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ORIGINAL PAPER

Removal of lead (II) from synthetic and batteries wastewater using agricultural residues in batch/column mode

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Abstract The present article explores the ability of five different combinations of two adsorbents (Arachis hypogea shell powder and Eucalyptus cameldulensis saw dust) to remove Pb(II) from synthetic and lead acid batteries wastewater through batch and column mode. The effects of solution pH, adsorbent dose, initial Pb(II) concentration and contact time were investigated with synthetic solutions in batch mode. The Fourier transform infrared spectroscopy study revealed that carboxyl and hydroxyl functional groups were mostly responsible for the removal of Pb(II) ions from test solutions. The kinetic data were found to follow pseudo-second-order model with correlation coefficient of 0.99. Among Freundlich and Langmuir adsorption models, the Langmuir model provided the best fit to the equilibrium data with maximum adsorption capacity of 270.2 mg g^{-1}. Column studies were carried out using lead battery wastewater at different flow rates and bed depths. Two kinetic models, viz. Thomas and Bed depth service time model, were applied to predict the breakthrough curves and breakthrough service time. The Pb(II) uptake capacity ($q_e = 540.41$ mg g^{-1}) was obtained using bed depth of 35 cm and a flow rate of 1.0 mL min^{-1} at 6.0 pH. The results from this study showed that adsorption capacity of agricultural residues in different combinations is much better than reported by other authors, authenticating that the prepared biosorbents have potential in remediation of Pb-contaminated waters.

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Keywords Lead acid batteries wastewater · Arachis hypogea · Eucalyptus cameldulensis · Biosorbents · Bed depth service model · Thomas model

Introduction

Industrial activities are principally responsible for generating large volume of effluents containing hazardous species. Among these hazardous species, the heavy metals ions are most toxic and are non-biodegradable (Yu 2005). Hence, their removal from aqueous effluents before being disposed in the environment is must (Jacques et al. 2007a). Amid these metal ions, lead is dominant in most of the effluent streams in India and all over the world. It is quite toxic to humans as it interacts with the sulfhydryl group of proteins, resulting in disruption of the metabolism and biological activities of different proteins in the body. It impairs hemoglobin synthesis, causes damage to liver and kidneys as well as leads to neurological disorders (Markowitz 2000). Hence, the elimination of lead from wastewater in economic and proficient way is of special concern.

Several treatment technologies have been developed to remove lead from wastewater, including ion exchange (Kopittke et al. 2007), chemical precipitation (Husein et al. 1998), electrochemical reduction (Lin and Navarro 1999), electrodialysis (Mohammadi et al. 2004), etc. However, all these methods involve high operating cost and may produce large volume of sludge. In this context, adsorption process could be helpful for the removal of Pb(II). A variety of the adsorbents have been reported in the literature for the removal of Pb(II) by waste materials of food and agricultural industry (Pehlivan et al. 2009; Saka et al. 2012).

The present research work was carried out in Haryana state of India, in 2012. In this work, the biosorption of

Pb(II) from synthetic solution was done in batch mode by using five different combinations, that is, A to E (by mixing activated *Eucalyptus cameldulensis* saw dust and *Arachis hypogea* shell powder). The combination B showed best adsorption capacity as compared to other four combinations. The influence of pH, adsorbent dose, initial metal ions concentration and contact time were studied. The obtained experimental data were evaluated and fitted using equilibrium isotherms and kinetic models. In fixed bed column operations, lead acid batteries wastewater was treated using combination B and the data were analyzed using Thomas and Bed depth service time (BDST) models.

Materials and methods

Preparation of biosorbents

Eucalyptus cameldulensis saw dust and *Arachis hypogea* shells were collected form Dinesh Wood Works Jagadhri and Trilok oil industry, Mustafabad (Haryana), India, respectively. Both the residues were washed extensively in deionized water to remove dirt and other particulate matter and then dried in the sun light for 7 days. *Arachis hypogea* shells were finally grinded separately in a vegetable grinder to obtain the biomass powder. Resulting powders were sieved through a 600-μm mesh sized sieve and the powder (500 g each) thus obtained was heated in an electric hot air oven at 105 °C for 12 h. The *Eucalyptus cameldulensis* saw dust (ECSD) and *Arachis hypogea* shell powder (AHSP) were mixed in different wt% (Table 1). The various combinations were prepared to analyze their adsorption capacity for multi-metal ion solutions.

Preparation of stock solutions

An aqueous stock solution of Pb(II) (1,000 mg L^{-1}) was prepared by dissolving requisite amount of $Pb(NO_3)_2$ (AR, Loba chmie, India) in 1.0 L deionized water. The known amount of stock solutions were further diluted with deionized water to prepare the solutions of desired concentrations. The pH of the solutions was adjusted by adding the appropriate amounts of 0.1 M HCl or 0.1 M NaOH solutions.

Table 1 Different combinations of agricultural residues

Combinations	Agricultural residues (wt%)
A	ECSD (10) + AHSP (90)
B	ECSD (30) + AHSP (70)
C	ECSD (50) + AHSP (50)
D	ECSD (70) + AHSP (30)
E	ECSD (90) + AHSP (10)

Instruments and software

The quantification of the Pb(II) in adsorbent-treated solutions has been performed on Atomic Absorption Spectrophotometer (AAS) AA630, Shimadzu, Japan. The Fourier transform infrared spectroscopy (FTIR) spectra of the adsorbent have been recorded on Thermo, Nicolet Is10 FTIR spectrophotometer, and field emission scanning electron microscopy (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 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 the data analysis and fitting the experimental data in Thomas model.

Batch studies

Batch experiments for Pb(II) biosorption from synthetic solutions were carried out at different pH values, viz. 1.0–8.0, for all the metal ions by agitating a known amount of five different combinations (A to E) in 250-mL screw-cap conical flasks with adsorbent dose of 2.0 g/0.1 L of metal ion solutions, respectively. The mixture so obtained was agitated in orbital shaker at 225 rpm speed for 300 min at 30 °C. After every 30 min of agitation, 2.0 mL of the suspensions was filtered through Whatman no. 40 filter paper and the filtrates were analyzed using AAS. Under optimized pH, rpm and temperature, the effect of adsorbent dose ranging from 0.5 to 3.0 g, initial metal ion concentration from 50 to 250 mg L^{-1} and contact time from 1 to 300 min have been studied.

The percent of the metal removal (*R%*) was calculated for each experiment using Eq. (1)

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

where C_i and C_e were the initial and equilibrium concentrations of Pb(II) metal ions in the solution, respectively. The metal biosorption capacity (q_e = mg/g) of each combination for biosorption of Pb(II) metal ions at equilibrium was determined using Eq.(2).

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

where V is the volume of the solution (L), and M_a is the mass of the adsorbent (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. 50 mL of 0.01 M NaCl solution was taken in 100-mL screw-cap conical flasks. The pH of each solution in each flask was adjusted to values of 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 the combinations A to E was added separately and the final pH measured after 48 h under agitation at room temperature.

The ion exchange of the combination B

Among all the five combinations studied, combination B showed maximum removal capacity of Pb(II) ions in the batch studies. To identify the ions involved in the sorption of Pb(II) onto different combination used, 1.0 g of the combination B was mixed with 100 mL Pb(II) solution in the screw-cap conical flasks with 200 mg L^{-1} initial concentration at pH 6.0. The mixture so obtained was agitated in orbital shaker at 225 rpm speed for 300 min. After 300 min, the mixture was centrifuged at 5,000 rpm for 10 min and analyzed for the release of Na^+, K^+, Ca^{2+} and Mg^{2+} and unabsorbed Pb(II) ions in the solution.

Blocking of carboxyl and hydroxyl functional groups

To study the role of carboxyl (–COOH) and hydroxyl (–OH) in metal sorption, they were blocked in combination B (Eqs. 3, 4, respectively). To protect the carboxylic group, 9.0 g of the combination B was treated with anhydrous CH_3OH (633 mL) in the presence of 5.4 mL HCl (5.0 M), with continuous stirring on magnetic stirrer at 225 rpm for 360 min. The combination B residue was then separated by centrifugation and washed thrice with deionized water to remove excess CH_3OH and HCl. The final biomass obtained was dried in hot air oven at 105 °C for 12 h and stored in for further use. Hydroxyl group of sorbent was protected by treating combination B with formaldehyde (Chen and Yang 2006). To do so, 5.0 g of the combination B was treated with HCHO (100 mL) under agitation on magnetic stirrer at 225 rpm for 360 min. The residual biomass was then separated and processed further following the same method as mentioned for the carboxylic group protection.

$$RCOOH + CH_3OH \rightarrow RCOOCH_3 + H_2O \quad (3)$$

$$2R - OH + HCHO \rightarrow (R - O)_2CH_2 + H_2O \quad (4)$$

Desorption studies

The regeneration of the adsorbent is one of the important factors in estimating its potential and feasibility for commercial use. Desorption of the adsorbed Pb(II) ions from the adsorbent was also studied in the batch mode. Three different desorption agents HCl, H_2SO_4 and HNO_3 were used in the concentration range of 0.1–0.5 M to recover Pb(II) from the adsorbents (combinations A to E) and the maximum desorption was studied and compared.

Characterization of lead acid batteries wastewater

Lead acid batteries effluent was collected from Singh battery manufacturer, Yamuna Nagar, Haryana, India. Analysis of effluent showed the concentration of Pb^{2+}, Fe^{2+} and Zn^{2+} as 645.15, 88.20 and 5.23 mg L^{-1}, respectively.

Column studies using lead acid batteries effluent

Continuous flow experiments were conducted in glass column having 50.0 cm length and 1.5 cm internal diameter. The packing of biosorbent was done with proper care to avoid any void spaces, channels and cracks in the bed. The packed column was held vertically with the help of stand and clamp. To stabilize the process, before each run, 2.0 L deionized water adjusted to pH 6.0 was passed through the columns for 12 h at a flow rate of 0.5 mL min^{-1} using peristaltic pump at room temperature. To measure the concentrations of the metal ions in the effluents of each column, 5.0 mL samples of the effluents was intermittently collected and analyzed. The percolation of the wastewater into each column was stopped as soon as the breakthrough point (BTP) in that particular column was achieved. Breakthrough occurs when the effluent concentration from the column is about 3–5 % of the influent concentration (Chen and Yang 2006). The column was recharged using 0.5 M HCl. The wastewater was treated till the concentration of all the metal ions reached to satisfy the Central Pollution Control Board standards (CPCB 1998).

Results and discussion

Characterization of the biosorbents

The *Eucalyptus cameldulensis* saw dust, *Arachis hypogea* shells and combination B used in the column studies for the Pb(II) biosorption from the lead battery waste have been recovered, dried and analyzed by the FTIR and SEM instruments.

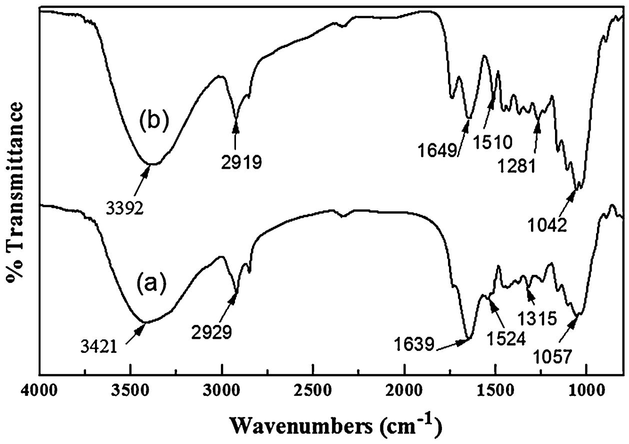

Fig. 1 FTIR spectra: **a** before biosorption of Pb(II) and **b** after biosorption of Pb(II) on combination B

FTIR analysis

In order to determine the main functional groups responsible for the biosorption of Pb(II) from the lead battery wastewater in column studies, the combination B was recovered from the column, dried and subjected to the FTIR studies. The recorded spectra have been compared as shown in Fig. 1. The broad and intense peak at 3,421 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 adsorbent. The band at 2,929 cm^{-1} indicates symmetric or asymmetric C–H stretching vibration of aliphatic acids. Peak observed at 1,649 cm^{-1} is the stretching vibration of C=O functional group and may be assigned to carboxylic acids that exist in with intermolecular hydrogen bond (Vaghetti et al. 2009; Jacques et al. 2007b; Jayaram et al. 2009). The peak observed at 1,524 cm^{-1} is assigned to C=C ring stretch of aromatic rings. Numerous bands ranging from 1,315 to 1,057 cm^{-1} refer to C–O bonding of phenols (Jacques et al. 2007b). FTIR spectra of Pb(II) sorbed on combination B showed that the peaks expected at 3,421, 2,929, 1,639, 1,524, 1,315 and 1,057 cm^{-1} had shifted to 3,392, 2,919, 1,649 and 1,042 cm^{-1}, respectively, attributed to Pb(II) ion adsorption. These groups may function as proton donors; hence, deprotonated hydroxyl and carbonyl groups may be involved in coordination with metal ions (Ashkenazy et al. 1997).

Scanning electron microscopy

Scanning electron microscopy along with energy dispersive X-ray (EDX) analysis has been done for the characterization of the adsorbent as well as for the elucidation of the probable mechanism of adsorption. SEM images and EDX spectra obtained from fresh combination B and lead-loaded combination B are shown in Fig. 2. SEM images of fresh combination B (Fig. 2a) reveal the nature of the biomass such as rough, uneven and porous with lots of ups and down and thus make possible for the adsorption of lead ions in different parts of the biomass. Lead-loaded combination B, SEM image (Fig. 2c), is comparably bit smooth, showing the presence of Pb(II) on it. EDX analysis provides the elemental analysis of fresh combination B and lead-loaded combination B. Figure 2b indicates the presence of C and O in blank biomass. EDX spectra in Fig. 2d revealed the additional signal, which confirms the binding of the metal ions to the surface of the biomass.

Batch studies

Effect of pH

The pH of the solution has a significant impact on the uptake of metal ions, since it determines the surface charge of the biosorbent, the degree of ionization and speciation of the metal ions (Boudrahem et al. 2009; Machida et al. 2005). To study the effect of pH on the biosorption of Pb(II) ions by all five combinations, that is, A to E, the batch equilibrium studies were carried out in the pH range of 1.0–8.0. This pH range was chosen to avoid metal solid hydroxide precipitation. The maximum biosorption of Pb(II) by all the combinations used was obtained at pH 6.0, and a significant decrease or increase in biosorption capacity was observed at pH values lower or higher than 6.0. This can be explained with the help of $\mathrm{pH_{PZC}}$ of the adsorbent. The $\mathrm{pH_{PZC}}$ is the point where the curve pH final versus pH initial crosses the line equal to pH final. The $\mathrm{pH_{PZC}}$ of all the five combinations (A to E) were experimentally found to be at pH 5.1, 4.9, 4.5, 5.3 and 5.5, respectively (Fig. 3). Further, at $\mathrm{pH} > \mathrm{pH_{PZC}}$, the combinations became negatively charged and the metal species were positively charged. Under such circumstances, the electrostatic attraction between the positively charged metal ions and the negatively charged adsorbent (combinations A to E) surface increases, consequently enhanced adsorption of the metal ions from the solution. On the other hand, at $\mathrm{pH} < \mathrm{pH_{PZC}}$, the surface of the adsorbent became positively charged, resulting in a decrease in the metal ions adsorption apparently due to the higher concentration of $\mathrm{H^+}$ ions in the solution that was challenging the positively charged metal for the active sites. The minimal adsorption was seen at $\mathrm{pH} > 6.0$. It was due to the Pb(II) hydrolysis and precipitation, so subsequent studies were conducted at pH 6.0.

Effect of contact time

The effect of contact time on biosorption of lead on different combinations was studied in the time range of

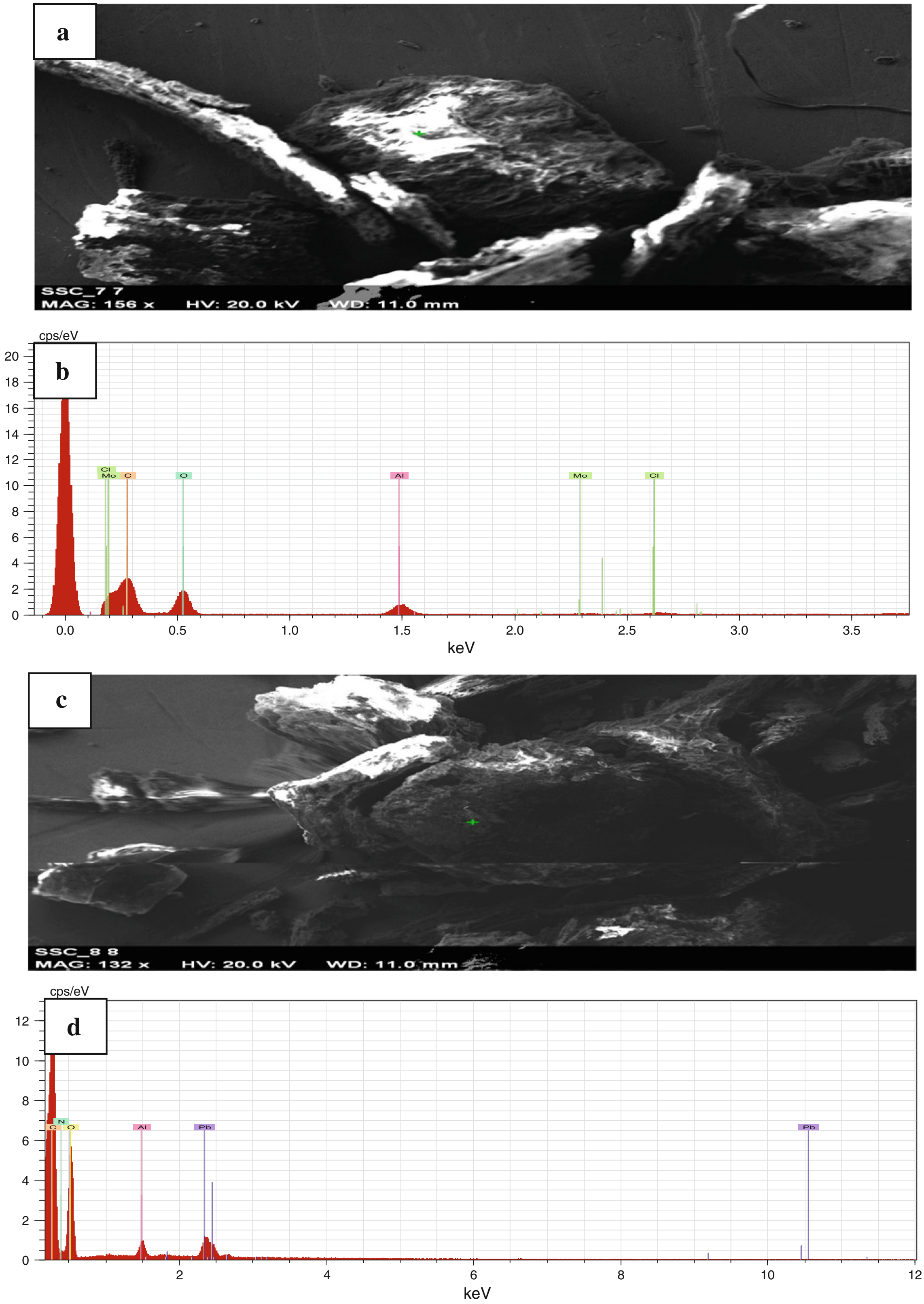

Fig. 2 SEM and EDX images of combination B before (**a**, **b**) and after (**c**, **d**) adsorption of Pb(II), respectively

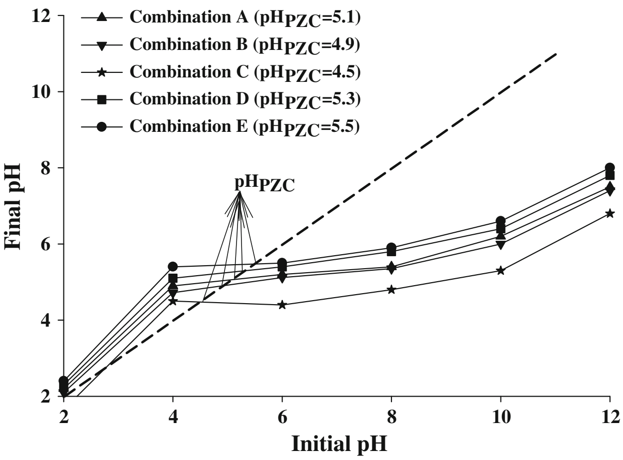

Fig. 3 Determination of pHpzc of all the combinations (*A* to *E*)

1–300 min by using 200.0 mg L^{-1} of Pb(II) solutions at pH 6.0 with 2.0 g/0.1 L of the adsorbent. The mixture was agitated at 30 °C with 225 rpm and the samples were taken after every 20 min, filtered and analyzed by AAS. About 80 % biosorption of Pb(II) took place in first 60 min and then it continued to increase at a lower rate until greater than 92 %, and biosorption was achieved for all the five combinations after 300 min of contact time. The rate of percent metal removal is higher in the beginning due to the availability of vacant-specific sites for metal ion binding. The two-stage sorption mechanism is consistent with the earlier literature reports (Boudrahem et al. 2009) which involve the first rapid and quantitatively predominant and the second slower and quantitatively insignificant step. Based on these results, a contact time of 300 min was assumed to be suitable for the subsequent biosorption experiments.

Adsorption kinetics

To analyze the adsorption kinetics of Pb(II) by all five combinations, the pseudo-first- and pseudo-second-order kinetic models were applied to the experimental data obtained. The first-order rate equation of Lagergren is one of the most widely used for the sorption of a solute from liquid solution and is represented in Eq. (5).

$$\mathrm{In}(q_e - q_t) = \mathrm{In}q_e - k_1 t \tag{5}$$

where q_t (mg g^{-1}) is the amount of metal ions adsorbed at time t, q_e is the amount of metal ions adsorbed at equilibrium (mg g^{-1}), and k_1 is the rate constant of the biosorption ($\min^{-1}$). The pseudo-first-order considers the rate of occupation of adsorption sites to be proportional to the number of unoccupied sites. The straight line in the graph of *ln* $(q_e - q_t)$ versus t suggests the applicability of the pseudo-first-order kinetic model. The amount of the adsorbed metal ions (q_e) and k_1 were determined from the intercept and slope of the plot, respectively, and are given in Table 2.

On the other hand, the pseudo-second-order kinetic model is based on adsorption equilibrium capacity as given in Eq. (6).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where k_2 (g $mg^{-1}min^{-1}$) is the rate constant of the second-order equation; q_t (mg g^{-1}) is the amount of adsorption at time t (min); and q_e is the amount of metal ions adsorbed at equilibrium (mg g^{-1}).

The plot of t/q_t versus t gave a straight line, and the pseudo-second-order rate constants k_2 and q_e were determined from slope and intercept of the plot, respectively, and are presented in Table 2. Among the two kinetic models used, the best fittings of the experimental values were obtained ($R^2 = 0.99$) by following the pseudo-second-order kinetic model. This implies that the data confirm the pseudo-second-order reaction, that is, the adsorption has two phases of reaction: a very rapid biosorption for shorter duration in initial stage followed by slow one for longer duration. It has been reported that the fast reaction is due to chemisorptions involving valency forces through sharing or exchange of electrons between sorbent and sorbate and slow one is by diffusion of ions into cell structure. Hence, the rate-limiting step is chemisorptions (Singh and Ali 2012).

Effect of adsorbent dose, initial Pb(II) concentration and isotherm modeling

The equilibrium adsorption isotherm models help to establish the relationship between the amounts of metal ions adsorbed on an adsorbent and its equilibrium concentration in aqueous solution. Among various adsorption isotherms models, Langmuir and Freundlich isotherm models are preferred in this study. The Langmuir model assumes that the uptake of the metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions and is given by Eq. (7).

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \tag{7}$$

where q_e (mg g^{-1}) is the amount of metal ions adsorbed per unit mass of adsorbent, C_e is the equilibrium concentration in the solution (mg L^{-1}) of Pb(II), respectively, q_{max} represents the maximum biosorption capacity(mg g^{-1}) under the experimental conditions, and b is a constant related to the affinity of the binding sites (L mg^{-1}).

Table 2 Pseudo-first- and second-order kinetic model for Pb(II) biosorption on different combination (A–E) at pH 6.0 ($C_i = 200$ mg L^{-1}, adsorbent dose = 2.0 g/0.1 L, contact time = 300 min, rpm = 225 at 30 °C)

Different combinations	Pseudo-first-order			Pseudo-second-order		
	k_1	q_e	R^2	k_2	q_e	R^2
A	0.010	4.19	0.933	0.058	192.30	0.99
B	0.046	5.17	0.944	0.024	192.30	0.99
C	0.008	4.20	0.931	0.058	192.30	0.99
D	0.009	3.79	0.762	0.039	192.30	0.99
E	0.007	3.81	0.767	0.039	188.67	0.99

Further, the shape of isotherm can be used to predict whether a sorption system is favorable or not. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant or separation factor (R_L) and the same could be defined by the Eq. (8).

$$R_L = \frac{1}{1 + bC_i} \tag{8}$$

where C_i (mg L^{-1}) is the initial amount of the adsorbate in the solution, and b (L mg^{-1}) is the Langmuir constant described above. There are four probabilities for the R_L value, viz. for (1) favorable adsorption $0 < R_L < 1$, (2) unfavorable adsorption $R_L > 1$, (3) linear adsorption $R_L = 1$ and (4) irreversible adsorption $R_L = 0$. On the other hand, Herbert Max Finley Freundlich derived an empirical adsorption isotherm equation, which is based on the biosorption on a heterogeneous surface and is given by Eq. (9).

$$\mathrm{In} q_e = \frac{1}{n} \mathrm{In} C_e + \mathrm{In} K_F \tag{9}$$

where K_F and n are the Freundlich constants and are indicators of adsorption capacity and adsorption intensity, respectively.

The influence of the adsorbent dose and initial Pb(II) concentrations on the present biosorption process was studied by employing Pb(II) solutions with initial concentrations in the range of 50–250 mg L^{-1}, pH 6.0 and adsorbent dose in the range of 0.5–3.0 g/0.1 L. Concentrations of Pb(II) from each batch were measured at equilibrium. Both Langmuir and Freundlich isotherms were applied to the data obtained, and it was seen that increase in adsorbent dose from 0.5 to 3.0 g/0.1 L resulted in a rapid increase in the uptake of Pb(II) ions. But no significant increase in adsorption was found beyond 2.0 g/0.1 L. It could be attributed to the presence of excess/surplus metal binding sites on the combination B than the available Pb(II) ions, or in other words, decrease in adsorption capacity could be due to the overlapping of the adsorption sites as a result of overcrowding of the adsorbent particles when the adsorbent dosage is increased above 2.0 g/0.1 L. This imposed a screening effect on the dense outer layer of the adsorbent, thereby shielding the binding sites from metals as explained by Babel and Kurniawan (2004). However, when the initial concentration of Pb(II) was continuously increased from 50 to 250 mg L^{-1} using the fixed amount of the adsorbent (2.0 g/0.1 L), the biosorption of the Pb(II) was found to decrease due to the early saturation of the binding sites of the biosorbent at high Pb(II) concentration. This may also be attributed to the increase in the number of Pb(II) competing for available binding sites of the adsorbent. The Langmuir and Freundlich constants and their correlation coefficients (r^2) evaluated from these isotherms for Pb(II) are given in Table 3.

The sorption characteristics of Pb(II) on the combination B followed more closely the Langmuir isotherm model with $q_{max} = 270.2$ mg L^{-1} than the Freundlich isotherm model. This observation is further supported by the assessment of the respective correlation coefficient values which are a measure of how well the theoretical values match with the experimental data. Also, the values of R_L were calculated using Eq. (6) with Pb(II) concentrations in the range of 50.0–250.0 mg L^{-1} and were found to fall between zero and one which is again an indication of the favorable biosorption for Pb(II) on all the five combinations used. The value of *n,* which is related to the distribution of bonded ions on adsorbent surface, represents beneficial adsorption if it is between 1 and 10 (Kadirvelu and Namasivayan 2000). The value of n was found to be >1, indicating that the adsorption of Pb(II) was favorable under studied conditions.

Comparison of the combination B with other adsorbents

The adsorption capacity values of various adsorbents used for Pb(II) adsorption have been shown in Table 4. The comparison between present results and with that of the literature reported one shows that agricultural residues used in combination in the present study exhibit very good sorption efficiency. The maximum biosorption capacity (q_{max}) was found to be 270.2 mg for Pb(II) when 2.0/.01 L of the combination B was used at pH 6.0, and this value is relatively better than most of the earlier reported results as

Table 3 Langmuir and Freundlich isotherm constants and correlation coefficients for the biosorption of Pb(II) on combination B at pH 6.0 with different adsorbent doses (contact time = 300 min, rpm = 225 at 30 °C)

Wt. of combination B (g)	Langmuir			Freundlich		
	q_{max} (mg g^{-1})	b (L mg^{-1})	R^2	n (mg g^{-1})	K_F	R^2
0.5	222.2	0.123	0.97	3.9	4.13	0.98
1.0	238.1	0.143	0.96	4.8	4.42	0.93
1.5	250.0	0.286	0.99	4.6	4.55	0.99
2.0	270.2	0.840	0.99	4.8	4.73	0.84
2.5	263.2	1.15	0.94	2.5	4.01	0.92
3.0	222.2	1.28	0.99	2.7	3.99	0.92

Table 4 Comparison of maximum adsorption capacity of Pb(II) on different adsorbents in the literature

Adsorbents	Mass of adsorbent (g L^{-1})	pH	Adsorption capacity (mg g^{-1})	References
Barely	6.25	6.0	23.20	Pehlivan et al. (2009)
Snowberry	4.0	5.5	62.16	Akara et al. (2009)
Rice husk	3.0	6.0	58.1	Krishnani et al. (2008)
Pecan nutshell	4.0	5.5	211.7	Vaghetti et al. (2009)
Macrofungus	4.0	5.0	38.4	Sari and Tuzen (2009)
Sawdust	7.5	5.0	88.49	Naiya et al. (2008)
Pinus sylvestris sawdust	1.0	5.0	22.22	Taty-Costodes et al. (2003)
Combination B (ECSD (30 %) + AHSP (70 %))	2.0	6.0	272.2	Present work

given in Table 4. Further additional advantages of ECSD and AHSP are their easy availability and cost effectiveness, which make them better biosorbent for the removal of Pb(II) in different combinations from aqueous systems.

The ion-exchange capacity of the combination B

More than 91 % removal of Pb(II) was due to the ion-exchange process involving Na^+, K^+, Ca^{2+} and Mg^{2+}. The remaining 9 % Pb(II) adsorption could be due to its ion exchange with protons, as pH of the supernatant was found to decrease at equilibrium. Hence, it may be concluded that the sorption process for Pb(II) on combination B occurs primarily through ion-exchange mechanism involving the replacement of alkali and alkaline earth metals. The protons bound to native carboxylate groups are also involved in ion-exchange process but to the lesser extent. Similar type of ion-exchange mechanism has also been reported and discussed for other agrowaste materials (Naiya et al. 2008).

Blocking of functional groups and computation of their role in metal sorption

To confirm and compute the role of carboxyl and hydroxyl groups in the removal of Pb(II), both the groups of the combination B were individually blocked in two separate experiments. It was observed that the metal removal capacity was badly inhibited when carbonyl groups were blocked and a decrease of 70.5 % in the adsorption of Pb(II) was observed. It clearly indicates that the carboxyl groups have the major role in the process of adsorption. On the other hand, 29.5 % of Pb(II) was removed by combination B, even after the blockage of carboxyl groups, indicating that other functional groups are also involved in adsorption of metal ions. To support the presence of other functional groups on the adsorbent, sorption of Pb(II) by combination B was carried out after blocking the hydroxyl groups. The adsorption capacity of the hydroxyl group-blocked adsorbent A was found to decrease 32.8 % for the removal of Pb(II). Further, the total metal uptake capacity of carboxylic and hydroxyl group-blocked adsorbent together was found to be almost equal to the total metal ions uptake by unblocked adsorbent. These results along with the functional groups study of adsorbent by the FTIR technique (Fig. 1) support that carboxyl and hydroxyl groups are mainly responsible for the uptake of Pb(II) by combination B.

Desorption studies

The 15.0 g of the combination B loaded with Pb(II) was collected and dried in an electric hot air oven at 105 °C for 12 h; 1.0 g of it was mixed with each 100 mL of HCl with varying concentration (0.1–0.5 M) in 250-mL screw-cap conical flasks. The mixtures so obtained were agitated in orbital shaker at 225 rpm speed for 300 min at 30 °C. After

300 min of agitation, the suspensions were filtered through Whatman no. 40 filter paper and the filtrates were analyzed for Pb(II) using AAS. Same procedure was repeated with H_2SO_4 and HNO_3. It was seen that the desorption efficiency increased with increase in the concentration from 0.1 to 0.5 M of desorption agents, viz. HCl, H_2SO_4 and HNO_3. Furthermore, it was noticed that HCl gave maximum desorption, about 99 % as compared to H_2SO_4 (83 %) and HNO_3 (74 %). The reusability of the combination B was tested in three consecutive adsorption–desorption cycles in batch mode, and the results suggested that the combination B has the potential to be used repeatedly for Pb(II) adsorption without much significant loss in total adsorption capacity.

Column studies

In this article, the effect of bed depth and flow rate on the breakthrough curves was investigated using bed depths of 25, 30 and 35 cm made by the uniform packing of 12, 14 and 16 g, respectively, of the combination B. The lead acid batteries effluent containing Pb(II), Fe(II) and Zn (II) metal ions with pH adjusted 6.0 was passed through the columns at the flow rate of 1.0, 2.0 and 5.0 mL min^{-1}.

Batch biosorption assays give fundamental information related to biosorption equilibrium and kinetics. However, in most industrial aqueous treatment units, a continuous flow biosorption experiments are preferred. Therefore, continuous biosorption experiments were conducted in fixed bed columns. The overall performance of the column is usually described through the concept of breakthrough curve, which is obtained by plotting the measured effluent concentration divided by the influent concentration (C_e/C_i) versus time (t). The column performance was studied by varying the flow rate and bed height at specific metal ion concentration.

Effect of effluent flow rate

Flow rate of the column could alter the residence time of the metal solution in the column and hence is an important parameter that could influence the sorption capacity of the biosorbent in fixed bed operations. To explore the effect of flow rate on Pb(II) biosorption, the lead battery wastewater with 645.15 mg L^{-1} Pb(II) initial concentration was passed through the column with fixed bed depth of 25 cm at pH 6.0 with different flow rates of 1.0, 2.0 and 5.0 mL min^{-1}. As shown in Fig. 4, the column performance was found to be better at lower flow rate. An earlier breakthrough and column exhaustion times were achieved, when the flow rate was increased from 1.0 to 5.0 mL min^{-1}. This behavior could be due to the decrease in the residence time, which restricted the contact of metal solution to the biosorbent (Singh and Ali 2012). Moreover, at higher flow rates, the metal ions did not have enough time to diffuse into the biosorbent and they leave the column before equilibrium occurred resulting in low metal uptake and which results in earlier breakthrough curves. At lower flow rates, the residence time of the metal solution in the column was increased, and hence, metal ions have enough time to diffuse into the biosorbent through intraparticle diffusion and resulting late breakthrough curves.

To predict the adsorption behavior of Pb(II) onto the combination B-packed fixed bed columns, the data obtained were analyzed by Thomas model as it is one of the most general and widely used models to explain the column performance theory. 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).

The expression by Thomas, for the adsorption by column, is given as follows in Eq. (10).

$$\frac{C_e}{C_i} = \frac{1}{1 + \exp\left(\frac{k_{TH} q_e s}{R} - k_{TH} C_i t\right)} \qquad (10)$$

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 (min), and $t = V_{eff}/R$ where V_{eff} is the effluent volume (mL) and R is the flow rate (mL min^{-1}). The values of k_{TH} and q_e were determined from the plot of C_e/C_i against time t using nonlinear regression analysis.

The value of the regression coefficient ($R^2 > 0.99$) as given in Table 5 indicates that the model describes the column performance data very well for the biosorption of Pb(II), Fe(II) and Zn (II) in all three sorption cycles. It was

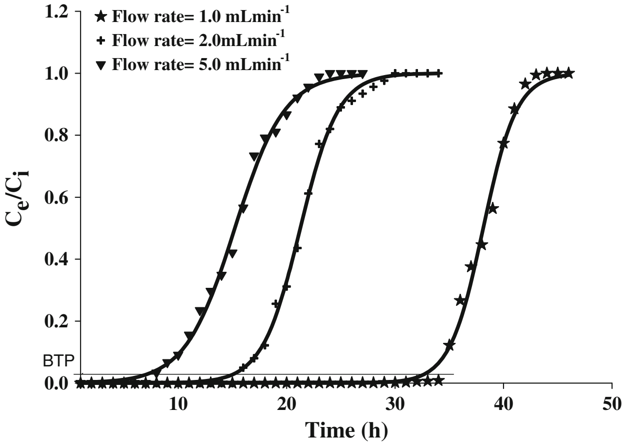

Fig. 4 Effect of flow rates on Pb(II) biosorption by combination B-packed fixed bed column at pH 6.0 ($C_i = 645.15$ mg L^{-1}, bed depth = 25.0 cm)

also found that the experimental and model predicted normalized values at experimental conditions were very close. Further, the metal uptake capacity found to decrease ($q_e = 512.45–204.74$ mg g^{-1}) in the successive cycles, whereas Thomas rate constant did not change significantly. This behavior was primarily attributed to gradual deterioration and depletion of binding sites caused by the acidic elution and continuous usage, or it might be due to blocking of the active sites for solute uptake by the organic moieties present in the lead battery effluents (Vinodhini and Das 2010). The effluent from first cycle showed complete biosorption of all three metals ions satisfying the Central Pollution Control Board standards (CPCB 1998) and making that water fit for reuse.

Effect of bed depth

The biosorption of the metal ions in fixed bed column studies is dependent on the quantity of biosorbent in the column. The continuous biosorption experiments were performed, at three different bed depths of 25, 30 and 35 cm, achieved by taking 12, 14 and 16 g of the combination B, in the columns as given in Fig. 5. The flow rate and initial Pb(II) concentration were kept constant at 1.0 mL min^{-1} and 645.15 mg L^{-1}, respectively, during the experiments. The shapes and gradient of the breakthrough curves change with the increase in bed depth from 25 to 35 cm. The metal ion concentration in the effluent was found to increase as the breakthrough time was reached and same was indicated by the sharp increase in the slope in each of the curves. The breakthrough time of 35.0 h was observed when the column of low bed depth of 25 cm was used for the biosorption study of Pb(II). On increasing the bed depth from 25 to 35 cm, the breakthrough time was found to increase from 35.0 to 47.0 h and metal uptake capacity q_e from 512.45 to 540.41 mg g^{-1}. This observation could be explained by considering the fact that with low bed depth, the metal ions do not have enough time to diffuse into the whole of the biosorbent mass, due to which the breakthrough time was achieved earlier by the column. However, the increase in bed depth of the column leads to increase the residence time of solution in the column and allowing the metal ions to diffuse deeper inside the biosorbent. Hence, higher values of the breakthrough time and q_e were achieved when a column of higher bed depth was used for the biosorption study.

Table 5 Thomas model parameters calculated constants for the Pb(II) biosorption by combination B at different bed depth and flow rates ($C_i = 645.15$, pH = 6.0)

R (mL min^{-1})	S (g)	k_{Th} (mL min^{-1}mg^{-1})	q_e (mg g^{-1})	R^2
1.0	12.0	0.001	512.45	0.99
2.0	12.0	0.009	285.76	0.99
5.0	12.0	0.007	204.74	0.99
1.0	14.0	0.007	514.37	0.99
1.0	16.0	0.005	540.41	0.99

The BDST model is one of the mathematical models proposed by Hutchins (1973), which states that bed depth (Z) and breakthrough service time (t_b) of a column bear a linear relationship. The equation can be expressed as follows:

$$t_b = \left(\frac{N_o}{C_i R}\right) Z - \left(\frac{1}{K_a C_i}\right) \mathrm{In}\left(\frac{C_i}{C_b} - 1\right) \tag{11}$$

where C_b (mg L^{-1}) is the breakthrough metal ion concentration, N_o (mg L^{-1}) is the adsorption capacity, K_a (L mg^{-1} h^{-1}) is the rate constant in BDST model, and the R (mL min^{-1}) is the flow rate. Equation (11) could be written in the form of the following Eq. (12):

$$t_b = mZ - K \tag{12}$$

where m is the slope of the BDST line ($m = N_o/C_i R$), and K is the intercept of this equation.

$$K = \frac{1}{k_a C_i}\left(\mathrm{In}\frac{C_i}{C_b} - 1\right) \tag{13}$$

A plot of t_b versus Z at flow rate of 1.0 mL min^{-1} was linear ($R^2 = 1.0$), indicating the validity of BDST model for the present system. The values of adsorption capacity N_o and rate constant K_a were evaluated from the slope and intercept of the plot and found to be 774.18 mg L^{-1} and 0.0006 L mg^{-1} h^{-1}, respectively. The value of K_a could be used to describe the capacity of biosorption column. A large value of K_a indicates that even a short bed could circumvent breakthrough, but as K_a decreases, a longer bed is required (Singh and Ali 2012) for maximum biosorption of the metal ions.

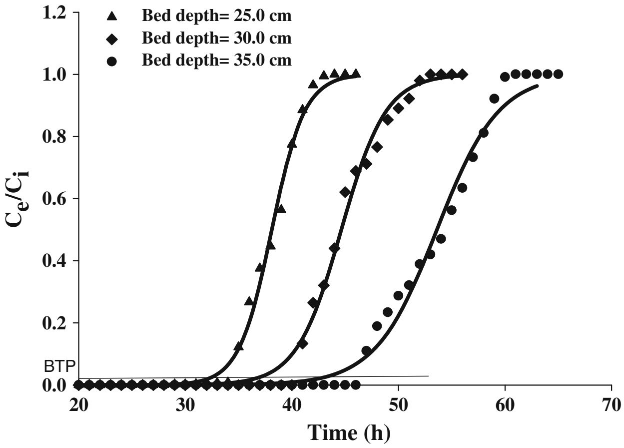

Fig. 5 Effect of bed depth on Pb(II) biosorption by combination B-packed fixed bed column at pH 6.0 ($C_i = 645.15$ mg L^{-1}, flow rate = 1.0 mL min^{-1})

Conclusion

The present article concludes that agricultural residues, viz. Eucalyptus cameldulensis saw dust and Arachis hypogea shell powder, used in different combinations have an excellent potential for the biosorption of Pb(II) from synthetic as well as lead battery effluents. The adsorption process was a function of pH, adsorbent dose, initial metal ion concentration and contact time. The effective pH for Pb(II) removal was found to be 6.0. Adsorption kinetics was found to follow pseudo-second-order kinetic model, and the equilibrium sorption data were satisfactorily fitted to Langmuir adsorption isotherms. Among the five different combinations used, combination B showed maximum biosorption capacity ($q_{\max} = 270.2$ mg g^{-1}) in batch mode. FTIR spectra analysis showed that the carboxyl and hydroxyl groups were the principal functional groups responsible for sorption of Pb(II) ions. The chemical blocking of the carboxyl and hydroxyl groups verified their participation in the metal sorption process. Further, the discharge of nearly equal amount of Na^+, K^+, Ca^{2+}, Mg^{2+} and H^+ during the uptake of Pb(II) ions showed that the adsorption process was entirely ion exchange. The column studies were carried out for treating lead battery effluent. Thomas and BDST models were applied to the data obtained, and the maximum metal uptake capacity ($q_e = 540.41$ mg g^{-1}) was obtained at flow rate of 1.0 mL min^{-1} with 35 cm bed depth. Present study reveals that the biosorbents used in different combinations are quite effective for the removal of different metal ions from the lead battery wastewater in continuous flow studies. The results obtained would be useful for the design of wastewater treatment plant for industrial purposes.

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