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Synthesis and application of chemically modified tamarind based TTPCA resin for removal of toxic metals from industrial effluents

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Abstract

TKP (Tamarind Kernel Powder) and its chemically modified derivatives are important biosorbents for removal of heavy metals such as lead, cadmium, iron, zinc, and copper from industrial effluents. TKP falls in natural gums category polymer which is completely non- toxic, bio-compatible and bio-degradable natural polymer. It has a hydrophilic polysaccharide matrix, which have been used for the synthesis of chelating resins. In present investigation a new Tamarind Kernel Powder based chelating resin {named as TTPCA) containing Proline group has been synthesized. Hear Proline group has been incorporated into TKP with the help of cyanuric chloride in the presence of dioxane medium. TKP resin serves the purpose of both flocculants as well as selective ion binders for heavy metals. This resin is totally eco-friendly and also supports green chemistry.

Keywords: Heavy metal ions, chelating resin, tamarind kernel powder, proline, industrial effluent treatment.

Introduction

The quality of water is of vital concern for mankind since it is directly linked with human welfare. Severe environmental problems are raised due to uncontrolled industrial development and urbanization. With the result that many rivers, water bodies have already been polluted with organic and inorganic pollutants, heavy metals, pesticides and solid particles [1]. Consequently, adverse effects, such as unbalancing solution pH, death of aquatic flora and fauna, infertility of soil and harmful effects to human's health would result.

There are a number of metal ions present in the environment. Some of these are toxic and the rest non- toxic. The toxic metal ions are discharged by industries into water. They get into the humans food chain from the environment. Once they enter our biological system they disturb the biological processes, leading in some cases to fatal results [2-4]. Some of the pollutants like lead (Pb), arsenic (As), mercury (Hg), chromium (Cr) specially hexavalent chromium, nickel (Ni), barium (Ba), cadmium (Cd), cobalt (Co), selenium (Se),vanadium (V), oils and grease, pesticides, etc. are very harmful, toxic and poisonous even in PPB (parts per billion) range [5, 6]. The presence of these pollutants cause alteration of water's physical/chemical/biological property includes acidity (change in pH), electrical conductivity, temperature, and eutrophication.

These heavy metal ions can neither be degraded nor destroyed but tend to bioaccumulation, causing an increase in its concentration in a biological organism over a period of time, compared to its amount in the environment. The treatment of heavy metals is of special concern due to their recalcitrance and persistence in the environment [13-16]. Innovative processes for treating industrial wastewater containing heavy metals often involve technologies for reduction of toxicity in order to meet technology-based treatment standards.

There are several methods available for heavy metal removal from wastewater like coagulation and precipitation, lime treatment, membrane filtration (such as ultra-filtration, nanofiltration, and reverse osmosis), ion exchange, electro dialysis, and photo catalysis and adsorption processes have been extensively used [7-10].

Various new low-cost adsorbents are derived from agricultural waste, industrial by-product, natural materials or modified biopolymers. They are known as biosorbents. These materials being highly efficient, low cost and renewable source of biomass can be exploited for metal ion remediation as inexpensive sorbents.

The present work describes the synthesis of chemically modified TKP resin and its application for the removal of heavy metal ions from effluent streams.

Materials and methods

Synthesis of TKP derived TTPCA resin

0.1 mole of Tamarind kernel powder was transferred to a round bottom flask containing 100 mL dioxane. Temperature was maintained at about 5^{0}C by external cooling and stirred. Further 7.2 g cyanuric chloride was added to this solution and by adding sodium bicarbonate, pH was brought to 7-8. The whole mass was then stirred for two hour.

0.1 Mole of Proline amino acid was added to above product and pH was brought 9-10 by adding 50% aqueous solution of NaOH. The temperature of the mixture was raised to 35-40^{0}C and stirred vigorously by magnetic stirrer for 3 hrs.

The derivative of Tamarind triazine pyrrolidine-2-carboxylic acid (TTPCA) resin, (IV) thus formed was filtered, washed with distilled water and finally dried at 110^{0}C. The Chemical reaction involved in synthesis is shown in figure: (I).

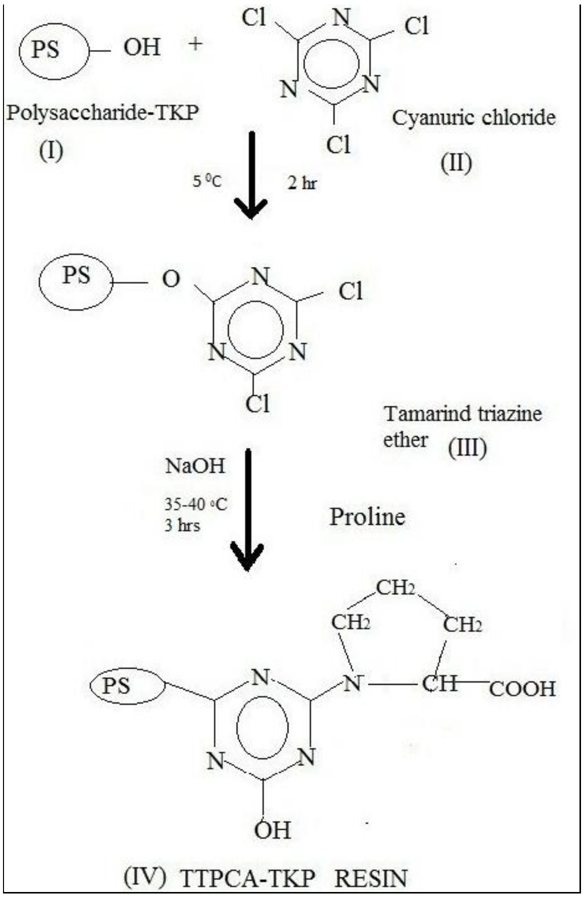

Fig 1: Synthesis of Tamarind triazine pyrrolidine-2-carboxylic acid (TTPCA) resin

FTIR spectra of TTCEA-TKP resin

TTCEA-TKP resin has been characterized by FTIR spectra analysis. The FTIR spectra is shown in figure (II) and reported in table (1).

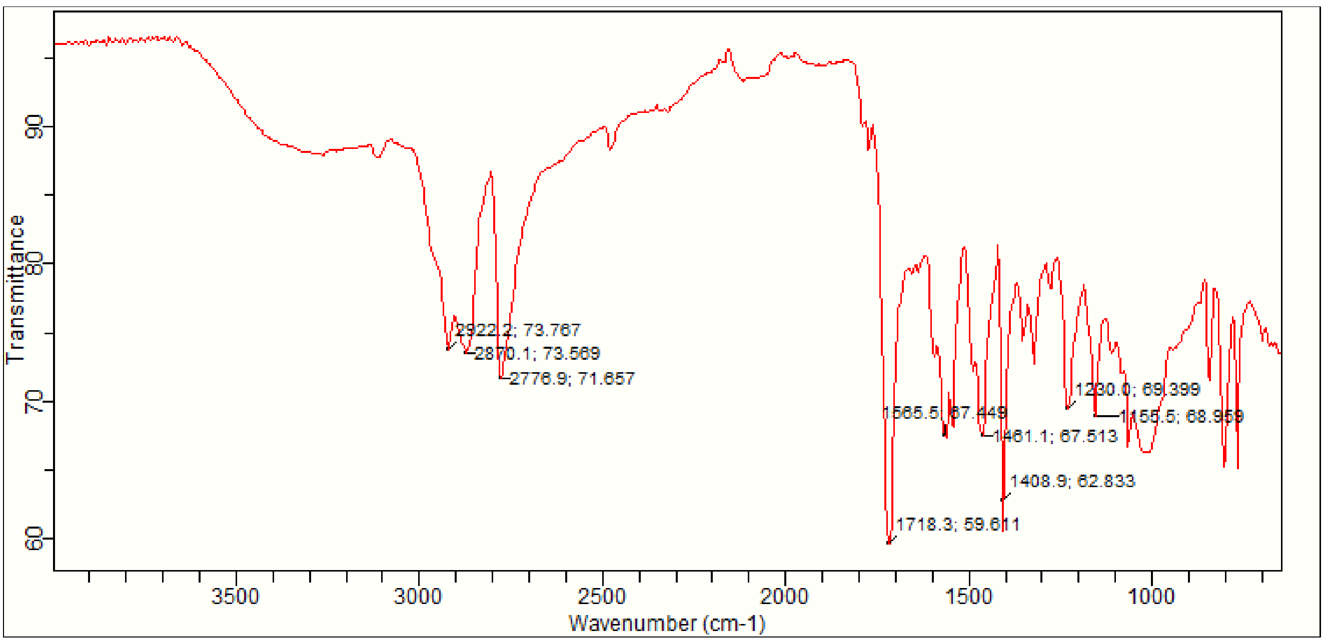

Fig 2: FTIR-Spectra of TTPCA resin

FTIR spectra shown above, shows various peaks from which resin TTPCA-TKP can be analysed:

Table 1: Characterization of Spectra

Assignment	K salt of ligands Bands
-C-H stretching	2870.1 cm^{-1} and 2922.2 cm^{-1}
–O-H stretching	2776.9 cm^{-1}
-C=O stretching	1718.3 cm^{-1}
-N-C-H stretching	1585.5 cm^{-1}
Corboxylate anion stretching	1408.9 cm^{-1}
- C-O stretching and O-H bending (secondary alcohol)	1230 cm^{-1}
C-N vibration aliphatic	1155.5 cm^{-1}

Experimental design and treatment of effluents using TTPCA resin:

Samples of industrial effluents containing heavy metal ions were collected from different metallurgical industries from Jodhpur region. Names of industries were not mentioned due to legal reasons. These samples contained heavy metal ions along with Ca^{2+} Mg^{2+}, Na^{+}, K^{+} and anions like CN^{-}, SO_4^{2-}, F^{-}, clay and turbidity. The characteristics of samples from industry A and industry B were reported in the table no. (II).

The procedural adopted for the removal of heavy metal ions from newly synthesized TTPCA –TKP resin was done with column method. In this method the diameter of the resin bed was less than one tenth of column height. Column was prepared by TKP derived resin of narrow size range. The resin was stored with water in an open beaker for several minutes, fine particles were removed by decantation then the slurry of resin was transferred portion wise to the column previously filled with water. 100 mL aliquots of samples were taken into clean beakers. First the sample is treated with 50 mg of clay and then treated with 50 mg of lime. After this the pH of sample was adjusted to 8 then the sample of metal ion solution was loaded in the column, polymer bound chelating agent was present in the form of sodium. Later, it formed chelate and released sodium ions.

When the solution travelled through the resin column, a colored band was formed which was further eluted by perchloric acid solution. In case of two or more cations the band which formed weaker complex was released first. The eluate was thus collected in flask and further these filtrates were treated for estimation of metal ions by AAS. The related results are reported in table (III).

Table 2: Characteristics of effluents contaminated with heavy metal ions obtained from various units of mineral and metal processing industries.

Characteristics	Industry A	Industry B
Colour	Brown	Green
pH	4.2	9.8
Total hardness (in ppm)	590	994
Zinc (in ppm)	4.90	1.72
Copper (in ppm)	0.78	1.01
Lead (in ppm)	0.92	0.76
Cadmium (in ppm)	0.52	0.11
Iron (in ppm)	76	45
Magnesium (in ppm)	81	63
Calcium (in ppm)	132	143
Sulphate (in ppm)	623	702
Fluoride (in ppm)	0.97	0.62

Table 3: Removal of toxic metal ions from the effluents from various minerals and metal processing industries

Source	Metal ions	Untreated effluents	After treatment with lime at 8.0 pH	After treatment with derivative of TKP 8.0 pH
Effluents of Industry A pH 4.2	Zinc (in ppm)	4.90	2.3	0.06
	Copper (in ppm)	0.78	0.23	0.02
	Lead (in ppm)	0.92	0.16	Nil
	Cadmium (in ppm)	0.52	0.09	0.01
	Iron (in ppm)	76	13	Nil
	Magnesium (in ppm)	81	81	81
	Calcium (in ppm)	132	132	132
Effluents of Industry B PH 9.8	Zinc (in ppm)	1.72	0.60	0.01
	Copper (in ppm)	1.01	0.71	0.02
	Lead (in ppm)	0.76	0.07	Nil
	Cadmium (in ppm)	0.11	0.04	0.01
	Iron (in ppm)	45	07	Nil
	Magnesium (in ppm)	63	63	63
	Calcium (in ppm)	143	143	143

Result and Discussion

The toxic metal ion concentration can be brought to a safer limit by effluent treatment technique. Polymeric reagents can be considered very good tertiary treatment.

TTPCA-TKP resin was successful in reducing the toxic metal ion concentration to the safer limit. This resin had good removal efficiency for lead and iron ions. Calcium and Magnesium metal ions were not removed from effluent sample after treating them with resin. The reason was incomplete dissociation of bivalent metals in these effluents.

Moreover, according to the FTIR analysis, the polysaccharide based TTPCA-TKP resin has a structure which facilitates the adsorption of heavy metals because it has C=O carbonyl groups, C-H stretching, O-H stretching, and -OH groups. So the resin has demonstrated outstanding removal capabilities for heavy metal ions from effluent by chelating, cross-linking and cation exchange. This resin has dual functioning as acting as flocculants cum selective ion binders. The TTPCA –TKP resin is very sustainable and inexpensive, also will not harm the environment.

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