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Research Article

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Chromatographic separation of Pb(II), Cr(II), Cd(II), Ni(II) and Fe(III) in aqueous solutions using *Lanchocarpus laxiflorus* plant leaves (LLL)

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ABSTRACT

This work assesses the potential of an adsorptive material LLL, for the separation of metal ions in aqueous solution. The adsorption behavior of LLL for lead, chromium, cadmium, nickel and iron ions was investigated. The effect of pH, initial concentration of metal ions, the biomass dose, and contact time on the sorption of each of the metal ions was determined. The result shows that the LLL biomass has a high selectivity for Pb, Cr and Ni with 99.86%, 98.75% and 99.49% at pH 5, 6 and 7 respectively. For cadmium the sorption capacity was low compared to Pb, Cr and Ni, While Fe (III) was slightly extracted (61%) at pH 4. The recovery of the metal ions is around 98% using 1M HNO_3 *acid as the best eluent.*

Keywords: Environment, Separation of metal ions, *Lanchocarpus Laxiflorus*, Immobilization, Fixed bed column

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INTRODUCTION

Environmental impact of heavy metals was mostly attributed to industrial sources, Major industrial sources include surface treatment processes with elements such as Cd, Pb, Mn, Cu, Zn, Cr, Hg, As, Fe and Ni,as well as industrial products that, at the end of their life, are discharged in wastes [1] Major urban inputs to sewage water include household effluents, drainage water, business effluents (e.g. car washes, dental uses, other enterprises, etc.), atmospheric deposition, and traffic related emissions (vehicle exhaust, brake linings, tires) transported into the sewerage system [2].The continual release of metal contaminants into the natural environment has led to environmental awareness and a need to develop analytical methods for selective separation of heavy metal ions.

Separation techniques for extraction of selective metal ions from the industrial effluents containing hazardous elements are of higher interest due to the increasing public attention and awareness towards their disposal into the environment. Although a variety of methods such as precipitation, electrolysis and ion exchange [3] can be used to remove dissolved metals from aqueous samples but they suffer from disadvantages like poor removal competence, high cost, generation of secondary pollution and ineffectiveness towards low metal concentrations [4]Recently, solid-phase extraction has gained increasing favor because of its simple procedure, higher preconcentration factor, rapid phase separation and ease of combination with different detection techniques. Solid phase extraction (SPE) has commonly been used as a technique for preconcentration/ separation of various inorganic and organic species [4].

The main requirements for substances to be used as solid-phase extractants are as follows : ability to extract a large number of elements over a wide pH range, fast and quantitative adsorption and elution, high capacity and ease of accessibility. Numerous substances have been proposed and utilized as solid-phase extractants, such as modified silica and alumina, magnesia, active carbon and cellulose [3].This technique has advantages of higher enrichment factor, absence of emulsion, safety with respect to hazardous samples, minimal costs due to low consumption of reagent, environmental friendly, flexibility and easier incorporation into automated analytical techniques

Most previous research using biosorbents for metal ions is based on batch kinetic and batch equilibrium studies. However, in the practical operation of full-scale biosorption processes, continuous-flow fixed bed columns are often preferred. In such systems, the concentration profiles in the liquid and adsorbent phases vary in both space and time. As a result, design and optimization of fixed bed columns are difficult to carry out a priori without a quantitative approach. From the perspective of process modeling, the dynamic behavior of a fixed bed column is described in terms of breakthrough curve [5]. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of an adsorption column.

The aim of this work is to investigate the adsorption behavior of heavy metals on Lonchocarpus Laxiflorus leaves and the conditions for separation of heavy metals from aqueous solution.

EXPERIMENTAL SECTION

Sample preparation

The leaves of *Lanchocarpus laxiflorus* plant were collected from a tree behind ModibboAdama Federal University of Technology Yola, Nigeria. The plant was wash thoroughly under running water to remove dust and any adhering particle and then rise with distilled water. The sample was air dry for 2 weeks and the dry leaves was grinded in analytical mill and sieve to obtain adsorbent of known particle size range [6].

Preparation of Heavy Metal Stock Solution

All reagents used in this study are of analytical grade. The stock solutions containing 1000mg/cm^3 of all the metals of interest will be prepared by dissolving appropriate quantity of each metal salt in grams in 250cm^3 of distilled water and make up to the mark in a 1 liter volumetric flask. The stock solution will be used to prepare dilute solutions of different working concentrations

Preparation of sodium alginate and calcium chloride stock solution

Sodium alginate was prepared by weighing 4.00 g and making it up to 100 cm^3 mark with distilled water in a volumetric flask and left overnight for complete dissolution. 0.12 M of calcium chloride was prepared by weighing 26.28g in to 1000cm^3 volumetric flask and making up to mark with distilled water according to a standard procedure described by [4].

Immobilization of the leaves of *Lonchocarpus Laxiflorus* plant

Sodium alginate was used for immobilization of the leaves of *Lonchocarpus Laxiflorus* plant. 50 cm^3 of sample solution prepared by dissolving 4g of each test sample in 100 cm^3 of distilled water and mix with 50 cm^3 of 4% stock solution of sodium alginate and stir vigorously in 250 cm^3 beaker, to obtain a homogenous mixture. After mixing, the solution the solution was drawn through hyperdemic needles and was added drop wise to a stirred solution of 1M $CaCl_2$. A retention time of 2 h was allowed for the reaction to obtain complete precipitation of the immobilized leave, stem bark and roots powder of *lonchocarpus laxiflorus* plant. The beads thus formed i.e sodium alginates were kept in fresh $CaCl_2$ solution. Before sorption studies, the beads were removed and allowed to dry at room temperature. The dried solid mass was stored in a polythene bag for further use [4]

Batch sorption studies

Batch sorption experiments of metal ion Pb^{2+}, Cu^{2+}, Cd^{2+}, Cr^{2+}, Fe^{2+}, Hg^{2+} and Ni^{2+} concentration were conducted to study effect of pH at 1-7, contact time 10-120 min at room temperature, The method by [7, 8] was adopted.

The amount of metal absorbed by the biosorbent is calculated as:

$$\mathbf{q_e = V(C_o - C_e)}/M \text{ --[1]}$$

Where, q is the amount of metal ion adsorbed in mg/g; C is the initial metal ion concentration in mg/cm^3; Ce is the final concentration in mg/cm^3 V is the volume of metal ion solution in liters; M is the mass of the leaves of *Lanchocarpus laxifloru s*powder used in gram. The percentage Removal of the metal ion was also determined using;

Removal % = $[(C_o\text{-}C_e)/C_o]\times\ 100$ -------------------------------------[2]
Where, R% is the percentage of metal removed.

Effect of pH on Immobilized Leaves of LLP
The effect of pH solution on the sorption capacity of immobilized (LLL, was investigated in this experiment at room temperature (30^{0}C) and equilibrium time of 2 h. 30 cm^3 of the prepared aqueous solution was measured in a conical flask, followed by the addition of 0.5 g of the sample in the flask. The pH was varied from 3 to 7. 0.1 M HCl or 0.1 M NaOH was used to adjust the pH of the metal ion solutions to the desired value of interest. The metal solutions containing the biosorbent in the conical flask were well corked and shake using Gallenkamp flask shaker for 2h and thereafter the mixture was filtered, and then the concentration of each metal ions removed was determined using Atomic Absorption Spectrometer, (model, Shimadz 6800).

The effect of contact time on immobilized leaves of LLP
The effect of contact time was studied using an initial concentration of 20 mg L^{-1}. The time intervals chosen for this experiment were 30, 60, 90, 120, and 150 minutes.

0.5g of the immobilized leaves sample was separately mixed with 50cm^3 solution of initial concentration 100 mg L^{-1}. The mixture was shaken constantly in a shaker at 180 rpm speed for the time period of 30, 60, 90, 120, and 150 minutes for all the metal ions. At the end of each contact time, the mixture was filtered and the concentration of the filtered was determined using AAS.(Shimdzu AA-680, Japan)

Fixed- bed adsorption column studies
Effect of sample flow rate
Effect of flow rate was investigated in a column with various liquid flow rate (10, 15, and 20 ml/ min) at room temperature. Working solution of metal ion with 100 mg/ L was run through the fixed bed column at various liquid flow rates. Effluent at the outlet of column was collected at predetermined time interval and analysed by AAS.

Column procedure
A fixed- bed column was made of Pyrex glass tube of length 50cm with an internal diameter of 2.5cm and a bed height of 40cm was used for the study. The method by Ali *et al*., 2014 was adopted. Two cm thick of glass wool was placed at the bottom and top of the adsorption column to increase the distribution of the solution onto the adsorbent surface and maintain a constant flow rate. The aqueous metal ion solution of Pb^{2+}, Cd^{2+}, Cr^{2+}, Fe^{2+}, $^{+}$ and Ni^{2+} ions at a concentration 80 mg/L was pumped through down ward direction in the column at 15ml.min^{-1} flow-rate. The columns were equilibrated with distilled water at the same flow rate. Fractions collected at regular intervals and metal ion concentration was analyzed using AAS. The column study was carried out at room temperature (30^{0}C. The column performance of heavy metals adsorption on LLL was used separately.

Quantitative Separations of Metal Ions
Separation of the metal ions was performed by an elution technique. LLL biomass (40g) was packed into three different glass column of 2.50 cm i.d., with a glass-wool support at the end, and washed 2–3 times with distilled water. Binary solutions of the metal ions were prepared by mixing 10 mg/ L solution of each ion. The binary mixture (5ml) was then poured on to the top of the column and the solution was left to flow slowly through the column. The retained metals on the column were eluted with 40 ml of 1 M $HNO_3$and the effluent was collected in 10-mL fractions. The metal ion content of each 10 ml fraction was determined by AAS.

RESULTS AND DISCUSSION

Effect of pH on metal ion uptake
The effect of pH in the range 3-7 in the binding of Cr, Cd, Ni, Pb, and Fe by LLL biomass was investigated. The result of the pH studied was represented in Figure 1. Table 1 shows the maximum pH value on different metal ions.

Table 1: The pH for maximum sorption of the metal ions studied by LLL and the corresponding % removal are given below

Metal ions	pH for maximum Sorption	Capacity %
LLL		
Cd	3.0	85.08
Ni	7.0	99.49
Pb	5.0	99.86
Cr	6.0	98.75
Fe	4.0	61.00

It can be seen that Fe was retained in solution at higher pH compared with other metal ions studied. In Table 1, the LLL sorption capacity for Fe reaches a maximum at 61% at pH 4. The sorption capacity for pb increased steadily as the pH increased while those of Ni, Cr and Cd decreased sharply and increased as their pH values increases. At lower pH values below 5, there was excessive protonation of the active site at LLL surface and this refuses the formation of links between metal ions and the active site [9]. At high pH values above 5-7. The Linked H^+ may have been released from the active sites and the adsorbed amount of metal ions will generally increase. From Table 1, comparing all the metal ions studied by LLL biomass, the LLL has a high selectivity for Pb, Cr and Ni with 99.86%, 98.75% and 99.49% at pH 5, 6 and 7 respectively. For cadmium the sorption capacity was low compared to Pb, Cr and Ni.

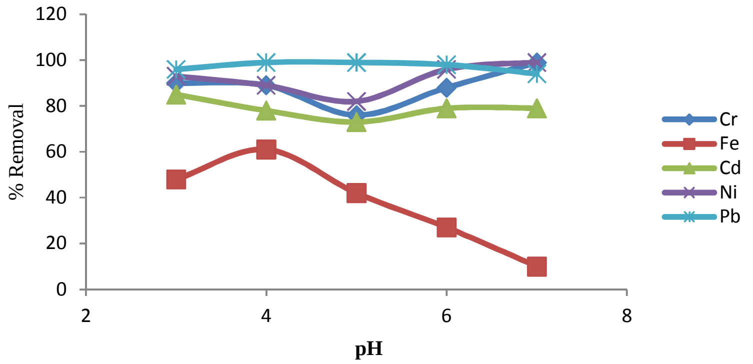


Fig: 1 Effect of pH on sorption of metal ions on LLL biomass

Effect of Contact Time

The percentage metal bound by the biomasses as a function of time was also determined. The effect of contact time on the uptake of chromium, iron, cadmium, nickel and lead by LLL biomasses are shown in figure 2. The adsorption of metal ions was increased at specific time and becomes constant when it reaches equilibrium. the rapid uptake is about 89.94 - 89.98% removal of chromium, 84- 86% removal of iron, 94.23- 95% removal of cadmium, 93.46- 94.98% removal of nickel and 97.75- 98.41% removal of lead by LLL biomass

Generally, metal biosorption consists of two phases: a very rapid initial sorption, followed by a long period of much slower uptake. During the initial stage of sorption, a large number of vacant surface sites are available for biosorption. After some time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules adsorbed on the solid surface and the bulk phase. Besides, the metal ions are adsorbed onto the mesopores that get almost saturated with metal ions during the initial stage of biosorption. Thereafter, the metal ions have to traverse farther and deeper into the pores, encountering much larger resistance. This results in the slowing down of the biosorption during the later period of biosorption. The results also indicate that the metal ion removal by the biomass is relatively rapid for all metals investigated. The optimum removal of each metal occurred between 20-40 min. The non uniform pattern of sorption observed could be attributed to non uniform surface area or binding of the biomass [10].

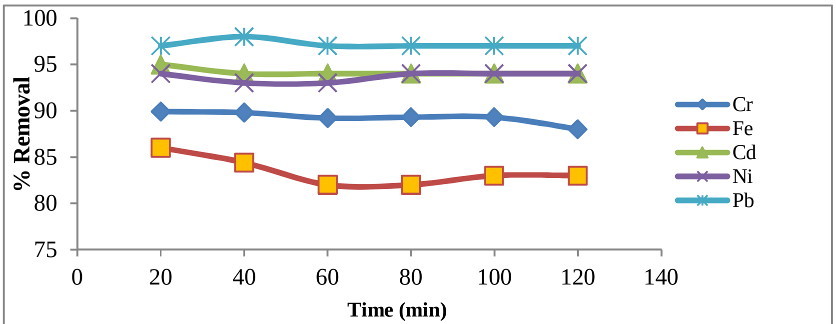


Fig: 2 : Effect of contact time on metal ion adsorption by LLL biomass

Breakthrough studies

Effect of sample flow rate

The sample flow rate is very important parameter since it controls the time of analysis. The retention of $Cr^{2+,}$ $Fe^{3+,}$ $Cd^{2+,}$, Ni^{2+} and Pb^{2+} on to LLL column was studied at different flow rates of 10, 15, and 20 $mL.min^{-1}$.

Figure 3, shows the retention of the metals with *Lonchocapus Laxiflorus* biomass at different sample flow rate. The results indicated that, the optimum flow rate for the metal ions studied is 10 – 15 ml/ min with LLL. Slower flow rates than 10ml/ min was not used to avoid longer analysis time. However, at flow rates greater than 15 ml/ min with LLL sorbents, a decrease was observed in the efficiency of retention onto the column. Probably because the metal ions couldn't be significantly equilibrated, since it needs longer time with the sorbents. According to the experimental results, the recovery of all metal ions reached 98-99 % at flow rate 10 -15 $mL.min^{-1}$. Therefore sample flow rate of $15mL.min^{-1}$ was chosen for further column experiment in order to ensure better retention along with relevant duration time. The results of effects of flow rate are directly correlated to the effects of contact time in the batch experiment, where the sorbent have showed fast contact of sorption with the metal ions.

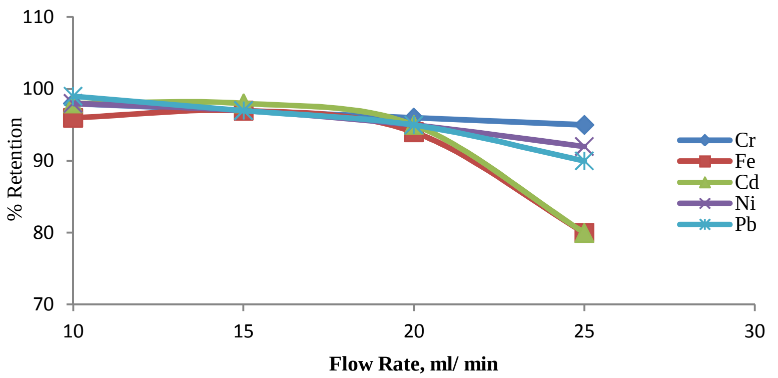


Fig: 3 Effect of sample flow rate on the retention of metal ions with 40g of LLL column

Breakthrough capacity

Figures 4 shows the breakthrough curve for the removal of metal ions from solution by 40g of each biomass in packed bed column. The breakthrough curves for different metal ions at the pH of maximum sorption at a flow rate of 15ml/min are given in Figure 4. All the breakthrough curves are steep at the breakthrough point.. Initially there was very good increases steadily as the column became more and more saturated. For calculating the 100% breakthrough time of LLL for each heavy metal, the Ce/Co was plotted against different time interval. From the figure 4, the saturation of the column was achieved after passing of 1.8 – 2.2 L of influent solution, therefore LLL can remove 100% of all the metal ions up to about 2.30 h. After 1 h the influent and effluent ratio of Cd, Ni, Fe, Pb and Cr was between 0.01-0.6 approximately. The breakthrough capacity of each sorbent was calculated using

$$q = (V_{50\%} - C_o)/m$$

Where V$_{50\%}$ is effluent volume (ml) at 5% breakthrough, Co is the concentration of the inlet solution (mg/ L) and m is mass of adsorbent in grams. Accordingly, the capacity (mg/ g) for Cr P(II) , Fe (III), Cd (II), Ni(II) and Pb (II) are estimated to be 14.3, 12.05, 12.45, 13.75 and 13.18 with LLL, Obviously the capacity of the column is generally good. It can be used to separate metal ions from dilute aqueous solutions. Similar trend was observed by [11]

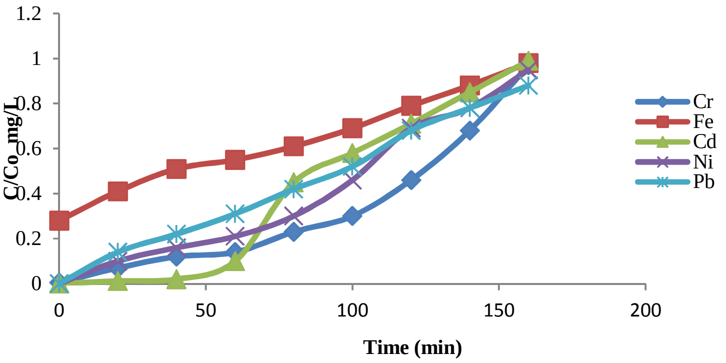


Fig: 4 Breakthrough curves for metal ions with LLL sorben at flow rate 15ml/min, concentration of metal ion solutions 80 mg/ L

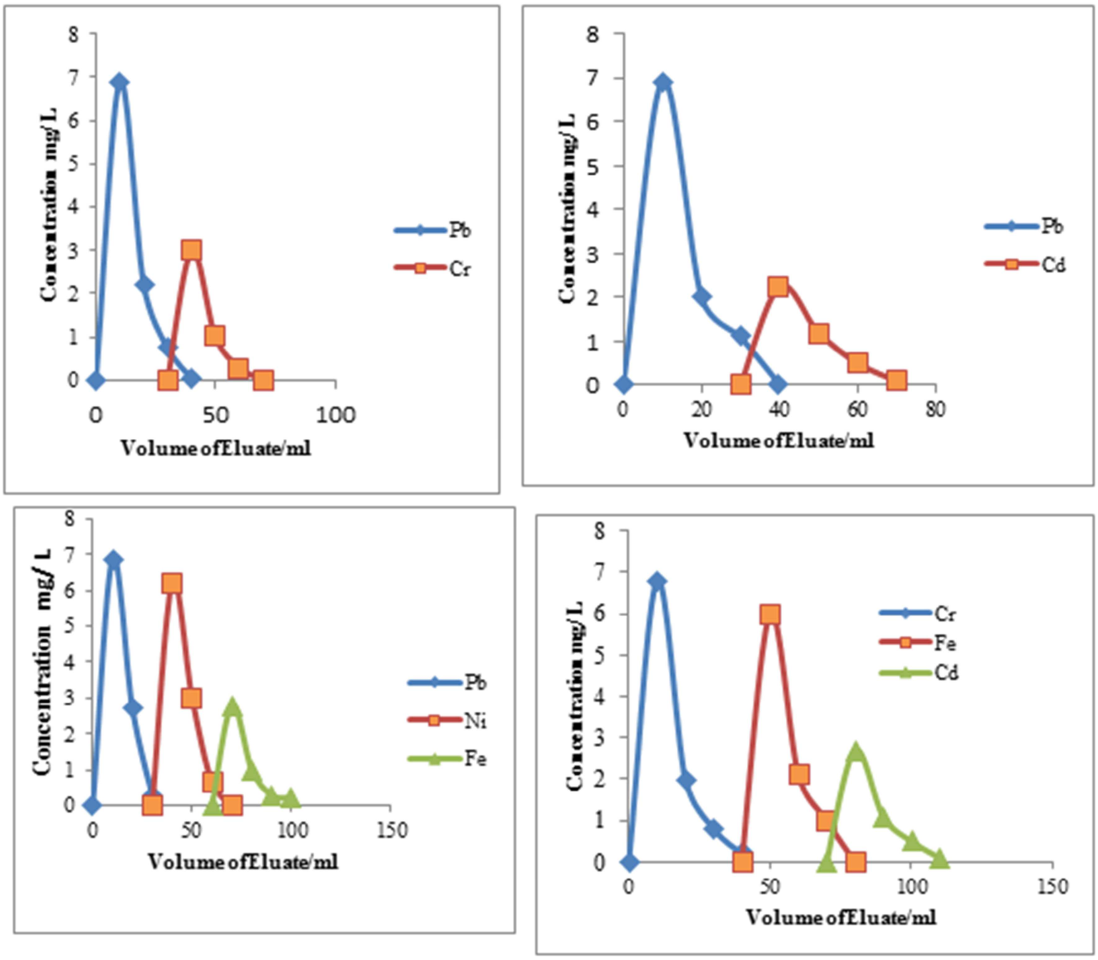
Separation of metal ions

From pH capacity curves, breakthrough capacities, the various metal ions confirm that the biomasses have different selectivity for the metal ions studied. pH of the maximum sorption for Ni(II) and Fe (II), Cr (II) and Ni (II), Pb (II) and Cr (II)-Fe (II)-Ni (II) are 7,6 .4 and 6 respectively. Since their sorption capacities are different, hence it is possible to separate these metal ions using HNO$_3$ as eluting agents with synthetic solutions. The results obtained are shown in Tables 2 and represented in Figures 5. 40 ml of acid eluent is efficient for almost complete desorption of the retained metals. Also is noted that the first aliquot of 10 mL elutes more than 70 % of retained ions on column, while the remaining eluant volume (30 mL) desorbed the rest of ions. The recovery of metal ions was 80-99%. The results indicate that the extraction and elution of the metal ions was little affected by the other ions. The separations are quite sharp and recovery was quantitative and reproducible. The chromatograms of these separations are given in Figs 5. Similar trend was observed by [11, 12].Table 2gives the results of the analysis of synthetic mixtures. In all instances good separations of the various metal ions were achieved and the standard deviations of the recoveries were low.

Table: 2 Qualitative separations of metal ions on a column of LLL biomass

Metal ion	Amount loaded(ppm)	Amount recovered (ppm)	Recovery of metal ion % ±SD	Volume of eluent(ml)	Eluent used
Ni	10	9.89	99±3 07	40	1.0MHNO$_3$ pH 7
Fe	5	4.30	86 ±1.34	40	
Cr	10	9.87	98±3.04	40	1.0MHNO3 pH 6
Ni	5	4.05	81±0.94	40	
Pb	10	9.90	99±3.18	40	1.0MHNO$_3$ pH 4
Cr	10	9.66	96±2.82	40	
Cr	10	9.80	98±3.02	40	1.0M HNO$_3$ pH 6
Fe	10	9.10	91±2.61	40	
Ni	5	4.40	88 ±1.14	40	

SD= standard deviation, N=3



Figures: 5 Eluation Curves for metal ions on LLL

CONCLUSION

The Lonchocarpus Laxiflorus biomass leaves was successfully applied to preconcentration and determination of Pb, Cd, Cr , Ni and Fe(III) metal ions. LLL showed good potential for the enrichment of these metal ions from various matrix as is evident from the column studies. The uptake and stripping of these metal ions on the LLl biomass was found to be fast, indicating a better accessibility of Pb, Cd, Cr , Ni and Fe(III) towards the chelating sites The separation of binary/ternary mixtures is possible by control of pH or gradient elution. The proposed method provides a simple, sensitive, precise, reliable and accurate method for the preconcentration and determination of Pb, Cd, Cr , Ni and Fe metal ions. The results show that LLL has a high sorption capacity for metals studied. The behavior of both metal ions on LLL depends on pH, the leave biomass enable the separation of all the metals by passing 1M HNO3 acid as eluent through the column. The biomass may be regenerated using 1M Nitric acid.

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