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Batch and Continuous Removal of Copper and Lead from Aqueous Solution using Cheaply Available Agricultural Waste Materials

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ABSTRACT: The potential of six economically cheap agricultural waste materials, viz. rice husk, betel nut peels, sugarcane molasses, tea waste, mustard oil cake and saw dust, was investigated for copper and lead removal from aqueous solutions under batch and continuous conditions. The effect of pH, contact time, sorbent dose and initial metal ion concentration on the uptake of copper and lead was first examined in batch mode. Rice husk was found to be the best among the tested biosorbents with a maximum removal of 72.17 % and 85.87 % for copper and lead, respectively. The batch sorption data correlated well with SIPS, Redlich-Peterson, Freundlich and Langmuir isotherms models. Heavy metal sorption kinetics was best explained by the diffusion based second order kinetics model. Fourier transform infrared analysis of rice husk, before and after heavy metal sorption, revealed the involvement of mainly hydroxyl, amine, and carboxyl functional groups in lead and copper removal by rice husk. Dynamic removal of lead and copper by rice husk was examined as a function of different bed height and flow rate using fixed-bed columns, which yielded a maximum saturation time of 14 hours. The metal breakthrough curves obtained were analysed using the Thomas, BDST, Yoon-Nelson and Clark breakthrough models. The simulation of breakthrough curve for the metals was successful with BDST, Yoon-Nelson and Clark models. Removal of bound lead/copper from the loaded column was finally achieved by using 0.1M HCl as the eluant, which yielded complete desorption of the metals in nearly 60 min.

Key words: Heavy meal removal, Biosorption, Breakthrough curve, Fixed-bed column, Desorption

INTRODUCTION

Increased usage of heavy metals in industrial activities has resulted in their widespread occurrence as a constituent in effluents from many industries. For example, lead copper, chromium, mercury and cadmium are commonly present in the wastewater from industries such as electroplating, plastic and paint manufacturing, mining, metallurgical process, petrochemical process, battery manufacturing etc. (Iqbal and Edyvean, 2004; 2005). Among the different heavy metals, toxicity due to lead and copper is well established, which at higher concentrations threaten human life. In addition, they accumulate in food chains and persist in the nature. The current Environmental Protection Agency (EPA) standard for lead in discharge wastewater and drinking water is 0.5 and 0.05 mg/L, respectively (Qaiser *et al.*, 2009; ATSDR, 2004; 2007). Due to their toxic effects on living species, treatment of industrial effluents containing metallic ions prior to their discharge into the environment is of great importance (Ko *et al.*, 2000).

Among the available methods to remove heavy metals from wastewaters, adsorptive removal of heavy metals from aqueous effluent has received much attention in recent years and is usually achieved by using activated carbon or activated alumina (Ali *et al.*, 1998; Monser and Adhoun, 2002). Other methods employed for the removal of heavy metals from wastewater include chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery, filtration, reverse osmosis, ion exchange and membrane technologies. However, all these processes suffer from one or more serious drawbacks such as inefficient removal of metals or they may be ineffective or expensive (Gavrilescu, 2004; Pino *et al.*, 2006; Qaiser *et al.*, 2009), especially when

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concentration of the heavy metal ions in solutions is in the order of 1-100 mg/L. Other drawbacks of these techniques may be secondary sludge production, high operational cost, etc. Hence there is an increasing interest in other heavy metal removal methods. One such promising method is biosorption which involves the use of biological materials such as plants and microbes. Due to the high uptake capacity and cost-effective nature of these natural raw materials, biosorption is seen to be the future for heavy metal removal from wastewaters. Although there are many studies conducted to remove heavy metals from aqueous solution using specially propagated bacteria, fungus, yeast and plant biomass, investigations on the use of cheap and easily available agricultural waste materials are highly limited. This is very important from the standpoint of the environment and sustainability of the process. Therefore, in the present study six different agricultural wastes, viz. rice husk, tea waste, sugarcane bagasse, mustard oil cake, betel nut peels and saw dust, were studied for evaluating the potential for removal of heavy metals from aqueous solution under batch and continuous conditions.

MATERIALS & METHODS

All the agricultural plant wastes, viz. rice husk, sugarcane bagasse, mustard oil cake, tea waste, betel nut coir and saw dust were collected from Gandhiya Village, Nalbari district, Guwahati (Assam, India). The collected biosorbents were manually cleaned to remove any unwanted impurities and debris, followed by washing with tap water and then by double distilled water. The materials were then dried under the sun to remove moisture followed by overnight drying in a hot air oven at 60°C. Completely dried materials were finally grinded using a mixer-grinder, sieved to obtain fine powder of 0.3-0.7 mm size and stored in an air tight container prior to use (Oboh *et al.*, 2009). Stock solution of lead and copper (1000 mg/L each) was prepared by dissolving $PbNO_3$ and $CuSO_4$’”$7H_2O$ (AR Grade), respectively, in double distilled water. Batch heavy metal biosorption experiments were performed to examine the effect of time, initial metal concentration, pH and biosorbent dose on their removal by the different biosorbents. For these batch experiments, the respective metal stock solutions were suitably diluted with distilled water to obtain 50 ml working volume of desired metal concentration in 250 ml Erlenmeyer flasks. All the batch experiments were carried out at an ambient room temperature of 25°C and under agitation (150 rpm) using an orbital rotary shaker (SI-300R, Rose scientific Ltd.). At the end of each batch experiment, the metal loaded biomass was separated by filtration using Whatman filter paper (4-7 µm pore size) and samples were analysed for lead and copper remaining in the solution using an atomic absorption spectrophotometer (AA 240, Varian, The Netherlands).

All the batch biosorption experiments were performed in triplicate and the results were expressed as either metal sorption capacity (mg/g of biosorbent) or removal efficiency (%) (Bansal *et al.*, 2009).

The amount of metal sorbed at equilibrium q_e (mg/g) was calculated by the equation:

$$q_e = \frac{[(C_o - C_e)V]}{W} \qquad (1)$$

where, q_e = sorption capacity (mg/g), V = volume of metal containing solution (L), W = Weight of biosorbent used (g), C_o = initial metal ion concentration (mg/L), C_e = equilibrium metal ion concentration (mg/L). The metal removal (%), also called as sorption efficiency was computed according to equation:

$$\% \text{ Removal} = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (2)$$

where, C_o = initial metal ion concentration (mg/L) and C_e = equilibrium metal ion concentration (mg/L). Sorption isotherms are plots between the sorption uptake (q_e) and the final equilibrium concentration of

Table 1. Sorption isotherm models tested in this study.

Model name	Equation	Estimable parameters	Reference
Langmuir	Non-linear form: $q_e = \frac{q_{max} b C_e}{1 + b C_e}$ Linear form: $\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{b q_{max}}$	$q_{max,}, b$	(Pakshirajan *et al.*, 2013)
Freundlich	Non-linear form: $q_e = K_F C_e^{1/n}$ Linear form: $\ln q_e = \ln(K_F) + (1/n)\ln(C_e)$	K_F, n	(Pakshirajan *et al.*, 2013)
Redlich- Peterson	$q_e = \frac{K_{RP} Ce}{1 + a_{RP} C_e^{\beta}}$	K_{RP} , a_{RP} , β	(Ho, 2006)
Sips	$q_e = \frac{q'_{max} b C_e^{1/n}}{1 + b C_e^{1/n}}$	$q_{max,}, b, n$	(Ho, 2006)

the residual sorbate remaining in the solution (C_e). In this study the Langmuir, Feundlich, Redlich-Peterson and SIPS models were applied to estimate the lead and copper sorption isotherm parameters. For each of these models, the isotherm parameters were determined by minimising the respective error function across the concentration range studied using the *solver* add-in function with Microsoft's excel spreadsheet (Microsoft, 2007). These isotherms relate the amount of metal sorbed at equilibrium per unit weight of biosorbent, q (mg/g), to the metal concentration at equilibrium, C_e (mg/L).These models are presented in Table 1.

Batch kinetic experiments were conducted to determine the rate of lead and copper sorption by the biosorbents. The experiments were carried in batch mode at 25°C for 3 hours at a constant pH of 6 and 5 for lead and copper, respectively (Cruz-Olivaresa *et al*., 2010; Daffalla, 2012). The experimental data was further fitted to pseudo first and pseudo second-order kinetic models to understand the sorption mechanism involved. These models are mentioned below.

The pseudo first-order (Lagergren model) equation is generally expressed as (Vijayaraghavan and Prabu, 2006)

$$\frac{dq_t}{d_t} = k_1(q_e - q_t) \qquad (3)$$

where q_e and q_t (mg/g) are the amount of metal sorbed at equilibrium and at time *t* (min), respectively, and k_1 (min$^{”1}$) is the rate constant of the pseudo first-order equation. After integration and applying the boundary conditions, i.e. $q_t = 0$ at t = 0 and $q_t = q_t$ at t = t, the linearised form of the equation is:

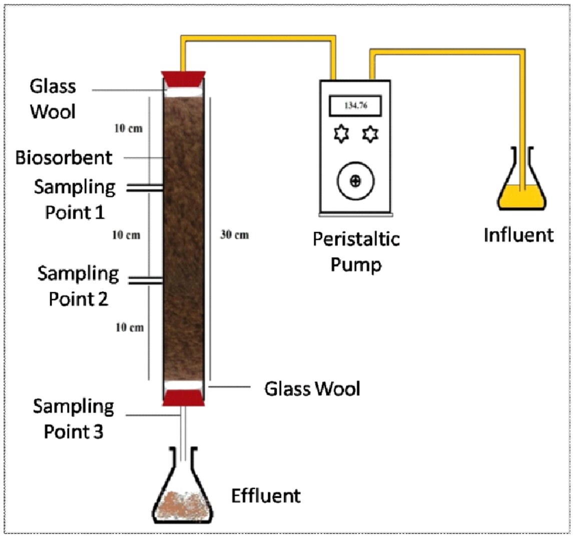

Fig. 1. Schematic of the fixed-bed column setup used in the continuous biosorption experiments.

$$q_t = q_e(1 - e^{-k_1 t}) \qquad (4)$$

Taking *ln* on both the sides, the linearised form of the equation is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (5)$$

The pseudo second-order equation is expressed as (Zhou and Kiff, 1991; Vijayaraghavan and Prabu, 2006):

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \qquad (6)$$

where k_2 is the equilibrium rate constant of the pseudo-second order equation (g/mg min).

Integrating the above equation gives the linearised form as follows:

$$\frac{t}{qt} = \frac{1}{k_2 qe^2} + \frac{1}{qe}t \qquad (7)$$

From the results of the batch tests, rice husk proved to be the best among all the biosorbents. Therefore, its morphological characteristics were observed by scanning electron microscopy (SEM) (LEO 1430VP), and its qualitative elemental constitution responsible for the metal uptake was analysed by Energy Dispersive X-ray (EDX) analysis coupled to SEM. For SEM analysis, raw rice husk and rice husk loaded with lead or copper following their biosorption, were taken and the samples were dried at 60 °C in a hot air oven for 24 hour to dehydrate the samples. Biosoprtion conditions followed were: initial metal concentration = 50 mg/L, biomass dose = 20 g/L, pH = 5 (copper) and 6 (lead). Sample fixing was then carried out by coating with a sticky carbon tape followed by cryofixation by plunging the specimen into slush nitrogen, i.e., liquid nitrogen cooled to its freezing point in a slush-nitrogen plunge (Qaiser *et al*., 2009).

Infrared spectra of raw and metal loaded rice husk, which showed best results among all other biosorbents, were obtained using a Fourier transform infrared (FTIR) spectrometer (Spectrum One, Perkin-Elmer, USA). For this analysis, the raw biosorbent was initially dried in an oven at 60 °C for 24 h before grinding. Approximately 5 mg of the finely ground biomass was encapsulated in 1000 mg of KBr pellet in order to prepare translucent sample disks using an eight ton force hydraulic press for 5 minutes (Elangovan etal., 2009). Similar procedure was followed for the metal loaded biosorbent obtained using the same conditions (initial metal concentration, biomass dose, pH, etc.) as mentioned earlier.

Column experiments were conducted for continuous removal of lead and copper using rice husk which proved to be the best among all the tested

Table 2. Models used to evaluate breakthrough curve in this study

Model name	Linearised model equation	Remarks	Ref.
BDST	$t = \frac{N_O}{C_O} Z - \frac{1}{K_a C_O} \ln\left(\frac{C_O}{C_B} - 1\right)$ $Z_O = \frac{F}{K_a N_O} \ln\left(\frac{C_0}{C_B} - 1\right)$	A plot of *t* Vs *Z*, should yield a straight line where N_o and K_a can be evaluated from slope and intercept, respectively. Z_o is the critical bed depth.	(Rio *et al*., 2002)
Thomas	$\ln\left(\frac{C_O}{C_t} - 1\right) = \frac{K_{TH} q_o W}{Q} K_{TH} C_O t$	A plot of $\ln[(C_o/C_t)-1]$ against *t* gives a straight line from which the value of K_{TH} and q_o can be determined from slope and intercept, respectively.	(Rio *et al*., 2002)
Yoon-Nelson	$ln\left(\frac{C_t}{C_O - C_t}\right) = K_{YN} t - \tau K_{YN}$	A plot of $\ln[C_t/(C_o-C_t)]$ against t gives a straight line from which the value of K_{YN} and τ can be determined from slope and intercept, respectively.	(Rio *et al*., 2002)
Clark	$ln[(\frac{C_O}{C})^{n-1} - 1] = \ln A - rt$	*A* and *r* are determined from the slope and the intercept of plots of $\ln[(C_o/C)^{n-1}-1]$ Vs *t*.	Zorica *et al*., 2011)

biosorbents from the batch studies. For this continuous experiment, aqueous solution containing lead/copper at 10mg/L concentration was used and the initial pH of the metal solution was adjusted at optimum for these metals based on the batch study, i.e. pH = 5 for copper and pH = 6 for lead.

The fixed column used in this study was made from a perspex tube of inner diameter (ID) = 3 cm and effective length (L) = 30 cm. Three sampling ports were provided at a distance of 10 cm each along the length of the column. The column was packed with rise husk (particle size 0.3-0.7 mm) between two supporting layers of glass wool and was operated in down flow mode using a peristaltic pump. A schematic of the setup is shown in Fig. 1. The outlet metal ion concentration was determined by collecting samples at regular time intervals from the different sampling ports. The column performance towards continuous copper and lead biosorption onto rice husk was investigated as a function of flow rate and bed depth. The effect of flow rate for copper was investigated in the range 5-15 mL/min, whereas for lead it was carried out at 30 and 40 mL/min. The effect of bed height was investigated at 10, 20 and 30 cm equivalent to 9.26, 18.52 and 27.78 g of biosorbent, respectively, for both copper and lead. The concentration of copper and lead in the samples was determined using an atomic absorption spectrometer (AA240, VARIAN, The Netherlands).

The maximum column capacity, q_{total} (mg) for a given set of condition in this continuous study was calculated from the area under the plot of sorbed metal concentration $C_{ad,}$(mg/L) versus time as given by the following equation (Vijayaraghavan and Prabu, 2006; Daffalla *et al*., 2012):

$$q_{total} = \frac{QA}{1000} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} C_{ad} dt \qquad (8)$$

where, C_{ad} is the metal sorbed in the column, which was calculated from the difference between the inlet (C_i, mg/L) and outlet (C_e, mg/L) metal concentration, t_{total} is the total flow time (min), Q is the flow rate (mL/min), A is the area under the breakthrough curve (cm^2).

The equilibrium uptake ($q_{e(exp)}$), i.e. the amount of metal sorbed (mg) per unit dry weight of biosorbent (mg/g) in the column was calculated using Eq. (8).

$$q_{e(exp)} = \frac{q_{total}}{W} \qquad (9)$$

where, W is the total dry weight of biosorbent in the column in gram.

The total volume treated V_{eff} (mL) was calculated from Eq.(9)

$$V_{eff} = Qt_{total} \qquad (10)$$

For predicting metal breakthrough in the column, the experimental data obtained was fitted to the Bed-Depth Service Time (BDST), Thomas, Yoon-Nelson and Clark models These models are presented in Table 2, and its more details can be found in the literature (Aksu *et al*., 2007; Cruz-Olivaresa *et al*., 2010; Daffalla *et al*., 2012; Acheampong *et al*., 2013).

To determine the reuse ability of rice husk as well as the recovery of lead and copper following biosorption, desorption experiments were performed with 0.1 M HCl as the eluant. The HCl solution was pumped from the top of the column along its length using a peristaltic pump with a defined inlet flow rate. Metal ion concentration in the outlet was determined at regular interval using an atomic absorption spectrometer (AA240, VARIAN, The Netherlands).

RESULTS & DISCUSSION

Fig. 2a shows the effect of contact time on the extent of lead and copper sorption by rice husk, which

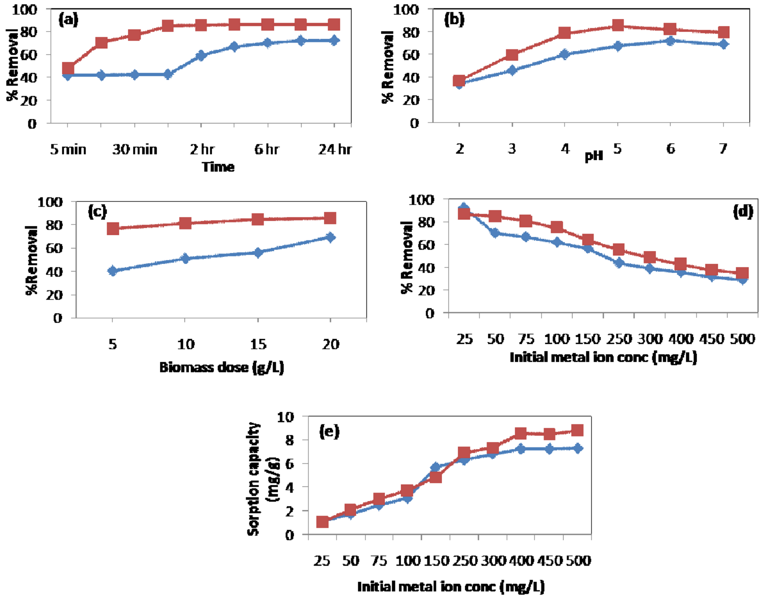

Fig. 2. Effect of different process parameters on batch removal of copper (♦) and lead (%) using rice husk as the biosorbent: (a) contact time (other conditions: initial metal concentration = 50 mg/L, biomass dose = 20 g/L, pH = unadjusted) , (b) pH (other conditions: initial metal concentration = 50 mg/L, contact time = 3 h, biomass dose = 20 g/L), (c) biomass dose (other conditions: initial metal concentration = 50 mg/L, contact time = 3 h, biomass dose = 20g/L, pH = 6.0 (for copper) and 5.0 (for lead)), (d) initial metal concentration (other conditions: contact time = 3 h, pH = 6 (for copper) and 5.0 (for lead), biomass dose = 20 g/L) and (e) initial metal concentration on metal sorption capacity (other conditions: contact time = 3 h, pH = 6 (for copper) and 5.0 (for lead), biomass dose = 20 g/L).

showed the best result among all the six biosorbents. It is observed that the metal sorption rate increased with an increase in the contact time. Maximum removal of these metals was achieved within 3 hr for copper and within 1 hr for lead, after which the residual metal concentration in solution remained the same. The initial rapid rate of the metal sorption is due to the abundant availability of the negatively charged functional groups on the surface of the rice husk. The later slow sorption rate is attributed to the electrostatic hindrance caused by already sorbed positively charged metal species and the slow pore diffusion of the metal (Saravanane *et al.*, 2002). In case of copper, rice husk showed a maximum removal of 72.16 % followed by saw dust (64.96%) and tea waste (62.26%). Similarly, lead removal was best with rice husk (85.87%) followed by tea waste (83.94%), sugarcane (83.28%), oilcake (80.27%), sawdust (79.57%) and betel nut peels (72.33%). Metal biosorption is critically linked with pH. From Fig. 2b, it is evident that maximum copper sorption is obtained at pH 6 with rice husk (72.16%). This was followed by tea waste (60.76%), betel nut (59.67%), sugarcane (52.94%), oil cake (52.19%) and saw dust (51.11%). In case of lead, the optimum pH was 5.0 with 85.21% removal using rice husk. At the same pH, sugarcane baggase showed 82.91% removal followed by tea waste (82.34%), saw dust (80.39%), oil cake (78.68%) and betel nut (72.89%). Both the biosorbent surface metal binding sites and the metal chemistry in solution are influenced by solution pH. At low pH values, metal cations and protons compete for binding sites on biosorbent surface which results in reduced uptake of metal. It has been suggested that at highly acidic condition, biosorbent surface ligands would be closely associated with H_3O^+ that restricts access to ligands by metal ions as a result of repulsive forces. It is expected that increase in pH values exposes a large numbers of negative charged ligands which attracts more of positively charged copper and lead ions. Hence pH 6.0 and 5.0 were found optimum for Cu(II) and Pb(II), respectively (Sekher *et al.*, 1998). In addition, at a high pH (above 6.0), the lower binding is attributed to the reduced solubility of copper and lead and their precipitation (Zhou and Kiff, 1991). The effect of biosorbent dose on copper and lead biosorption by rice husk is depicted in the Fig 2c. It is observed that the metal removal increased with an increase in the sorbent dosage with a maximum removal obtained at 20.0 g/L biosorbent dose, which can be explained due to more availability of binding sites for lead and copper biosorption (Rio *et al.*, 2002). A similar trend in the metal removal was observed for other biosorbents as well (data not shown). Fig. 2d shows the effect of initial metal concentration on copper sorption by rice husk. It is observed that copper sorption decreases from 92.23% to 29.18% for rice husk with an increase in the metal concentration from 25 to 500 mg/L. Similarly, lead sorption decreased from 87.27% to 33.3% for rice husk with a same increase in the metal ion concentration. However metal sorption capacity (expressed as mg/g) increases with an increase in the initial metal concentration for both copper and lead removal by rice husk (Fig. 2e). The metal removal results followed a similar trend for other biosorbents. At a high initial metal concentration, most of the metal ions are left unadsorbed due to saturation of their binding sites on the biomass. As the ratio of sorptive surface to ion concentration decreases with an increase in the metal ion concentration, metal ion removal efficiency gets reduced. Thus, at a low initial metal concentration, more binding sites are available, but at a higher initial concentration, the number of ions competing for available binding sites on the rice husk surface increases, thereby reducing its uptake (Fig.2(d)) (Zorica *et al.*, 2011).

The metal biosorption experimental data obtained using the six different biosorbents was fitted to the non-linear Langmuir model, which revealed q_{max} mostly in the range 6.34-11.51 mg/g for copper. Similarly, for lead biosorption q_{max} values were obtained mainly in the range 7.56-10.43 mg/g. The highest value was obtained due to rice husk for both the metals. The affinity factor b was obtained in the range 0.004-0.017 L/mg and 0.011-0.028 L/mg for copper and lead biosorption, respectively, with the highest value obtained again due to rice husk. Table 3 presents the estimated Langmuir model parameters using rice husk as the biosorbent for copper and lead. The Langmuir sorption isotherm, which is probably the best known and most widely applied, supposes a monolayer sorption by physical forces with a homogeneous distribution of sorption sites and sorption energies, without any interaction between the sorbed molecules (Pino *et al.*, 2006; Bansal *et al.*, 2009). Thus, high values of q_{max} and b is obtained for copper and lead biosorption using rice husk indicated a high metal uptake and high affinity between the biosorbent and the metal ions, respectively (Table 3).

In contrast to the Langmuir model, the Freundlich isotherm is originally empirical in nature, but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities i.e. multilayer adsorption (Pino *et al.*, 2006; Bansal *et al.*, 2009). The applicability of this isotherm model to describe the metal sorption process was judged by the correlation coefficient R^2 value which is highest for rice husk i.e. 0.96 and 0.97 for copper and lead sorption, respectively (Table 3). The value of K_F obtained from the linearised Freundlich equation using the different biosorbent was mainly in the range 9.70-48.41 L/g for copper and 11.32-34.69 L/g for lead. The value of the affinity constant (*1/n*) was in the range 0.32-0.50 and 0.43-0.52 for copper and lead, respectively. The highest values of K_F and *1/n* were obtained due to rice husk among all the biosorbents for both copper and lead biosorption. The high values of adsorption capacity K_F and heterogeneity factor *n* obtained using this model for suggest a high affinity of both copper and lead for rice husk as well as a high distribution of metal binding sites on its surface. Redlich and Peterson (Ho, 2006) incorporated the features of Langmuir and Freundlich isotherm into a single equation.. This isotherm reduces to a linear isotherm in the case of low surface coverage for β =0, and to the Langmuir isotherm

Table 3. Estimated sorption isotherm model parameters for copper and lead removal using rice husk as the biosorbent

Isotherm	Parameter	Copper	Lead
Langmuir non-linear	q_{max} (mg/g)	11.51	9.29
	b (L/mg)	0.017	0.028
	R^2	0.97	0.97
Freundlich	K_f (L/g)	48.41	33.94
	1/n	0.50	0.52
	R^2	0.955	0.97
SIPS	q'max (mg/g)	11.07	14.79
	b'(L/mg)	0.12	0.69
	$1/n'$	0.78	0.61
	R^2	0.97	0.99
Redlich-Peterson	K_r (L/mg)	14.29	20.54
	a_R (L/µg)	408.71	391.56
	β	0.56	0.58
	R^2	0.96	0.98

Table 4. Estimated biosorption kinetic parameters for (a) copper and (b) lead removal using the different biosorbents.

(a)

Biosorbent		Pseudo first-order kinetic model			Pseudo second-order kinetic model		
	$q_e(exp)$	K_1	$q_e(cal)$	R^2	K_2	$q_e(cal)$	R^2
Rice husk	1.804	0.003	1.04	0.206	0.016	1.970	0.949
Tea waste	1.519	0.001	1.14	0.085	0.020	1.587	0.927
Sugarcane bagasse	1.324	0.001	1.04	0.030	0.025	1.434	0.970
Oil cake	1.565	0.003	1.03	0.083	0.033	1.571	0.989
Betel nut peels	1.490	0.001	1.12	0.103	0.018	1.580	0.928
Saw dust	1.330	0.001	1.56	0.015	0.033	1.380	0.973

(b)

Biosorbent		Pseudo first-order kinetic model			Pseudo second-order kinetic model		
	$q_e(exp)$	K_1	$q_e(cal)$	R^2	K_2	$q_e(cal)$	R^2
Rice husk	2.346	0.005	1.29	0.290	0.014	2.60	0.979
Tea waste	2.058	0.007	1.17	0.220	0.012	2.43	0.979
Sugarcane bagasse	2.072	0.006	1.26	0.260	0.010	2.40	0.964
Oil cake	1.987	0.009	1.19	0.205	0.010	2.43	0.950
Betel nut peels	1.822	0.005	1.19	0.254	0.008	2.27	0.960
Saw dust	2.00	0.006	1.25	0.261	0.010	2.43	0.970

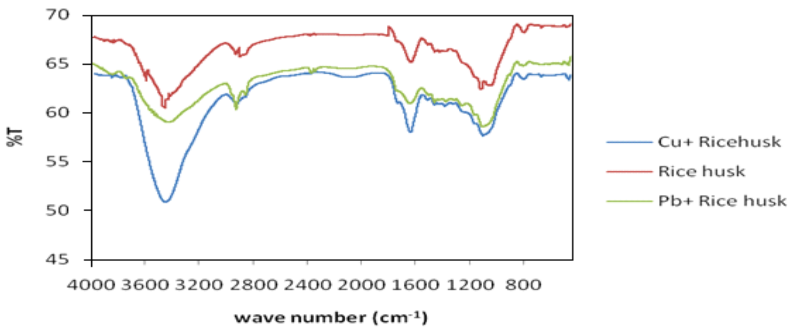

Fig. 3. FTIR spectra of raw rice husk and metal loaded rice husk.

form when β=1. However Freundlich form is evident at β >1. The Redlich-Peterson isotherm constants for copper and lead biosorption are presented in Table 3. The value of the isotherm constant K_R obtained from the experimental data for the different biosorbents was in the range 1.42-14.29 L/mg in case of copper and for lead it was in the range 7.6-20.54 L/mg. The values of the exponent β obtained varied from 0.38 to 0.56 for copper and in case of lead it was in the range 0.51-0.60. The highest values of these parameters corresponded to rice husk among all the biosorbents. On the contrary, a reverse trend was observed with a_R for both the models. The β value obtained in the present study using this isotherm further confirmed that the metal biosorption by rice husk follows the Langmuir isotherm. A high K_R value obtained for rice husk again confirmed high affinity of rice husk for copper and lead. SIPS isotherm at a low metal concentration effectively reduces to Freundlich isotherm when $1/n \lll 1$, and at a high metal concentration when $1/n = 1$ it predicts a monolayer sorption capacity characteristics of the Langmuir isotherm (Pakshirajan *et al.*, 2013). By fitting the experimental data to SIPS isotherm model (Eq. 8), the model *b* value was obtained the range 0.002-0.12 L/mg and 0.004-0.69 L/mg for copper and lead, respectively; whereas the value of $1/n'$ was in the range 0.48-0.78 and 0.42-0.61 for copper and lead, respectively. The highest values of *b* and $1/n$ were obtained due to rice husk among all the biosorbents for both the metals (Table 3). Furthermore, the value of $1/n$ greater than 0.5 indicates that the biosorption of copper and lead by rice husk is more of a Langmuir form than that of Freundlich.

Table 5. Possible range of IR-wavelength (cm^{-1}) with respect to presence of functional group from FTIR spectra of native rice husk and metal loaded rice husk (Numerical values corresponds to peaks obtained from Fig. 3).

IR Range	Functional group	Functional moiety	Raw rice husk	Rice husk loaded with copper	Rice husk loaded with lead
3700-3000	Free and intermolecular-OH	OH stretch	3610		
3520–3320	NH_2 in aromatic amines	NH stretch	3516	3488	3492
2990–2850	CH_3 and CH_2 in aliphatic compound	CH antisym and asym stretch	2936	2944	2937, 2911
2700–2250	Amine salts	NH_2 stretch	2383		
1680–1620	C O and NH_2 in primary amides	C O stretch	1640	1660	1681
1400–1310	COO- group in carboxylic acid	Antisym stretch	1397	1382	1386
1285–1240	AR O in alkyl ethers	C-O stretch	1274	1274	
1260–1150	Hydrated sulphonic acid	SO_3 stretch			1161
1060–1025	CH_2-OH in primary alcohols	C O stretch	1055	1045	
950–865	CH-CH_2 in vinyl compounds	CH_2	845	866	866

The data on metal sorption kinetics using rice husk and other biosorbents was first fitted to the linearised form of the pseudo first-order model (Eq. 11). The sorption rate constants k_1 and q_e for copper and lead were estimated from the slope and intercept of the plot of *ln (qe-qt)* versus *t*, as per Eq. 11 and are presented in Table 4 for all the biosorbents; the R^2 values, which clearly showed a poor fit of this model to the experimental data. The data was then fitted to the pseudo-second order model which is based on the assumption that the filling rate of sorption sites in a biosorbent is proportional to the square of the number of unoccupied sites as defined in Eq. 7.

A plot of t/q_t vs. *time* yields a straight line, from which the values of k_2 and q_e can be obtained from intercept and slope of the straight line, respectively. These model parameters are also presented in Table 4.

The experimental equilibrium specific uptake of copper and lead q_e(exp) was compared with the q_e(cal) obtained using the Lagergren first-order and second-order equation and are given in Table 4 (a) and (b), respectively. A higher degree of R^2 (>0.9) was obtained for the pseudo second-order kinetic model for the sorption of copper and lead compared with that obtained using the pseudo-first order kinetic model. All these results indicate that copper and lead biosorption by rice husk involves a diffusion controlled process based on chemical reaction, such as that involving ion exchange between the biosorbent and the metals (Ho, 2006; Preetha and Viruthagiri, 2007; Bansal *et al.*, 2009).

FTIR spectra of raw rice husk and metal loaded rice husk are shown in Fig 3. Table 5 presents infrared adsorption wavelength range and the corresponding functional groups (Luo *et al*., 2011). It also shows the various functional groups that were recognised in the FTIR spectra of native rice husk and rice husk loaded with the metals. The FTIR analysis (Fig. 3 and Table 5) reveals a peak around 3610 cm^{-1} which shows the existence of free and intermolecular bonded hydroxyl groups that were absent in the spectra of metal loaded rice husk indicating participation of these groups in binding copper and lead. The peak obtained around 3516 cm^{-1} and 2936 cm^{-1} shows (-NH) and (–CH) stretch, respectively, in the rice husk. Presence of peak around 2383 cm^{-1} shows NH_2 bending. These were however absent in the spectra of metal loaded rice husk indicating their involvement in both copper and lead uptake. Presence of peak around 1640 cm^{-1} and 1397cm^{-1} in native rice husk confirms (-CO) and (-COO) stretch. Absence of –C-O stretch and presence of –SO stretch in the spectra of rice husk loaded with lead reveals the complex nature of biosorption. Presence of intense band at 1055 cm^{-1} can be assigned to the C–O of alcohols and carboxylic acids which is absent in the spectra of rice husk loaded with lead. Peak around 845 cm^{-1} shows the presence of (-CH_2) bending. Following biosorption, the intensity of many peaks was either minimized or shifted in case of the spectra of metal loaded rice husk. Variation in the FTIR peaks of the biomass following metal biosorption suggests the participation of its various functional groups in the metal removal process. Fig. 4(a) illustrates the SEM image of rice husk which shows irregular groove and ridges in fibrous network that is considered helpful for the binding of copper and lead on to the biosorbent surface. In Fig 4(a) and 4(b) the micrographs enabled the direct observation of the changes in the surface microstructures of the rice husk before and after metal biosorption.

EDX measurements of the samples (with and without metal ion) were recorded for qualitative

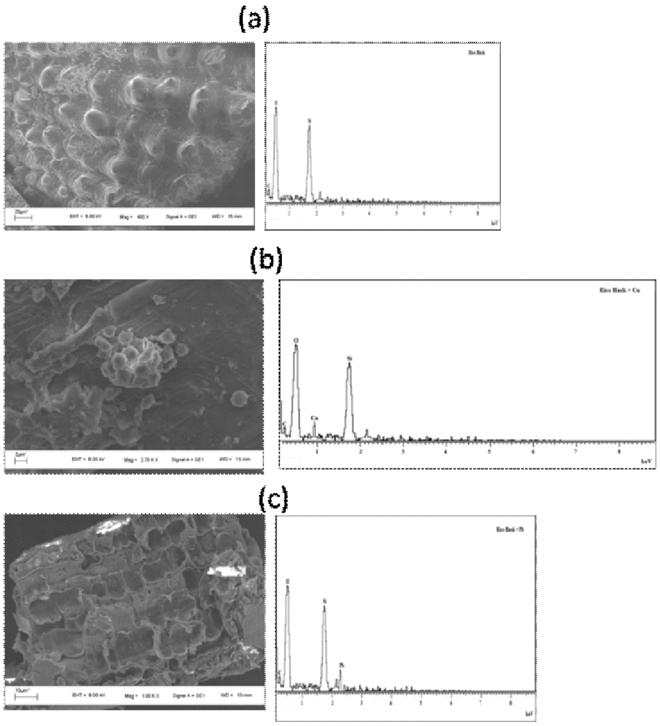

Fig. 4. SEM image and EDX diffractogram of (a) native rice husk (EDX full scale = 115 counts, Cursor = 8.834 KeV), (b) rice husk loaded with copper (EDX full scale = 103 counts, Cursor = 8.834 KeV), (c) rice husk loaded with lead (EDX full scale = 105 counts, Cursor = 8.834 KeV).

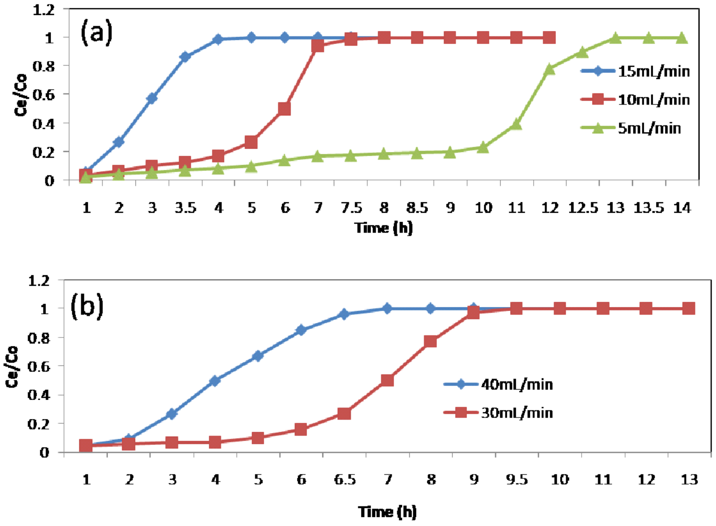

Fig. 5. Effect of flow rate on continuous metal biosorption by rice husk using the fixed bed columns: (a) copper and (b) lead (bed-depth = 10 cm, inlet metal concentration (C_0) = 10 mg/L, particle size = 0.3-0.7 mm, inlet solution pH = 6 (for copper) and 5 (for lead)).

analysis of the elemental constitution of the rice husk. Fig. 4(a) shows the EDX spectra for native rice husk where as Fig 4(b) and Fig 4(c) shows the EDX spectra of rice husk loaded with copper and lead, respectively. The samples equilibrated with metal ion solution showed distinct peaks for copper and lead confirming these metal ions were sorbed onto the rice husk as they were absent in the native rice husk.. EDX analysis provided direct evidence for the copper and lead sorption onto the biosorbent. In continuous column experiments, as the metal containing solution moves, its sorption zone also starts moving and after some

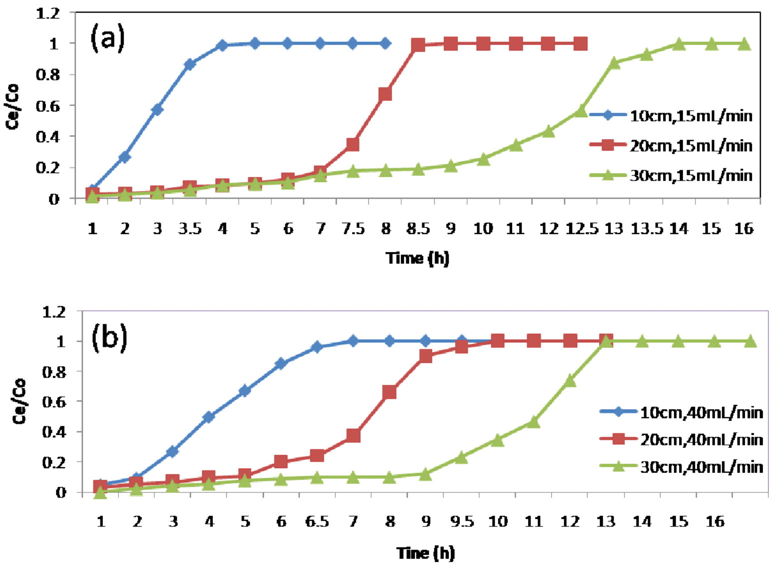

Fig. 6. Effect of bed depth on continuous metal biosorption by rice husk using the fixed bed columns: (a) copper and (b) lead (flow rate = 40 ml/min, inlet metal concentration (C_0) = 10 mg/L, particle size = 0.3-0.7 mm, inlet solution pH = 6 (for copper) and 5 (for lead)).

Table 6. Uptake of metal ions by rice husk in the dynamic column experiment conducted at different conditions.

		Copper			
Z (cm)	*Q* (mL/min)	C_o (mg/L)	V_{eff} (mL)	q_{total} (mg)	q_e(exp) (mg/g)
10	15	10	75	81.18	8.76
10	10	10	80	262.32	28.32
10	5	10	70	477.00	51.51
20	15	10	135	638.04	34.41
30	15	10	210	1613.52	58.08
		Lead			
Z (cm)	*Q* (mL/min)	C_o (mg/L)	V_{eff} (mL)	q_{total} (mg)	q_e(exp) (mg/g)
10	40	10	280	664.8	71.79
10	30	10	300	1136.22	122.70
20	40	10	400	1665.6	89.92
30	40	10	480	2776.2	99.93

time, concentration of metal in the effluent sharply raises, which is termed as the breakthrough point. Breakthrough time (t_b) is therefore defined as the time required for achieving a specific breakthrough concentration in the column, which is generally (10% of initial concentration *Co*). The loading behaviour of metal ions to be removed from solution in a fixed-bed is usually expressed in terms of C_e/C_O as a function of time, giving a breakthrough curve (Luo *et al.*, 2011). The breakthrough curves obtained at different flow rates, at a constant inlet metal concentration of 10 mg/L and bed height of 10 cm for both copper and lead are shown in Fig. 5(a) and 5(b), respectively. These curves show that the breakthrough time and exhaustion time increase with a decrease in flow rate. As the influent flow rate in the column was increased the breakthrough curve of both the metals turned steeper. Fig. 5 reveals that the column performed well for copper and lead biosorption at lower flow rates. This is mainly because at lower flow rates residence time of the feed solution increases allowing more time for the metal ions to interact with the rice husk particles enabling diffusion of more ions into its pores via inter-particle diffusion (Vijayaraghavan and Prabu, 2006). Further, an increase in flow rate reduces the volume of treated effluent before the bed is saturated and, therefore, decreases the bed service time to breakthrough. Breakthrough curves for copper and lead biosorption onto rice husk were evaluated for different bed-depth for an inlet metal concentration of 10 mg/L and at a flow rate of 15 mL/min for copper and at 40 mL/min for lead. Three bed-depths (10, 20 and 30 cm), corresponding to 9.26, 18.52

Table 7. Estimated BDST model parameters for metal biosorption in the fixed bed column study (initial metal concentration (C_O) =10 mg/L, particle size = 0.3-0.7mm, flow rate = 15 ml/min (for copper) and 40 ml/min (for lead), inlet solution pH = 6 (for copper and 5 (for lead))

Copper			Lead		
Parameters	10% saturation	50% saturation	Parameters	10% saturation	50% saturation
N_O	931.515	1361.445	N_O	2484.07	2866.24
Ka	0.11	0.002	Ka	0.21	0.007
Z_o	5.1438	4.21	Z_o	4.10	4.00
R^2	0.99	0.99	R^2	0.99	0.99

Table 8. Breakthrough model parameters for copper and lead biosorption onto rice husk

Copper											
Experimental conditions			Thomas model parameters			Yoon-Nelson model parameters			Clark model parameters		
Z (cm)	Q (mL/min)	C_O (mg/L)	q_o (mg)	K_{TH} (mL/mg min)	R^2	K_{YN} (mg/g)	R^2	τ (h)	A	R^2	r (per min)
10	15	10	43.82	17.2×10^{-2}	0.99	1.724	0.99	2.70	571.92	0.99	2.013
10	10	10	61.99	8.74×10^{-2}	0.96	0.874	0.87	5.74	1136.83	0.96	1.060
10	5	10	74.09	2.88×10^{-2}	0.86	0.609	0.84	8.42	369.81	0.86	0.378
20	15	10	68.26	6.09×10^{-2}	0.93	0.319	0.90	14.01	1645.82	0.93	0.770
30	15	10	75.67	3.19×10^{-2}	0.95	0.288	0.87	13.72	765.86	0.95	0.419
Lead											
Experimental conditions			Thomas model parameters			Yoon-Nelson model parameters			Clark model parameters		
Z (cm)	Q (mL/min)	C_O (mg/L)	q_o (mg)	K_{TH} (mL/mg min)	R^2	K_{YN} (mg/g)	R^2	τ (h)	A	R^2	r (per min)
10	40	10	162.48	11.3×10^{-2}	0.93	1.138	0.92	4.4	325.70	0.93	1.266
10	30	10	236.26	6.4×10^{-2}	0.86	0.646	0.87	7.29	252.39	0.86	0.857
20	40	10	185.27	5.12×10^{-2}	0.90	0.612	0.92	7.52	222.51	0.90	0.925
30	40	10	191.44	3.17×10^{-2}	0.90	0.317	0.90	12.86	135.77	0.90	0.888

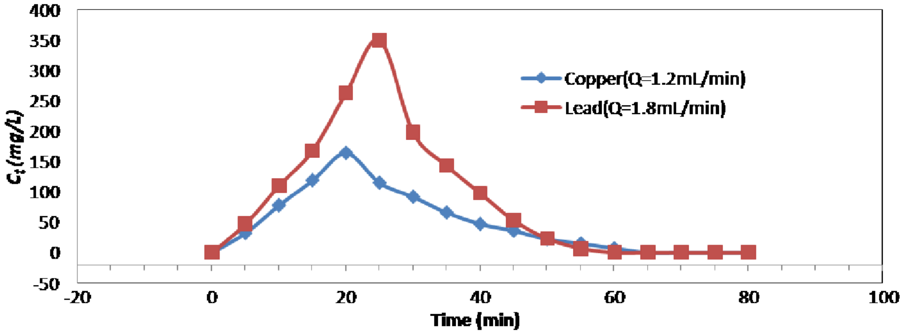

Fig. 7. Desorption of bound metals from loaded rice husk in the column study (Q = flow rate, eluant pH = 2 for both the metals).

and 27.78 g dry weight of rice husk were evaluated and, the breakthrough curves obtained showed that breakthrough time and exhaustion time increases with an increase the in bed-depth (Fig. 6(a) and 6(b)). Fig. 6 indicated that an increased in the column bed height enabled the metal ions to interact with more rice husk particle resulting in a high uptake of the metals (Ho, 2006). Therefore, an increase in the metal sorption capacity is observed with bed height in the column, which is attributed to an increase in available surface area and the number of binding sites. Table 6 further presents the metal sorption data obtained by using rice husk in the dynamic column experiment at different condition. This data clearly shows a better uptake of lead than copper by rice husk. The volume treated in case of lead containing solution is as well better compared to that of copper.Thus, a maximum sorption capacity value of 58.08 mg/g for copper and 122.70 mg/g for lead was obtained using the fixed bed columns (Table 6). These values are 7.96 and 14.10 times higher than that obtained from the batch study for copper and lead, respectively. This significant increase in the metal sorption capacity in the fixed bed columns can be attributed to the continuously increasing concentration gradient in the interface of the sorption zone as the metal containing solution passes through the column, whereas the gradient concentration decreases with time in the batch system.

The most important criterion in the design of a fixed-bed sorption system for heavy metal removal is the prediction of the column breakthrough, which determines the operating life-span of the bed (Preetha and Viruthagiri, 2007). BDST model was evaluated from the plot of the service time verses bed height for both copper and lead biosorption onto rice husk for 10% and 50% saturation. The BDST parameters calculated from the slope and intercept of the plots are presented in Table 5. The variation of the service time with bed depth is linear for the 10% and 50% saturation plots with very high correlation coefficient (R^2) values indicating the validity of the BDST model in the present study. Thus, the BDST model, in general gave an idea of the efficiency of the column under constant operating condition for achieving desired metal breakthrough level in the column. The value of sorption rate constant K_a and sorption capacity N_O are high and match closely for both 10% and 50% metal breakthrough in the column (Table 6). This indicates a favourable continuous removal of copper and lead by rice husk using the fixed bed column even under the different operating conditions adopted in this study.

Thomas model was applied to describe the experimental data on dynamic sorption of the metals with respect to flow rate and bed height of the column. The model parameters were determined from the plot of linear form of Eq.13, and are presented in Table 6. It reveals that the value of K_{TH} increased with an increase in the flow rate and decreased with an increase in the bed height; whereas, q_o value followed a reverse trend, i.e. decreased with an increase in the flow rate and increased with the increase in bed height at a constant initial metal ion concentration.

The values of Yoon-Nelson parameters (K_{YN} and τ) were determined from the plot of *ln[(Ct/(Co-Ct)]* versus *t* under different conditions for operating the column, and are presented in Table 6. The K_{YN} value increased with an increase in the flow rate, whereas the τ value decreased with an increase in the flow rate. The R^2 values obtained for both copper and lead at all conditions indicated a good fit of this model in describing the continuous biosorption of these metals onto rice husk (Daffalla *et al.*, 2102). The values of the Clark model parameters *A* and *r* obtained by fitting the experimental data for copper and lead biosorption under different conditions for operating the column are presented in Table 7. As expected the values of *r* increased with increase in flow rate and decreased with increase in bed height, while the *A* values are inversely related to the experimental conditions. The R^2 value obtained due to this model indicated an accurate fit of this model to the experimental data. The parameters estimated from this model revealed that the entire breakthrough curve can be accurately predicted for continuous removal of both copper and lead using fixed bed column operated at a low flow rate and for a low bed height in the column (Ahceampong *et al.*, 2013).

Desorption experiments were performed to evaluate the regeneration potential of the metal loaded rice husk and recovery of metal from the column. Fig. 7 shows that both copper and lead were fully recovered in less than 80 min using 0.1M HCl as the eluant. The concentration of copper and lead in the respective eluant was 156 mg/L and 340 mg/L, respectively. The eluant metal concentration thus obtained was 15.6 and 34 times, respectively, higher than the initial concentration of copper and lead, thus revealing a very good potential for metal recovery and column regeneration for repeated use (Han *et al.*, 2006).

CONCLUSIONS

Among the six different agricultural waste materials examined for copper and lead biosorption, rice husk proved to be the most effective. Among the various parameters studied for their effect on biosorption of metal in batch, pH and initial metal ion concentration were found to be most influential. FTIR analysis of raw and metal loaded rice husk revealed the participation and presence of -NH, -CH, -CO, -COO, and -SO groups in the metal biosorption process. SEM-EDX analyses further confirmed the metal biosorption on to the biomass. In addition biosorption of both the metal by rice husk was found to be governed by the intra-particular diffusion controlled pseudo second-order kinetics. Dynamic column studies with rice husk as the biosorbent yielded a very high sorption capacity for the continuous removal of copper and lead. In the column experiments, an increase in the feed flow rate decreased the remaining time to breakthrough of the metal ions, whereas an increase in the bed depth led to an increase in the remaining time to breakthrough. Among the different breakthrough models applied to describe the dynamics of metal biosorption by rice husk in their respective columns, the BDST, the Yoon-Nelson and the Clark models were found to be accurate. Finally, desorption using 0.1M HCl proved highly effective for continuous recovery of bound metals from the biosorbent in their respective column.

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NOMENCLATURE

A	Cross sectional area of the bed (cm^2)
A	Clark model parameter
a_R	Redlich-Peterson model parameter (L/µg)
b	Constant in SIPS model (L/mg)
b	Langmuir model constant (L/mg)
C_B	Effluent concentration at breakthrough point (mg/ L)
C_e	Equilibrium metal concentration in solution (mg/L)
C_i	Initial metal concentration in solution (mg/L)
F	Linear flow rate (cm/ h)
K_a	Sorption rate constant in BDST model (L/mg h)
k_1	Langergen model constant (per min)
k_2	Rate constant of the second-order equation (g /mg min)
K_F	Freundlich constant (L/g)
K_R	Redlich-Peterson model parameter (L/mg)
k_{TH}	Thomas model rate constant(mL/min’” mg)
n	Dimensionless parameter in Freundlich model
N_O	Sorption capacity in BDST model (mg/L)
Q	Volumetric flow rate (mL/min)
q_o	Sorption capacity in Thomas model (mg/g of biomass)
q'_{max}	Maximum sorption capacity in SIPS model (mg/g)
q_B	Sorption capacity in BET model (µg/g)
q_e	Equilibrium sorption capacity (mg/g)
q_{max}	Maximum sorption capacity (mg/g)
q_t	Adsorption capacity after time (t) (mg/g)
q_{total}	Total amount of metal ions loaded into the column (mg/L)
r	Clark model parameter (per min)
R^2	Determination coefficient
t_{total}	Total time (min)
V	Volume of adsorbate solution (L)
V_{eff}	Total volume of the effluent (mL)
W	Weight of biosorbent used (gram)
X	Amount of solute at equilibrium (mg)
Z	Bed depth of the column (cm)
Z_O	Critical bed depth (cm)
β	Redlich-Peterson model parameter
τ	Time required for retaining 50% of the initial adsorbate (h)

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