Comparison of Pb(II) uptake by coir and dye loaded coir fibres in a fixed bed column

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Abstract

The possibility of adsorbing Pb(II) from solution using coir, a cheap lignocellulosic fibre, was assessed in a fixed bed column. The coir fibres were also chemically modified by covalent loading of a reactive dye, C.I. Reactive Orange 13, and used as adsorbent. Column adsorption studies were carried out at different initial Pb(II) concentrations and it was observed that the breakthrough time decreased with increase in the initial Pb(II) concentration. The column packed with dye loaded coir fibres was operated for longer duration than the one packed with unmodified coir fibres. The total Pb(II) adsorbed was also higher in a column packed with dye loaded coir fibres. The desorption level in the fixed bed column packed with coir fibres was of the order of 85%, whereas the one packed with dye loaded coir fibres was more than 90%. Both the columns were regenerated and used upto five cycles.
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1. Introduction

Lead, a heavy metal, finds extensive applications in day-to-day commodities like batteries, paints, ceramics, soldering, etc. It is an essential component for the production of many other highly technical products. As the use of lead increases, the waste generated is also tremendous due to the inappropriate waste disposal practices. The dumping of these wastes without monitoring the permissible limits into sewers and drainage causes hazardous effects on life, both aquatic and land. Lead is a very toxic element even at low concentrations. It affects central nervous system, kidneys, gastrointestinal system, etc. [1]. The removal of such a heavy metal from the effluent in an effective and economic manner is a must for a healthy living.

Generally, heavy metals are removed from wastewaters by chemical precipitation [2], ion exchange [3], floatation [4], membrane systems [5], and adsorption [6]. However, these techniques have their advantages and inherent limitations, like high cost, sludge formation, etc. Hence, other unconventional methods like use of activated carbon from cheap throwaway agricultural/biological wastes [7], biosorption [8], adsorption on to minerals [9,10], etc., have been sought after. Natural bio polymeric materials also are effective in removal of heavy metal ions [11,12].

The application of dye loaded polymeric materials for heavy metal removal is being explored widely. It has been reported that dye loaded synthetic polymeric materials were quite promising in removal of heavy metals from aqueous solutions [13,14]. The reactive dye loaded cheap cellulosic and lignocellulosic materials were quite efficient for heavy metal removal from their aqueous solutions [15–20]. The use of fibrous lignocellulosic materials for removal of heavy metals has been explored recently by a number of researchers [21,22]. Coir and jute fibres loaded with a reactive dye were found efficient in removing heavy metals like Pb(II), Cu(II), Ni(II) and Zn(II) from their aqueous solution in a batch wise manner [23,24]. Very little literature is available where in

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the use of unconventional materials, of agricultural and biological origin, for removal of heavy metals has been studied in a continuous manner in a fixed bed column. Shukla and Sakhardande [25] used dye loaded jute fibres packed in a fixed bed column for removal of different heavy metal ions. Black gram husk, fungal biomass and modified rice husk has also been used in a fixed bed column for removal of different heavy metal ions [26–28].

The present work explores the use of a lignocellulosic fibre, coir, for removal of Pb(II) from lead nitrate solution in a fixed bed column. The efficiency of coir fibre, after loading with a specific reactive dye, CI Reactive Orange 13, for Pb(II) removal in a fixed bed column is also assessed. The desorption and regenerative capacity of dye loaded coir column is also reported.

2. Materials and experimental methods

2.1. Adsorbents

Coir fibre waste was collected from a local industry in Kerala and cut into approximately 1 cm long pieces. It was cleaned thoroughly by washing with water. The cleaned coir fibres as well as the dye loaded coir fibres were used as adsorbents.

2.2. Chemicals

Lead nitrate was of Analytical Reagent grade, supplied by Merck (India) Ltd. A stock solution of 4.8 mmol/L Pb(II) was prepared by dissolving 1.6 g of anhydrous lead nitrate in 1 L of demineralised water. The experimental solutions ranging from 2.13 to 4.16 mmol/L Pb(II) were prepared by approximately diluting the stock solution. The other chemicals used, sodium hydroxide, sodium carbonate, nitric acid were also of Analytical Reagent grade, supplied by Merck (India) Ltd. Glauber's salt was supplied by S.D. Fine Chemicals, Mumbai, and the non-ionic detergent, Auxipon NP was supplied by Auxichem Ltd., Mumbai.

Demineralised water was used for all experiments.

2.3. Dye

A commercially available monochlorotriazine-type reactive dye, C.I. Reactive Orange 13, procured from Atul (I) Ltd. was used for covalent loading of coir. The structure and the covalent reaction of this dye with cellulose have been given in Fig. 1.

2.4. Methods

2.4.1. Dyeing of coir fibres

The technique used for dye loading was that of dyeing a monochlorotriazine type reactive dye on cellulosic materials like cotton [29]. Cleaned and uniformly cut coir fibres,

100 g were added to 4 L of the diluted dye solution containing 0.5 g predissolved dye powder. The dyeing reaction was started at 40 °C and the temperature was slowly raised to 85 °C for uniform dye loading. After about 10 min, 65 g/L of sodium sulphate deca hydrate (Glauber's salt) was added for further improving the dye exhaustion onto coir. After another 20 min, for covalent fixation of the dye onto the material, 15 g/L of sodium carbonate was added to the same bath and the treatment continued at 85 °C for further 30 min. In the end, the material was filtered, washed thoroughly with hot water and then with cold water to remove the loosely held dye on coir. This was followed by boiling the dye loaded coir fibre with 1 g/L solution of a non-ionic detergent, Auxipon NP, for 20 min and thorough washing with water to remove completely the unfixed dye and the by product of the reaction, the hydrolysed dye. The material was then dried in an oven at 50 °C overnight and used as an adsorbent.

2.4.2. Estimation of dye loading on the materials

The estimation of the amount of dye loaded on to the coir fibres was carried out by measuring the absorbance values of the dye solution used for the dye loading reaction using Techcomp UV–vis spectrophotometer, (Model 8500 Hong Kong). Each dyestuff gives the colour absorption value at a particular λ_{max} specific to it. A calibration plot was developed by plotting known quantities of dye concentrations (mmol/L) against their absorbance (%) values at the particular λ_{max}, which is linear at lower concentrations. The absorbance of initial dye liquor used for dye loading was measured at λ_{max} of 495 nm (A). After completion of the dyeing process, the coir fibres were carefully removed from the bath without spilling any drop of spent liquor. Water after washing, the soap liquor as well as final washings were carefully collected together, added to the exhausted dye bath and its absorbance was measured (B). This absorbance equals the amount of dye not loaded on the adsorbent. Thus, (A–B) is related to the dye loaded onto the material. By making use of the calibration curve, the amount of dye loaded on to coir was determined. The dye loading observed for coir fibres was 2.16 µmol/g.

2.4.3. Column adsorption studies

2.4.3.1. Adsorption cycle. The coir fibres and dye loaded coir fibres, were used for adsorption of Pb(II) in a fixed bed column. 100 g of coir was filled in a glass column of 4.8 cm inner diameter to yield a bed length of 43 cm. Glass beads were used as support at bottom and top. The feed containing known concentration of Pb(II) ion was given from bottom using a peristaltic pump (Electrolab, Mumbai). A constant flow rate of 40 mL/min was used for the entire study. The liquor coming out from the top of the column was collected at regular intervals and the amount of Pb(II) adsorbed was estimated. The estimation of Pb(II) was carried out using flame type atomic absorption spectrophotometer (Model GBC 932 Plus, Australia). Three different Pb(II)
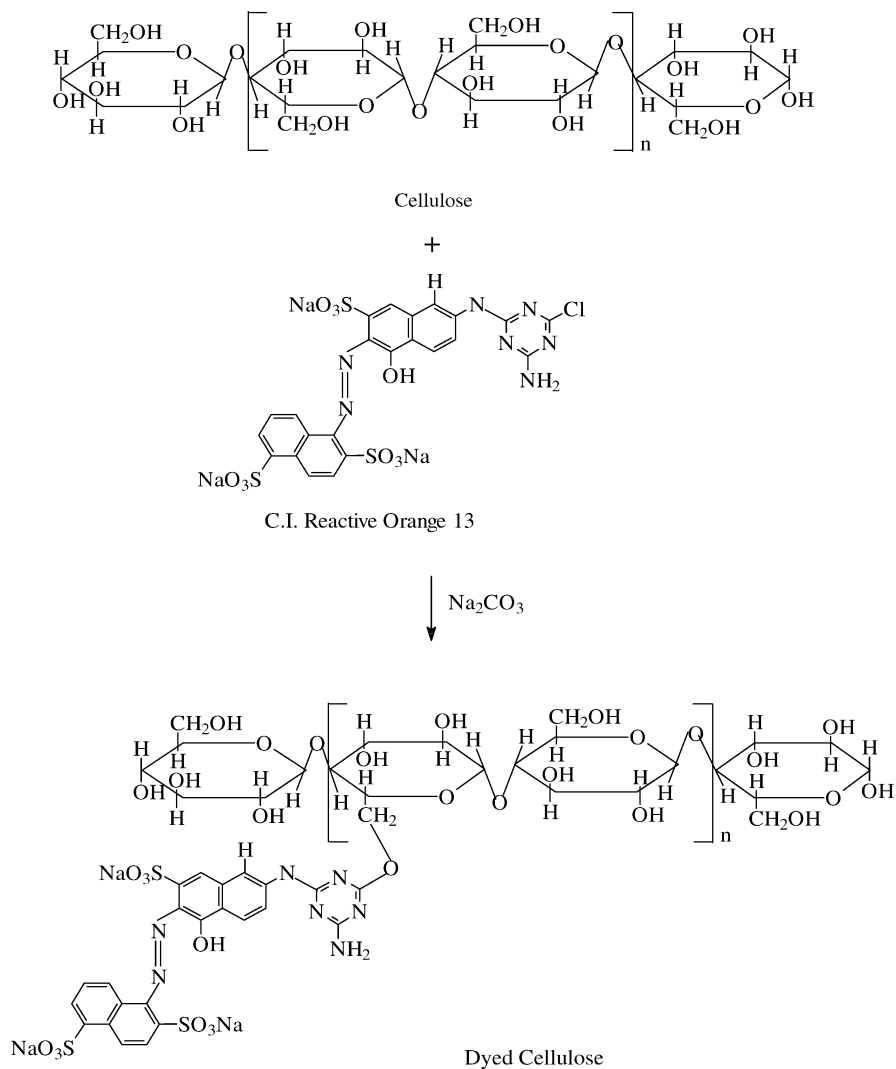
Fig. 1. Structure of C.I. Reactive Orange 13 and its reaction with cellulose.

concentrations of 2.13, 3.21 and 4.16 mmol/L were used in the present study. Breakthrough curves were developed by plotting C/C_o versus t, where C_o and C are the inlet and outlet concentrations of Pb(II) in mmol/L and t is the time in min.

2.4.3.2. Desorption cycle. After adsorption, the column was given a wash with demineralised water to remove any unabsorbed Pb(II). This was followed by desorption using 0.25N nitric acid. The amount of the acid was calculated stoichiometrically and a slight excess (5%) was added in order to ensure complete desorption of Pb(II). The acid feed was given from top of the column and the flow rate of addition was kept constant at 10 mL/min. The acid addition was followed by addition of demineralised water, which serves the purpose of pushing down the desorbed Pb(II) ion and clearing off the acidity of the bed. The addition of water was continued till the Pb(II) concentration coming out was less than 0.01 mmol/L.

The liquor coming out at the bottom of the column was collected at regular intervals (t) and was estimated for Pb(II) desorbed (C). Desorption curves were developed by plotting C versus t.

Concentration factor was calculated as the ratio of desorbed Pb(II) concentration to initial Pb(II) concentration in mmol/L.

2.4.3.3. Regeneration and reusability study of fixed bed column. The regenerative treatment was given to the adsorbent after complete desorption of Pb(II) was achieved. One liter of 0.025N NaOH was circulated in the bed with a flow rate of 40 mL/min. The final step was washing the column with 600–900 mL of demineralised water.

The adsorption, desorption and regeneration step was considered as one cycle. The reusability of the column was studied for five cycles with an initial Pb(II) concentration of approximately 2.13 mmol/L.

Table 1
Chemical composition of coir fibres

Contents	(%)
Lignin	45.84
Cellulose	43.44
Hemicellulose	0.25
Pectin	3.00
Water soluble matter	5.25
Ash	2.22

3. Results and discussion

3.1. Pb(II) adsorption on to dye loaded coir

The material selected in the present study, coir, is a ligno-cellulosic fibre. The components present in coir are given in Table 1 [30]. Cellulose is a natural polymer made up of β-glucose units with abundant primary and secondary hydroxyl groups, whereas lignin has a network type of structure with majority of methoxy and free hydroxyl groups. Both these chemical entities have been shown to be capable of adsorbing various types of heavy metal ions [17]. This adsorption was observed to be of ionic nature and even dilute acids were capable of fully desorbing them [25].

In the present study, coir was subjected to a chemical modification by covalent bonding of the reactive dye used. Fig. 1 gives the structure of the reactive dye used to load on to coir fibres. The dye reacts covalently by substitution of the −Cl group of the dye by primary −OH of the cellulose portion in coir [31]. The reaction takes place under alkaline pH (10.5–11) achieved by addition of Na_2CO_3, which converts the −OH to −ONa, the later being capable of forming a firm covalent bond with a reactive dye. The coir thus gets modified chemically to a combined dye-fibre moiety. The salient features of the dye used in the present study are: (i) the presence of azo group with a hydroxy group in ortho position to it, and (ii) the presence of sulphonic acid groups. These groups take part in binding a heavy metal ion through formation of a six membered ring chelate and through cation exchange, respectively. The detailed mechanism of fibre-dye-metal chelate formation and ion exchange has been explained earlier [23].

3.2. Adsorption cycle

Our studies on batch wise adsorption for removal of Pb(II) from its aqueous solution have revealed that the dye loaded coir fibres were more efficient than the unmodified ones [23]. The present work deals with column studies for the same.

Fig. 2 depicts the breakthrough curves for Pb(II) adsorption from lead nitrate solutions of different initial concentrations on to the coir and dye loaded coir fibres in a fixed bed column. The inlet flow rate was kept at 40 mL/min. For both the columns, the breakthrough time decreased with increase in the concentration of Pb(II) solution. For a given initial Pb(II) concentration, the dye loaded coir fibres performed more efficiently. Thus, for a low Pb(II) concentration of 2.13 mmol/L, the breakthrough time was 75 min for column packed with dye loaded coir fibres as against only 50 min using unmodified coir. Similar were the observations at higher concentrations. In the present study, the Pb(II) adsorption was continued till complete exhaustion of the bed for both unmodified and modified coir fibres. It may also be observed that the column packed with unmodified coir got fully exhausted within a shorter time when compared to the column packed with dye loaded coir fibres, especially at higher initial Pb(II) concentrations. Table 2 indicates that the later column gave higher total amount of Pb(II) adsorption and its degree of saturation reduced at higher initial Pb(II) concentrations. No such trend was followed by the column packed with unmodified coir fibres.
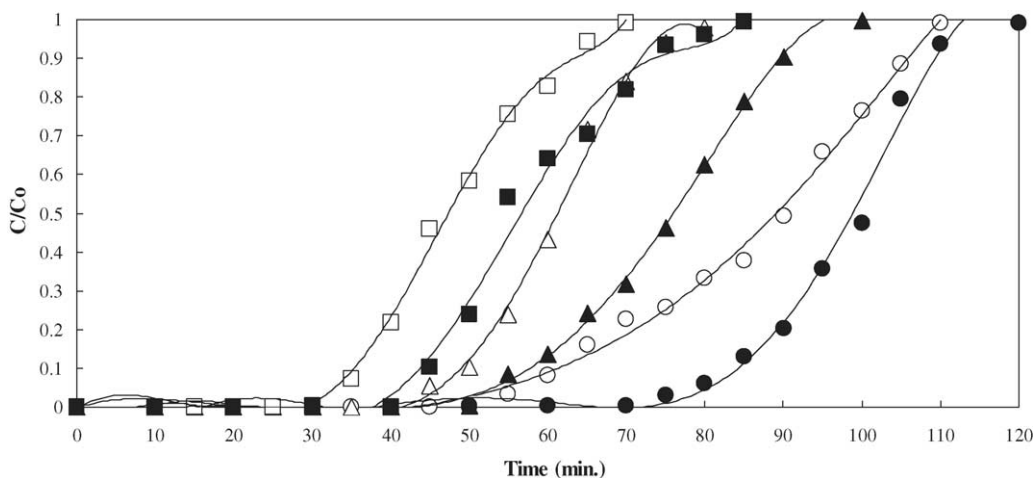

Fig. 2. Breakthrough curves for adsorption of Pb(II) at different initial concentrations in a fixed bed column: ○, Pb(II) concentration 2.13 mmol/L on coir fibres; △, Pb(II) concentration 3.21 mmol/L on coir fibres; □, Pb(II) concentration 4.16 mmol/L on coir fibres; ●, Pb(II) concentration 2.13 mmol/L on dye loaded coir fibres; ▲, Pb(II) concentration 3.21 mmol/L on dye loaded coir fibres; ■, Pb(II) concentration 4.16 mmol/L on dye loaded coir fibres.

Table 2
Adsorption and desorption of Pb(II) in a fixed bed column packed with different coir samples at different initial concentrations

| Material	Initial Pb(II) concentration (mmol/L)	Break-through time (min)	Pb(II) adsorbed up to breakthrough point (mmol)	Total Pb(II) adsorbed (mmol)	Degree of saturation (%)	Pb(II) desorbed (mmol)	Eluent used (mL)		Desorption (%)	Total concentration factor
							0.25 N HNO$_3$	Water		
Coir fibres	2.13	50	4.26	7.34	58.03	6.42	65	635	87.42	4.31
	3.21	45	5.78	7.92	72.94	6.80	75	925	85.80	2.11
	4.16	30	4.98	8.01	62.24	7.09	75	925	88.58	1.70
Dye loaded coir fibres	2.13	75	6.20	8.28	75.00	7.66	75	625	92.59	5.13
	3.21	50	6.43	9.15	70.18	8.43	80	920	92.03	2.63
	4.16	40	6.65	9.47	70.21	8.50	100	900	89.75	2.04
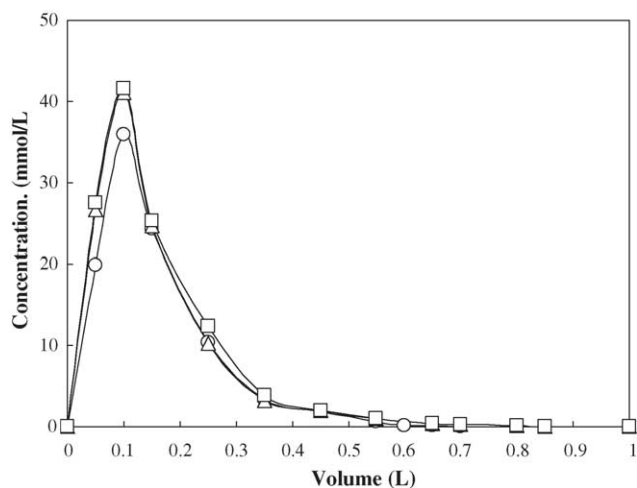
Fig. 3. Desorption curves of Pb(II) from a fixed bed column packed with coir fibres: ○, desorbed from bed adsorbed with 2.13 mmol/L of Pb(II); △, desorbed from bed adsorbed with 3.21 mmol/L of Pb(II); □, desorbed from bed adsorbed with 4.16 mmol/L of Pb(II).

3.3. Desorption cycle

The desorption cycles for Pb(II) from these columns packed with unmodified and dye loaded coir fibres are depicted in Figs. 3 and 4, respectively. It may be noted that majority of Pb(II) was desorbed by 500 mL of the eluent. The exact amounts of acid and the demineralised water used for desorption are given in Table 2. The desorption efficiency of both the materials was found to be quite good, being >85% for the unmodified coir fibres and >90% for the dye loaded coir fibres. Also, the concentration factor was higher for the column packed with dye loaded coir fibres and it decreased with increase in the initial Pb(II) concentration. Thus, at a low initial concentration of 2.13 mmol/L, it was possible
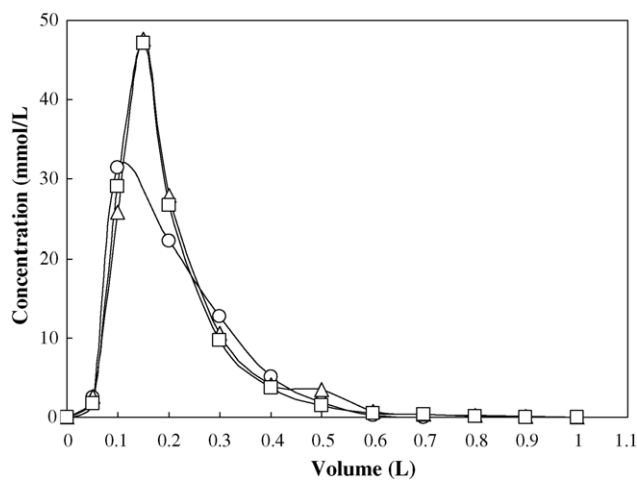

Fig. 4. Desorption curves of Pb(II) from a fixed bed column packed with dye loaded coir fibres: ○, desorbed from bed adsorbed with 2.13 mmol/L of Pb(II); △, desorbed from bed adsorbed with 3.21 mmol/L of Pb(II); □, desorbed from bed adsorbed with 4.16 mmol/L of Pb(II).

Table 3
Repeated adsorption–desorption of column for Pb(II) adsorption

Cycle no.	Initial concentration (mmol/L)	Material			
		Coir fibres		Dye loaded coir fibres	
		Adsorption (%)	Desorption (%)	Adsorption (%)	Desorption (%)
1	2.13	76.73	87.46	86.56	92.51
2	2.17	75.84	87.87	83.41	95.46
3	2.08	77.16	87.82	88.69	93.26
4	2.15	75.97	85.44	84.66	92.06
5	2.19	73.11	85.41	82.35	94.69

to concentrate the Pb(II) solution up to five times with this column.

3.4. Reusability study of fixed bed columns

Although the coir fibre was obtained as a waste material, the cost incurred in loading with dyestuff has to be taken into account while making the adsorption process economically viable. The cost incurred in modifying the coir fibres by a specific reactive dye is justifiable in terms of the enhanced metal ion adsorption. The effluent generated during dye loading is of a known quality, being similar to that of any textile dyeing process, and a number of effluent treatment processes for the coloured textile waste water are already being practiced [32–34]. Thus, the pollution problem arising out of dye loading process can be tackled easily. Nevertheless, it is always advisable to reuse the adsorbent as many times as possible, which has the advantage of further bringing down the level of pollution caused due to loading of the dye on adsorbents, apart from the economy of the process.

Thus, the reusability of both the columns was studied up to five cycles, with intermediate alkali regeneration, using an initial concentration of approximately 2.13 mmol/L of Pb(II). The adsorption and desorption values for both types of columns were almost constant up to five cycles, as indicated by the data in Table 3.

4. Conclusion

In a fixed bed column packed with coir fibres, it was possible to achieve good adsorption of Pb(II) from its aqueous solution. The column packed with dye loaded coir fibres showed higher efficiency. The breakthrough time decreased with increase in the initial Pb(II) concentration. The desorption efficiency of column packed with unmodified coir fibre was of the order of 85%, which enhanced to >90% for the dye loaded coir column. A concentration factor of five was achieved in a column packed with dye loaded coir fibres. Both the columns retained their adsorptive capacities for removing Pb(II) up to five adsorption–desorption cycles.

Acknowledgement

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