandarin peel, maple leaves and garden grass, individually were compared in regard to the biosorption capacities for Cd(II), Cu(II), Pb(II) and Zn(II) uptake in Fig. 1. The results indicate TW, ML and MP showed satisfying biosorptive capacity for all heavy metal ions (cadmium, copper, lead and zinc). SD and CC had quite less biosorptive potential in comparison with GG and GS and PS.AP, SC and EU results for Pb, Zn, Cd and Cu were very unsatisfactory that this type of waste will not be considered for study in combination with other biosorbents. TW:ML:MP combination was selected to apply for further batch experiments.



	TW	GS	MP	ML	PS	GG	AP	SC	SD	CC	Eu
Cd	3.65	3.17	3.59	3.33	2.37	2.70	0.80	2.24	1.60	1.72	1.20
Cu	6.86	3.93	6.02	5.78	6.92	3.46	2.45	2.86	4.60	4.08	3.16
Pb	10.66	8.53	10.24	10.41	9.89	10.13	3.97	5.33	7.30	6.34	5.27
Zn	3.52	2.48	3.37	2.35	1.80	1.91	0.20	1.35	0.90	0.81	1.30

Fig. 1. Biosorption capacity of different agro-industrial wastes and by-products.

The effect of proportions for each biosorbent (TW:ML:MP) for heavy metal removal was carried out with the different ratios tabulated in the Fig. 2. All materials were separately weighed and mixed for removing any error and inaccuracy. To test the significance and adequacy of the model, statistical testing of the model in the form of analysis of variance (ANOVA) was done.



	1:1:1	2:1:1	1:2:1	1:1:2	3:1:1	1:3:1	1:1:3	4:1:1	1:4:1	1:1:4	2:2:1	1:2:2	2:1:2	1:2:3	1:3:2	2:3:1	3:2:1
Cd	2.58	2.02	1.78	1.51	1.71	1.16	1.28	1.27	0.72	1.16	1.33	1.02	1.11	3.02	2.92	2.98	3.21
Zn	2.46	1.90	1.68	1.96	1.56	1.35	1.44	1.35	1.35	1.53	1.09	1.27	1.22	2.33	2.26	2.31	2.38
Cu	6.67	6.73	6.46	6.47	6.67	6.37	6.26	6.69	6.26	6.26	6.33	6.10	6.38	6.60	6.46	6.71	6.91
Pb	10.0	10.0	9.86	9.71	9.89	9.99	9.66	10.0	9.88	9.67	9.85	9.71	9.85	9.85	10.0	10.2	10.0

Fig. 2. Effect of ratio of tea waste: maple leaves: mandarin peel on Cd(II), Cu(II), Pb(II) and Zn(II) adsorption(initial pH 5.0–5.5 ± 0.1; room temperature, 22 ± 1 °C; contact time: 24 h; initial metal conc.: 50 mg/L; biosorbent dose: 5 g/L; rotary speed: 150 rpm).

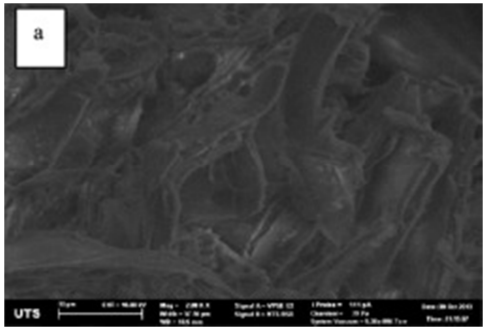
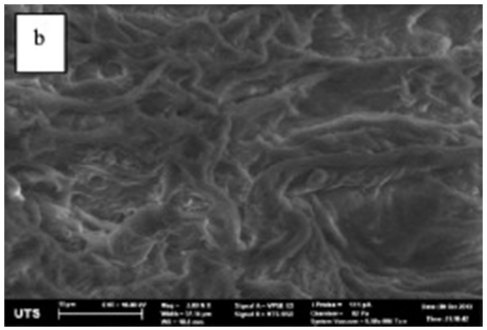
Apparently, there are no significant differences between the equal proportions of 1:1:1 and the others, especially for lead and copper. This was despite the fact that ANOVA results for each metal indicated the rejection of the null hypothesis due to P value was less than 0.05. The observed data are inconsistent with the assumption that the null hypothesis is true. Moreover, the ratio of 3:2:1 for TW:ML:MP showed the highest metal biosorption capacity. This is illustrated in Fig. 2 and will be referred as MMBB, hereinafter. The pH, moisture content (%), loss of mass and bulk density (g/cm^3) of MMBB were 4.97, 18.86, 0.93 and 0.36, respectively.

3.2. Characterization of adsorbents by FTIR

The FTIR spectrum of MMBB exhibited a large number of absorption peaks, indicating the complexity in nature of this adsorbent. It also confirmed changes in functional groups and surface properties of MMBB. The shift of some functional groups bands and their intensity significantly changed after heavy metal biosorption (Table 1).

These shifts may be attributed to carboxylic (C═O) and hydroxylic (O–H) groups on the MMBB's surface. They were dominantly active groups in Cd(II), Cu(II), Pb(II)and Zn(II) biosorption process, suggesting that acidic groups, carboxyl and hydroxyl, are main contributors in the complexation of metal cations and ion exchange processes. Amine and amide groups were found between medium intensity peaks in the frequency range of 1640–1560 with 132.13 cm^{-1} shift after biosorption process. The peaks detected in spectra were laid between 1320 and 1000 cm^{-1}, which is related to C═O stretch in amides, ketones, aldehydes, carboxylic acids and esters (Hossain et al., 2012 and Feng et al., 2011). A shift of 32.79 cm^{-1} was in the range of 1500–1450, and is attributed to C═C–C asymmetric stretching aromatic rings. In addition, a big change (78.12 cm^{-1}) occurred on the biosorbent after metal loading. This is reflected in the strong and broad band present between 3500 and 3200 cm^{-1}. This may be assigned to complexation of metal ions with the ionized O–H groups of polymeric compounds (i.e. alcohols, phenols and carboxylic acids) of cellulose and lignin of lignocellulosic materials (Hossain et al., 2012 and Feng et al., 2011). The changes of peaks in the range of 3000–2850 cm^{-1} and 3100–3000 cm^{-1} indicated the involvement of H–C–H asymmetric and symmetric stretch and C–H stretch of aromatic rings, respectively, which can be found in the molecular structure of MMBB. The other detected peaks represent existence of H–C═O:C–H stretch in aldehydes in the range of 2850–2700 cm^{-1}.

Table 1. FTIR spectra and SEM images of (a) unloaded and (b) metal loaded-biosorbents.

Frequency (cm^{-1})		**Transmittance (%)**		**Bond/functional group**	**SEM images**
Unloaded	Loaded	Unloaded	Loaded		
514.05	510.19	21.469	16.457	C–Br stretch/Alkyl halides	
1005.92	1007.85	84.401	76.065	C═O stretch/alcohols, carboxylic acids, esters and ethers	
1491.04	1458.25	83.572	74.933	C–C stretch (in-ring)/aromatics	
1590.38	1458.25	84.227	74.933	N–H band/1° amines and amides	
1654.03	1654.03	78.747	72.344	–C═C– stretch/alkanes	
2721.68	2820.05	85.77	77.181	H–C═O: C–H stretch/aldehydes	
2958.93	2957	83.061	75.485	H–C–H asymmetric and symmetric stretch/alkanes	
3096.85	3096.85	82.54	75.043	C–H stretch/aromatics	
3348.57	3230.91	81.419	74.193	–C≡C–H: C–H stretch/alkynes	
3482.63	3404.51	81.609	74.247	O–H stretch, H-bonded/alcohols and phenols	

3.3. SEM analysis

From Table 1, SEM depicts the morphology changes of unloaded and loaded biosorbent. After biosorption of heavy metal ions, the surface became smoother with less porosity with probable metal entrapping and adsorbing on biosorbent. The SEM/EDS was reported in previous study (Abdolali et al., 2015).

3.4. Effect of different physico-chemical parameters

3.4.1. Influence of pH

Fig. 3(a) represents the effect of pH of the adsorption of cadmium, copper, lead and zinc altering in the range of 2.0–5.5.

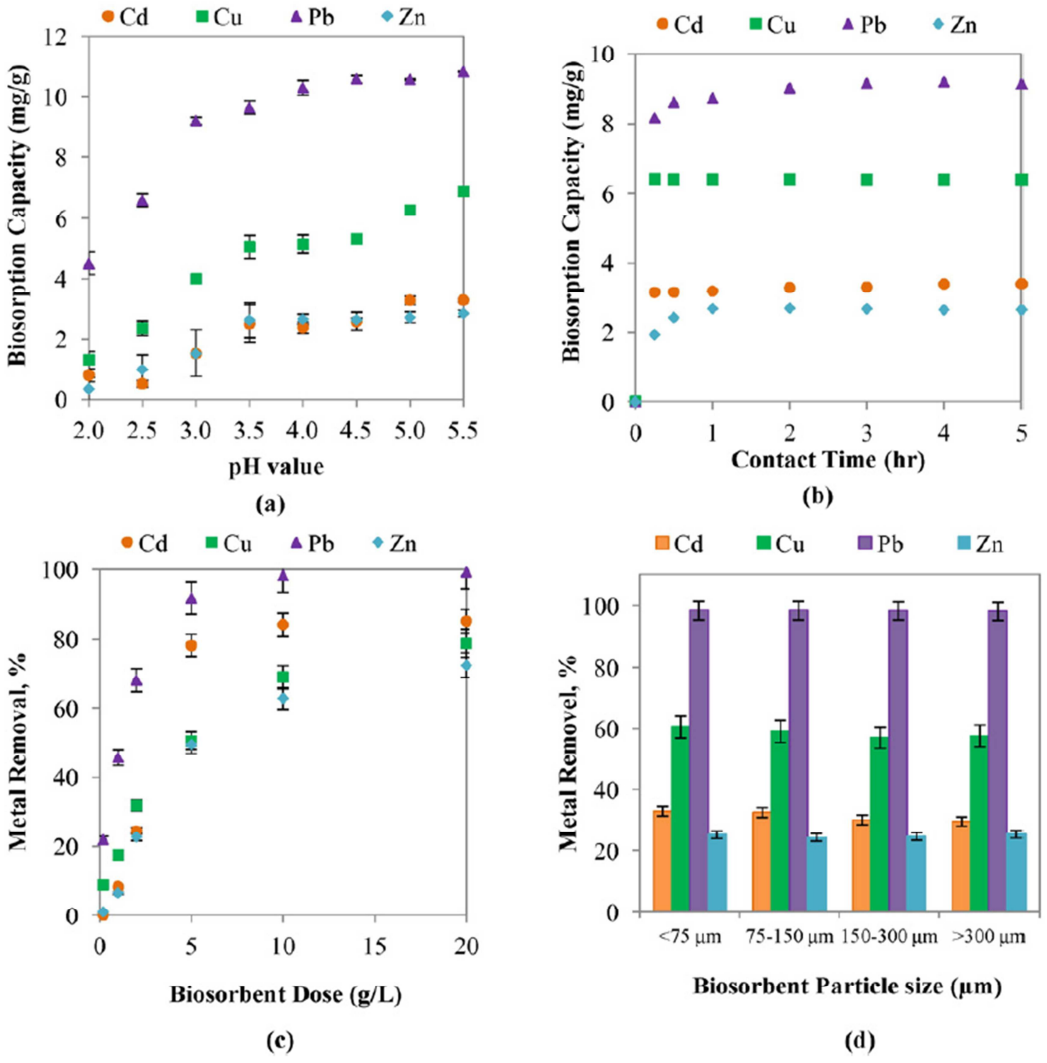


Fig. 3. Effect of (a) initial pH of solution, (b) contact time, (c) biosorbent dose and (d) biosorbent particle size on Cd(II), Cu(II), Pb(II) and Zn(II) adsorption (room temperature, 22 ± 2 °C; initial metal conc.: 50 mg/L).

The initial pH values above 5.5 are not preferable due to the observed presence of metal hydroxide precipitation, so as the experiments were not conducted beyond pH 5.5. Although all metal adsorption followed a similar pattern, the adsorption capacity of Cu and Pb increased significantly by an increase in pH values which are 1.30 to 6.90 mg/g and 4.51 to 10.84 mg/g, respectively, while Cd and Zn uptake gradually increased up to 3.28 and 2.83 mg/g for Cd and Zn, respectively. The results indicated that the optimum pH value was 5.5 for all metals.

3.4.2. Influence of contact time

It is evident from Fig. 3(b) that the rate of metal uptake was very fast within first 30 min as a result of the exuberant number of available active sites on adsorbent surfaces and then decreased until equilibrium was reached. Biosorption capacity leveled off at equilibrium state within 180 min. Therefore, the biosorption time was set to 180 min in each experiment.

3.4.3. Influence of adsorbent dose

Biosorption capacity was also affected by biosorption dose and amount of available active sites and this effect is shown in Fig. 3(c). The experimental results indicate that the percentage removal of all metal ions on MMBB represents an equilibrium pattern for biosorbent amounts of 5 g/L and more. Furthermore, the removal efficiency decreased by increasing initial metal ion solution with similar trends. The highest removal efficiencies changed in the range of 70%, 84%, 98% and 61% for Cd, Cu, Pb and Zn, with an initial concentration of 50 mg/L, on 5 g/L MMBB.

3.4.4. Effect of biosorbent particle size

The effect of particle size of biosorbent was conducted for 5 g/L adsorbent dose and an initial concentration of 50 mg/L. The results of different particle sizes of < 75 μm, 75–150 μm, 150–300 μm and > 300 μm are shown in Fig. 3(d). It was found that biosorption capacity did not significantly change by varying particle sizes. The reason was that these particle size distributions were very small (less than 300 μm). The smaller biosorbent size exhibits better performance in regard with metal removal due to a higher surface area for metal adsorption; however the mechanical stability reduces particularly in column (Liu et al., 2012).

3.5. Adsorption kinetics

A kinetic investigation was carried out to quantify the adsorption rate controlling steps in Cd(II), Cu(II), Pb(II) and Zn(II) uptake on MMBB. The pseudo-first-order and pseudo-second-order kinetic models were applied for kinetic study (Febrianto et al., 2009).

The pseudo-first-order kinetic model known as the Lagergren equation and takes the form as:

$$q_t = q_e[1 - \exp(-K_1 t)] \quad (2)$$

where, q_t and q_e are the metal adsorbed at time t and equilibrium, respectively, and K_1 (min^{-1}) is the first-order reaction rate equilibrium constant.

The pseudo-second-order kinetic model considered in this study is given as:

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad (3)$$

where, K_2 (g mg^{-1} min^{-1}) is the second-order reaction rate equilibrium constant.

The experimental data and obtained parameters of these models were measured by MATLAB® and summarized in Table 2. These kinetic models were exploited to describe the probable mechanism of biosorption. As shown in Table 2, with comparison between adsorption rate constants, the estimated *qe* and the coefficients of correlation associated with the Lagergren pseudo-first-order and the pseudo-second-order kinetic models at room temperature for MMBB, it is obvious that both kinetic models well described all metal biosorption. However, the coefficients of correlation (R^2) of pseudo-second-order kinetic model were slightly larger than those of pseudo-first-order kinetic model for Cu in all initial concentrations. For lead and zinc ions, the Lagergren pseudo-first-order described equilibrium state and experimental data better than the other kinetic model. In addition, while pseudo-first-order kinetic model well fit the lower cadmium concentrations, pseudo-second-order kinetic model outlined better description for higher Cd concentrations. Totally, the kinetic models indicated that chemical reaction would be presumably the rate limiting step of Cd, Cu, Pb and Zn biosorption on MMBB.

3.6. Adsorption isotherm

The correlation between the adsorbed and the aqueous metal concentrations at equilibrium has been described by the Langmuir, Freundlich, Dubinin–Radushkevich, Sips, Redlich–Peterson and Khan adsorption isotherm models. All the model parameters which were evaluated by non-linear regression using MATLAB® software are presented in Table 3. Furthermore, residual root mean square error (RMSE), error sum of square (SSE) and correlation of determination (R^2) were used to measure the exactness of fitting.

The Langmuir equation describes the equilibrium condition better than the other models (R^2: 0.99 and small RMSE values). The maximum amounts of biosorption capacity by monolayer adsorption assumption for Cd, Cu, Pb and Zn obtained from Langmuir equation are 31.73, 41.06, 76.25 and 26.63 mg/g, respectively. Furthermore, it was understood that the Langmuir isotherm corresponded to a dominant ion exchange mechanism while the Freundlich isotherm showed adsorption–complexation reactions taking place at the outer heterogeneous surface of the adsorbent (Asadi et al., 2008 and Kazemipour et al., 2008).

Among three-parameter isotherm models, for Cu(II) and Zn(II), Khan isotherm describes biosorption conditions moderately better than Sips and Redlich–Peterson models, while for Cd(II) and Pb(II), the Sips model was found to provide the best correlation of the biosorption equilibrium data. The foregoing analysis of isotherm models shows that the better fit for Cd(II), Cu(II), Pb(II) and Zn(II) biosorption is produced by three-parameter isotherm models rather than two-parameter isotherm models.

Table 2. Adsorption rate constants, the estimated q_e and the coefficients of correlation associated with the Lagergren pseudo-first and pseudo-second order, kinetic models.

Metal	**Kinetic models**	**Parameter**	**Metal concentration**			
			10 mg/L	20 mg/L	50 mg/L	100 mg/L
Cd	Experiment	*qe* (mg/g)	1.63	2.92	3.30	5.40
	Pseudo-1st-order	*qe* (mg/g)	1.62	2.92	3.36	5.29
		K_1 (h^{-1})	12.66	8.55	10.70	10.57
		R^2	0.997	0.999	0.990	0.990
		SSE	0.005	0.001	0.104	0.245
		RMSE	0.019	0.008	0.089	0.137
	Pseudo-2nd-order	*qe* (mg/g)	1.63	2.94	3.40	5.34
		K_2 (mg/gh)	55.25	12.24	11.08	7.355
		R^2	0.998	0.997	0.995	0.995
		SSE	0.004	0.022	0.044	0.126
		RMSE	0.018	0.043	0.058	0.098
Cu	Experiment	*qe* (mg/g)	1.35	4.30	6.40	7.16
	Pseudo-1st-order	*qe* (mg/g)	1.34	4.24	6.39	7.16
		K_1 (h^{-1})	8.50	11.73	8.047	9.02
		R^2	0.993	0.999	0.999	0.999
		SSE	0.011	0.009	0.005	0.174
		RMSE	0.029	0.027	0.006	0.115
	Pseudo-2nd-order	*qe* (mg/g)	1.35	4.26	6.39	7.20
		K_2 (mg/gh)	2.09	2.21	3.32	5.99
		R^2	0.996	0.998	0.999	0.996
		SSE	0.006	0.026	0.532	0.174
		RMSE	0.021	0.046	0.006	0.115
Pb	Experiment	*qe* (mg/g)	1.81	4.15	9.02	13.58
	Pseudo-1st-order	*qe* (mg/g)	1.81	4.14	9.06	13.76
		K_1 (h^{-1})	9.27	15.29	8.93	7.17
		R^2	0.985	0.999	0.995	0.999
		SSE	0.046	0.001	0.354	0.109
		RMSE	0.059	0.009	0.165	0.091
	Pseudo-2nd-order	*qe* (mg/g)	1.80	4.15	8.99	13.57
		K_2 (mg/gh)	1.22	0.79	0.72	1.21
		R^2	0.976	0.999	0.985	0.971
		SSE	0.073	0.021	1.149	5.081
		RMSE	0.074	0.013	0.297	0.625
Zn	Experiment	*qe* (mg/g)	1.38	2.43	2.88	3.72
	Pseudo-1st-order	*qe* (mg/g)	1.32	2.43	2.64	3.77
		K_1 (min^{-1})	9.05	8.25	5.17	12.78
		R^2	0.989	0.999	0.998	0.996
		SSE	0.015	0.008	0.007	0.043
		RMSE	0.035	0.012	0.024	0.057
	Pseudo-2nd-order	*qe* (mg/g)	1.32	2.45	2.68	3.79
		K_2 (mg/g min)	0.75	0.23	0.08	0.30
		R^2	0.982	0.996	0.988	0.998
		SSE	0.028	0.021	0.076	0.023
		RMSE	0.046	0.042	0.76	0.42

Table 3. Isotherm constants of two- and three-parameter models for Cd(II), Cu(II), Pb(II) and Zn(II) adsorption (initial metal conc.: 10–500 mg/L).

Models		Metal			
		Cadmium	Copper	Lead	Zinc
Two-parameter models					
Langmuir					
	$q_e = \frac{q_{m,L} b_L C_e}{1+b_L C_e}$				
	$q_{m,L}$ (mg/g)	31.73	41.06	76.25	26.63
	b_L (L/mg)	0.005	0.010	0.034	0.050
	SSE	35.74	62.35	13.50	0.84
	R^2	0.99	0.99	0.99	0.99
	RMSE	3.45	4.56	2.12	0.53
Freundlich	$q_e = K_F C_e^{1/n}$				
	K_F	0.92	1.64	7.80	0.46
	n	1.88	1.96	2.38	1.80
	SSE	50.37	44.37	50.11	2.92
	R^2	0.79	0.92	0.98	0.97
	RMSE	4.09	3.84	4.08	0.98
Dubinin–Radushkevich	$q_e = q_{D\text{-}R} \exp(-B_{D\text{-}R}\varepsilon_{D\text{-}R}^2)$				
	q_{DR} (mg/g)	22.78	32.17	56.32	12.19
	B_{DR}	0.075	0.042	0.016	0.067
	SSE	13.94	32.99	33.5	7.81
	R^2	0.96	0.94	0.87	0.92
	RMSE	2.15	3.31	10.57	1.61
Three-parameter models					
Khan	$q_e = \frac{q_{m,K} b_K C_e}{(1+b_K C_e)^{a_K}}$				
	$q_{m,K}$ (mg/g)	21.53	43.04	85.43	16.30
	a_K	0.013	0.23	0.09	0.68
	b_K (L/mg)	0.006	0.097	0.003	0.004
	SSE	15.2	1.02	28.66	1.39
	R^2	0.95	0.99	0.96	0.99
	RMSE	2.74	0.71	3.78	0.83
Redlich–Peterson	$q_e = \frac{K_{RP} C_e}{1+a_{RP} C_e^{\beta_{RP}}}$				
	β_{RP}	0.21	3.03	0.81	0.44
	K_{RP} (L/g)	0.08	0.20	4.17	0.18
	a_{RP} (L/mg)	0.67	0.02	0.15	0.41
	SSE	66.39	27.45	1.02	3.91
	R^2	0.79	0.95	0.99	0.97
	RMSE	5.76	3.70	0.71	1.21
Sips	$q_e = \frac{K_S C_e^{\beta_S}}{1+a_S C_e^{\beta_S}}$				
	β_S	3.56	1.80	0.77	1.13
	K_S (L/g)	0.028	0.017	4.457	0.051
	a_S (L/mg)	1.29	5.14	0.05	0.02
	SSE	7.59	15.01	0.43	1.45
	R^2	0.97	0.97	0.99	0.98
	RMSE	1.95	2.74	0.46	0.85

Various kinds of agro-industrial wastes and by-products were studied for heavy metal removal. A comparison between maximum adsorptive capacities of MMBB and some other

adsorbents is shown in Table 4. These study results are compatible with other adsorbents by higher or at least equal sorption potential for heavy metal removal from aqueous solutions. Furthermore, combination of several types of low-cost agro-industrial waste might provide more selectivity as a result of increase in different effective functional groups involved in metal binding. Hence, this kind of adsorbent will be recommended for its significant advantages.

Table 4. Biosorption capacities of various adsorbents.

Adsorbent	Adsorbate	q_{max} (mg/g)	Reference
MMBB	Cd(II)	31.73	Present study
	Cu(II)	41.06	
	Pb(II)	76.25	
	Zn(II)	26.63	
Cashew nut shell	Zn(II)	24.98	Kumar et al. (2012)
Rice straw	Cd(II)	13.89	Ding et al. (2012)
Sugarcane bagasse	Cd(II)	69.06	Garg et al. (2008)
Sawdust	Cu(II)	6.88	Šćiban et al. (2007)
	Zn(II)	0.96	
	Cd(II)	0.15	
Olive stone	Pb(II)	92.6	Fiol et al. (2006)
	Cd(II)	77.3	
	Ni(II)	21.3	
	Cu(II)	20.2	
Orange peel	Pb(II)	113.5	Feng et al. (2011)
	Cd(II)	63.35	
	Ni(II)	9.82	
Tea waste	Cu(II)	48	Amarasinghe and Williams (2007)
	Pb(II)	65	

3.7. Biosorption mechanism

The main mechanisms known for metal sorption on lignocellulosic biosorbents are chelating, ion exchanging and making complexion with functional groups and releasing $[H_3O]^+$ into aqueous solution. Ionic exchange is known as a mechanism which involves electrostatic interaction between positive metallic cations and the negatively charged groups in the cell walls. The ion exchange reaction could be represented as (Fiol et al., 2006):

$$\equiv S - M_{2/n}(s) + Me^{2+}(aq) \Longleftrightarrow \equiv S - M\,(s) + \frac{2}{n}M^{2+}(aq)$$

where M^+ represents K^+, Mg^{2+} or Ca^{2+} and Me^{2+} is heavy metal ions like Pb^{2+}, Cd^{2+}, Ni^{2+}, and Cu^{2+}. On the other hand, many characterization studies confirmed that ion exchange mechanism was included in heavy metal biosorption process rather than complexation with functional groups on the biosorbent surface and also showed the role of sodium, potassium, calcium and magnesium present in the adsorbent in ion exchange mechanism (Ding et al., 2012 and Akar et al., 2012).

The amount of adsorbed heavy metal ions and released alkali ions (Na^+, K^+, Mg^{2+} and Ca^{2+}) concentration (mg/L) is shown in Fig. 4. Apparently, metal adsorption on biosorbent surface made Na^+, K^+, Mg^{2+} and Ca^{2+} ions release in aqueous medium. It confirmed the possibility of ion-exchange mechanism in biosorption process by comparing total amount of adsorbed heavy metal ions (1.43 mmol/L) and released alkali ions (1.51 mmol/L) which were approximately equal.

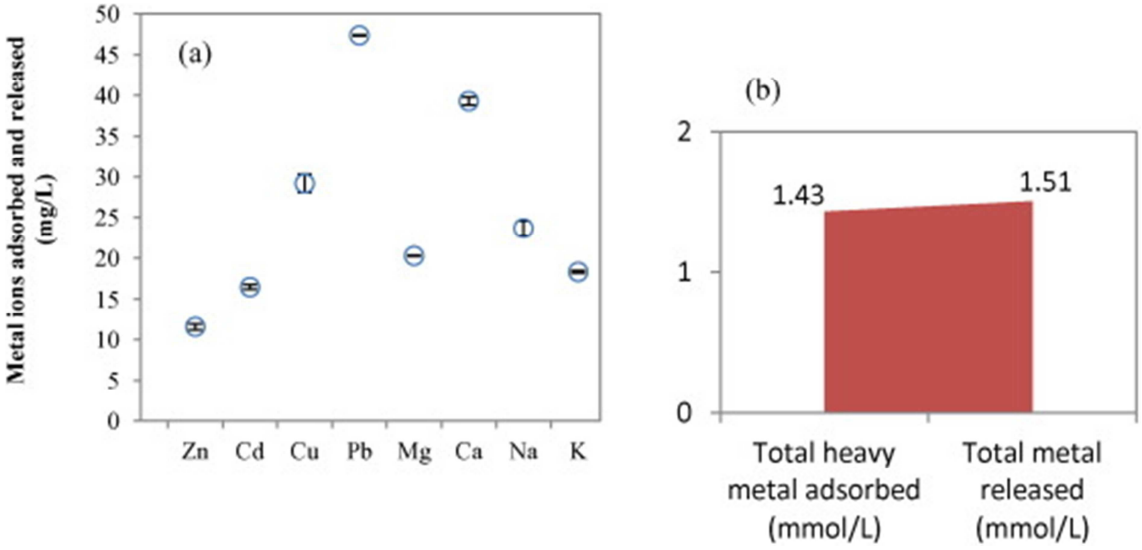


Fig. 4. Comparison of (a) individual and (b) total metal ions adsorbed and released in biosorption process (initial heavy metal conc.: 50 mg/L).

In a previous study on this MMBB (Abdolali et al., 2015), SEM/EDS analysis confirmed that the variance in intensity of K, Na and Ca peaks might be due to ion-exchange mechanism of metal uptake.

In addition, the mean free energy of adsorption $E = \frac{1}{\sqrt{2B_{D-R}}}$ calculated from Dubinin–Radushkevich isotherm can evaluate sorption properties and main mechanism. Based on hypothesis of Dubinin–Radushkevich isotherm, it is concluded that *E* values between 8 and 12 kJ/mol mean chemical adsorption whereas *E* values less than 8 kJ/mol means physical adsorption or ion exchange process at the cell surface. Hence, according to calculated *BD–R* for Cd, Cu, Pb and Zn, *E* values show physical adsorption or ion exchange for four metal removal process whose calculated values are 2.58, 3.45, 5.59 and 2.73 kJ/mol for Cd, Cu, Pb and Zn respectively which are all less than 8 kJ/mol.

With respect to kinetic modeling, it also established that metal uptake by the micro-organisms takes place in two consecutive stages: a passive and quick uptake that follows by an active and very slow uptake. The first step is regarded to be physical adsorption or ion exchange (Witek-Krowiak, 2012) which was well represented by pseudo-second-order kinetic model.

3.8. Adsorption thermodynamics

The biosorptive potential of MMBB for Cd(II), Cu(II), Pb(II) and Zn(II) removal was studied at the temperatures of 25, 30, 40 and 50 °C.

Table 5. Thermodynamic parameters, ΔG° (kJ/mol), ΔH° (kJ/mol) and ΔS° (kJ/mol K), for adsorption of Cd(II), Cu(II), Pb(II) and Zn(II) adsorption.

Metal	***T* (K)**	$q_{m,L}$ **(mg/g)**	$k_c = q_e/C_e$	**ΔG°**	**ΔH°**	**ΔS°**
Cd	298	2.93	1.14	− 17.44	− 4.11	0.87
	303	3.15	1.07	− 17.57		
	313	3.18	1.00	− 17.98		
	323	3.40	0.90	− 18.27		
Cu	298	10.00	0.59	− 15.81	− 15.45	2.75
	303	7.48	0.58	− 16.03		
	313	11.08	0.55	− 16.42		
	323	10.11	1.3	− 19.25		
Pb	298	10.47	8.29	− 22.35	− 11.93	0.90
	303	7.74	6.91	− 22.27		
	313	12.63	6.89	− 23.00		
	323	11.35	10.43	− 24.85		
Zn	298	3.75	0.23	− 13.47	− 3.64	− 0.54
	303	3.76	0.23	− 13.70		
	313	3.61	0.22	− 14.04		
	323	4.05	0.2	− 14.23		
Metal	***T* (K)**	$q_{m,L}$ **(mg/g)**	$k_c = 1/b_L$	**ΔG°**	**ΔH°**	**ΔS°**
Cd	298	2.93	2.97	− 19.81	− 10.06	0.61
	303	3.15	3.24	− 20.36		
	313	3.18	3.28	− 21.07		
	323	3.40	3.56	− 21.96		
Cu	298	10.00	14.29	− 23.70	− 18.30	2.58
	303	7.48	17.01	− 24.54		
	313	11.08	30.77	− 26.89		
	323	10.11	25.51	− 27.25		
Pb	298	10.47	1.13	− 17.41	− 12.65	1.65
	303	7.74	1.12	− 17.70		
	313	12.63	2.48	− 20.34		
	323	11.35	1.42	− 19.50		
Zn	298	3.75	5.32	− 21.26	− 17.72	2.62
	303	3.76	13.00	− 23.86		
	313	3.61	11.72	− 24.38		
	323	4.05	13.23	− 25.48		
Metal	***T* (K)**	$q_{m,L}$ **(mg/g)**	$k_c = K_F^{\,n}$	**ΔG°**	**ΔH°**	**ΔS°**
Cd	298	2.93	1.01	− 17.13	− 6.95	0.02
	303	3.15	0.98	− 17.34		
	313	3.18	0.98	− 17.92		
	323	3.40	1.01	− 18.57		
Cu	298	10.00	0.37	− 14.66	− 16.58	3.20
	303	7.48	0.45	− 15.40		
	313	11.08	0.37	− 15.42		
	323	10.11	1.00	− 18.55		
Pb	298	10.47	14.35	− 23.71	− 12.68	0.92
	303	7.74	14.92	− 24.21		
	313	12.63	18.25	− 25.53		
	323	11.35	17.65	− 26.26		
Zn	298	3.75	0.33	− 14.38	− 2.57	− 0.91
	303	3.76	0.22	− 13.55		
	313	3.61	0.23	− 14.13		
	323	4.05	0.24	− 14.68		

The experimental results indicated dependency of adsorption on the temperature and are listed in Table 5. The thermodynamic parameters for the adsorption process such as free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔG°) were calculated to evaluate thermodynamic feasibility of the sorption process and to confirm its nature. The Gibbs free energy indicates the degree of spontaneity of sorption process, and the higher negative value reflects a more energetically favorable sorption. ΔH° and ΔS° were obtained from the slop and intercept of the Van't Hoff plots (Fig. 5). The negative values of (ΔG°) for all metal ions indicate the spontaneous nature of metal biosorption on MMBB. The negative value of ΔH° showed that the sorption process was exothermic in nature.

Except for zinc, calculated ΔS° values for cadmium, copper and lead were positive, reflecting the increased randomness at the solid/solution interface during sorption. It also indicates an affinity of the sorbent towards Cd, Cu and Pb ions. In addition, the low value of ΔS° may imply that no remarkable change in entropy occurred during the sorption of Cd, Cu, Pb and Zn ions on MMBB.

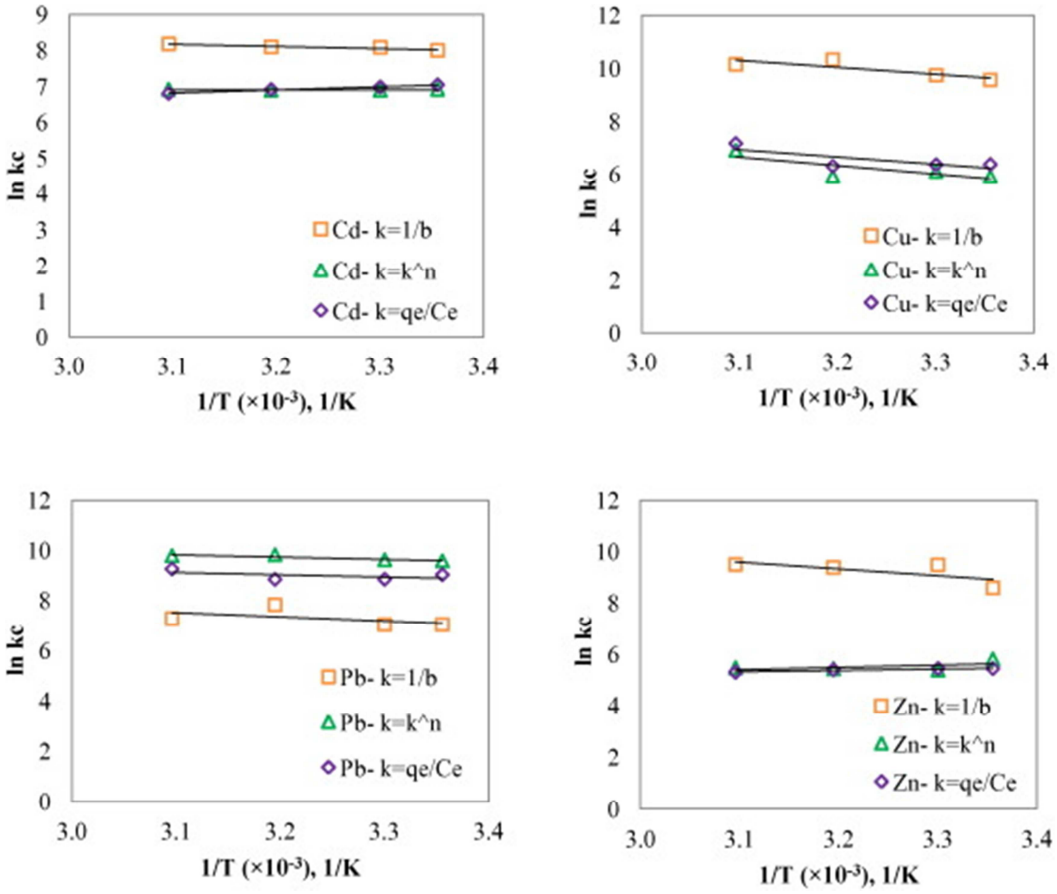


Fig. 5. Van't Hoff plots for Cd(II), Cu(II), Pb(II) and Zn(II) adsorption(initial pH 5.5 ± 0.1; initial metal conc.: 1–50 mg/L; contact time: 3 h; biosorbent dose: 5 g/L).

4. Conclusions

The present work explores a new economical and selective lignocellulosic biosorbent containing tea waste, maple leaves and mandarin peels as an alternative to costly adsorbents for the removal of Cd(II), Cu(II), Pb(II) and Zn(II) ions. The low cost, rapid attainment of phase equilibrium (within 3 h) and high sorption capacity values may be cited among the main advantages. Adsorption kinetics follows a pseudo-second-order kinetic model and negative values of $\Delta H°$ and $\Delta G°$ prove the exothermic and spontaneous nature of the biosorption phenomenon. Hence, this novel MMBB can be a promising adsorbent to eliminate heavy metal ions from aqueous solutions.

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