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ORIGINAL PAPER

Desalination of Cd^{2+} and Pb^{2+} from paint industrial wastewater by *Aspergillus niger* decomposed *Citrus limetta* peel powder

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Abstract The present research was conducted to study the column mode (down flow and up flow) of *Aspergillus niger* decomposed *Citrus limetta* peels powder for desalinating Cd^{2+} and Pb^{2+} from synthetic and paint industrial wastewater. The batch mode was carried out to optimize pH, contact time, initial metal ion concentration and adsorbent doses. The column studies (both down flow and up flow) were performed with paint manufacturing industrial wastewater at optimized conditions. The percentage removal, metal uptake capacity and exhaustion time of the column in up flow mode were found to be far better as compared to down flow mode. The value of metal uptake capacity for Cd^{2+} and Pb^{2+} was achieved to be 722 and 596 mg g^{-1} at pH 5.0 and 6.0, respectively, in the first cycle using Thomas model. The comparison of adsorption in single- and multi-metal ion systems showed that *A. niger* decomposed *C. limetta* peels powder have an excellent potential for the removal metal ions from industrial effluents.

Keywords Wastewater · Biomass · Desalination · Thomas model

Introduction

The health status of an individual, a community, or a nation is determined by the interplay and integration of two ecological factors, i.e., internal environment and external environment of human. The increased standard of living is creating a great threat to both environments by generating a huge amount of contaminants. The rapid industrialization is undoubtedly successful but unfortunately adding poisoned rivers, darkened sky and wastelands to our universe. One of the reasons for these worsening is the release of heavy metals (Ni, Zn, Pb, Cd, Hg) into environment. These metals are highly toxic, and their oral exposure thorough potable water can result in significant morbidity and mortality. Hence, it is worthwhile to treat the industrial wastewater to permissible limits before its disposal into natural water bodies.

The wastewater from paint manufacturing industry is rich in Cd^{2+} and Pb^{2+}. Both the metal ions are highly toxic, non-biodegradable, tend to accumulate in the tissues of the human body and have potential to be noxious even at relatively minor levels of exposure. Hence, their removal to an environmentally safe level in a cost effective and environment friendly manner is of greater significance. Biosorption seems to be an eco-friendly technology to clean up contaminated water (Galun et al. 1987; Mullen et al. 1989).

Applications of fungal species for removal of metal ions from aqueous media have been reported by various research groups (Huang and Huang 1996; Zouboulis et al. 1997). The use of dead cells for metal removal has received greater attention compared to living ones as former is non-hazardous and does not demand the growth media (Awofolu et al. 2006). The fungal biomass of *Penicillium* (Galun et al. 1983), *Rhizopus arrhizus* (Tsezos and Velosky 1982; Tobin et al. 1984), *Rhizopus oryzae*, *Aspergillus oryzae* (Huang and Huang 1996) and *Aspergillus niger* (Kapoor et al. 1999; Park et al. 2005; Awofolu et al. 2006) have been used for desalinating the metal ions from

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aqueous solutions, and it has emerged as one of the most promising process.

In this study, *A. niger* was cultivated on *Citrus limetta* peels powder, and the dead biomass obtained was used for desalinating synthetic and paint manufacturing industrial (PMI) wastewater containing Cd^{2+} and Pb^{2+} in column studies. The batch mode was carried out to optimize pH, adsorbent dose, contact time, initial metal ion concentration and temperature so that the same conditions can be used to carry out continuous column studies which is applicable at industrial level for water purification. The characterization of the dead biomass was done using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM)–energy-dispersive X-ray (EDX) analysis. The present research was carried out at MM University, Mullana (Haryana), and Thapar University, Patiala (Punjab), India, from August to December, 2012.

Materials and methods

Preparation of biosorbent

The *C. limetta* peels were collected and washed in running tap water followed by deionized water to remove dirt and other particulate matter. The peels were then dried in the hot air oven at 60 °C for 48 h and finally grinded in a vegetable grinder to obtain the powder. Resulting powder was sieved through a 150-µm mesh-sized sieve, and powder (100.0 g) thus obtained was preserved in a sealed glass container for further use at 4 °C.

Aspergillus niger was obtained from the department of microbiology, MMMC, Mullana (India), and was cultivated in medium of 200.0 mL deionised water and 100.0 g *C. limetta* peel powder at room temperature. After 20 days of incubation, living fungi were killed by autoclaving at 121 °C for 20 min. The biomass thus obtained was washed thrice by using deionized water to remove the residual growth medium and then dried at room temperature. The dried *A. niger* decomposed biomass (ANDB) (88.5 g) was grounded in a mortar and pestle, and sieved through a sieve with 150-µm opening and stored in a desiccator for further uses.

Preparation of stock solutions

The synthetic stock solutions of Cd^{2+} and Pb^{2+} were prepared by dissolving requisite amount of AR grade $CdSO_4$ and $Pb(NO_3)_2$ in deionized water, respectively. The stock solutions were further diluted with deionized water to prepare the solutions of the desired concentrations. The pH of the solutions was adjusted by the addition of appropriate amounts of 0.1 M HCl or 0.1 M NaOH solutions.

Table 1 Different parameters of the PMI wastewater

Parameters analyzed	Results
pH	5.5
Temperature (°C)	30
Total Hardness (mg L^{-1})	870.5
Biological oxygen demand (BOD) (mg L^{-1})	350.25
Chemical oxygen demand (COD) (mg L^{-1})	420.6
Cadmium (mg L^{-1})	205.66
Lead (mg L^{-1})	197.60
Chloride (mg L^{-1})	288.20
Sulfates (mg L^{-1})	290.45
Nitrates (mg L^{-1})	305.42
Turbidity (NTU)	163.0

Analysis of paint manufacturing industrial wastewater

Paint manufacturing industrial wastewater was collected from the paint manufacturing unit situated in Panipat, Haryana (India), and the physicochemical parameters of the same were analyzed (Table 1) using standard analytical methods (Smith 1963). The concentration of heavy metals was analyzed using Atomic Absorption Spectrophotometer (AAS).

Instruments and software

The quantifications of Cd^{2+} and Pb^{2+} in solutions have been performed on AAS AA630, Shimadzu, Japan. The FTIR spectra of the adsorbent have been recorded on Thermo, Nicolet Is10 FTIR spectrophotometer, and field emission SEM was performed on JEOL JSM 6510LV to collect the SEM images. The pH of the solution has been measured by Cyber scan, Eutch pH meter. The orbital shaker incubator made by Metrex scientific instruments has been used for shaking the samples during batch operations at desired temperature and rpm. Software Sigma plot 11 has been used for plotting the graphs and data analysis.

Batch studies

Batch studies were opted merely to optimize the parameters such as pH, adsorbent dose, contact time, initial metal ion concentration and temperature for maximum biosorption of Cd^{2+} and Pb^{2+} from synthetic aqueous solutions. The same parameters were utilized to carry out continuous column studies for actual applicability at industrial scale. Batch experiments for Cd^{2+} and Pb^{2+} biosorption from synthetic solutions were carried out at different pH values (1.0–8.0) by agitating 2.0 g of ANDB in 250-mL screw-cap conical flasks with 100.0 mL of metal ion solutions. The mixtures so obtained were agitated in orbital shaker at 225 agitation speed for 300 min at 30 °C. After every 20 min of agitation, 2.0 mL of the suspensions were centrifuged at 3,000 rpm for 10 min and analyzed by AAS. Further, the effect of initial metal ion concentration (50–250 mg L^{-1}), adsorbent dose (0.5 g–3.0 g/0.1 L), contact time (1–300 min) and temperature (10–40 °C) were studied. The percent of the metal removal (*R %)* was calculated for each experiment using Eq. (1)

$$R(\%) = [(C_i - C_e)/C_i] \times 100 \quad (1)$$

where C_i and C_e were the initial and equilibrium concentrations of metal ions in the solution, respectively. The metal biosorption capacity (q_e) of ANDB for biosorption of Cd^{2+} and Pb^{2+} metal ions at equilibrium was determined using Eq. (2)

$$q_e = \frac{(C_i - C_e)}{M_a} \times V \quad (2)$$

where V is the volume of the solution (L) and M_a is the mass of the biosorbent (g) used.

Point of zero charge

The charge on the biomass surface is a function of pH. Point of zero charge (pHpzc) is the pH at which the charge of the solid surface is zero. About 50 ml of 0.01 M NaCl solutions were taken in 100-mL screw-cap conical flasks. The pH of each solution was adjusted to 2, 4, 6, 8, 10 and 12 by adding 0.1 M HCl or NaOH solutions (Rivera-Utrilla et al. 2001). Then, 0.15 g of ANDB was added to each flask, and the final pH was measured after 48 h of agitation at room temperature. The graph was plotted between the initial pH and the final pH obtained and point of zero charge was determined.

Column studies

Column studies (both down flow and up flow) were conducted in glass columns (internal diameter = 3.0 cm and height 25.0 cm) at room temperature (around 30 °C). Columns of desired bed depth of ANDB were packed over a sheet of glass wool. The pH of the columns was adjusted to pH 5.0 and 6.0 for Cd^{2+} and Pb^{2+}, respectively, by circulating 3.0 L buffer solution of appropriate pH for 12 h at a flow rate of 1.0 mL min^{-1} by means of peristaltic pump.

The effect of bed depths on the breakthrough curves were studied, using bed depths of 8.0, 10.0 and 12.0 cm made by uniform packing of 15.40, 19.25 and 23.10 g of ANDB, respectively. The feed solution of 200 mg L^{-1} initial metal concentration for both metal ions was circulated in down flow and up flow mode with 1.0 mL min^{-1} flow rate. The effect of effluent flow rates (1.0, 3.0 and 6.0 mL min^{-1}) on breakthrough were investigated with columns of 12.0 cm bed depth.

The PMI wastewater was treated by passing through the column 1 (bed depth 12.0 cm) at 5.0 pH with the flow rate of 1.0 mL min^{-1}. Samples were collected at regular time intervals and analyzed for Cd^{2+} and Pb^{2+}. The percolation of the wastewater into the column 1 was stopped on achieving the breakthrough point (BTP). Effluent of the column 1 was readjusted to pH 6.0 using a 0.1 M NaOH solution and then passed through the column 2 up to the BTP. The wastewater was treated till the concentration of both the metal ions fall below the detection limit.

The columns (1 and 2) used for treating PMI wastewater were regenerated using 0.1 M HCl. A mean effluent flow rate of 1.0 mL min^{-1} was maintained, and the effluents from both the columns were collected in 5.0 ml fractions and were analyzed for Cd^{2+} and Pb^{2+}. Thereafter, the column 1 was treated with water adjusted to pH 5.0 and column 2 with water of pH 6.0. The reactivated columns were then used again for another two cycles, for the treatment of the PMI wastewater.

Comparison of biosorption of Cd^{2+} from synthetic and PMI wastewater

The comparison of biosorption of Cd^{2+} in synthetic solution (single-metal ion system) and paint manufacturing wastewater (multi-metal ion system) was studied in columns (bed height 12.0 cm) fed with synthetic solution containing Cd^{2+}alone (C_i = 200.0 mg L^{-1}) and industrial wastewater containing Cd^{2+} and Pb^{2+} at flow rate of 1.0 mL min^{-1} at pH 5.5.

Results and discussion

Characterization of ANDB

Chemical and physical characterization of blank and Cd^{2+}, Pb^{2+} loaded ANDB was carried out with the help of FTIR and SEM instruments.

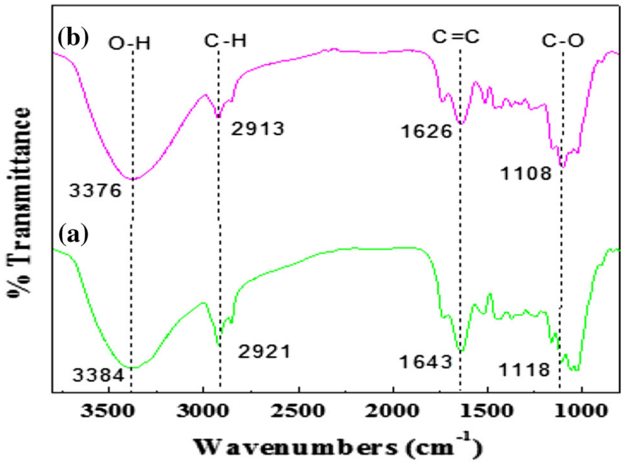

Fig. 1 FTIR spectra of ANDB: *a* before and *b* after Cd^{2+} and Pb^{2+} biosorption

FTIR analysis

The FTIR spectra were recorded before and after biosorption of Cd^{2+} and Pb^{2+} to find out the functional groups involed in metal binding during the metal biosoption. Changes in intensity and shift in position of the peaks were observed in the spectra after Cd^{2+} and Pb^{2+} biosorption on ANDB (Fig. 1). The broad and intense peak at 3,384 cm^{-1} was assigned to the presence of free or hydrogen-bonded O–H groups (from carboxylic acids or alcohols) on the surface of the biosorbent (Singh et al. 2013). The band at 2,921 cm^{-1} indicates symmetric or asymmetric C–H stretching vibration of aliphatic acids. Peak observed at 1,643 cm^{-1} assigned to C=C stretching in aromatic ring. The peak observed at 1,118 cm^{-1} represents C–O bonding of phenols (Jacques et al. 2007). FTIR spectra of Cd^{2+} and Pb^{2+} biosorbed ANDB showed the shift in peaks from 3,384, 2,921, 1,643 and 1,118 cm^{-1} to 3,376, 2,913, 1,626 and 1,108 cm^{-1}, respectively. These observations confirmed the interaction of Cd^{2+} and Pb^{2+} with the biosorbent through –OH and –CO– functional groups.

SEM

Scanning electron microscopy with EDX analysis has been done before and after biosorption of Cd^{2+} and Pb^{2+} on ANDB (Fig. 2). The EDX spectra obtained after biosorption revealed the additional signals of Cd^{2+} and Pb^{2+}, thereby confirming the binding of the metal ions to the surface of the biomass.

Batch studies

The maximum removal of Cd^{2+} and Pb^{2+} by ANDB was obtained at pH 5.0 and 6.0, respectively, as shown in Fig. 3, and a significant decrease in biosorption capacity

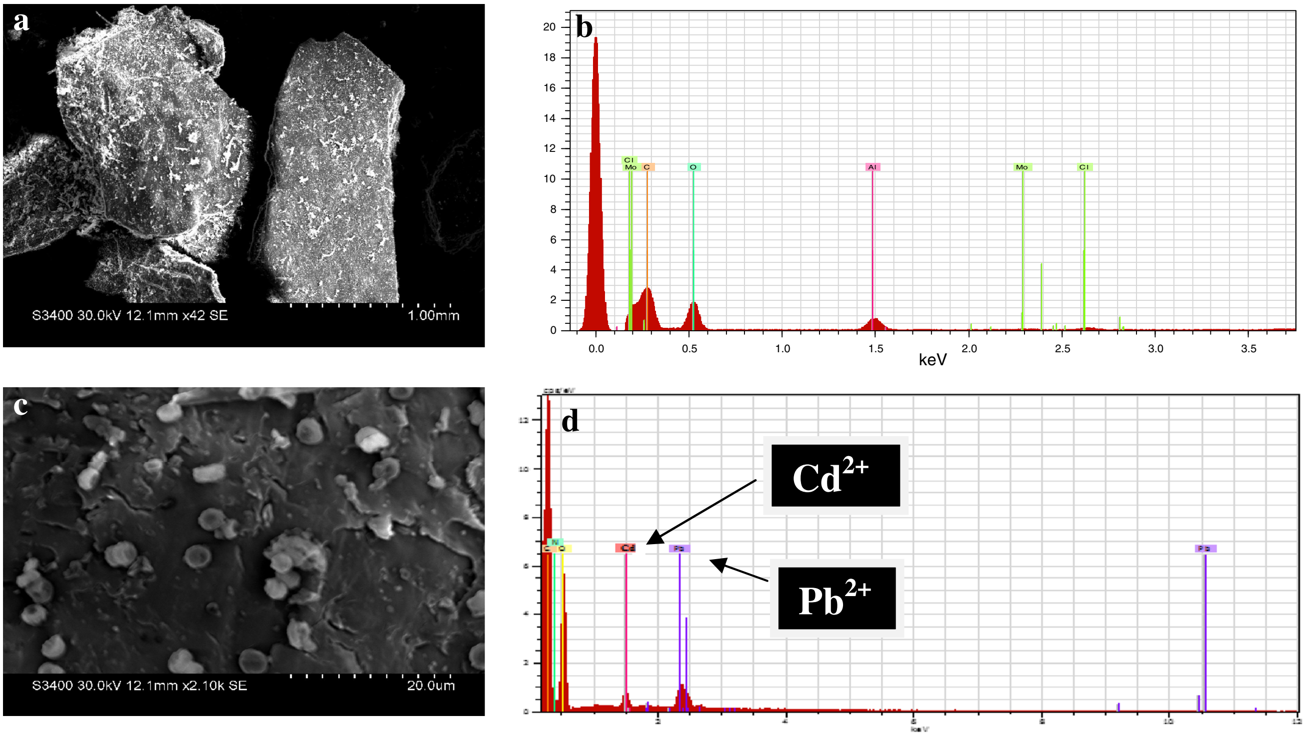

Fig. 2 SEM image of ANDB **a** before and **c** after $Cd^{2+}$and Pb^{2+} biosorption, and respective EDX is shown in **b** and **d** images

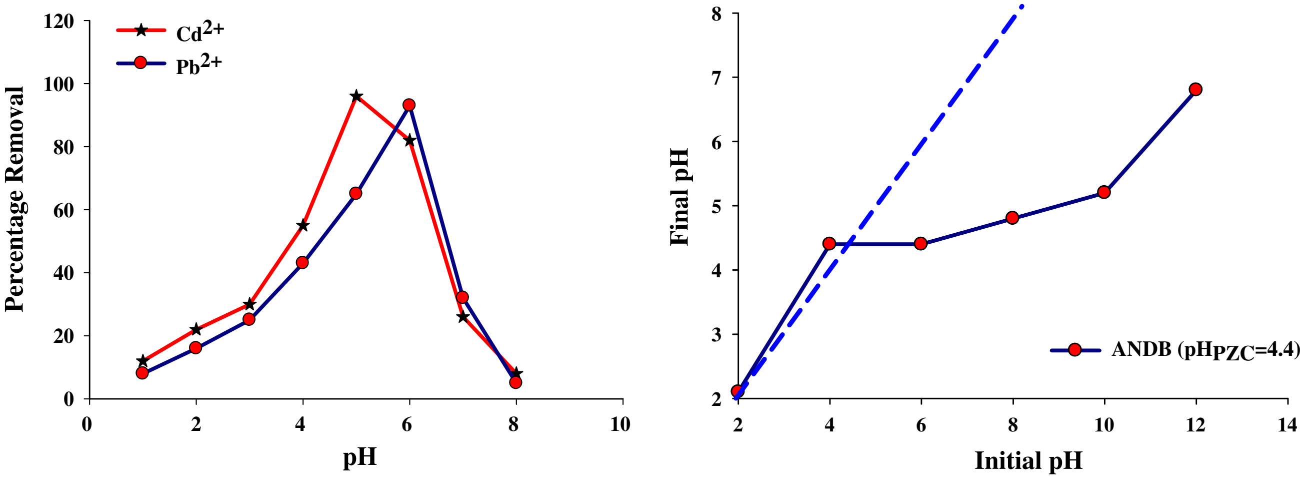

Fig. 3 Effect of pH on $Cd^{2+}$and Pb^{2+} percentage removal and determination of point zero charge (pH_{PZC}) of ANDB

was observed at pH values other than 5.0 and 6.0. The pH_{PZC} of ANDB (Fig. 3) was experimentally found to be 4.4, supporting that biosorption would be better at pH higher than 4.4 for both Cd^{2+} as well as Pb^{2+}. Negligible adsorption was seen at pH > 7.0 for both the metal ions due to the metal hydrolysis and precipitation. So the subsequent studies were conducted at pH 5.0 and 6.0 for $Cd^{2+}$and Pb^{2+}, respectively.

The effect of contact time on biosorption of Cd^{2+} and Pb^{2+} on ANDB was studied in the time range of 1–300 min. It was observed that 65 % biosorption of Cd^{2+} and Pb^{2+} took place in first 60 min, and then, it continued to increase at a lower rate until 96 and 90 % biosorption of Cd^{2+} and Pb^{2+}, respectively, was achieved after 300 min of contact time. The two-stage biosorption mechanism was observed that involves the first rapid and quantitatively predominant, and the second slower and quantitatively irrelevant (Boudrahem et al. 2009). Hence, it was concluded here that lower flow rate would be more effective for biosorption in column experiments.

The influence of the adsorbent dose and initial metal concentrations on the present biosorption process was studied, and both Langmuir and Freundlich isotherms were applied to the data obtained. It was noticed that increase in adsorbent dose from 0.5 to 3.0 g/0.1 L resulted in a rapid increase in the uptake of Cd^{2+} and Pb^{2+}. But no considerable increase in biosorption was found beyond 2.0 g/0.1 L adsorbent dose. The presence of additional biomass resulted in overlapping of the biosorption sites or overcrowding of the biosorbent particles when the biosorbent dosage was increased beyond 2.0 g/0.1 L (Garg et al. 2003; Babel and Kurniawan 2004). However, when the initial concentration of Cd^{2+} and Pb^{2+} was continuously increased from 50.0 to 250 mg L^{-1} using the fixed amount of the adsorbent (2.0 g/0.1 L), the uptake of Cd^{2+} and Pb^{2+} was found to decrease due to the early saturation of the binding sites of the biosorbent at high metal concentration. This may also be accredited to the increase in the number of Cd^{2+} and Pb^{2+} competing for available binding sites of the biosorbent. The biosorption characteristics of Cd^{2+} and Pb^{2+} on ANDB followed more closely the Langmuir isotherm model with metal uptake

Table 2 Thermodynamic parameters of Cd^{2+} and Pb^{2+} biosorption on ANDB at different temperatures with pH 5.0 and 6.0, respectively

Metal ion	T (°C)	K_d	$\Delta G°$ (kJ mol^{-1})	$\Delta S°$ (Jmol^{-1} K^{-1})[a]	$\Delta H°$ (kJ mol^{-1})[a]
Cd^{2+}	10	1.21	−2.26	245.52	0.69
	15	1.42	−0.84		
	20	1.58	−1.09		
	25	2.58	−2.33		
	30	24.96	−8.01		
	35	16.61	−7.26		
	40	16.61	−7.26		
Pb^{2+}	10	1.28	−0.57	218.49	0.62
	15	1.42	−0.84		
	20	1.56	−1.07		
	25	2.81	−2.55		
	30	9.96	−5.77		
	35	9.04	−5.67		
	40	9.04	−5.67		

[a] Measured between 10 and 40 °C

Table 3 Comparison of maximum biosorption capacity of Cd^{2+} and Pb^{2+} on different biosorbents

Adsorbents	Metal	Adsorption capacity[a] (mg g^{-1})	References
Pleutrotus platypus	Cd	14.28	Vimala and Das (2011)
Tea waste	Cd	46.0	Amarasinghe and Williams (2007)
L. hyperborean	Cd	52.4	Yu et al. (1999)
Padina sp.	Cd	46.9	Sheng et al. (2004)
Sargassum siliquosum	Cd	49.4	Hashim and Chu (2004)
ANDB	Cd	370.4	Present work
Barely	Pb	23.20	Pehlivan et al. (2009)
Snowberry	Pb	62.16	Akara et al. (2009)
Rice husk	Pb	58.10	Krishnani et al. (2008)
Hazelnut shell	Pb	28.18	Pehlivan et al. (2009)
Pecan nutshell	Pb	211.7	Vaghetti et al. (2009)
Macrofungus	Pb	38.40	Sari and Tuzen (2009)
Sawdust	Pb	88.49	Naiya et al. (2008)
ANDB	Pb	286.0	Present work

[a] Batch mode

Table 4 Thomas model parameters for Cd^{2+} and Pb^{2+} biosorption from synthetic solution in down flow/up flow mode at pH 5.0 and $C_i = 200$ mg L^{-1}

Parameters varied Bed depth (cm^{-1}) (g)	q_e (mg g^{-1})		R^2		BTP (h)		VWT (mL)	
	DF	UF	DF	UF	DF	UF	DF	UF
Cd^{2+}								
8.0 (15.40)	520	575	0.99	0.99	28	32	1,680	1,920
10.0 (19.25)	565	605	0.99	0.99	35	39	2,100	2,340
12.0 (23.10)	588	633	0.99	0.99	45	47	2,700	2,820
Flow rate (mL min^{-1})								
1.0	588	633	0.99	0.99	45	47	2,700	2,820
3.0	358	412	0.99	0.99	12	13	2,160	2,340
6.0	213	261	0.99	0.99	5	6	1,800	2,160
Pb^{2+}								
8.0 (15.40)	490	544	0.99	0.99	25	29	1,500	1,740
10.0 (19.25)	532	571	0.99	0.99	31	36	1,860	2,160
12.0 (23.10)	532	600	0.99	0.99	41	44	2,460	2,640
Flow rate (mLmin^{-1})								
1.0	532	600	0.99	0.99	41	44	2,460	2,640
3.0	312	367	0.99	0.99	9	11	1,620	1,980
6.0	189	233	0.99	0.99	4	5	1,440	1,800

DF down flow, *UF* up flow, *VWT* volume of water treated

capacity (q_{max}) of 370.4 and 286 mg L^{-1}, respectively, than the Freundlich isotherm model.

The effect of temperature on the uptake of Cd^{2+} and Pb^{2+} on ANDB was studied at different temperatures, ranging from 10 to 40 °C with fixed initial concentration of 200 mg L^{-1} and adsorbent dose 2.0 g/0.1 L at pH 5.0 and 6.0, respectively (Table 2).The biosorption capacity of Cd^{2+} and Pb^{2+} on ANDB was better at 30 °C, and this may possibly be attributed due to the increase in molecular diffusion or due to the availability of more active sites on the surface of the ANDB by expansion of the pores at the same temperature (Gundogdu et al. 2009). The observed values of $\Delta H°$ and $\Delta G°$ as given in Table 2 supported the physical nature and spontaneity of the biosorption of Cd^{2+} and Pb^{2+} on ANDB.

Hence, it was concluded from the batch studies that continuous biosorption experiments can be conducted using ANDB at specific pH (pH 5.0 and 6.0 for Cd^{2+} and Pb^{2+}, respectively) with lower flow rates (1.0 mL min^{-1}) and appropriate biosorbent dose at 30 °C.

Comparison of ANDB with few literature reported biosorbents

On the basis of batch studies, the comparison was done between the biosorption capacity of ANDB and that of the literature reported biosorbents. It was observed that ANDB exhibit very good sorption efficiency for Cd^{2+} and Pb^{2+} (Table 3). The maximum biosorption capacity (q_{max}) was found to be 370.4 and 286 mg g^{-1} for Cd^{2+} and Pb^{2+} when 2.0/0.01 L of ANDB was used at pH 5.0 and 6.0, respectively.

Column studies

Effect of bed depth and flow rate

The increase in bed depth and decrease in flow rate resulted in increase of Cd^{2+} and Pb^{2+} biosorption on to ANDB with fixed initial metal ion concentration and specific pH. The data obtained by varying the bed depth and flow rate in both down flow and up flow modes for Cd^{2+} and Pb^{2+} were analyzed using Thomas model. The Thomas model assumes the Langmuir kinetics of sorption and desorption, with no axial dispersion. It assumes that the rate-driving force in sorption obeys second-order reversible reaction kinetics (Thomas 1944).

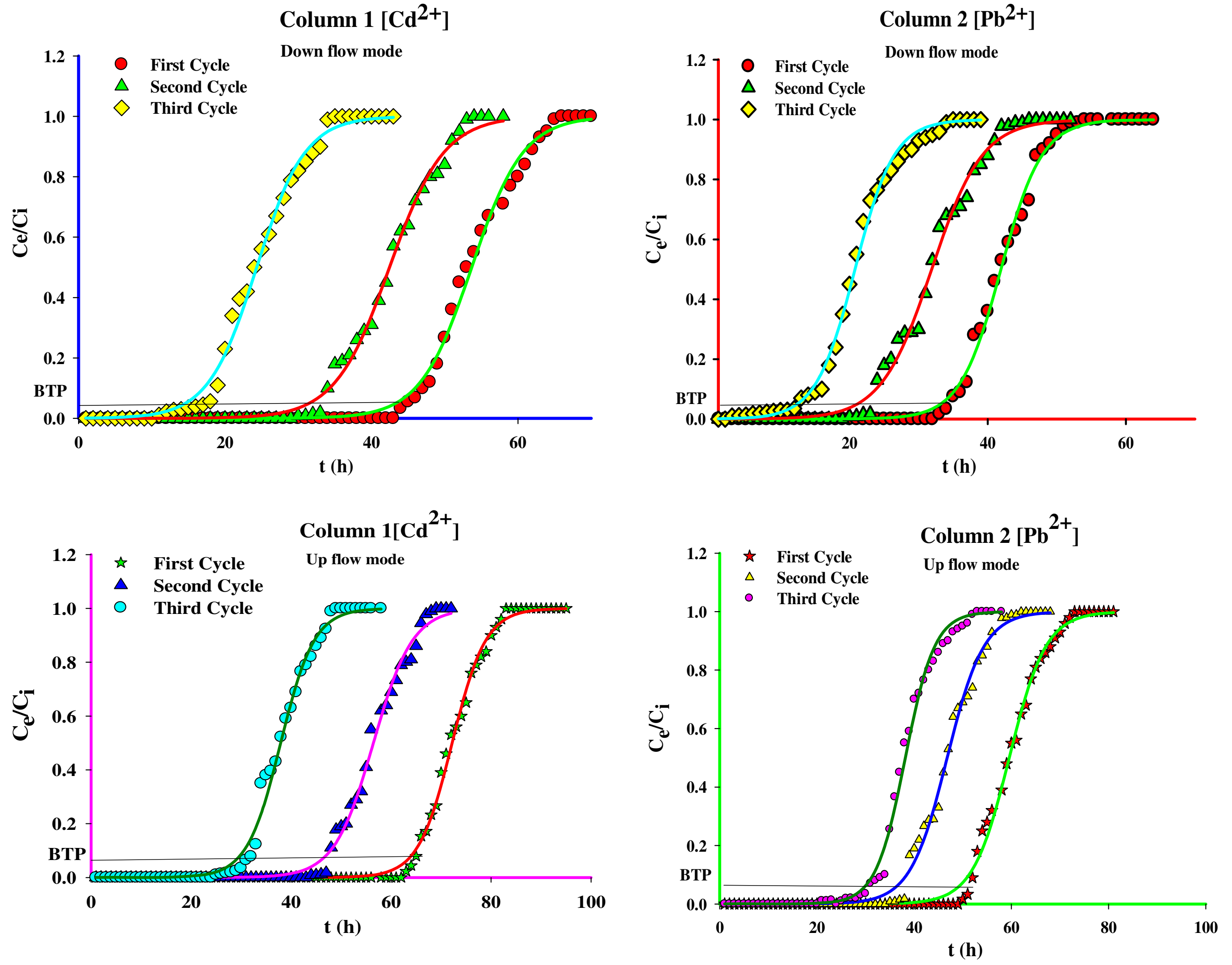

Fig. 4 Down flow/up flow biosorption of Cd^{2+} and Pb^{2+} from PMI wastewater by ANDB packed columns at pH 5.0 and 6.0, respectively

The expression by Thomas, for the adsorption by column, is given as follows:

$$\frac{C_e}{C_i} = \frac{1}{1 + \exp\left(\frac{k_{TH} q_e s}{R} - k_{TH} C_i t\right)} \tag{3}$$

where k_{TH} is the Thomas rate constant (mL min^{-1} mg^{-1}), q_e the maximum metal uptake per gram of the adsorbent (mg g^{-1}), s the amount of adsorbent in gram in the column, C_i and C_e are the influent and the effluent concentrations (mg L^{-1}) of the metal ions, respectively, at time t, $t = V_{eff}/R$ where V_{eff} is the effluent volume (mL) and R is the flow rate (mL min^{-1}). The value of k_{TH} and q_e was determined from the plot of C_e/C_i against time t using nonlinear regression analysis.

The Thomas model parameters are given in Table 4 for Cd^{2+} and Pb^{2+}, respectively. It was observed from Table 4 that the metal biosorption capacity, BTP, and volume of water treated increased with increase in bed depth and decreases with increase in flow rate of the ANDB columns in both the modes. The increase in metal biosorption capacity with increase in bed depth (increase in the biosorbent mass) is obvious as more biosorbent will provide more binding sites resulting in higher metal uptake capacity (Singh et al. 2013). With increase in bed depth from 8.0 to 12.0 cm, the BTP shifted from 28 to 45 h in down flow, 32 to 47 h in up flow for Cd^{2+} and 25 to 41 h in down flow, 29 to 44 h in up flow for Pb^{2+}. Thus, an increase in bed depth causes the solution to spend more

Table 5 Thomas model parameters for Cd^{2+} and Pb^{2+} biosorption from PMI wastewater

Columns (DF/UF)	Cycles (DF/UF)	q_e (mgg^{-1})		BTP (h)		Volume of Water Purified (mL)		% Removal of			
								Cd^{2+}		Pb^{2+}	
		DF	UF	DF	UF	DF	UF	DF	UF	DF	UF
Column 1 (influent pH = 5.0)	1st	673	722	43	64	2,580	3,840	93	100	28	32
	2nd	532	565	32	47	1,920	2,820	84	94	19	23
	3rd	305	379	15	31	900	1,860	73	89	14	17
Column 2 (influent pH = 6.0)	1st	525	596	33	51	1,980	3,060	0.0	0.0	95	100
	2nd	399	468	21	38	1,260	2,280	6.0	4.5	90	100
	3rd	260	382	13	30	780	1,800	10.2	7.6	83	85

The value of k_{TH} in both the columns was 0.0013 to 0.0017

time in the column, resulting in maximum biosorption and late column exhaustion. The volume of treated water and metal uptake capacity was higher in up flow mode as compared to down flow mode, signaling that the biosorption against gravitational force is more effective as the metal ions get comparably more time for binding to the active sites on the surface as well into the interior of the biosorbent. The value of R^2 for all the experiments was 0.99 which indicated that Thomas model described the column performance data very well for the biosorption of Cd^{2+} and Pb^{2+} in both the modes.

Removal of Cd^{2+} and Pb^{2+} from PMI wastewater

Thomas model was also applied to the data obtained during three sorption desorption cycles for treating PMI wastewater in two separate columns 1 and 2 maintained at pH 5.0 and pH 6.0, respectively. The breakthrough curves obtained for Cd^{2+} and Pb^{2+} biosorption in both down flow and up flow modes were shown in Fig. 4. The value of Thomas rate constant (k_{TH}), metal uptake capacity (q_e), BTP and water treatment capacity is given in Table 5. From there, it can be summarized that the value of Thomas rate constant has not changed significantly, but the total metal uptake capacity, breakthrough time and volume of treated water showed a variation between the two modes as well as among the three cycles carried out. The metal uptake capacity, breakthrough time and volume of water treated in both the columns were maximum in the first cycle, and their value decreased in second and third cycles. It could be either due to the partial blocking of the active sites of ANDB in first and second cycles or due to the deterioration of the ANDB by acid washing during its regeneration process (Singh et al. 2013).

Further, comparing down flow and up flow modes, it was seen that in up flow mode, the metal uptake capacity, breakthrough time and volume of water treated were better than the down flow mode. This enhancement in the performance of the column in up flow mode may be due to increase in the residency time of the metal solution in the column while moving against the gravitational force and also due to the diffusion of the metal ions into the interior of the biosorbent utilizing the biosorbent binding sites completely.

After the third cycle, the exhausted biomass was removed from the columns and taken in 1,000-mL beaker. The 200 mL of 1.0 M HCl was added to it, and the mixture was agitated on the shaker for 2 h. The mixture was than filtered and again agitated with 200 ml of deionised water for same duration. Finally, the biomass was filtered and dried, and EDX analysis confirmed the absence of Cd^{2+} and Pb^{2+}. This powder was used as a manures in the rice fields.

Comparison of biosorption of Cd^{2+} in synthetic and PMI wastewater

The comparison of biosorption of Cd^{2+} in synthetic solution (single-metal ion system) containing Cd^{2+} only with PMI wastewater (multi-metal ion system) containing Cd^{2+}, Pb^{2+} and other ions was studied in up flow mode. It was observed that Cd^{2+} biosorption was 100 % in case of synthetic solution, and it decreases to 95 % in case of PMI wastewater. Additionally, the BTP was also reduced to 63 h from 89 h. This may be due to the presence of a variety of metal ions in PMI wastewater. All metal ions are now competing for the adsorption sites, and hence, lesser sites would be available for Cd^{2+} adsorption. However, the uptake capacity ($q_e = 722$ mg g^{-1}) in PMI wastewater was still reasonably good indicating the efficacy of the ANDB for the removal of Cd^{2+}, even from multi-metal ion solution.

Conclusion

High metal uptake capacity and reusability of ANDB make it promising biosorbent for desalinating Cd^{2+} and Pb^{2+} from synthetic and PMI wastewater. The column studies conducted with PMI wastewater at optimized pH, contact time and temperature showed that metal removal (722 mg g^{-1}) and overall water purification (3,840 mL) were maximum in up flow mode. The effect of co-ions in PMI wastewater proved that the biosorption of Cd^{2+} and Pb^{2+} was more effective in synthetic solution (single-metal system) as compared to PMI wastewater (multi-metal system). Hence, it can be concluded that ANDB has an excellent capacity to sequester metal ions from industrial effluents and can be used as an alternative adsorbent at commercial scale.

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References

Akara ST, Gorgulu A, Anilan B, Kaynak Z, Akara T (2009) Investigation of the biosorption characteristics of lead(II) ions onto Symphoricarpus albus: batch and dynamic flow studies. J Hazard Mater 165:126–133

Amarasinghe BMWPK, Williams RA (2007) Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. Chem Eng J 132:299–309

Awofolu OR, Okonkwo JO, Merwe RR, Badenhorst J, Jordaan E (2006) A new approach to chemical modification protocols of *Aspergillus niger* and sorption of lead ion by fungal species. Electron J Biotechnol 9:341–348

Babel S, Kurniawan TA (2004) Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. Chemosphere 54:951–967

Boudrahem F, Aissani-Benissad F, Ait-Amar H (2009) Batch sorption dynamics an equilibrium for the removal of lead ions from aqueous phase using activated carbon developed from coffee residue activated with zinc chloride. J Environ Manag 90:3031–3039

Galun M, Keller P, Malki D, Feldstein H, Galun E, Siegel S, Siegel B (1983) Recovery of uranium (VI) from solution using precultured Penicillium biomass. Water Air Soil Pollut 20:221–232

Galun M, Galun E, Siegel BZ, Keller P, Lehr H, Siegel SM (1987) Recovery of metal ions from aqueous solutions by Penicillium biomass: kinetic and uptake parameters. Water Air Soil Pollut 33:359–371

Garg VK, Gupta R, Yadav AB, Kumar RD (2003) Dye removal from aqueous solution by adsorption on treated sawdust. Bioresour Technol 89:121–124

Gundogdu A, Ozdes D, Duran C, Bulut VN, Soylak M, Senturk HB (2009) Biosorption of Pb(II) ions from aqueous solution by pine bark (*Pinus brutia Ten.*). Chem Eng J 153:62–69

Hashim MA, Chu KH (2004) Biosorption of cadmium by brown, green and red seaweeds. Chem Eng J 97:249–255

Huang C, Huang CP (1996) Application of *Aspergillus oryzae* and *Rhizopus oryzae* for Cu(II) removal. Water Res 30:1985–1990

Jacques RA, Bernardi R, Caovila M, Lima EC, Pavan FA, Vaghetti JCP, Airoldi C (2007) Removal of Cu(II), Fe(III) and Cr(III) from aqueous solution by aniline grafted silica gel. Sep Sci Technol 42:591–609

Kapoor A, Viraraghavan T, Cullimore DR (1999) Removal of heavy metals using the fungus *Aspergillus niger*. Bioresour Technol 70:95–104

Krishnani KK, Meng X, Christodoulatos C, Boddu VM (2008) Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk. J Hazard Mater 153: 1222–1234

Mullen MD, Wolf DC, Ferris FG, Beveridge TJ, Flemming CA, Bailey GW (1989) Bacterial sorption of heavy metals. Appl Environ Microbiol 54:3143–3149

Naiya TK, Bhattacharya AK, Das SK (2008) Adsorption of Pb(II) by sawdust and neem bark from aqueous solutions. Environ Prog 27:313–328

Park D, Yun Y, Jo JH, Park JM (2005) Mechanism of hexavalent chromium removal by dead fungal biomass of *Aspergillus niger*. Water Res 39:533–540

Pehlivan E, Altun T, Parlayıcı S (2009) Utilization of barley straws as biosorbents for Cu^{2+} and Pb^{2+} ions. J Hazard Mater 164:982–986

Rivera-Utrilla J, Bautista-Toledo I, Ferro-Garcy'a MA, Moreno-Castilla C (2001) Activated carbon surface modifications by adsorption of bacteria and their effect on aqueous lead adsorption. J Chem Technol Biotechnol 76:1209–1215

Sari A, Tuzen M (2009) Kinetic and equilibrium studies of biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Amanita rubescens*) biomass. J Hazard Mater 164:1004–1011

Sheng PX, Ting YP, Chen P, Hong L (2004) Sorption of lead, copper, cadmium, zinc and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. J Colloid Interface Sci 275:131–141

Singh J, Ali A, Prakash V (2013) Removal of lead(II) from synthetic and batteries wastewater using agricultural in batch/column studies. IJEST. doi:10.1007/s13762-013-0326-9

Smith AH (1963) The mushroom hunter's field guide, revised and enlarged. The University of Michigan Press, Ann Arbor, p 67

Thomas HC (1944) Heterogeneous ion exchange in a flowing system. J Am Chem Soc 66:1446–1664

Tobin JM, Cooper DG, Neufeld RJ (1984) Uptake of metal ions by *Rhizopus arrhizus*. Appl Environ Microbiol 47:821–824

Tsezos M, Velosky B (1982) The mechanism of thorium biosorption by *Rhizopus arrhizus*. Biotechnol Bioeng 29:955–969

Vaghetti JCP, Lima EC, Royer B, da Cunha BM, Cardoso NF, Brasil JL, Dias SLP (2009) Pecan nutshell as biosorbent to remove Cu(II), Mn(II) and Pb(II) from aqueous solutions. J Hazard Mater 162:270–280

Vimala R, Das N (2011) Mechanism of Cd(II) adsorption by macrofungus *Pleutrotus platypus*. J Environ Sci 23:288–293

Yu Q, Matheickal JT, Yin P, Kaewsarn P (1999) Heavy metal uptake capacities of common marine macro algal biomass. Water Res 33:1534–1537

Zouboulis AI, Matis KA, Lanara BG, Neskovic CL (1997) Removal of cadmium from dilute solutions by hydroxyapatite. II. Flotation studies. Sep Sci Technol 32:1755–1767