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Equilibrium Uptake and Column Studies of Pb^{+2}, Cu^{+2} and Cd^{+2} Using Waste Eucalyptus Charcoal

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Abstract: The potential of charcoal prepared from waste Eucalyptus wood has been investigated for the biosorption of Pb^{+2}, Cu^{+2} and Cd^{+2} metal ions in aqueous solution. Physico-chemical parameters like pH, biosorbent dosage, biosorbent regeneration and contact time were optimized by batch mode. Langmuir and Freundlich isotherm models were tested to the equilibrium data. Freundlich isotherm model fits the biosorption of Cu^{+2} and Cd^{+2} ions, while Langmuir isotherm model fitted more for biosorption of Pb^{+2} ions. The surface morphology of charcoal was studied by FTIR spectra. Fixed-bed column studies were performed to obtain the breakthrough curve. The removal of Pb^{+2}, Cu^{+2} and Cd^{+2} by eucalyptus wood charcoal was found to be favorable and can be employed as an alternative technique for the removal of heavy metals from industrial waters.

Key words: Eucalyptus wood charcoal, Pb^{+2}, Cu^{+2} and Cd^{+2}, biosorption isotherms, metal uptake, fixed-bed column, breakthrough curve.

INTRODUCTION

Increased use of chemicals and heavy metals, in industries has resulted in generation of high concentration of heavy metals in waste waters. Inputs of these trace metals into ecosystem are largely as a result of mining operations, refining ores, sludge disposal, fly ash from incinerators, processing of radioactive materials, metal plating, manufacture of electrical equipment, paints, alloys, batteries, pesticides, preservatives and e-wastes. Heavy metal pollution poses public health and environmental problems due to their toxic and carcinogenic effects as they are non biodegradable. Hence, it is necessary to remove these metals from industrial effluents before discharging aqueous waste into environment (Johnson *et al.*, 2007). Excess copper accumulates in the liver, brain, skin, pancreas and myocardium (Davis *et al*., 2000). Intake of cadmium-contaminated food causes acute gastrointestinal effects, such as vomiting and diarrhea (Godt *et al*., 2006). Lead has been the most dreaded toxic heavy metal causing anemia, encephalopathy, hepatitis and nephritic syndrome.

The conventional removal methods are sedimentation, filtration, flocculation, neutralization, electro dialysis, reverse osmosis, adsorption, biosorption etc. Conventional adsorbents like activated carbon find limited application as they are expensive for industrial applications. Therefore, the past two decades have seen a tremendous upsurge in the search for cost effective and environmentally sound alternatives to the conventional methods for dealing with these wastes (Igwe *et al.,* 2007).

The present work is an attempt to Indigenously Prepare Eucalyptus Carbon (IPEC) from the locally available timber waste *viz.,* waste Eucalyptus wood and study the suitability of eucalyptus carbon for the removal of Cu^{2+}, Cd^{2+} and Pb^{2+} ions by determining the effect of contact time, dose, initial pH , desorption pH, isotherm studies and continuous fixed bed studies.

MATERIALS AND METHODS

Preparation of Synthetic Aqueous Solution:

The synthetic aqueous solution with a concentration of 20mg/L was prepared by dissolving 20mg each of analytical grade Lead nitrate (Loba Chemie), Cadmium chloride (Merck) and Copper sulphate pentahydrate (Merck) in 1000ml distilled water.

Preparation of Biosorbent:

The waste eucalyptus wood was obtained from the nearby timber market and burnt at a temperature of 400^0-600^0C. The charcoal (IPEC) was washed thoroughly with distilled water to remove the dust and dirt

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adhered to it, sun dried for a week and oven dried at 75 ^{o} C for two days. The dried biomass was ground in a blender to fine particles and sieved to different sizes. This was kept in an air-tight bottle and used as per experimental requirement (Igwe *et al.,* 2007).

Characterisation of Biosorbent by Ftir Spectra:

To analyze and understand the binding mechanism of sorption, FTIR studies were carried out. FTIR investigation gives an idea of functional groups present on the surface of the biosorbent. The FT-IR spectrum was recorded by Perkin- Elmer spectrum 100.

Batch Studies:

Batch experiments were conducted at fixed metal ion Pb^{+2}, Cu^{+2} and Cd^{+2} concentration of 20 mg/L to study effect of pH at 3,5,7,9; biosorbent dosage from 1g to 2g/50ml; contact time from 15 to 240 minutes at 35^{0}C. Desorption studies were carried out with 20 mg/L metal ion Pb^{+2}, Cu^{+2}, Cd^{+2} concentration in pH range 1 to 11. Batch experiments were agitated in a Remi orbital shaker at 180 rpm usually for 1 hr. After 1 hr the biosorbent was separated from metal ion solution through Whatman filter paper No: 42. The filtrate was analyzed for residual metal ion concentration using AAS (Perkin-Elmer). Percentage removal and metal uptake were evaluated from the given equation as:

$$\%\text{Percentage removal of metal} = [(Ci–Ce)/Ci]*100 \quad (1)$$

Where, Ci is the initial metal ion concentration before biosorption process in mg/L, Ce is the equilibrium metal ion concentration after biosorption process in mg/L.

$$\text{Metal uptake } q = [(Ci - Ce)/M] * V \quad (2)$$

Where, V is the volume of metal ion solution in ml, M is the mass of biosorbent taken in gm.

Equilibrium Isotherm Studies:

The biosorption isotherm is important from practical view in order to design the biosorption system. The effect of initial metal ion concentration on the biosorption of metal ions by IPEC was studied in the range (20mg/L-120mg/L) for Pb^{2+}, Cd^{2+} and Cu^{2+} using 1g/100ml dose of biosorbent, pH 7 and temperature of 35^{0}C for 1 hr at 180 rpm. After 1 hr the biosorbent was separated from the metal ion solution using Whatman filter paper no.42 and the filtrate estimated for metal ion concentration using Perkin Elmer AAS. Isotherms studied are:

a) Langmuir model is the most popular one due to its simplicity. The Langmuir isotherm is represented as:

$$1/q_e = 1/qo + 1/(qob)Ce \quad (3)$$

Where, C_e is the concentration of metal ions (mg/L) at equilibrium, q_e is the amount of metal ion adsorbed per unit mass of adsorbent at equilibrium (mg/g), q_o is the maximum adsorption at monolayer coverage (mg/g), b is the adsorption equilibrium constant related to the energy of adsorption. To predict whether the biosorption is favorable or unfavorable for the Langmuir type R_L, a dimensionless constant separation factor is calculated as:

$$R_L = 1/(1+bC_o) \quad (4)$$

Where, $R_L$is dimensionless separation factor, Co is the highest initial concentration of the metal ion (mg/L) in the investigated concentration range and b is the Langmuir constant (L/mg).

b) Freundlich isotherm model gives an expression encompassing the exponential distribution of active sites and their energies. The Freundlich isotherm was tested in the following linear form:

$$\log q_e = \log K_f + (1/n) \log C_e \quad (5)$$

where, q_e is the amount of metal ion adsorbed per unit mass of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration of the metal ion (mg/L), K_f is the Freundlich constant related to the adsorption capacity, n is the adsorption intensity (N. Kannan *et al*., 2008).

Column Studies:

A polypropylene column of length 18cm with an inner diameter of 2.5cm was used as a column. Glass wool was used on both the ends of the column to prevent the leakage of biosorbent leakage. The biosorbent material of 5g was filled in the column to make fixed bed. The metal ion solution was made to run in an upward direction in the column using a peristaltic pump. The column was initially equilibrated with distilled water at a flow rate of 20ml/min. The aqueous metal ion solution of Pb^{2+}, Cd^{2+} and Cu^{2+} ions at a concentration 150mg/L was pumped through the column from the reservoir bottle at a fixed flow-rate of 20ml/min. Fractions were collected at regular intervals and metal ion concentration were evaluated using AAS.

Modeling of Column Biosorption:

Breakthrough studies were carried out to find the column residence time and continuous column biosorption capacity. Yoon Nelson model was used to analyze the behavior of the biosorption system. The linear form of Yoon Nelson model is given as:

$$\ln (Ct/Co\text{-}Ct) = k_{YN}.t - \tau.\ k_{YN} \qquad (6)$$

where, k_{YN} is Yoon Nelson's rate constant, τ is time required for 50% adsorbate breakthrough and t is sampling time, Ct is the concentration of metal ion at time t, Co is the initial metal ion concentration. A plot of ln (Ct/Co-Ct) vs. t gives a straight line. For a given bed:

$$q_{oYN} = Co.Q.\tau\ /\ 1000X \qquad (7)$$

where, q_{oYN} is adsorption capacity, Co is initial metal ion concentration, Q is the flow rate, X is the weight of biosorbent and τ is the 50% breakthrough time (Sivakumar *et al*., 2009).

RESULTS AND DISCUSSIONS

Ftir Spectra of Eucalyptus Wood Charcoal (IPEC):

FTIR spectra obtained for Eucalyptus wood charcoal (IPEC) revealed the probable binding mechanism for biosorption. The frequencies of vibrations and their corresponding groups are listed in Table 1. According to the fig. 2, the metal binding properties of Eucalyptus wood charcoal are largely due to the existence of alkanes, carboxylate ions and primary alcohols which are likely to be present on the surface of the charcoal.

Batch Studies:

The biosorption was optimized with various parameters. The effect of pH is one of the controlling factors in biosorption. As pH increases the extent of removal increases and reaches an optimum value and then decreases, as at higher pH the metal ions precipitate. The effect of pH is shown in fig.3. The optimum pH for Pb^{+2} and Cu^{+2} was 7 and Cd^{+2} was 9. The effect of biosorbent dosage on the extent of removal of metal ions has been studied. The percentage removal of metal ions increases with the increase in biosorbent dosage as seen in fig. 4. This may be due to increase in the effective surface area. The removal lowers down at higher doses which may be due to conglomeration of the biosorbent particle at higher dosage. The optimum dosage becomes an important parameter for biosorption (Kannan *et al.*, 2002). It is seen that optimum biosorption of Pb^{2+} and Cu^{2+} was at the dosage of 1 g/50ml and for Cd^{2+} the percentage removal increased with increasing dose.

Effect of contact time is one of the most important parameters for an economic waste water treatment. Contact time studies for uptake of Pb^{2+}, Cd^{2+} and Cu^{2+} ions by IPEC revealed that biosorption is rapid and fast. The percentage removal against contact time is presented in fig.5. From the results of the biosorption Pb^{2+} ions had the optimum contact time at 10 mins , Cd^{2+} at 1 hr 30 mins and Cu^{2+} at hr. After attaining optimum, the biosorption slightly decreases due to decrease in pH as seen in fig.5.

Desorption and regeneration of biosorbent is of crucial importance in industrial practice for metal removal from wastewater. Desorption in batch mode was eluted in pH range 1 to 11. It was observed that at pH1 there is maximum desorption, indicating that acidic pH is unfavorable for biosorption. This strategy could be harnessed for regeneration of biosorbent. At pH 1, 93.18% Cd^{2+}, 73.26% Cu^{2+} and 71.61% of Pb^{2+} was desorbed as seen in fig.6. The quantitative recovery of metal ion indicated that regeneration of IPEC was possible and also it is evident that ion exchange mechanism is involved in biosorption (Shanmugavalli *et al*., 2006).

Equilibrium Studies:

Isotherms are useful in calculating how much carbon is needed to achieve desired removal by biosorption. The classical and popular isotherm for homogeneous flat surface is Langmuir isotherm and for heterogeneous flat surface, the classical isotherm studied is Freundlich isotherm (Prasanna Kumar *et al*., 2006). Both these isotherms were fitted for removal studies using Eqns. 2, 3, 4 and 5. The results are given in the table no.2 as summary of equilibrium isotherms data. The equilibrium data obtained showed a good fit. The experimental data for Cu^{2+} and Cd^{2+} ion biosorption fits with Freundlich isotherm and for Pb^{2+} ion fits with Langmuir model with high R^2 values. The R_L values are between 0 and 1, indicating that the biosorption is favorable. The equilibrium studies for Cd^{2+}, Cu^{2+} & Pb^{2+} are shown in fig.7, 8 and 9.

Column Studies:

Fixed-bed column studies were evaluated for efficiency and applicability of continuous column mode for large scale operation. The biosorbent packed in the bed removes metal ion until the attainment of equilibrium and is dependent on the transfer mechanism and the rate of adsorption (Kaushik *et al.*, 2007). For mathematical modeling biosorption breakthrough curves were studied for 150mg/L metal ion concentration at a flow rate of 20ml/min and a bed height of 5.5cm. Fig.10 shows the breakthrough curve for the metal ions Cd^{2+}, Cu^{2+} and Pb^{2+}. The breakthrough time for Cd^{+2} was in the range of 90 to 300 mins, while for Cu^{2+} and $Pb^{2+}$was in the range 135 to 360 mins (Purnomo *et al*., 2007). Mathematical model by Yoon Nelson's results are given in table no.3. The τ and q_{oYN} were calculated using eqns.6 and 7. The continuous column studies reveal this to be an efficient biosorbent for industrial application for metal ion removal from waste water and are also promising for scale-up process.

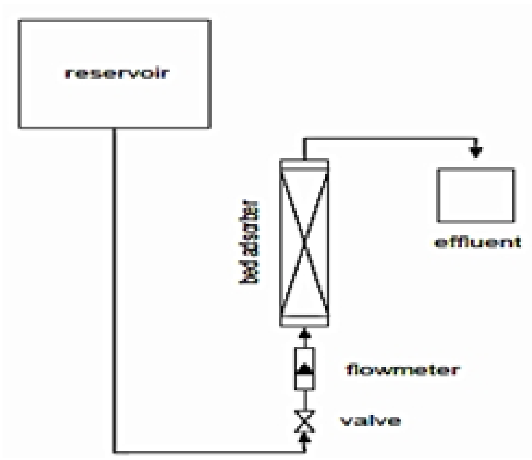

Fig. 1: Experimental apparatus for continuous studies.

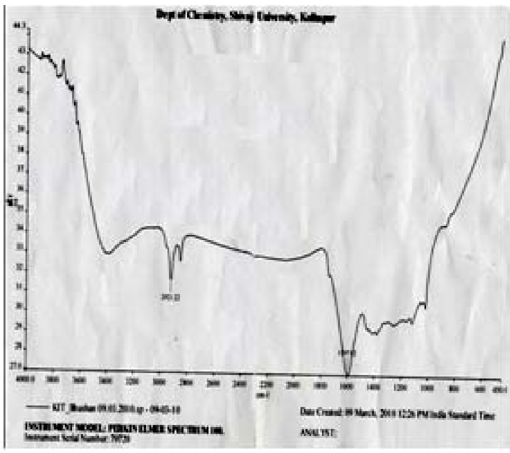

Fig. 2. FTIR analysis of Eucalyptus charcoal.

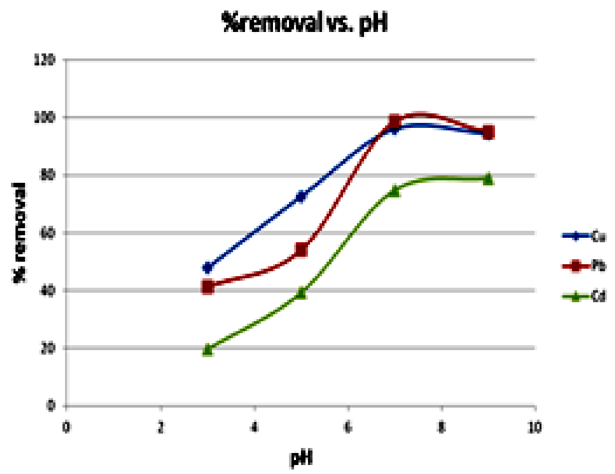

Fig. 3: % removal vs. pH

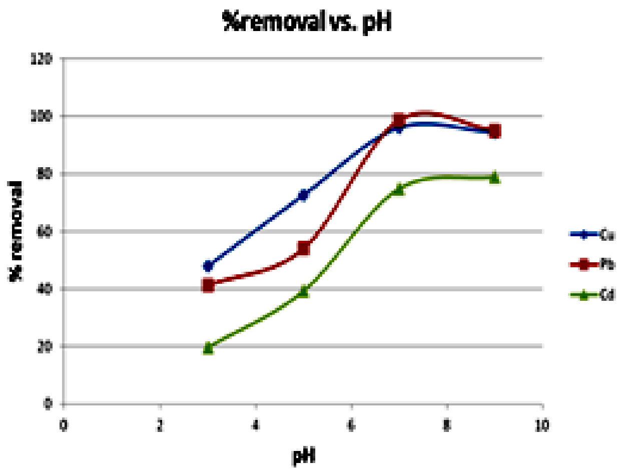

Fig. 4: % removal of vs.biosorbent dosage

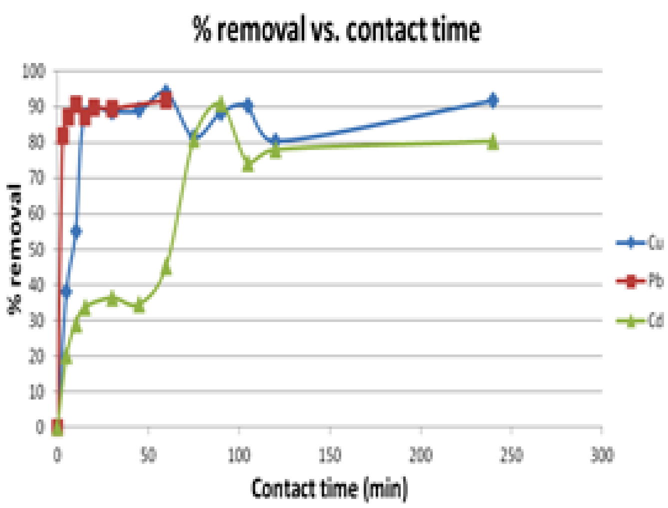

Fig. 5: Effect of contact time on % removal.

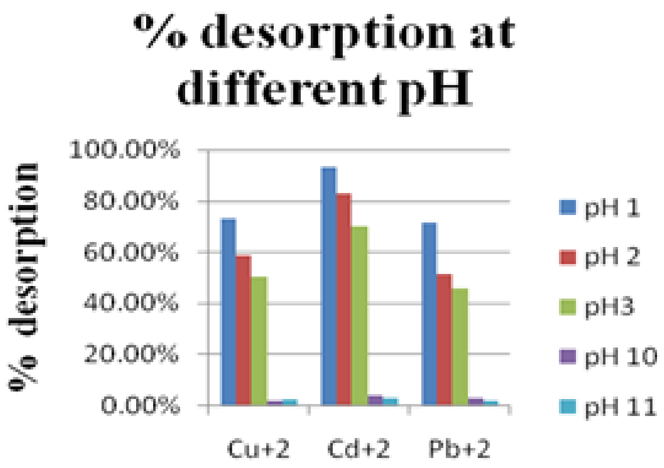

Fig. 6: Desorption studies at different pH.

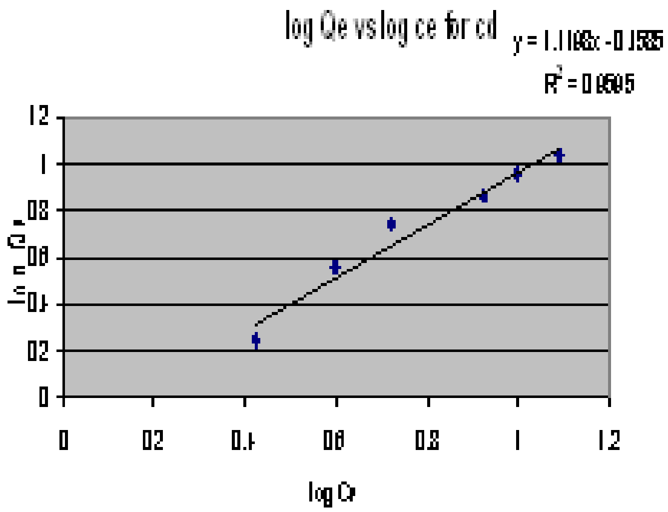

Fig. 7: Freundlich Isotherm for Cd^{2+}

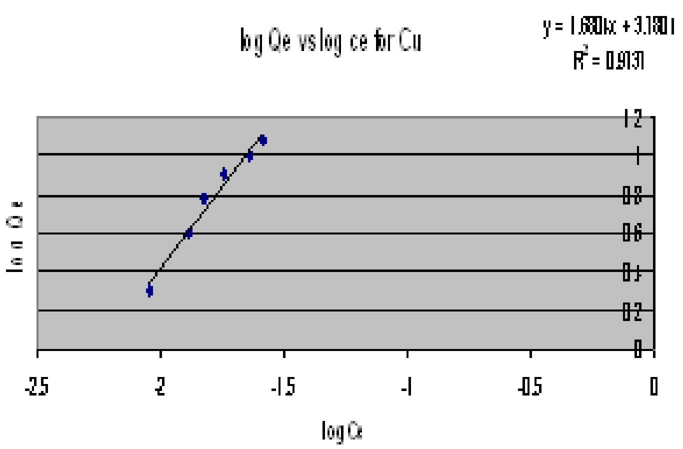

Fig. 8: Freundlich isotherm for Cu^{+2}

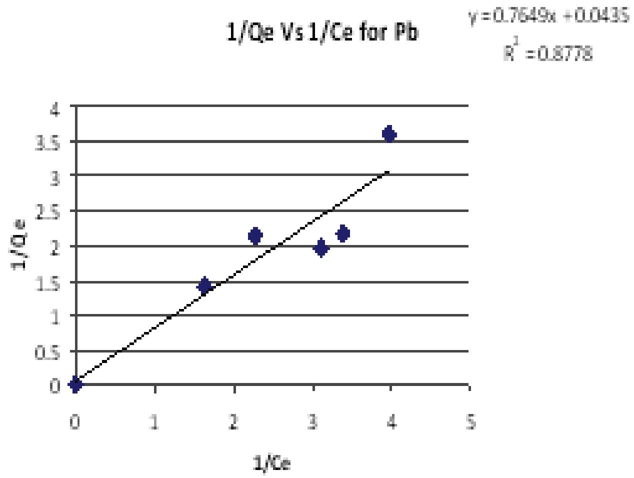

Fig. 9: Langmuir isotherm for Pb^{+2}

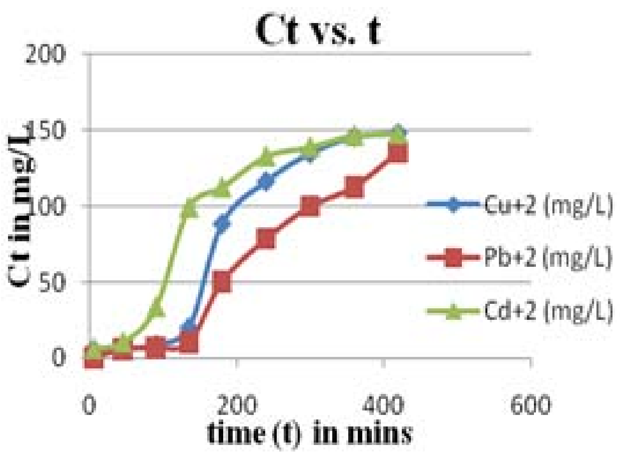

Fig. 10: Breakthrough curve column studies.

Table 1:

R_l	Value type of isotherm
$R_l > 1$	Unfavourable
$R_l = 1$	Linear
$R_l = 0$	Irreversible
$0 < R_l < 1$	Favourable

Table 1: FTIR analysis & functional groups

Functional groups	Vibration mode	Frequency (cm-1)
-CH2-	C-H str., asym	2921.22
Carboxylate ion	O=C-O str.,asym	1597.12
-CH2-	C-H str., sym	2860
Primary alcohols	C-OH str.	1025

Table 2: Summary of equilibrium isotherms data.

	Langmuir 1/qe vs. 1/Ce			Freundlich logqe vs. logCe		
	qo mg/g	B	R^2	Kf mg/g	N	R^2
Cd^{+2}	-16.15	-0.04	0.9441	0.8534	0.893	0.9595
Cu^{+2}	-5.793	-29.76	0.9539	43.833	0.5951	0.9737
Pb^{+2}	22.998	0.0568	0.8778	1.0064	1.2886	0.8598

Table 3: Yoon Nelson kinetic model's result.

	kYN (l/min)	τ (min)	qoYN (mg/g)	R^2
Cu^{2+}	0.02	193.8	116.28	0.0971
Cd^{2+}	0.018	152.166	91.2996	0.952
Pb^{2+}	0.021	273.619	91.1714	0.805

Conclusion:

This investigation showed that IPEC is very effective adsorbent in removal of Cd^{2+}, Pb^{2+} and Cu^{2+} from aqueous solutions. Biosorption is pH dependent with maximum removal for Pb^{2+} and Cu^{2+} at pH 7, while for Cd^{2+} optimum pH is pH 9 and maximum desorption at pH1 indicating biosorption is based on ion-exchange mechanism and there is a good possibility of biosorbent regeneration. The biosorption capacity of IPEC for Cd^{2+}, Pb^{2+} and Cu^{2+} is 0.8534, 43.833 and 22.998 mg/g respectively. The sorption is very rapid. For a bed height of 5.5cm and flow rate of 20ml/min in the continuous mode, the adsorption capacity for Cd^{2+} is 91.30 mg/g, Pb^{2+} is 164.17 mg/g and Cu^{2+} is 116.28 mg/g. The residence time, τ for Cd^{2+} is 152.16 mins, Pb^{2+} is 273.61 mins and Cu^{2+} is 193.8 mins. The continuous column studies reveal this to be an efficient biosorbent for industrial application for metal ion removal from waste water and are also promising for scale-up process.

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