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Characterization of a multi-metal binding biosorbent: Chemical modification and desorption studies

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HIGHLIGHTS

- A novel multi-metal binding biosorbent (MMBB) was prepared and characterized.
- Carbonyl and carboxylate groups are involved in metal binding of MMBB.
- Desorption and regeneration have been evaluated.
- The obtained results recommend this MMBB as potentially low-cost biosorbent.

ARTICLE INFO

ABSTRACT

This work attends to preparation and characterization of a novel multi-metal binding biosorbent after chemical modification and desorption studies. Biomass is a combination of tea waste, maple leaves and mandarin peels with a certain proportion to adsorb cadmium, copper, lead and zinc ions from aqueous solutions. The mechanism involved in metal removal was investigated by SEM, SEM/EDS and FTIR. SEM/EDS showed the presence of different chemicals and adsorbed heavy metal ions on the surface of biosorbent. FTIR of both unmodified and modified biosorbents revealed the important role of carboxylate groups in heavy metal biosorption. Desorption using different eluents and 0.1 M HCl showed the best desorption performance. The effectiveness of regeneration step by 1 M $CaCl_2$ on five successive cycles of sorption and desorption displays this multi-metal binding biosorbent (MMBB) can effectively be utilized as an adsorbent to remove heavy metal ions from aqueous solutions in five cycles of sorption/desorption/regeneration.

1. Introduction

Heavy metal ions are one of the most toxic aquatic pollution discharging from various industries. They are very harmful for all plants, animals and human life due to their high environmental mobility in soil and water and also strong tendency for bioaccumulation in the living tissues through food chain (Akar et al., 2012). In order to remediate polluted water and wastewater streams, a wide range of physicochemical/biological treatment technologies are employed in industry (e.g. chemical precipitation, extraction, ion-exchange, filtration, reverse osmosis, membrane bioreactor and electrochemical techniques). 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 (Abdolali et al., 2014a; Montazer-Rahmati et al., 2011; Gupta et al., 2009).

Recently, the attention has been addressed towards cheap agro-industrial wastes and by-products as biosorbents. Therefore, introducing a properly eco-friendly and cost effective technology for wastewater treatment has provoked many researchers into this matter (Abdolali et al., 2014b; Hossain et al., 2014; Tang et al., 2013; Ding et al., 2013; Ronda et al., 2013; Kumar et al., 2012; Hossain et al., 2012; Gadd, 2009; Gurgel and Gil, 2009; Volesky, 2007).

The metal binding takes place as a passive mechanism based on the chemical properties of surface functional groups. The mechanisms involved in metal bioaccumulation are complicated; therefore the interpretation is very difficult. Usually these mechanisms are related to electrostatic interaction, surface complexation, ion-exchange, and precipitation, which can occur individually or in combination (Oliveira et al., 2014). Moreover, pretreatment of adsorbents improves physical and chemical properties of biosorbent, increases the adsorption capacity and prevents organic leaching, while chemical modification makes some improvements on surface active sites, liberates new adsorption sites and enhances mechanical stability and protonation (Yargıç et al., 2014; Anastopoulos et al., 2013; Velazquez-Jimenez et al., 2013).

However, the major disadvantage of biosorption is producing huge amount of solid biomass or aqueous solutions with high concentration of heavy metals to environment. To tackle the problem attributing to solid biomass, applying proper desorbing and regenerating agent would be effective. Desorption can be carried out by proton exchange using mineral and organic acids such as HCl, HNO$_3$, H$_2$SO$_4$ and acid acetic, by exchange with other ions like applying CaCl$_2$ or by chelating agents (for example EDTA). An efficient eluant is one that desorbs the metal completely without any damaging the biomass structure and functionality to be able to reuse (Mata et al., 2009).

All of the previous attempts have been made to study the agro-industrial wastes and by-products individually. The present work is therefore novel as it uses the combination of selected agro-industrial multi-metal binding biosorbents for removal of cadmium, copper, lead and zinc ions from aqueous solutions. The purpose of blending different lignocellulosic materials is to have all potentials of biosorbents for heavy metal uptake. Also these wastes were selected because of the good results reported in other literatures for heavy metal removal. Additionally, they are properly available in Australia and also all over the world.

This work mainly explored characterization of this new biosorbent to find the principal surface functional groups and possible biosorption mechanisms involved in the biosorption in terms of chemical modification and desorbing agents using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDS). Desorption studies were carried out in terms of eluent type, concentration and contact time of desorption process. The effect of regeneration step by CaCl$_2$ was taken into consideration as well.

2. Methods

2.1. Preparation of 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$_3$)$_2$·4H$_2$O, Cu$_3$(NO)$_2$·3H$_2$O, Pb(NO$_3$)$_2$ and Zn(NO$_3$)$_2$·6H$_2$O 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).

2.2. Preparation of adsorbents

The biosorbent was a combination of tea waste (TW), maple leaves (ML) and mandarin peel (MP). These biosorbent displayed better biosorptive capacity for cadmium, copper, lead and zinc among a group of low-cost and very available lignocellulosic wastes and by-products. Maple leaves (ML) was collected in

Sydney area. Tea (TW) and mandarin (MP) were bought from a local market and after using the useful parts were washed by tap water and then by distilled water to remove any dirt, color or impurity. All biosorbents were dried in oven (Labec Laboratory Equipment Pty Ltd., Australia) over night. Having crushed, ground and sieved (RETSCH AS-200, Germany) to the particle size of <75, 75–150, 150–300 and >300 μm, the natural biosorbents were kept in desiccator prior to use. Biosorbent was physical modified by heating (50–150 °C in a drying oven for 24 h) and boiling (100 g biosorbent in 150 mL water). For chemical modification, HCl (1 M), NaOH (1 M), HNO$_3$ (1 M), H$_2$SO$_4$ (1 M), CaCl$_2$ (1 M), formaldehyde (1%) and mixture of NaOH (0.5 M) and CaCl$_2$ (1.5 M) in ethanol were used as the modification agents. 10 g of each biosorbent was soaked in 1 L of each solution and thoroughly shaken (150 rpm) for 24 h at room temperature. Pretreatment with the mixture of 250 mL NaOH (0.5 M) and 250 mL CaCl$_2$ (1.5 M) solutions in 500 mL ethanol was same as other chemicals hereinabove. Afterwards, all materials were filtered and rinsed several times with distilled water to remove any free chemicals until the neutral pH to be obtained and dried in oven over night. All biosorbents were kept in a desiccator prior to use in future experiments.

2.3. Biosorption studies

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 150 rpm. After equilibration, to separate the biomasses from solutions, the solutions were filtered and final concentration of metal was measured using MP-AES. All the experiments were carried out in duplicates.

The experimental conditions of Cd(II), Cu(II), Pb(II) and Zn(II) applied for current study were pH 5.5 ± 0.1, room temperature, biosorbent dose of 5 g/L and biosorbent particle size of 75–150 μm.

2.4. Desorption studies

Desorption study was carried out in a similar way to the biosorption studies. After adsorption step, metal-loaded biosorbent (5 g/L) was filtered, dried, weighed and shaken with 50 mL of desorbing agents in 250 mL Erlenmeyer flasks at 150 rpm on an orbital shaker. The suspension of metal-loaded MMBB and eluent was centrifuged and the supernatant was filtered and analyzed for metal ions desorbed.

In order to evaluate the regeneration properties of 1 M CaCl$_2$, desorption experiments were performed with and without regeneration step in five consecutive sorption/desorption cycles with modified MMBB.

2.5. Characterization of adsorbents by FTIR and SEM/EDS

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 place 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) and Energy Dispersive X-ray Spectrometry (EDS) of the free and loaded MMBB was performed on ZEISS EVO|LS15 (Germany) at an electron beam voltage of 15 kV, pressure of about 7×10^{-6} Torr, temperature of 20 °C, spot size of 10–200 μm and with the working distance of 9–11 mm. The MMBB samples were examined before and after modification, biosorption, desorption and regeneration to observe the porous properties of the biosorbents.

2.6. Biosorption kinetics and isotherm study

A series of contact time experiments for cadmium, copper, lead and zinc adsorption on modified MMBB from 0 to 3 h were carried out at pH 5.5 ± 5.5 and room temperature. Each sample was taken each 15 min from 1 L solution containing Cd, Cu, Pb and Zn ions with initial concentration of 10, 50 and 100 mg/L and 5 g of biosorbents. Experimental data of kinetic studies were fitted to the pseudo-first and pseudo-second order kinetic model.

The relationship between metal biosorption capacity and metal concentration at equilibrium has been described by very common Langmuir and Freundlich isotherm models. The kinetic and isotherm constants were evaluated by non-linear regression using MATLAB® software.

2.7. Calculation

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

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

where C_f and C_i (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.

After each biosorption, the final amount of metal adsorbed (C_{ads}, mg/L) was calculated with the following expressions (Mata et al., 2010):

$$C_{ads} = (C_i + C_{res}) - C_f \tag{2}$$

where C_{res} (mg/L) is the residual amount of metal retained from the previous desorption (when applicable).

After each desorption, the desorption efficiency, % was determined as follows:

$$\% \text{ Desorption efficiency} = \frac{C_{des}}{C_f} \times 100 \tag{3}$$

where C_{des} is the amount of metal ion concentration in desorbing agent after each desorption step.

3. Results and discussion

3.1. Effect of biosorbent ratio

The effect of proportions for each biosorbent (TW:ML:MP) for heavy metal removal was fulfilled with different proportions (Fig. 1a). All materials were separately weighed and mixed for removing any error and inaccuracy. In order to test the significance and adequacy of the model, statistical testing of the model in the form of analysis of variance (ANOVA) was conducted. 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.

Moreover, the ratio of 3:2:1 for TW:ML:MP showed the highest metal biosorption capacity. This ratio will be used for further

studies. The pH, moisture content (%), loss of mass and bulk density (g/cm³) of MMBB were 4.97, 18.86, 0.93 and 0.36, respectively.

3.2. Effect of biosorbent particle size

The tests for studying the effect of particle size of biosorbent were conducted for 5 g/L adsorbent dose and an initial concentration of 1–50 mg/L. The results of different particle sizes of <75 μm, 75–150 μm, 150–300 μm and >300 μm are indicated in Fig. 1b. It was found that biosorption capacity slightly increased by decreasing particle size. The reason was that these particle size distributions were very small (less than 300 μm). The smallest biosorbent size (<75 μm) exhibited better performance in regard with metal removal. Nonetheless, the smaller size provides a higher surface area for metal adsorption, the mechanical stability reduces particularly in column (Liu et al., 2012). Hence, the size of 75–150 μm MMBB was selected for the experiments.

3.3. Effect of drying temperature

All of biosorbents were dried at various temperatures to investigate the influence of drying temperature on drying rate and remaining weight. As can be expected, increasing drying temperature made a significant improvement of drying rate. The drying time was reduced remarkably with an increase in temperature within 50–150 °C.

The drying time of tea leaves and mandarin peels have very similar pattern. For tea leaves, at 150 °C the remaining weight plateaued after 2 h while at 75 °C, the constant weight could be achieved within 6 h. For maple leaves, due to low content of moisture, there were no remarkable differences between drying time in different drying temperature which were within 3 h for lower drying temperatures and 2 h for higher temperatures. However, when the temperature was higher than 105 °C, there is no significant change in the drying rate for all three types of biosorbent after 2 h of drying in oven.

3.4. Effect of physical and chemical pretreatment

A few researchers investigated the effect of temperature of drying on biosorptive capacity of biosorbent for metal removal. In some literatures, biosorption performance was enhanced by increase in drying temperature. Thermal pretreatment can make larger surface sites and improve biosorbent surface activity and kinetic energy (Liu et al., 2012). However, in this study for metal concentration of 50 mg/L, the temperature did not affect the amount of Cd, Cu, Pb and Zn biosorption on MMBB (Fig. 1c).

Therefore, as mentioned in the Section 3.3, for low energy consumption in a short time of drying and also to avoid any physical damage of biosorbent structure, all biosorbent was dried at lower temperature (105 °C) as an optimum temperature in this study.

NaOH has been used to hydrolyze protein of biosorbents and methyl esters of cellulose, hemicellulose, pectin and lignin (Calero et al., 2013; Ronda et al., 2013; Feng et al., 2009). Methyl ester bonds can be saponified to carboxyl (–COOH), carboxylate (–COO) and alcoholic (–OH) ligands. It also leads to a decrease in the degree of polymerization and crystallinity as follows:

$$R - COOCH_3 + NaOH \rightarrow R - COO^- + CH_3OH + Na^+$$
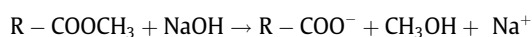
Strong acids such as HCl, H_2SO_4 or HNO_3 can protonate unavailable functional groups in the structure of biosorbents by oxidizing functional groups and transforming them to carboxylic groups (Chatterjee and Schiewer, 2014; Ronda et al., 2013; Schiewer and Balaria, 2009; Nadeem et al., 2008).
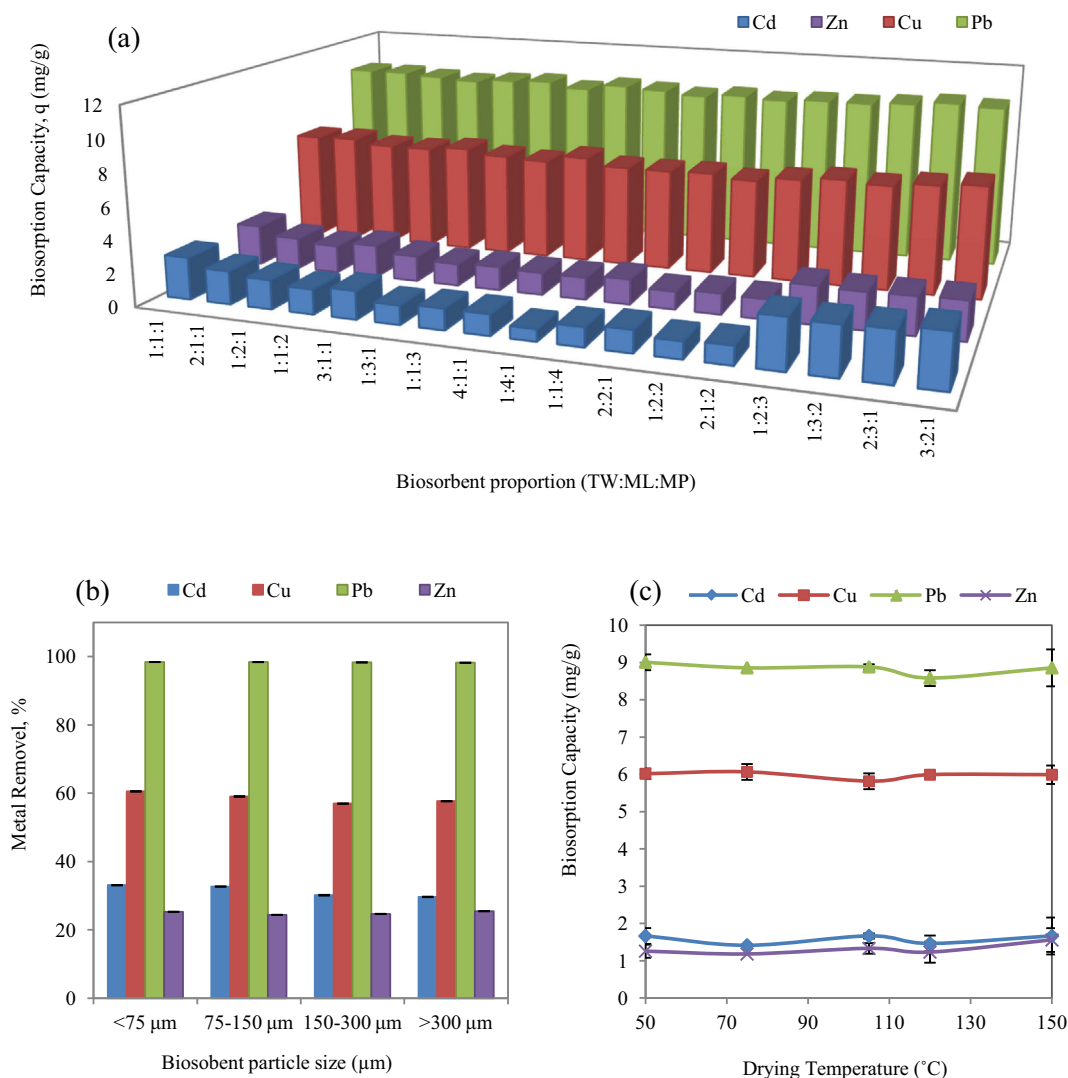
Fig. 1. (a) Effect of ratio of tea waste: maple leaves: mandarin peel, (b) biosorbent particle size and (c) drying temperature on Cd(II), Cu(II), Pb(II) and Zn(II) adsorption (initial pH 5.0–5.5 ± 0.1; room temperature, 22 ± 1 °C; initial metal conc.: 50 mg/L; biosorbent dose: 5 g/L; rotary speed: 150 rpm).

Besides, alkali treatments in comparison with acidic ones at the same conditions were more effective on metal ion removal and made the functional groups denser and thermodynamically more stable (Velazquez-Jimenez et al., 2013). Dilute NaOH treatment leads to an increase in surface area, while treatment with nitric acid reduces the surface area and total pore volume (Ronda et al., 2013).

Formaldehyde can increase stability of the material and surface structure. It can be applied to pretreatment for prevention of organic leaching and metal uptake enhancement. Chen and Yang (2005) reported that formaldehyde reacts with the hydroxyl group of biosorbent to form acetyl groups and increase the structural stability of the biomass.

Pectin acid of lignocellulosic materials is precipitated and by treating with calcium chloride and its solubility in solution decreases. In addition, $CaCl_2$ makes biosorbent stable in term of mechanical structure by releasing organic compounds and volatiles (Feng et al., 2009). It has been also reported that the formation of reactive carboxyl groups cross-links with calcium might increase by adding a given amount of calcium ions (Sriamornsak, 2003).

Finally, it should be noted that the enhancement obtained in biosorption capacity with pretreatments of MMBB by mineral acids

was due to the functional groups replacement with more soluble compounds and improvements of surface characteristics (Velazquez-Jimenez et al., 2013; Ofomaja and Naidoo, 2011). The calculated biosorption capacities for each metal ion were shown in Fig. 2. The biosorption capacity of all metals increased after modification by NaOH which are 10.58, 9.00, 13.42 and 10.70 mg/g for Cd, Cu, Pb and Zn, respectively. HCl, HNO_3 and H_2SO_4 indicated reverse results due to probable damage of biosorbent structures by these mineral acids. $CaCl_2$ and formaldehyde improve lead removal whereas cadmium, copper and zinc removal decreased by formaldehyde-treated MMBB.

It can be concluded that, chemical modification by sodium hydroxide and the solution containing sodium hydroxide, calcium chloride and ethanol were more effective than the other chemical and physical pretreatment. Since calcium chloride made biosorbent structure more durable for reusing in successive and continuous processes, all biosorbents were pretreated by NaOH, $CaCl_2$ and ethanol.

3.5. FTIR

FTIR analysis was performed to investigate the major functional group in cadmium, copper, lead and zinc binding process. The FTIR
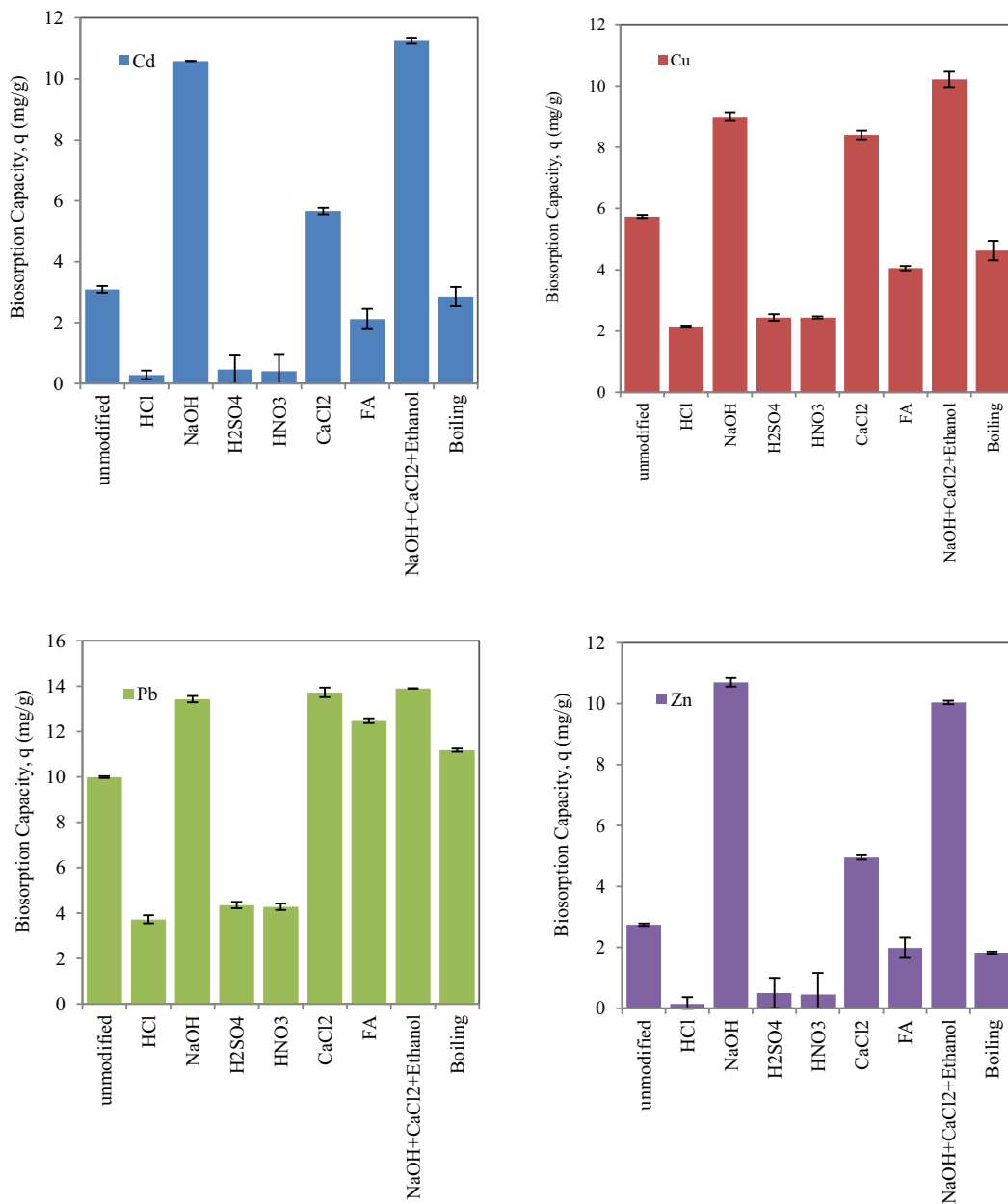
Fig. 2. Biosorption capacity of modified MMBB by different chemical and physical methods.

spectra of the unmodified and modified MMBB by NaOH, CaCl$_2$ and ethanol before and after metal loading were compared. The major band assignments and functional groups are as follows. A medium band at about 1051–1012 cm^{-1} corresponds to deformation vibration of groups C–N stretch of aliphatic amines. Broad bands at 1300–1000 cm^{-1} have been assigned to C–O stretching in acids, alcohols, phenols, ethers and esters. Two bands (<200 cm^{-1} apart) were the appearance of N=O bend of nitro compounds between 1400 and 1300 cm^{-1}. The bands at 1579 and 1523 cm^{-1} for modified MMBB and at 1546 and 1533 cm^{-1} for unmodified MMBB, respectively, correspond to stretching of carbonyl group and carboxylic acid (C=O) of primary amide (1° amide). The band at 1589 cm^{-1} corresponds to deformation vibration of N–H bends of primary amines (1° amine). The region between 2000 and 3000 cm^{-1} presents two major adsorption bands. At about 2341 and 2343 cm^{-1} for modified MMBB and at 2345 and 2353 cm^{-1}

for unmodified MMBB, a doublet peak can be seen due to the existence of B–H stretch. The band around 2916 cm^{-1} was exhibited in presence of C–H stretching of CH$_2$ groups (asymmetric and symmetric stretches). Besides, a very broad weak band at 3144 and 3487 cm^{-1} might attribute to the presence of intermolecular hydrogen bonded O–H stretch of phenols and alcohols.

The changes after modification can be obviously seen in FTIR spectra as the fingerprint of sodium hydroxide pretreatment due to the formation of the intermolecular hydrogen bond and complexation of heavy metal ions by carboxylate groups. According to literature (Tan and Xiao, 2009; Gurgel and Gil, 2009), ester product and carboxyl acid compounds will have a strong sharp peak at ∼2900 cm^{-1} (alkyl C–H) and a strong and sharp peak at ∼1700 cm^{-1} (C=O). The absorption band wave number of the carboxylate groups (COO$^-$) is about 1670–1600 cm^{-1}, which shifted to low wave number because of the formation of the intermolecular

hydrogen bond. This confirms that basic modification of biosorbent makes methyl ester hydrolyze, ester groups decrease and subsequently carboxylate groups increase. The FTIR analysis of the chemically modified MMBB in comparison with unmodified form also confirmed that carboxylate groups play an important role in heavy metal adsorption.

3.6. Effect of contact time and kinetic study

It is evident from Fig. 3 that the rate of metal uptake was very fast within first 60 min for initial metal concentrations of 10 and 50 mg/L in comparison with 100 mg/L. The reason is exuberant number of available active sites on adsorbent surface. The biosorption capacity levelled off after 120 min of contact time for cadmium, copper and zinc ions with initial concentration of 100 mg/L while for lead, there is no difference between metal removal in different initial content.

The experimental kinetic results were fitted to pseudo first-order and pseudo second-order kinetic models. The 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. According to calculated kinetic model parameters in Table 1, with comparison between adsorption rate constants, the estimated q_e and the coefficients of correlation associated with the Lagergren pseudo-first-order and the pseudo-second-order kinetic models, cadmium, copper, lead and zinc biosorption process followed pseudo second-order kinetic model. It is obvious that chemical reaction would be presumably the rate limiting step of Cd, Cu, Pb and Zn biosorption on both modified and unmodified MMBB. The calculated values of q_e for pseudo-second-order kinetic model (modified MMBB) are 10.94, 10.75, 13.56 and 9.68 mg/g for Cd(II), Cu(II), Pb(II) and Zn(II), respectively, approximately close to the experimental values (11.69, 11.63, 13.75 and 10.33 mg/g).

3.7. Adsorption isotherm

The correlation between the adsorbed and the aqueous metal concentrations at equilibrium was described by the Langmuir and Freundlich (Table 2a). The Langmuir equation describes the equilibrium condition better than Freundlich model (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, for unmodified MMBB. These amounts were 69.56, 127.70, 345.20 and 70.55 mg/g for Cd(II), Cu(II), Pb(II) and Zn(II), respectively, for modified MMBB. 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 (Cay et al., 2004).

From Table 2b, this modified MMBB biosorptive potential is compatible with other adsorbents by higher biosorption capacity for heavy metal removal from aqueous solutions. Besides, 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.

3.8. Desorption studies

It is desirable to desorb and recovered the adsorbed metals and also regenerate the adsorbent materials for another cycle of application. The regeneration of the adsorbent can be achieved by washing loaded adsorbent with an appropriate desorbing solution. Desorbing agent must be cheap, effective, non-polluting and non-damaging to the adsorbent structure (Ozdes et al., 2006).

In Fig. 4, the desorption potential of the eluents is compared for first cycle of sorption/desorption to select the best desorbing agent. It is apparently that milli-Q water was very ineffective for releasing
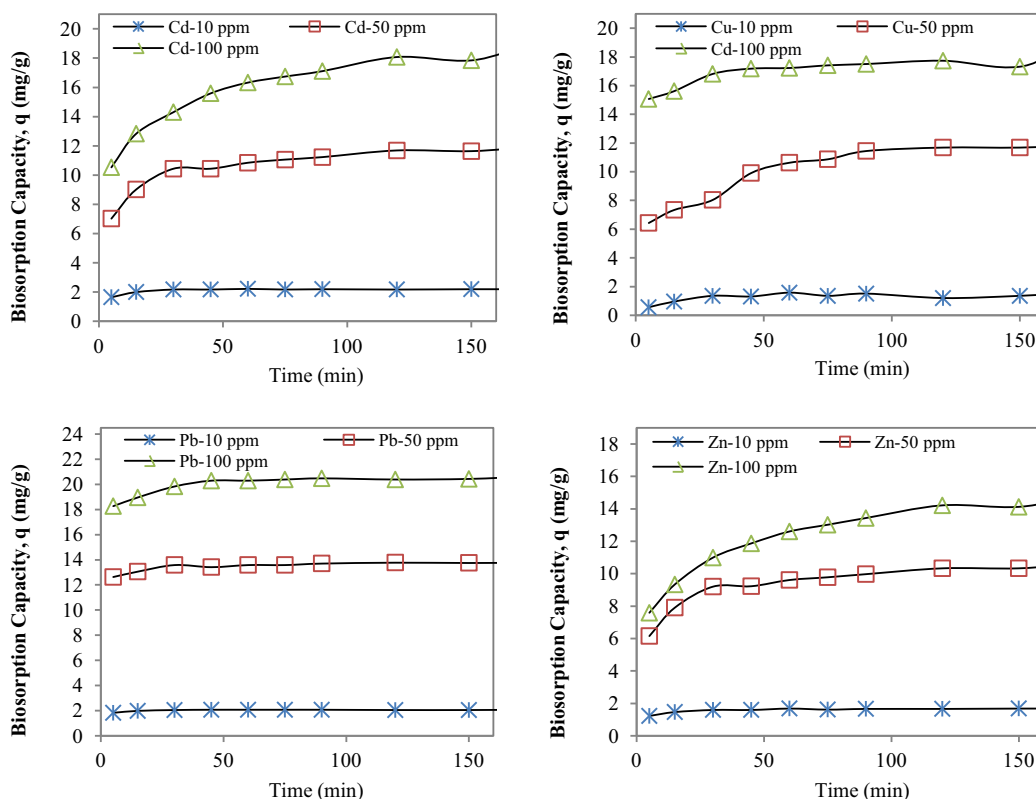

Fig. 3. Effect of contact time on Cd(II), Cu(II), Pb(II) and Zn(II) adsorption.

Table 1

Comparison between adsorption rate constants, the estimated q_e and the coefficients of correlation associated with the pseudo-first-order and pseudo-second order kinetic models (initial conc.: 50 ppm).

Kinetic models	Parameter	Metal							
		Cd[a]	Cd[b]	Cu[a]	Cu[b]	Pb[a]	Pb[b]	Zn[a]	Zn[b]
Experiment	q_e (mg/g)	3.30	11.63	6.40	11.69	9.02	13.75	2.88	10.33
Pseudo-1st-order	$q_t = q_e[1 - \exp(-K_1 t)]$								
	q_e (mg/g)	3.36	10.94	6.39	10.75	9.06	13.56	2.64	9.68
	K_1 (h^{-1})	10.70	11.02	8.047	5.95	8.93	3.33	5.17	10.62
	R^2	0.99	0.99	0.99	0.88	0.99	0.99	0.99	0.97
	SSE	0.10	3.47	0.005	13.99	0.354	0.37	0.007	2.91
	RMSE	0.08	0.65	0.006	1.32	0.165	0.21	0.02	0.60
Pseudo-2nd-order	$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t}$								
	q_e (mg/g)	3.40	11.63	6.39	11.74	8.99	13.7	2.68	10.32
	K_2 (mg g^{-1} h^{-1})	11.08	1.46	3.32	0.78	0.72	9.83	0.08	1.57
	R^2	0.99	0.99	0.99	0.95	0.98	0.99	0.98	0.99
	SSE	0.04	0.62	0.53	6.27	1.14	0.12	0.07	0.53
	RMSE	0.05	0.28	0.006	0.88	0.29	0.12	0.76	0.25

[a] Un-modified MMBB.
[b] Modified MMBB.

Table 2

(a) Isotherm constants of non-linear Langmuir and Freundlich models for Cd(II), Cu(II), Pb(II) and Zn(II) adsorption on unmodified and modified MMBB and (b) maximum biosorption capacities of various adsorbents.

(a)

Isotherm models	Metal							
	Cd[a]	Cd[b]	Cu[a]	Cu[b]	Pb[a]	Pb[b]	Zn[a]	Zn[b]
Langmuir $\quad q_e = \frac{q_{m,L} b_L C_e}{1 + b_L C_e}$								
$q_{m,L}$ (mg/g)	31.73	69.56	41.06	127.70	76.25	245.20	26.63	70.55
b_L (L/mg)	0.005	0.004	0.010	0.001	0.034	0.060	0.050	0.004
R^2	0.99	0.98	0.99	0.99	0.99	0.99	0.99	0.99
RMSE	3.45	2.59	4.56	2.87	2.12	0.71	0.53	2.25
Freundlich $\quad q_e = K_F C_e^{1/n}$								
K_F	0.92	1.24	1.64	0.75	7.80	0.37	0.46	1.17
n	1.88	1.71	1.96	1.40	2.38	1.15	1.80	1.67
R^2	0.79	0.95	0.92	0.97	0.98	0.99	0.97	0.95
RMSE	4.09	4.49	3.84	4.26	4.08	1.36	0.98	9.06

(b)

Adsorbent	Adsorbate	$q_{m,L}$ (mg/g)	References
Tomato waste[b]	Cu(II)	34.48	Yargıç et al. (2014)
Olive tree pruning[a]	Pb(II)	33.90	Anastopoulos et al. (2013)
Olive tree pruning[b]	Pb(II)	82.64	Anastopoulos et al. (2013)
Cabbage waste[a]	Cd(II)	20.56	Hossain et al. (2014)
Cabbage waste[a]	Cu(II)	10.31	Hossain et al. (2014)
Cabbage waste[a]	Pb(II)	60.56	Hossain et al. (2014)
Cabbage waste[a]	Zn(II)	8.97	Hossain et al. (2014)
Orange peel[b]	Pb(II)	113.5	Feng et al. (2011)
Orange peel[b]	Cd(II)	63.35	Feng et al. (2011)
Cashew nut shell[a]	Zn(II)	24.98	Kumar et al. (2012)
Rice straw[a]	Cd(II)	13.89	Ding et al. (2012)

[a] Un-modified MMBB.
[b] Modified MMBB.

bonded metal onto MMBB. Sodium chloride and sodium hydroxide showed very weak potential for detaching adsorbed metal in comparison with the acids. It is well known that under acidic conditions the adsorbent surface is protonated by H_3O^+ ions to make possible desorption of positively charged metal ions from the adsorbent surface (Ozdes et al., 2006). Among these three mineral acids, HCl was slightly better than HNO_3 and H_2SO_4 for all metals.

Copper was almost completely desorbed with 0.1 M HCl. Other metal ions recovery cannot thoroughly fulfilled by desorption. This might be due to heavy metal ions being trapped in the adsorbent porous structure and therefore difficult to release (Ozdes et al., 2006). According to the Langmuir parameter presented in Table 2a, lead biosorption presented the highest affinities for MMBB, therefore desorbed in longer time than other metals. The lead recovery was the lowest and copper showed the highest amounts which were 76.26 and 99.93%, respectively by applying HCl as he desorbing agent. Cadmium and zinc desorption efficiency were 96.33% and 91.93% respectively for HCl, and 96.90% and 92.90%, respectively for HNO_3.
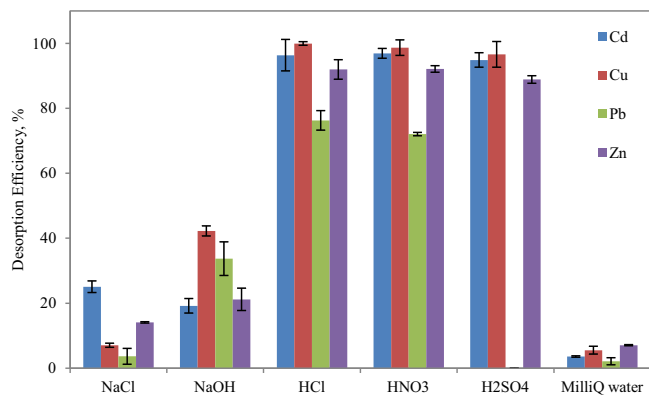
Fig. 4. Comparison between Cd, Cu, Pb and Zn elution from metal-loaded modified MMBB using different desorbing agents (C_i: 50 ppm).

Generally, desorption efficiency of all metals did not tangibly change by using these three acids. It is necessary to note that because of low solubility of lead sulfate, H_2SO_4 could not be utilized for lead recovery.

For desorption study, the optimum conditions were determined and metal loaded modified MMBB was desorbed using HCl, HNO_3 and H_2SO_4 (0.1 M) for enough time within that the outlet metal concentration remained constant and equal or close to zero.

Fig. 5 shows the elution curves of metal-loaded modified MMBB with HCl, HNO_3 and H_2SO_4 until desorption efficiency amount levelled off. Lead desorption by HCl was slower than other metal desorption. The lead desorption equilibrium took place within 3 h

whereas other metal desorption efficiency reach equilibrium state in 2 h.

The effect of HCl concentration was indicated in Fig. 6a. Metal desorption efficiency increased by about 9, 47, 70 and 26% for Cd, Cu, Pb and Zn, respectively, when HCl concentration increased from 0.01 M to 0.1 M. Higher acid concentration might damage the biosorbent structure and reduce the sorption and desorption efficiency due to biosorbent mass loss.

The metal-desorbed modified MMBB was used as the regenerated sorbent in five repeated sorption and desorption cycles and five successive cycles of sorption, desorption and regeneration to determine reusability potential of the adsorbent. After adsorption, the metal-loaded modified MMBB were filtered, oven dried, weighed and soaked in 0.1 M HCl desorption solution with biosorbent concentration of 5 g/L. After each desorption step, biosorbents was washed properly by distilled water, then contacted with 1 M $CaCl_2$ for 12 h at 4 °C to be regenerated. In each cycle, the biosorbent was repeatedly washed with distilled water after each desorption to eliminate any excess chemical. Biosorbent stability or any probable weight loss was controlled by weighing MMBB after drying in oven.

The results were very promising. Calcium chloride can increase the stability and reusability of MMBB and repairing the damage caused by the desorbing agents and removing the excess protons after each elution providing new binding sites. HCl was the best eluent for the reutilization of MMBB among all studied chemicals without destroying its sorption capability. MMBB were successfully reused (5 cycles) without any significant loss in both biosorption capacity and biosorbent mass. Metals uptake levelled off or increased after using a 1 M $CaCl_2$ regeneration step after each
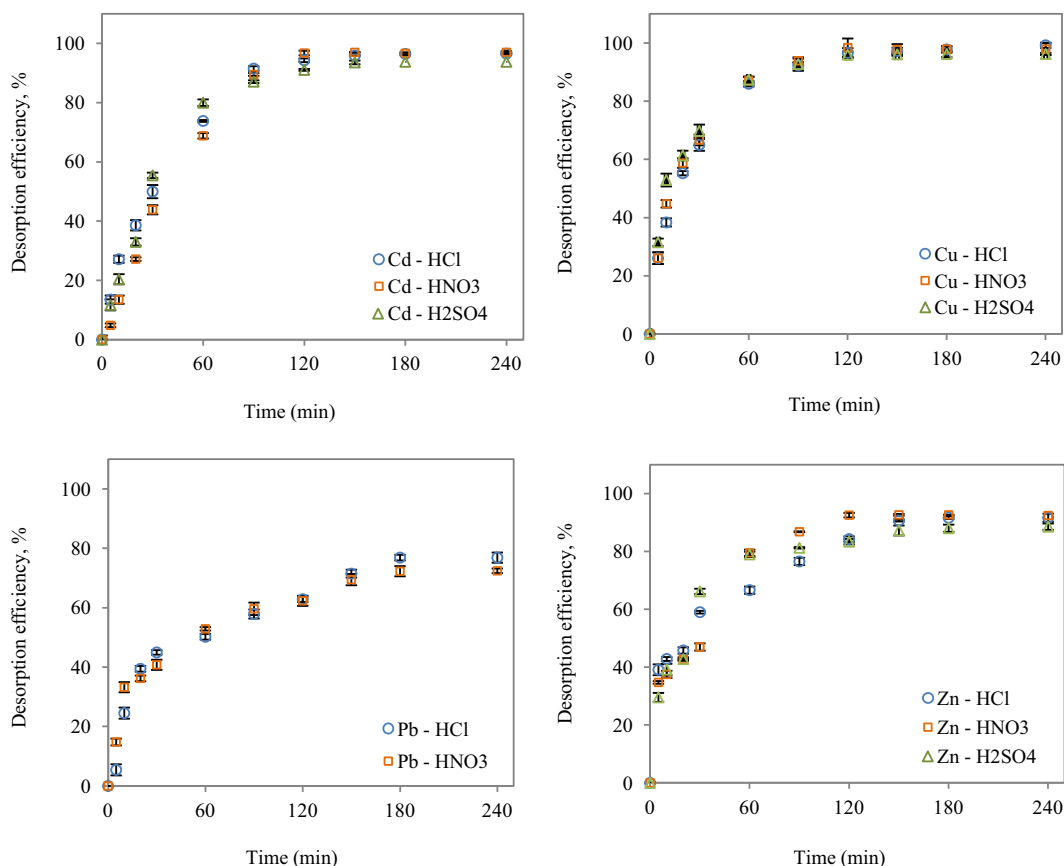

Fig. 5. Elution of Cd, Cu, Pb and Zn from metal-loaded modified MMBB using different mineral acids: 0.1 M HCl, H_2SO_4 and HNO_3.
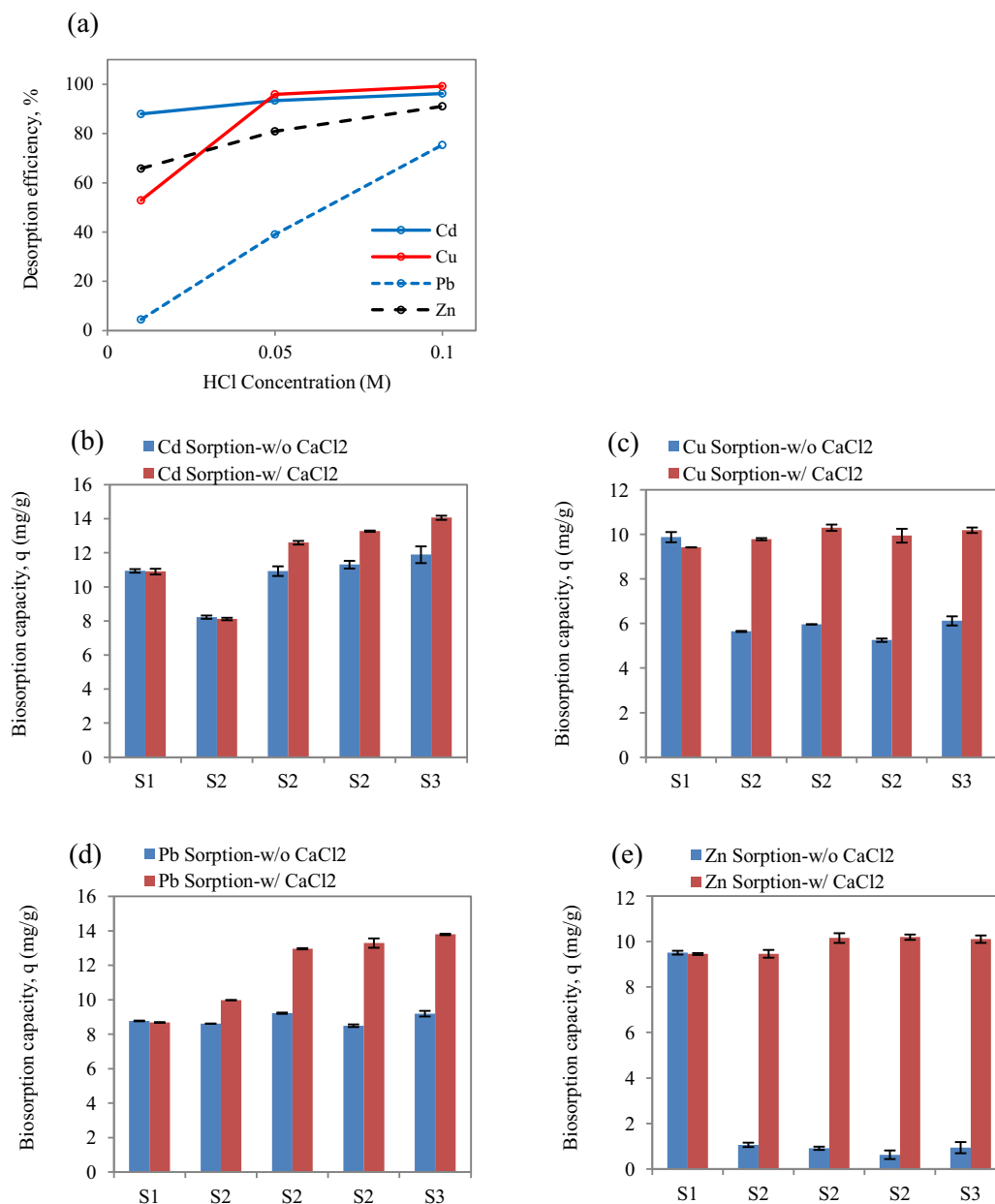
Fig. 6. (a) Effect of HCl concentration on desorption efficiency. (b–e) Desorption efficiency of modified MMBB after each sorption/desorption step without and with regeneration by CaCl₂ and (f–i) biosorption capacity of modified MMBB after each sorption/desorption step without and with regeneration step by CaCl₂.

desorption. After the fifth step of sorption and desorption, for Cd and Pb ions, biosorption capacity increased from 10.95 mg/g to 11.90 mg/g and 8.78 mg/g to 9.20 mg/g, respectively, while Cu and Zn removal decreased by 3.76 and 8.57 mg/g, respectively (Fig. 6b–e).

Desorption efficiency of cadmium, copper, lead and zinc decreased by about 26, 37, 29 and 36%, respectively (Fig. 6f–i). During desorption by hydrochloric acid, biosorbent can become swollen in the acid and the mass loss of MMBB was the result of this damage that was observed between the first and fifth cycles. After five cycles, however, biosorbent mass decreased by 32%, without regeneration by CaCl₂.

The biosorbent surface remained coarsely porous to entrap the metal ions, CaCl₂ could repair the damage caused by the acid during desorption and remove the excess protons remaining from that step (Mata et al., 2009, 2010). In addition, it was seen that the metal desorption efficiency and biosorption capacity remained

constant or increased to a slight extent for all metals. This might be due to a result of slightly chemical modification by CaCl₂. Similarly, Mata et al. (2009, 2010) using 0.1 M HNO₃ as desorbing agent and 1 M CaCl₂ as regenerating agent for pectin gel beads in order to Cd, Cu and Pb uptake. It was very successful to reuse pectin gel beads after nine cycles of sorption/desorption/regeneration. In other study, calcium chloride was successfully applied as an eluant to desorbed cadmium, lead and nickel adsorbed on brown algae of *Cystoseira indica*. In that investigation, calcium chloride was compared with sodium chloride and acetic acid for five consecutive cycles of sorption and desorption (Montazer-Rahmati et al., 2011). Therefore, when regeneration step by calcium chloride added to sorption and desorption experiments, the mass loss of biosorbent decreased only 18%. It was obvious that after five cycles of sorption/desorption/regeneration, the biosorbent appearance, visible structure and mechanical stability did not demolish at all.
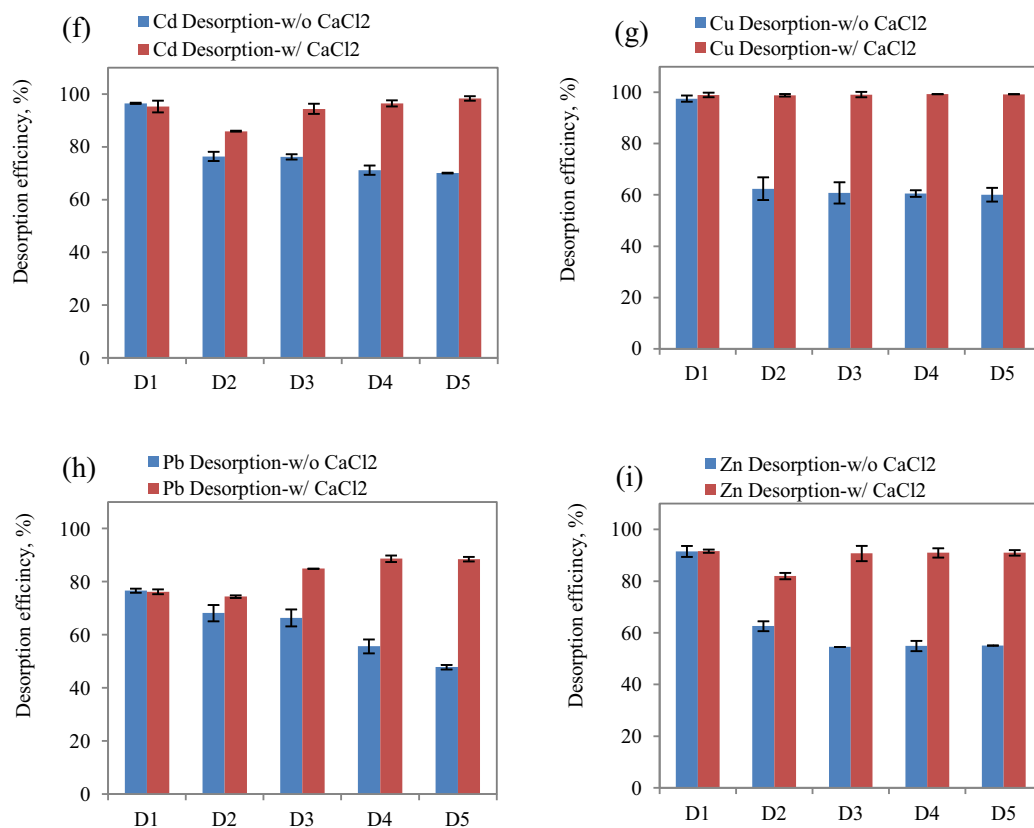
Fig. 6 (*continued*)

3.9. SEM/EDS

SEM analysis 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 electron micrograph of the biosorbent before and after modification by NaOH and $CaCl_2$ after metal adsorption presents several sites on MMBB. The EDS graphs of MMBB samples clearly show a strong peak of Ca and a moderate peak of Na after chemical modification. The distribution of peaks changed in element and intensity. Besides, after metal adsorption the strong peaks attributing to Cd, Cu, Pb and Zn appeared significantly. The variance in intensity of K, Na and Ca peaks might be due to ion-exchange mechanism of metal uptake. Overall, the Cd(II), Cu(II), Pb(II) and Zn(II) intake by biosorbent was confirmed by SEM/EDS analysis.

4. Conclusions

The results of the present study show that modified MMBB may be efficiently used as a renewable biosorbent to remove Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} ions from aqueous solutions. As shown in FTIR studies, unmodified and modified MMBB have similar surface functional groups where by carboxylic acid groups involved in heavy metal binding. Modified MMBB revalues as an agricultural based biosorbent. It was proven to have excellent desorption performance for reutilization by following regeneration step with $CaCl_2$ in five cycles. SEM represent biosorbent surface remained coarsely porous to entrap the metal ions after five cycles of sorption/desorption/regeneration.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2015.06.123.

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