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APPLICATIONS OF A NOVEL GREEN ADSORBENT FOR ENVIRONMENTAL MONITORING

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Abstract

In this paper preparation of a novel Calotropis procera based adsorbent and green chemical technology for the removal of zinc, cadmium and lead in different matrixes including polluted water has been described. The developed technology is based on the nanoparticles obtained from latex of Calotropis procera. Investigations were carried out either by batch method or by column method. Effects of different parameters like pH, amount of modified latex, flow rate, inert electrolyte, and temperature and adsorption time were also investigated. The distribution coefficients for Zn, Cd and Pb were found as 3.6 x 10^2; 3.9 x 10^2 and 2.8 x 10^2 respectively. The results of preconcentration and recovery of the metal ions using column method are found to be 98.7% for zinc, 98.4% for cadmium and 97% for lead. The working conditions are very easy and modified latex can be regenerated and reused.

Keywords: *Calotropis procera, Green chemical technology, Pre concentration, Water.*

1. Introduction

The chelating resins are a group of materials having chelating or complexing group embodied on their surface such as iminosalicylsilica, chemical modification of a resin surface (i.e. silica) with salicyldehyde [1] or o-vanillin [2]. In recent years a wide range of these materials has been developed, based not only on soft resin cores but also on more rigid materials such as controlled pore glass [3] and silica [4-6]. Many other materials such as chitosan [7], chelex [8], cyanex [9], amberlite [10], cellulose [11], starch [12], polystyrene [13] and Dowex [14] etc. have also been used as a supporting agent to load with various chemicals or organic complexing agents like alkyldiamines, diamines, dithiocarbamates, thioanilide and these have been used for preconcentration and separation of metal ions.

The chelating resins are preferred over conventional ion exchange resin because of their high selectivity and capability of binding metals through multiple coordination group attached to support. The multiple coordinations of a ligand on a chelating resin make it particularly suitable for the collection of polyvalent metal ions. The chelating resins are largely prepared by immobilization of ligands on the resin matrix. In general few essential properties are required for a good quality and selective chelating resin such as - the complexing agent to be incorporated should yield with the support matrix a stable system, it must be stable over a wide range of pH values, the solid support must have high chemical stability, so that during the synthesis of chelating resins their functional structure is not changed and the steric structure of the chelating group should be compact, so that the formation of chelate ring with metal ion is not hindered with the resin matrix. Synthetic or Inorganic resins provides good results but their limitations related with environmental issues provides an area for evolution of natural resins / adsorbents.

In front of above facts the present paper describes the potential use of three green *Calotropis procera* adsorbents i.e. CPB (*Calotropis procera Bark),* CPR (*Calotropis procera Root)* and CPDL (*Calotropis procera* dried Latex) for the separation and estimation of

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metal ions (i.e. zinc, cadmium and lead). The studies have been carried out by batch and column techniques. The new Green adsorbents are better and developed method has been successfully used for the trace determination of these metal ions in various samples.

2. Experimetal

2.1 Apparatus

A digital (ECIL model) pH meter 5651A and a Shimadzu AA-640-13 atomic absorption spectrometer were used. A glass tube of 100 mm and 7 mm i.d. was used as a chromatographic column.

2.2 Materials and solvents

All chemicals were used of AR grade. A stock solution of following metal ions Zn (II), Cd (II) and Pb (II) were prepared by dissolving their salts in double distilled water or acids and used after standardization. Three Green adsorbents were prepared and have been used as adsorbents. i.e. CPB (*Calotropis procera Bark),* CPR (*Calotropis procera Root)* and CPDL (*Calotropis procera* dried Latex). In case of CPDL two types of particles were obtained and nanoparticles obtained by micellar technique have been used after characterization.

2.3 General Procedure.

Two types of methods were used for investigations i.e. Batch and Colum method

2.3.1 Batch method

Preconcentration of Zn (II), Cd (II) and Pb (II) was performed by a batch technique at $25^{o}C$. Fixed amount of Green adsorbent (0.08g) was equilibrated with 10 ml (10 μg/ml) solution of metal ions, Zn (II), Cd (II) and Pb (II) in a shaker thermostatted to the desired temperature and adjusted to the desired shaking speed. The pH of each mixture was maintained in between 4-8.5 (zinc 6.0-6.8, cadmium 5.5-8.5 and for lead 3.7-8.0) either by sodium acetate or borate buffer. After a fixed time the green adsorbent was allowed to settle down, supernatant solution was separated and metal ions in the supernatant solution were estimated by means of atomic absorption spectrophotometer (AAS).

2.3.2 Dynamic method

In a dynamic experiment glass column with a length of 100 mm and internal diameter of 7 mm were packed with 0.08g of Green adsorbent to a height of about 12 mm. It was eluted by 5.0 ml of appropriate buffer solution (pH 4 to 9, depending on the optimum pH range of metal ion), thereafter, 10ml (10ppm) solution of metal ion (Zn (II), Cd (II) and Pb (II)) was maintained for 25 minutes at the same pH and then allowed to pass through column at a flow rate of 2 ml per minute. The adsorbed metal ions were eluted from the column using 20 ml of 0.1 N HNO_3 and the metal ions were determined by means of atomic adsorption spectrophotometer (AAS).

3. Result and Discussion

3.1. Effect of type and amount of green adsorbent

In order to explore the effect of type and amount of green adsorbent, investigations have been carried out on different amounts of three green adsorbents prepared from different parts of *Calotropis procera*, which were prepared by a method developed earlier by our group.

3.2 Effect of pH

Retention of metal ions on a column packed with green adsorbent was studied as a function of pH. Zinc, cadmium and lead have been retained quantitatively from aqueous solution in the pH range of 6.0-6.8, 7.0-8.0 pH and 6-8 respectively. The optimum pH selected for further investigation is 6.5 for Zn, 7.0 for Cd and 6.0 for Pb.

3.3 Optimization of adsorption time

The speed with which solid phase adsorbs metal ions from the solution and attains the equilibrium condition is of considerable importance. It was found that time necessary to reach the equilibrium is about 8 minutes for Zn and Pb and 10 minutes for Cd.

3.4 Adsorption isotherms

The uptake of Zn (II), Cd (II) and Pb (II) by green adsorbents as a function of metal ion concentration in aqueous solution was determined by using a batch technique. The adsorption isotherms represent a good linear relationship over a relatively wide range of tested ion concentrations (Fig. 2) . The distribution coefficient, D, defined as $D = N_1 C$. Here N_1 is expressed in mmol per gram and C in mmol per ml. The average value of D (ml per g calculated for each metal in the concentration

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range 2 x 10^{-5} M to 2.5 x 10^{-3} M have been found to be: Zn: 3.6 x10^2, Cd:3.8 x10^2, Pb:3.9 x10^2). Plots of adsorption capacity of green adsorbents particularly CPDL against the concentration of metal ions had an almost zero intercept (0.0017). Regression analysis of the adsorption isotherm plot revealed the correlation was good, r = 0.998. The sensitivity sequence was in order Zn(II)>Pb(II)>Cd(II) (Fig. 2).

3.5 Effect of temperature

Adsorption of metal ion is also affected by temperature. The percentage adsorption and distribution coefficient of the complexation reaction have been found to increase with increase in temperature upto 35°C then it remained constant upto 45°C, thereafter it decreased marginally.

3.6 Effect of flow rate

Adsorption of the metal ions on green adsorbent column was studied at different solution flow rates. For each metal ion solutions (100 ml) containing 40 µg of the ion were passed through the column at a flow rate varying from 0.5 ml to 5 ml per minute. Adsorption was quantitative and reproducible in the given range. The flow rate, maintained at 2 ml per minute, was most suited for better adsorption.

3.7 Preconcentration and recovery of metal ions

To study the performance of green adsorbent for preconcentration Zn (II), Pb (II) and Cd(II), each of metal (50 mg) in different volumes of samples (25-100 ml) was passed through a column at 2 ml per min. Elution of the metal ions from the columns resulted in recoveries Zn (II), Pb (II) and Cd(II) was 98.7%, 97.5% and 98.4% respectively. The uptake of metal ion decreased with increasing sample volume. These results show that these metal ions can be concentrated effectively from large volumes of dilute aqueous solutions by use of green adsorbent. (Table 1)

3.8 Effect of electrolytes

The effect of various electrolytes such as sodium chloride, potassium nitrate, calcium chloride and magnesium sulphate on the adsorption of metal ions by green adsorbents was investigated. Electrolytes had no effect on the adsorption of the metal ions by the green adsorbents.

3.9 Determination of Zinc in milk and lead in water samples

Solutions of the samples of milk and water were prepared as described previously [15]. Aliquots from this solution were taken and 2.5 ml of buffer solution was added to it then the volume was made upto 10 ml and the solution was passed through a column packed with green adsorbent. Metal ions were eluted from the column using 0.1N HNO_3. The amounts of metal ions were determined by means of AAS. The recovery was found to be 97-98%. Results are given in Table 2 and 3.

Table 1. Preconcentration and recovery of metal ions

Metal ion	Concentration (µg/ml)	Volume of eluent (ml)	Recovery	
			µg/ml	%
Zn	10	20	9.87	98.7
Cd	10	20	9.75	97.5
Pb	10	20	9.84	98.4

Table 2.Determination of Zn various milk samples

Sample	Zinc added (µg/g)	Zinc determined (µg/g)	% Recovery
Cow milk	- 0.040	0.365* 0.402*	- 99.1
Dairy Milk	- 0.040	0.420* 0.454*	- 98.5
Milk Powder (A)	- 0.040	0.056* 0.095*	- 99.0
Milk Powder (B)	- 0.040	0.052* 0.091*	- 98.6
Milk Powder (C)	- 0.040	0.056* 0.093*	- 96.8

* Mean of five simultaneous determinations

Table 3. Determination of Lead in water

Sample	Pb added (µg /ml)	Pb determined (µg / ml)	% Recovery
(A)	- 0.10	0.58* 0.66*	- 96.5
(B)	- 0.10	0.25* 0.34*	96.0
(C)	- 0.10	0.28* 0.37*	- 96.5
(D)	- 0.10	0.35* 0.44*	- 97.1

* Mean of five simultaneous determinations

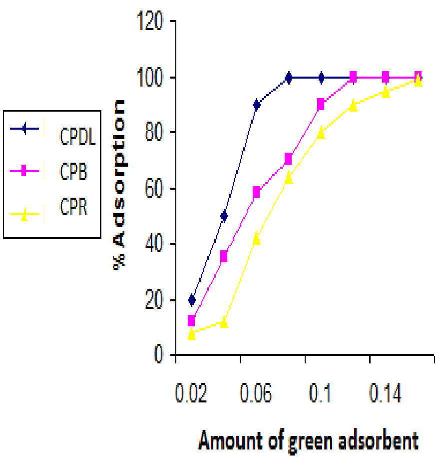
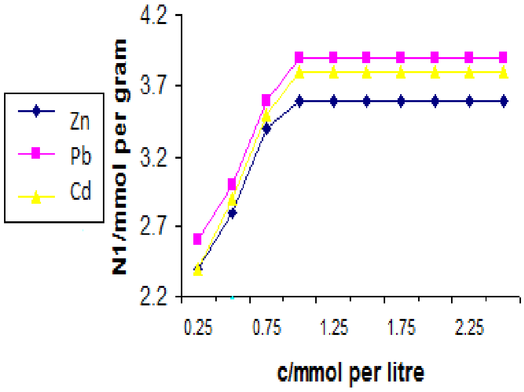


Figure 1. Effect of type and amount of green adsorbent on the adsorption of zinc



4. Conclusion

Zn, Cd and Pb can be readily determined by using these green adsorbents. The solid phase extraction method shows fast metal ion-exchange kinetics and high sorption efficiency. The proposed method is widely applicable for the measurement of trace Zn, Cd and Pb in a variety of samples. There is further scope for the investigation on other metals, which is in progress.

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