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ORIGINAL PAPER

Enhanced biosorption of metal ions from wastewater by Fenton modified *Hydrilla verticillata* dried biomass

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Abstract Present study deals with the biosorption of metal ions (Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+}) from aqueous solutions as well as from wastewater using Fenton modified *Hydrilla verticillata* dried biomass. Fenton modification process was optimized by varying different parameters such as pH, temperature, contact time, and Fe^{2+}/H_2O_2 ratio. The modified biosorbent was characterized by using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy, and Malvern particle size analyzer. Energy-dispersive X-ray spectroscopy analysis revealed the enhancement in weight percent of Cu^{2+} (47.53 %), Zn^{2+} (41.82 %), Pb^{2+} (43.76 %), and Cd^{2+} (43.15 %) ions on the surface of modified biosorbent after the biosorption process. The experimental data obtained from the batch study were modeled using Langmuir and Freundlich isotherm models. Experimental data showed best fitting to Freundlich isotherm model. The increase in biosorption capacity after the Fenton modification was observed, which follows the sequence: $Cu^{2+} > Pb^{2+} > Cd^{2+} > Zn^{2+}$. The biosorption process followed the pseudo-second-order kinetics, suggesting that the chemisorption may be the rate-limiting step in this study. The thermodynamic study revealed that the biosorption process was spontaneous and exothermic in nature. The biosorption capacity for multi-metal solution was found to be relatively lower than the single-metal solution. Performance of batch reactor in treating wastewater showed significant increase in removal efficiency of Cu^{2+} (from 74 to 96 %), Zn^{2+} (from 67 to 84 %), Pb^{2+} (from 71 to 92 %), and Cd^{2+} (from 71 to 89 %) ions after the modification of biosorbent as compared to raw biomass.

Keywords Isotherms · Kinetics · Metal ions · Thermodynamics · Wastewater

Introduction

Contamination of surface water bodies by the discharge of untreated industrial effluents laden with toxic metals has become a very important matter of concern in the developing countries like India. Due to their persistent nature, these metals do not eliminate easily and gets accumulated in the different parts of the environment (Saygideger et al. 2005; Sasmaz and Obek 2009). Several methods are reported for the elimination of metals from wastewater such as ion exchange, chemical precipitation, solvent extraction, reverse osmosis, electrochemical treatment, membrane technologies, and flotation (Janson et al. 1982; Lundh et al. 2000; Ku and Jung 2001; Lai and Lin 2003; Cardoso et al. 2004; Medina et al. 2005; Mohsen-Nia et al. 2007; Li et al. 2008; Yuan et al. 2008). Use of these methods, however, is occasionally restricted owing to their technical or economical limitations (Puranik and Paknikar 1999). Thus, it becomes indispensable to develop simple, cost-effective, and environment-friendly technique for the removal of metal ions from wastewater. Recently, removal of metal ions using biosorption technique has gained significant interest because of their high effectiveness, low cost, and simplicity (Vijayaraghavan et al. 2006; Dekhil et al. 2011; Santos et al. 2011; Ekmekyapar et al. 2012; Mane and Bhosle 2012; Zan et al. 2012; Deng et al. 2013; Bhatti and

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Hamid 2014). To augment the biosorption capacity and to reduce organic contents of low-cost natural biosorbents, different modification techniques have been utilized by previous researchers (Argun and Dursun 2008; Fatima et al. 2013). Among them, the Fenton's oxidation process has attracted considerable interest. Fenton's reagent is a mixture of ferrous iron and hydrogen peroxide (Fe^{2+}/H_2O_2), which generates highly reactive hydroxyl radical, capable of degrading a wide range of organic and inorganic pollutants (San Sebastian et al. 2003; Pignatello et al. 2006). In addition to this, Fenton process has numerous significant advantages; for instance, reagents are inexpensive, short reaction time among all advanced oxidation processes (Pouran et al. 2013), iron is highly abundant, hydrogen peroxide is easy to handle and environmentally benign (Munter 2001; Venny et al. 2012), high efficiency of mineralization facilitates the conversion of organic pollutants into non-toxic carbon dioxide (Nidheesh et al. 2013), and the overall procedure is easy to execute and control (Argun and Dursun 2008; Miretzky and Munoz 2011). Hydrogen peroxide used in the Fenton process would cause no environmental or ecological threat because diluted and stabilized hydrogen peroxide (5–20 %) was applied, which not only promotes a safer working environment during exothermic in situ application of Fenton reaction, but also results in enhanced treatment efficiency throughout the in situ remediation compared to concentrated H_2O_2 (30–35 % commercial grade), as already reported elsewhere (Kakarla et al. 2002; Venny et al. 2012).

It is very well documented that both living or dead aquatic plants are hyper-accumulators of metals (Singh et al. 2011; Li et al. 2013). Therefore, the application of these aquatic plants for metal removal from wastewater has gained considerable interest. Since *Hydrilla verticillata* is a submerged invasive aquatic plant that interferes with navigation, irrigation, recreation, and power generation, it could be interesting to reinforce its use as biosorbent as a strategy to control invasion episodes. Therefore, in the present research work, *H. verticillata* plant was selected for the study because of its wide spread availability throughout the year and very fast growth rate (2.5 cm per day; Nigam et al. 2013). Various literatures on biosorption of different metals utilizing *H. verticillata* as biosorbent suggest that these aquatic plants possess hydroxyl groups in their cellulosic matrix (Huang et al. 2010; Li et al. 2013; Naveen et al. 2011). Modification or pre-treatment of biosorbent using Fenton's reagent technique can be used to oxidize these hydroxyl groups of cellulose into carboxyl groups by creating a weak cationic ion exchanger (Shukla and Pai 2005), which ultimately could enhance the metal removal efficiency up to many folds as compared to the other previous research studies (Nasernejad et al. 2005; Kumar et al. 2007; Li et al. 2007; Singh et al. 2007; King et al. 2008; Mohammadi et al. 2010; Liang et al. 2011; Momcilovic et al. 2011; Tay et al. 2011; Zhang 2011; Verma et al. 2013; Kumar 2014; Tasar et al. 2014) without imposing much burden on the economy. Furthermore, the use of Fenton modified dried biomass of *H. verticillata* (FMDBH) for the removal of metal ions from aqueous solution and their application for treating wastewater does not exist. Therefore, the aim of the present research study was to investigate the potential of FMDBH in removing metal ions (Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+}) from aqueous solutions as well as from wastewater. Various mathematical models related to biosorption isotherm, kinetics, and thermodynamic parameters were utilized for the better perception of the overall biosorption process. Moreover, these models were also used to compare the biosorption capacity of FMDBH with non-modified/raw *H. verticillata* dried biomass (RB). Batch experiments for the present study were performed at Pollution Ecology Research Laboratory (PERL), Centre of Advanced Study in Botany, Banaras Hindu University, Varanasi, India, from July 2013 to January 2014.

Materials and methods

Wastewater sample collection and analysis

Representative wastewater samples were collected from the effluent channel of Bhagwanpur sewage treatment plant, Varanasi, India, in polytetrafluoroethylene (PTFE) bottles (pre-washed with acid), preserved and transported to the laboratory in ice boxes. Concentration of metal ions in samples (Table 1) was analyzed by using standard protocols (APHA 2012).

Biosorbent preparation

The live biomass of *H. verticillata* was collected from the Agro-farm pond of the Banaras Hindu University, Varanasi, India. The biomass was washed under the running tap water followed by ultrapure water (Milli-Q) several times

Table 1 Concentration of Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} in wastewater samples with their maximum effluent discharge standards

Metal ions	Concentration in wastewater samples (mg L^{-1})	[A]EPA (2004) (mg L^{-1})	[B]BIS specification IS 10500 (mg L^{-1})
Cu^{2+}	4.64	0.25	3.00
Zn^{2+}	3.75	1.00	5.00
Pb^{2+}	1.34	–	0.10
Cd^{2+}	3.28	0.01	2.00

[a] EPA (Environmental Protection Agency) (2004), USA

[b] BIS (Bureau of Indian Standard Specification), IS 10500 (1993), India

to remove dust particles adhered to its surface, dried in sunlight for 2 days followed by oven drying at 70 °C for 48 h. After drying, the biomass was crushed and sieved through mesh to get particles below 1 millimeter in size. The dried biomass of *H. verticillata* (biosorbent) was further subjected to Fenton modification process.

Fenton modification of biosorbent

Fenton modification of dried biomass was carried out by the method as illustrated elsewhere (Argun and Dursun 2008). After determining the optimum Fe^{2+}/H_2O_2 ratio, pH, temperature, and contact time, 20 mg of dried biomass of *H. verticillata* was added into 500-ml Erlenmeyer flask containing 250 ml Fenton's reagents and agitated on rotatory shaker at 250 rpm for 60 min. After agitation, the solution was filtered and the dried biomass was washed with ultrapure water followed by oven drying at 80 °C for 2 h.

Metal solutions

Analytical reagent grade chemicals were used in the present research study. Metal stock solutions (1,000 mg L^{-1}) of Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} were prepared by dissolving known quantity of $Cu(NO_3).2.5H_2O$, $ZnSO_4.7H_2O$, $PbNO_3$, and $CdCl_2.0.5H_2O$, respectively, in ultrapure Milli-Q water. Standard solutions of different concentrations were finally prepared by diluting the stock solutions. 0.1 M NaOH and HNO_3 were used for the pH adjustment.

Characterization of FMDBH

Fourier transform infrared spectroscopy (FT-IR)

The FT–IR spectra of RB, FMDBH before and after biosorption were obtained using PerkinElmer Spectrum version 10.03.05 to determine the alteration in peaks of functional groups of the biosorbent.

Scanning electron microscopy (SEM)–energy-dispersive X-ray spectroscopy (EDX) analysis

The alteration in surface morphology and elemental composition of FMDBH before and after the biosorption process was analyzed by using SEM coupled with EDX (FEI QUANTA 200 F).

Experimental design

Biosorption batch experiment

Biosorption batch experiments were performed in Erlenmeyer flask previously cleaned with dilute nitric acid, containing 250 ml solution of metal ions at the desired pH of 5. 250 mg of RB and FMDBH was then added to the flask separately and agitated at 250 rpm for 60 min. After agitation, the solution was centrifuged at 2,000 rpm for 10 min and finally filtered by cellulose acetate membrane (0.45 µm). Atomic absorption spectrophotometer was employed for the measurement of initial and final metal ions concentration. All the batch experiments including the effect of pH, initial metal ion concentration, and contact time on biosorption were performed in triplicate to avoid errors in measurement, and the results were reported as the mean values of replicates in the subsequent sections. The standard deviation from the means of all batch experiments was within 3 %. Hence, mean values were presented along with the error bars of ±3 % in the graphs, all through the manuscript. Under the similar experimental conditions, metal ions-free and dried biomass-free blanks were also carried out as controls. The quantity of metal ion biosorbed onto raw biomass (RB) and Fenton modified dried biomass of *H. verticillata* (FMDBH) was calculated by using subsequent mass balance expression (Davis et al. 2000):

$$Q_{\mathrm{MA}} = \frac{V_{\mathrm{s}}(C_i - C_f)}{W_{\mathrm{DB}}}$$

where Q_{MA} is the quantity of metal biosorbed (mg g^{-1}), V_{S} is the volume of solution (L), $C_{\mathbf{i}}$ and C_{f} are initial and final metal ion concentration (mg L^{-1}), and W_{DB} is the weight of dried biomass (g). The removal efficiency of metals (RE_{M}) onto RB and FMDBH was calculated by using the following equation (Miretzky and Munoz 2011):

$$RE_{\mathrm{M}} = \frac{(C_{\mathrm{i}} - C_{\mathrm{f}})}{C_{\mathrm{f}}} \times 100$$

Performance of batch reactor in treating secondary effluent

Performance of batch reactor in treating secondary effluent containing metal ions collected from the effluent channel of Bhagwanpur sewage treatment plant was assessed by utilizing wastewater samples instead of metal solutions under same experimental conditions.

Results and discussion

Characterization of biosorbent

The average particle size of the RB and FMDBH was analyzed using Malvern Matersizer 2000. The FT–IR spectral characteristics of RB, FMDBH before and after biosorption are given in Fig. 1. After Fenton modification of biomass and biosorption process, shift in different peaks was observed, suggesting the combination of functional groups and metal ions (Baral et al. 2009; Huang et al.

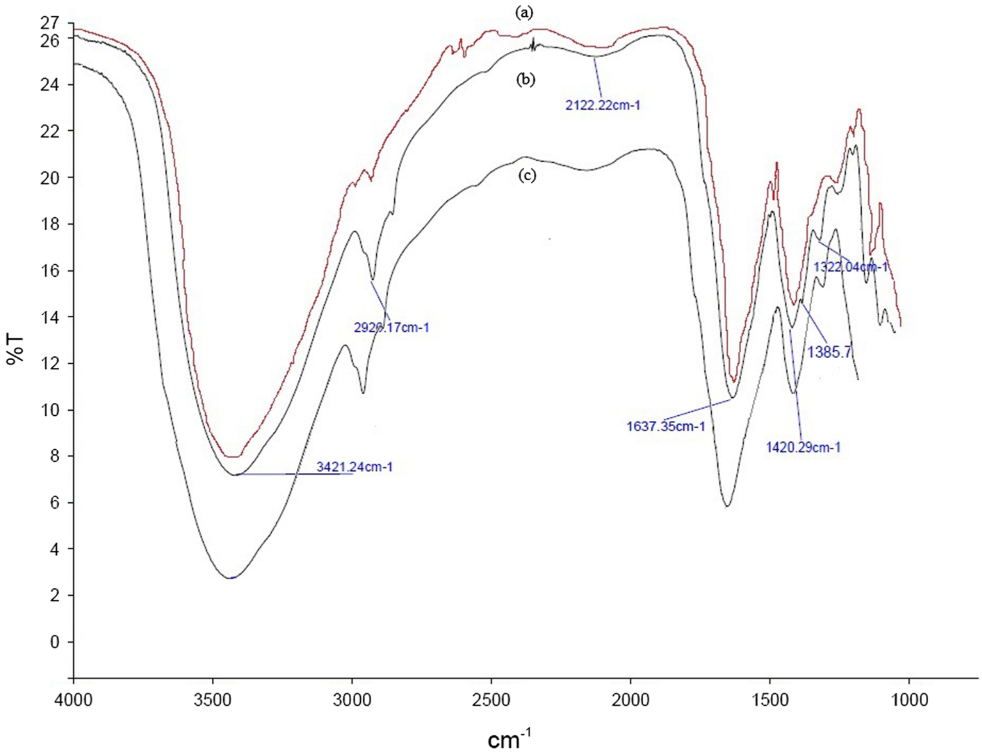


Fig. 1 FT–IR spectra of *a* RB *b* FMDBH before biosorption *c* FMDBH after biosorption

2010). SEM images of FMDBH are shown in Fig. 2a, b. It can be observed from the figures that the surface was rough before biosorption process, which becomes smooth after the process. EDX images of FMDBH before and after biosorption are given in Fig. 2a, b. The weight percent of the Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} ions on the surface of Fenton modified biosorbent before biosorption were observed to be 0.41, 0.43, 0.38, and 0.35 %, respectively. But after the process of biosorption, significant increase in the weight percent of Cu^{2+} (47.53 %), Zn^{2+} (41.82 %), Pb^{2+} (43.76 %), and Cd^{2+} (43.15 %) ions was observed. This clearly confirms the biosorption of metal ions on the surface of FMDBH. Moreover, the reduction in the peaks of potassium and sodium suggests (Fig. 2a, b) that there might be the involvement of an ion-exchange mechanism in the process (Huang et al. 2010).

Effect of Fenton oxidation process parameters on modification of biosorbent

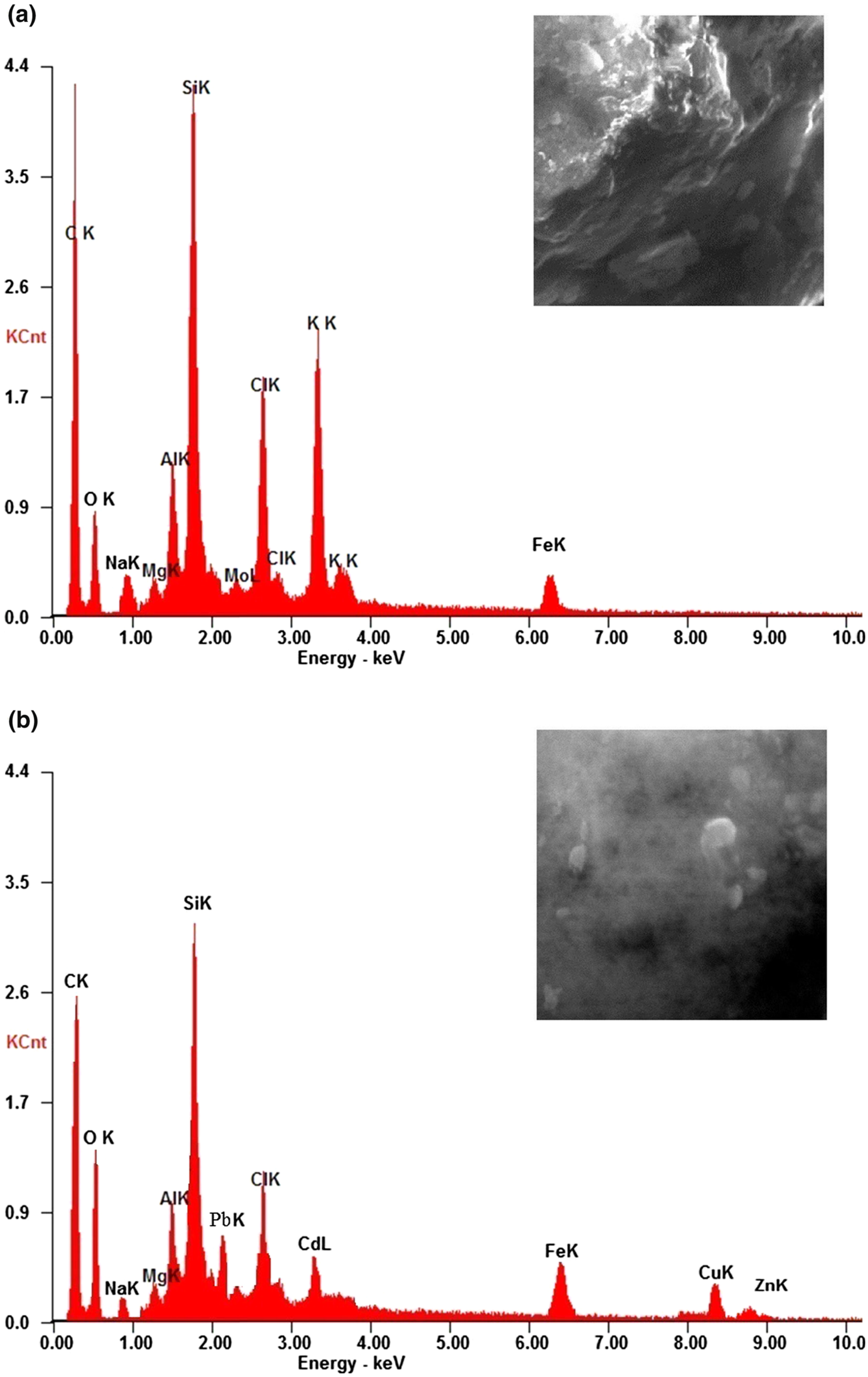
The effectiveness of the overall Fenton oxidation process in terms of hydroxyl radical formation and utilization is governed by process parameters, viz., pH, temperature, Fe^{2+}/H_2O_2 ratio, and contact. Therefore, it becomes necessary to optimize these parameters. For the modification process, the removal of Cu^{2+} ions was considered and results were applied in all the following batch experiments. The effect of pH on the Fenton modification of *H. verticillata* dried biomass was evaluated by the efficiency of Cu^{2+} removal (Fig. 3a). The maximum biosorption of metal ion was achieved at pH value 3.5 (Fig. 3a). At pH values <3.5, the excess production of H^+ ion suppresses the hydroxyl radical formation. On the other hand, generation of metal hydroxides at pH values >4 hinders the whole catalytic process suppressing the formation of hydroxyl radical (Miretzky and Munoz 2011). Thus, it can be concluded that for the modification of biosorbent, the optimum pH value was 3.5. Since there was no significant effect on the biosorption of metal ions with rise in temperature from 20 to 70 °C (Fig. 3b), therefore room temperature was selected as an optimum temperature for the modification process. The optimum biosorbent dose for modification process was observed to be 80 g L^{-1} (Fig. 3c). Also, Fe^{2+}/H_2O_2 ratio of 0.01 (w/w) was found to be optimum for the process. Figure 3d suggests that 60-min contact time was optimum for the modification reaction.

Biosorption batch studies

Effect of initial metal solution pH on biosorption

Earlier studies have shown that the pH of the metal solution greatly influences the metal ion solubility, counter ion concentration present on the biosorbent surface, and the extent of ionization of biosorbate (Gupta

Fig. 2 SEM–EDX image of FMDBH **a** before biosorption **b** after biosorption



et al. 2010). Thus, the effect of initial metal solution pH on the biosorption process using RB and FMDBH was studied. In order to examine the effect, the pH range was varied from 1 to 7. For RB, the optimum pH value was found to be 5.2 for Cu^{2+}, 4.5 for Zn^{2+}, 5.0 for Pb^{2+}, and 6.0 for Cd^{2+}, whereas the optimum biosorption capacity

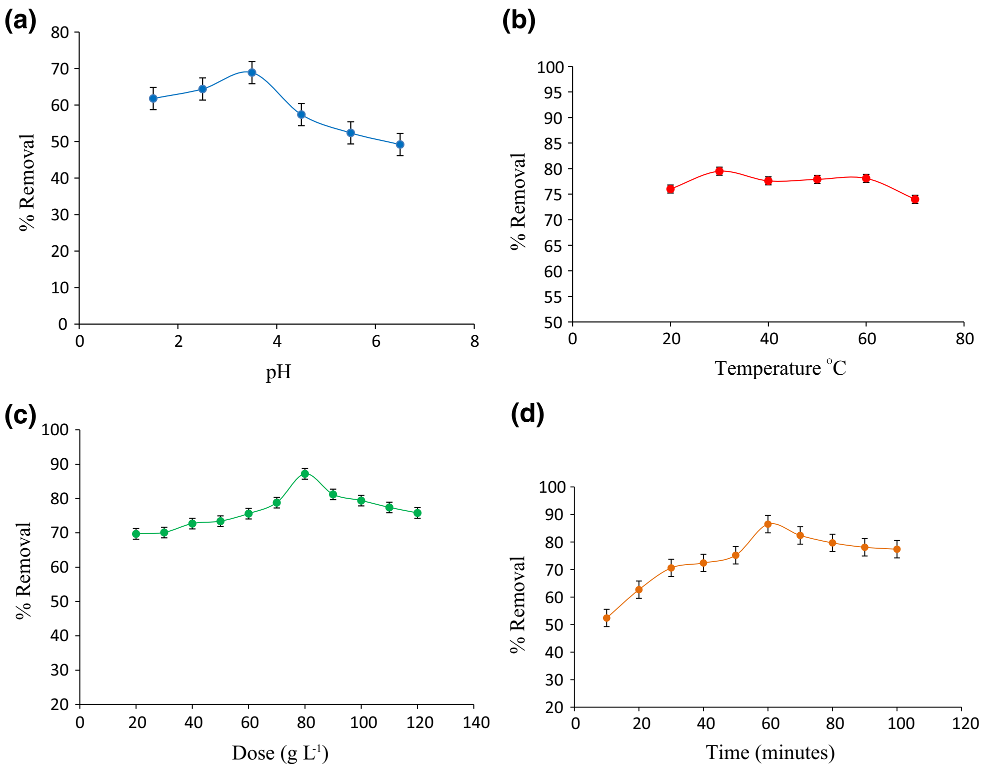


Fig. 3 Effect of **a** pH **b** temperature **c** dose **d** contact time on the Fenton modification process

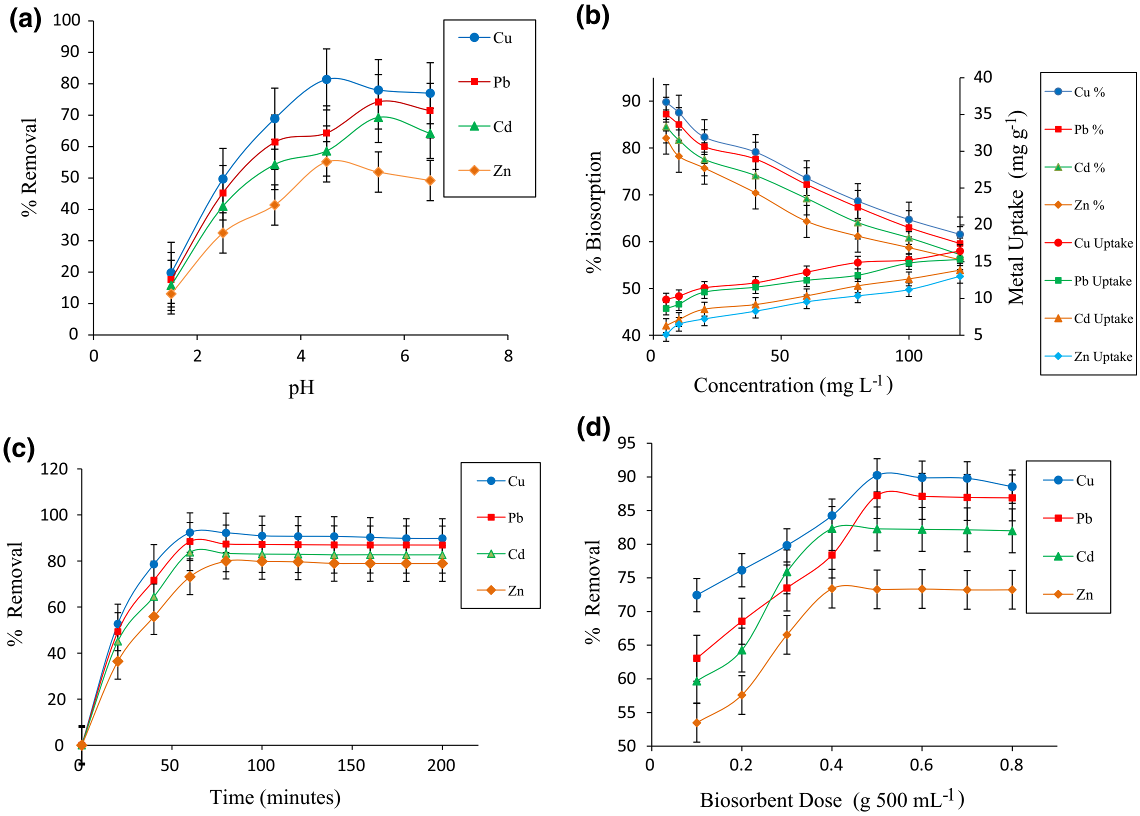


Fig. 4 Effect of **a** pH **b** initial metal ion concentration **c** time **d** biosorbent dose on the removal of metal ions using FMDBH

of metals using FMDBH was observed at pH value 4.5 for Cu^{2+} and Zn^{2+} and pH 5.5 for Pb^{2+} and Cd^{2+} (Fig. 4a). Sharp decrease in biosorption capacity was observed below pH 2.5. This might be because of the development of repulsive force due to the protonation of active binding sites which restricts the binding of metal ions under acidic condition (Aldor et al. 1995; Gupta et al. 2000; Hawari and Mulligan 2006). Similarly, formation of metal hydroxides at pH values above neutral results in the precipitation of metal ions from the solution, thereby decreasing the overall biosorption capacity (Hawari and Mulligan 2006; Gupta et al. 2010).

Effect of initial metal ion concentration on biosorption

The efficiency of Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} biosorption by FMDBH at different concentrations was examined at the most suitable experimental conditions. The results are shown in Fig. 4b. From figure, it is clear that as the metal concentration increases, Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} uptake by FMDBH increases from 9.86 to 16.45 mg g^{-1}, 8.63 to 15.32 mg g^{-1}, 6.32 to 13.85 mg g^{-1}, and 5.11 to 13.01 mg g^{-1}, respectively, but the biosorption percentage of Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} ions decreases from 89.81 to 61.55 %, 87.23 to 59.60 %, 84.62 to 57.24 %, and 82.11 to 56.12 %, respectively. The increase in metal uptake could be attributed to the differences in concentration gradient across the two phases. Decrease in biosorption percentage might be due to the lack of availability of more active sites and sufficient surface area to hold more metal ions present in the solution (Kumar et al. 2006; Gupta et al. 2010). Similarly, the effect of initial metal ion concentration on biosorption of Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} using RB showed the similar trend but is less efficient as compared to FMDBH.

Effect of contact time on biosorption

The effect of contact time on the biosorption of Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} ions using FMDBH is presented in Fig. 4c. Throughout the experiment, the other parameters, viz., pH (4.5 and 5.5), temperature (30 °C), initial metal concentration (10 mg L^{-1}), and biosorbent dose (0.5 g 500 mL^{-1} and 0.4 g 500 mL^{-1}), were kept constant. It can be concluded from the figure that the biosorption process was very fast initially for a period of 20 min thereafter the process becomes slow and reached the equilibrium at 60 min (for Cu^{2+}, Pd^{2+}, and Cd^{2+} removal) and 80 min (for Zn^{2+} removal) using FMDBH. Very fast process of biosorption initially could be attributed to the availability of more free surface active sites. Once these sites are blocked, the intra-particle diffusion of biosorbate takes place, which might be responsible for the slower biosorption process at the later stage (Baral et al. 2009). For biosorption using RB, the optimum contact time was found to be 80 min for Cu^{2+} removal, 90 min for Pb^{2+} and Cd^{2+} removal, and 120 min for Zn^{2+} removal.

Effect of biosorbent dose

The effect of varying biosorbent dosage on the removal efficiency of Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} using FMDBH is shown in Fig. 4d. The percentage of metal removal increased from 72.44 to 90.24 % for Cu^{2+}, from 63.06 to 87.24 % for Pb^{2+}, from 59.67 to 82.34 % for Cd^{2+}, and from 53.47 to 73.40 % for Zn^{2+} with increase in biosorbent dose from 0.1 to 0.8 g 500 mL^{-1} with adsorbate concentration of 10 mg L^{-1}. The increase in biosorption of metal ions with increasing biosorbent dosage can be attributed to the rise in overall surface area due to increase in more active sites on the biosorbent. The optimum biosorbent dose was found to be 0.5 g 500 mL^{-1} for Cu^{2+} and Pd^{2+} and 0.4 g 500 mL^{-1} for Cd^{2+} and Zn^{2+} ions. With further increase in biosorbent dose beyond the optimum level, the removal efficiency of metal ions remained almost constant, this may be due to the reaching of equilibrium state at given experimental conditions (Baral et al. 2009). Likewise, for RB, the optimum biosorbent dose was found to be 0.7 g 500 $mL^{-1}$for Cu^{2+} and Zn^{2+} ions and 0.5 g 500 mL^{-1} for Pd^{2+} and Cd^{2+} ions.

Effect of particle size

Particle size is one of the main parameters which influence the biosorption capacity. The effect of varying average particle size of RB and FMDBH on biosorption was studied with three different particle sizes (100, 250, and 500 μm), keeping other parameters constant. For FMDBH, the amount of metal ion biosorbed at equilibrium increased from 11.42 to 19.67 mg g^{-1}, 7.84 to 12.14 mg g^{-1}, 9.55 to 15.90 mg g^{-1}, and 8.26 to 15.22 mg g^{-1} for Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} ions, respectively, with decrease in particle size from 500 μm to 100 μm. Similarly, for RB, the metal uptake increases with decrease in particle size (8.34 to 10.63 mg g^{-1} for Cu^{2+}, 5.38 to 8.66 mg g^{-1} for Zn^{2+}, 5.25 to 8.52 mg g^{-1} for Pb^{2+}, 7.16 to 10.88 mg g^{-1} for Cd^{2+}). Similar behavior was also reported by other researchers for different metals using powdered stem of *Arundo donax* (Song et al. 2014), dried prickly pear cactus (*Opuntia ficus indica*) cladodes (Barka et al. 2013), pine cone shell (Blazquez et al. 2012), defatted *Carica papaya* seeds (Gilbert et al. 2011).

Table 2 Langmuir and Freundlich isotherm constants and correlation coefficients of isotherm models

Metal ions	Treatment	Langmuir			Freundlich		
		Q_{max}	b	R^2	K_f	$1/n$	R^2
Cu^{2+}	Raw biomass	27.86	0.108	0.896	18.35	0.624	0.922
	Fenton modified biomass	106.23	0.459	0.996	22.16	0.964	0.999
Zn^{2+}	Raw biomass	50.66	0.156	0.858	14.76	0.523	0.879
	Fenton modified biomass	109.32	0.521	0.982	19.75	0.826	0.989
Pb^{2+}	Raw biomass	32.14	0.122	0.877	17.13	0.573	0.903
	Fenton modified biomass	108.56	0.498	0.992	21.47	0.949	0.996
Cd^{2+}	Raw biomass	40.43	0.135	0.865	15.91	0.556	0.894
	Fenton modified biomass	110.78	0.566	0.988	20.33	0.872	0.995

Biosorption isotherm studies

Single-component system

The equilibrium biosorption data obtained from the batch study were modeled using Langmuir (Langmuir 1916) and Freundlich (Freundlich 1906) isotherm model. Langmuir model is expressed by equation as follows:

$$Q_e = \frac{Q_{max} \times b \times C_e}{1 + b \times C_e}$$

where Q_e is the amount of metal ions biosorbed (mg g^{-1}), Q_{max} is the maximum biosorption capacity (mg g^{-1}), C_e is the metal ions concentration in the solution at equilibrium (mg L^{-1}), and b is the constant related to the energy or net enthalpy of biosorption (L mg^{-1}). In order to fit the experimental data, the linear form of Langmuir expression was used, which is described by the equation given as follows:

$$\frac{1}{Q_e} = \frac{1}{Q_{max}} + \frac{1}{Q_{max} \times b} \times \frac{1}{C_e}$$

The Langmuir isotherm fitting parameters and correlation coefficient (R^2) values for different metal ions biosorption onto raw (RB) and Fenton modified biosorbent (FMDBH) are shown in Table 2. Langmuir Q_{max} values as obtained were 27.86, 50.66, 32.14, and 40.43 mg g^{-1} for RB and 106.23, 109.32, 108.56, and 110.78 mg g^{-1} for FMDBH for Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+}, respectively. This clearly shows that the Fenton modification of the biomass significantly enhanced the biosorption capacity.Freundlich model is expressed by the equation

$$Q_e = K_f \times C_e^{1/n}$$

where K_f (mg g^{-1}) is the Freundlich constant or biosorption capacity and n denotes the biosorption intensity. In order to fit the experimental data, the linearized Freundlich expression was utilized, which is described by the equation given as follows:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e$$

Freundlich isotherm constants and correlation coefficients (R^2) values are given in Table 2. The value of K_f increased after the Fenton modification process, which shows that modification process enhances the biosorption capacity. The percentage increase in the biosorption capacity after modification process follows the sequence: $Cu^{2+} > Pb^{2+} > Cd^{2+} > Zn^{2+}$. The elevated affinity of the modified biomass for metal ions was also imitated by $1/n$ values. The value of $1/n < 1$ shows the favorable biosorption. Both the isotherm models fit the experimental data reasonably well, but after comparing R^2 values, it can be observed that the Freundlich isotherm model fits the experimental data better than the Langmuir model.

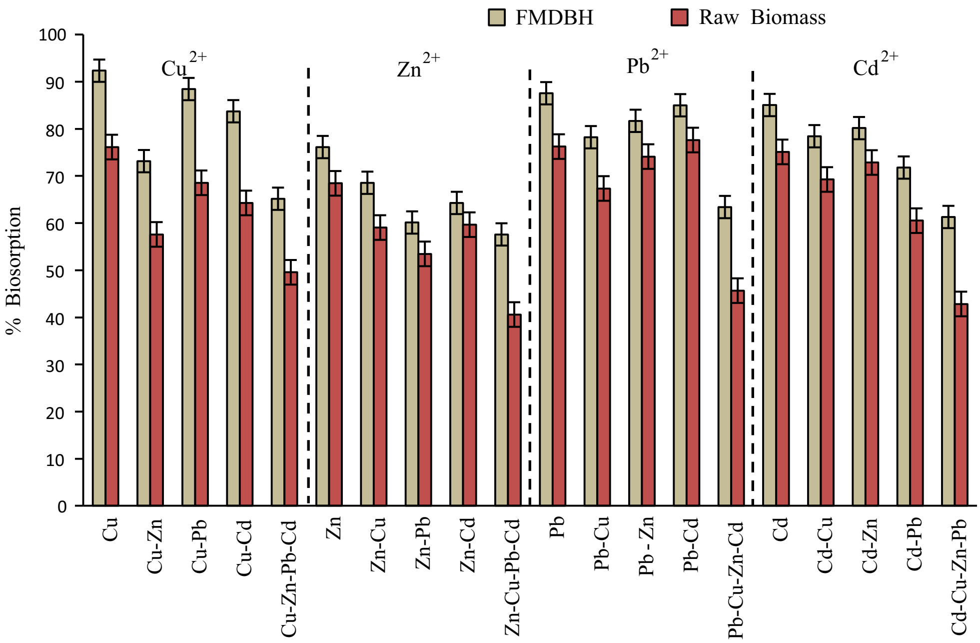
Multi-component system

For multi-metal system studies, RB and FMDBH were suspended separately in 50 ml of multi-metal solution containing 10.0 mg $L^{-1}$of each metal ion (Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+}) at pH 5. The results are shown in Fig. 5. The biosorption capacities of both RB and FMDBH for multi-metal solution were relatively lower in comparison with the single-metal solution. This may be due to differences in ionic charge, radii, and electrode potential of different metals which affects the overall multi-metal ions biosorption (Saygideger et al. 2005). Further, the biosorption capacity of FMDBH for multi-metal solution was better than the RB, suggesting the increase in biosorption capacity after Fenton modification process.

Biosorption kinetic studies

In the present research study, two different biosorption kinetic models, viz, pseudo-first-order and pseudo-second-order models, were employed to the experimentally obtained biosorption data. The biosorption kinetic studies were performed separately for RB and FMDBH. The

Fig. 5 Effect of single- and multi-metal ions on biosorption capacities of FMDBH and raw biomass



pseudo-first-order (Lagergren 1898) rate equation which is expressed as follows:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1 t}{2.303}$$

was used to fit the experimental data, where Q_e (mg g^{-1}) and Q_t (mg g^{-1}) are the amount of metal ions biosorbed at equilibrium and at time *t*, respectively. k_1 ($\min^{-1}$) is the biosorption rate constant. The values of k_1 and Q_e (cal.) can be obtained from the slope and intercept of the plot between log (Q_e–Q_t) and t. The biosorption rate constant (k_1) and their corresponding correlation coefficient (R^2) values is given in the Table 3. As it can be observed from the Table 3, the calculated values of $\mathbf{Q_e}$ (cal.) obtained from the intercept of plot greatly differ from the experimental values of $\mathbf{Q_e}$. Moreover, the R^2 values were relatively low for all the studied metal ions. Hence, it can be concluded that the pseudo-first-order model cannot be appropriate to predict the biosorption reaction kinetics in this case. As a consequence of the non-suitability of pseudo-first-order rate equation, the experimental data were further analyzed using pseudo-second-order model. The linear form of the pseudo-second-order model is expressed as (Ho and McKay 1999):

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2}$$

where Q_e (mg g^{-1}) and Q_t (mg g^{-1}) are the amount of metal ions biosorbed at equilibrium and at time *t*, respectively. k_2 (g mg^{-1} $\min^{-1}$) is the biosorption rate constant and *t* is the contact time (min). The values of k_2 and Q_e (cal.) can be obtained from the slope and intercept of the plot between t/Q_t and *t*. The rate constant k_2, the calculated values of Q_e (cal.), and their corresponding correlation coefficient (R^2) values are shown in the Table 3. The calculated values of Q_e (cal.) determined from the intercept of plot matches with the experimental values of Q_e. Furthermore, the correlation coefficient (R^2) values were higher for all the metal ions studied. Thus, it can be concluded that the pseudo-second-order rate equation fits the experimental data relatively better than the pseudo-first-order rate equation, supporting the postulation that the chemisorption may be the rate-limiting step in this case.

Comparative studies

Comparison of raw and Fenton modified *H. verticillata* dried biomass with other adsorbents or biosorbents for Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} ions removal was presented in Table 4. From the table, it can be concluded that the FMDBH is much more efficient in removing Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} ions from wastewater compared to other adsorbents or biosorbents reported earlier. Although many bacterial biosorbents have shown their potential (Table 4) for metal removal from wastewater, they present some disadvantages such as requirement of centrifugation for biomass concentration stage and chemical agents for immobilization process for the production of granulated or agglomerated products. Both are very expensive processes that demand a high energetic cost and utilize toxic chemical products or environmental contaminants. Moreover, the other difficulties are production and transportation of

Table 3 Fitting parameters for pseudo-first-order and pseudo-second-order along with their correlation coefficients (R^2) values

Metal ions	Treatment	Temperature (K)	Q_e (mg g^{-1}) experimental	Pseudo-first-order model			Pseudo-second-order model		
				K_1 (min^{-1})	Q_e (mg g^{-1})	R^2	K_2(g mg^{-1} min^{-1})	Q_e (mg g^{-1})	R^2
Cu^{2+}	Raw biomass	293	45	0.1267	29	0.745	0.0728	46	0.932
		303	42	0.0745	26	0.667	0.0956	42	0.999
		313	41	0.0785	24	0.632	0.0945	40	0.969
	Fenton modified biomass	293	78	0.0582	58	0.768	0.0778	78	0.995
		303	75	0.0680	61	0.792	0.0834	72	0.992
		313	71	0.0459	55	0.831	0.0952	73	0.984
Zn^{2+}	Raw biomass	293	37	0.0521	30	0.714	0.0743	39	0.976
		303	32	0.0478	26	0.798	0.0690	32	0.988
		313	31	0.0715	24	0.663	0.0561	30	0.969
	Fenton modified biomass	293	59	0.0638	47	0.827	0.0814	59	0.997
		303	57	0.0587	44	0.705	0.0674	57	0.994
		313	55	0.0668	39	0.749	0.0755	53	0.932
Pb^{2+}	Raw biomass	293	43	0.1024	31	0.803	0.0429	46	0.999
		303	40	0.1035	30	0.796	0.0530	41	0.969
		313	38	0.0953	26	0.751	0.0468	37	0.978
	Fenton modified biomass	293	69	0.0732	49	0.711	0.0542	68	0.991
		303	68	0.0581	45	0.725	0.0567	68	0.999
		313	68	0.0554	48	0.818	0.0535	66	0.987
Cd^{2+}	Raw biomass	293	41	0.0916	25	0.682	0.0764	41	0.983
		303	40	0.0632	29	0.667	0.0854	42	0.977
		313	35	0.0805	27	0.694	0.0837	34	0.982
	Fenton modified biomass	293	68	0.0457	46	0.708	0.0698	68	0.993
		303	64	0.0428	41	0.738	0.0871	63	0.995
		313	61	0.0586	39	0.712	0.0982	60	0.992

inoculants to the decontamination site as this is restricted by the low stability of the inoculant culture and their requirement in huge volume (Cotoras and Viedma 2011). Since these kinds of disadvantages are not associated with current method suggested for the removal of metal ions form wastewater, it can be concluded that the current method is better, economically cheaper, and environment-friendly than the aforesaid biosorbent as this has already been discussed previously in the introduction section.

Thermodynamic studies

Experiments were carried out at 293, 303, and 313 K to examine the thermodynamic characteristics of metal ions biosorption process using only FMDBH. To assess the feasibility of the process, different thermodynamic parameters were estimated using the equation given as follows:

$$\Delta G^{\mathrm{o}} = -RT\ \ln K_{\mathrm{o}}$$

where ΔG^{O} is standard free energy change, R is the universal gas constant (8.314 J/mol/K), T is the absolute temperature, and K_{o} is the thermodynamic constant. K_{o} values can be determined by plotting a graph between ln Q_e/C_e versus Q_e at different temperatures, where Q_e is the amount of metal ions biosorbed by FMDBH and C_e is the metal ions concentration in the solution at equilibrium. The change in enthalpy ($\triangle H^{\mathrm{O}}$) and entropy ($\triangle S^{\mathrm{O}}$) was determined by the following equation:

$$\ln K_{\mathrm{o}} = \frac{\Delta S^{\mathrm{o}}}{R} - \frac{\Delta H^{\mathrm{o}}}{RT}$$

The change in enthalpy ($\triangle H^{\mathrm{O}}$) and entropy ($\triangle S^{\mathrm{O}}$) was estimated from the slope and intercept of the plot between ln K_{o} versus 1/T. With increase in temperature from 293 to 313 K, the value of Gibbs free energy decreases from −3.63 to −7.45, −1.56 to −6.21, −3.92 to −5.66, and −2.58 to −4.96 for Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} ions, respectively (Table 5). This might be due to increase in the degree of protonation of carboxylic and amine groups on the surface of FMDBH with rise in temperature (Biesuz et al. 1997; Donais et al. 1999). The change in enthalpy ($\triangle H^{\mathrm{O}}$) and entropy ($\triangle S^{\mathrm{O}}$) was found to be −68.46, −59.42, −65.18, and −61.83; and −0.344, −0.198, −0.384,

Table 4 Comparison of raw biomass (RB) and Fenton modified *H. verticillata* dried biomass (FMDBH) with other adsorbent or biosorbent

Biosorbent	Biosorption capacity (mg g^{-1})				References
	Cu^{2+}	Zn^{2+}	Pb^{2+}	Cd^{2+}	
Dairy manure compost	–	–	95.31	–	Zhang (2011)
Pseudomonas putida CZ1	15.8	17.7			Chen et al. (2005)
Pseudomonas putida		6.9	56.2		Pardo et al. (2003)
Bacillus circulans				26.5	Yilmaz and Ensari (2005)
Thiobacillus ferrooxidans		82.6			Celaya et al. (2000)
Marine green algae (*Ulva fasciata* sp.)	–	13.5	–	–	Kumar et al. (2007)
Sulfured orange peel		80	164	–	Liang et al. (2011)
Saw dust	6.58	–	21.05	–	Li et al. (2007)
Activated carbon from sea-buckthorn stones	–	–	25.91	–	Mohammadi et al. (2010)
Spirogyra neglecta	40.83	31.51	90.19	27.95	Singh et al. (2007)
Peanut shell	–	–	38.91	–	Tasar et al. (2014)
Carrot residue	–	29.61	–	–	Nasernejad et al. (2005)
Pine cone activated carbon	–	–	27.53	–	Momcilovic et al. (2011)
Azadirachta indica bark	–	33.49	–	–	King et al. (2008)
Penicillium citrinum (immobilized biomass)	25	–	–	–	Verma et al. (2013)
Jute fibers treated with H_2O_2	–	8.02	–	–	Shukla and Pai (2005)
Lemna minor L. (Alkali-treated)	69	–	–	83	Saygideger et al. (2005)
Pithophora odeogonia	23.08	8.98	71.13	13.07	Singh et al. (2007)
Cashew nut shell	–	–	17.82	–	Kumar (2014)
Pleurotus ostreatus	–	–	–	4.05	Tay et al. (2011)
RB	27.86	50.66	32.14	40.43	Present study
FMDBH	106.23	109.32	108.56	110.78	Present study

Table 5 Thermodynamic parameter for biosorption of Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+}

Metal ions	Temperature (K)	ln K_o	ΔG^O (KJ mol^{-1})
Cu^{2+}	293	45	−3.63
	303	42	−5.84
	313	41	−7.45
Zn^{2+}	293	37	−1.56
	303	32	−4.34
	313	31	−6.21
Pb^{2+}	293	43	−3.92
	303	40	−4.27
	313	38	−5.66
Cd^{2+}	293	41	−2.58
	303	40	−3.63
	313	35	−4.96

Table 6 Percentage removals of metal ions from wastewater using RB and FMDBH

Metal ions	Concentration (mg L^{-1}) before biosorption	% Removal after raw biomass biosorption	% Removal after FMDBH biosorption
Cu^{2+}	4.64	74 %	96 %
Zn^{2+}	3.75	67 %	84 %
Pb^{2+}	1.34	71 %	92 %
Cd^{2+}	3.28	71 %	89 %

and −0.275 for Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} ions, respectively. Thus, it can be concluded that the biosorption process using FMDBH was spontaneous, chemically governed and exothermic in nature. Similar results were also reported by the other researchers (Huang et al. 2010).

Performance of batch reactor in treating wastewater

Since the main aim of the biosorption technology was to treat the wastewater laden with several metal ions, the batch experiments were also carried out by utilizing wastewater samples instead of metal solutions under same experimental conditions. Significant increase in removal efficiency of Cu^{2+} (from 74 to 96 %), Zn^{2+} (from 67 to 84 %), Pb^{2+} (71–92 %), and Cd^{2+} (71–89 %) ions were observed after the modification of biosorbent as compared to RB (Table 6).

Conclusion

In order to enhance the biosorption capacity of *H. verticillata* dried biomass, Fenton reagent was used. For Fenton modification process, the optimum values of pH, biosorbent dose, contact time, and Fe^{2+}/H_2O_2 ratio were 3.5, 80 g L^{-1}, 60 min, and 0.01 w/w, respectively. EDX analysis revealed the enhancement in the weight percent of Cu^{2+} (47.53 %), Zn^{2+} (41.82 %), Pb^{2+} (43.76 %), and Cd^{2+} (43.15 %) ions on the surface of FMDBH after the biosorption. Results revealed that the Freundlich isotherm model fits the data better than the Langmuir isotherm model. The biosorption process followed the pseudo-second-order kinetics, suggesting that the chemisorption may be the rate-limiting step in this study. Thermodynamic study showed that the biosorption process was spontaneous and exothermic in nature. In case of multi-metal solution, the biosorption capacity was found to be relatively lower than the single-metal solution. Performance of batch reactor in treating secondary effluent using FMDBH showed significant reduction in the concentration of Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} ions after the biosorption process. Thus, it can be concluded that the FMDBH could be efficiently used to remove metal ions from wastewater.

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