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Bioremediation of industrial toxic metals with gum kondagogu (*Cochlospermum gossypium*): A natural carbohydrate biopolymer

V T P Vinod[1] and R B Sashidhar[2]*

[1]Jonaki, Board of Radiation and Isotope Technology, Department of Atomic Energy
Center for Cellular and Molecular Biology Campus, Uppal Road, Hyderabad 500 007, India

[2]Department of Biochemistry, University College of Science, Osmania University, Hyderabad 500 007, India

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The ability of gum kondagogu [*Cochlospermum gossypium* (L.) DC.], a natural carbohydrate biopolymer, was investigated for adsorptive removal of toxic metal ions Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+} and total Cr present in industrial effluents. Various physico-chemical parameters, such as, *p*H, temperature, equilibrium contact time, % biosorption and adsorption capacity, were investigated. Metal biosorption (%) and adsorption capacity of the biopolymer was determined by ICP-MS. Gum kondagogu was capable of competitively biosorb 8 toxic metal ions from the samples of industrial effluents tested. The adsorption capacity was observed to be in the following order, $Cd^{2+} > Cu^{2+} > Fe^{2+} > Pb^{2+} > Hg^{2+} >$ total Cr $> Ni^{2+} > Zn^{2+}$. The maximum adsorption capacity of metals by gum kondagogu varied in the range of 31-37 mg g^{-1} for Fe^{2+} and minimum of 5.5-9.3 mg g^{-1} for Hg^{2+} in the effluent samples tested. The equilibrium adsorption data were fitted to Langmuir isotherm models for all the metal ions adsorbed. FT-IR studies were carried out to understand the type of functional groups in gum kondagogu responsible for metal biosorption process. Desorption studies on biosorbed metal ions showed that HCl was a good eluant for all metals tested. The re-adsorption capacity of the recycled gum kondagogu biopolymer sustained its biosorption property at 90% level, even after 3 cycle of desorption. Gum kondagogu biopolymer has the potential to be used as an effective, non-toxic, economical and an efficient biosorbent clean-up matrix for removal of toxic metals from industrial effluents.

Keywords: Adsorption, biosorption, *Cochlospermom gossypium,* desorption, regeneration, FT-IR, ICP-MS, SEM-EDXA, gum kondagogu

Introduction

The continuously increasing demand for the commodities produced by chemical industries has triggered heavy metals accumulation in the ecosystem. Mining and metallurgical wastewaters are considered to be the major sources of heavy metal contamination in the environment. Biosorption is a potentially attractive technology for removal of toxic heavy metals form industrial effluents, which utilizes environmental biosorbent to sequester metal contamination[1]. Heavy metal contamination exists in aqueous waste streams from diverse industries, such as, metal plating, mining, tanneries, painting, car radiator manufacturing, batteries as well as agricultural sources, where fertilizers and fungicidal sprays are intensively used. Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Hg^{2+} and Cr are harmful wastes produced by industry that pose a risk of contaminating groundwater and other water resources. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders[2,3].

Safe and effective disposal of effluents containing heavy metals based on green chemistry is always a challenging task for industrialists and environmentalists as cost-effective treatment alternatives are not available. Conventional technologies for the removal of toxic heavy metals, such as, chemical precipitation, ion exchange or electrochemical processes, are often uneconomical, especially, when used for the reduction of heavy metal ions at low concentrations. Biosorption technology based on the ability of certain biomasses to remove metallic ions from aqueous solutions and its potential for industrial effluents treatment has received wide attention[4]. Different types of biomass, such as, algae, bacteria, fungi, yeast and plant based polysaccharides, have been successfully employed to clean-up the industrial effluents[5,6].

*Author for correspondence:
Tel/Fax: +91-40-27097044
E-mail: sashi_rao@yahoo.com

Gum kondagogu [*Cochlospermum gossypium* (L.) DC.] is an Indian tree gum derived as an exudate and belongs to the family *Bixaceae*. In recent past, gum kondagogu has been established as a biosorbent to remove toxic metals like lead, cadmium, nickel and total chromium from aqueous solutions[7,8]. The morphological, physico-chemical, structural and rheological properties of gum kondagogu have been comprehensively studied[9-11]. The primary structure of this biopolymer contains sugars, such as, arabinose, rhamnose, glucose, galactose, mannose, glucuronic acid and galacturonic acid. This gum has been grouped under substituted rhamnogalacturonans. Based on the spectroscopic categorization, the probable structural feature consigned to gum kondagogu is (1→2) β-D-Gal *p*, (1→6) β-D-Gal *p*, (1 → 4) β-D-Glc *p* A, 4-0-Me-α-D-Glc *p* A, (1→ 2) α-L-Rha and (1→ 4) α-D-Gal *p* A. Gum kondagogu is an acidic gum with high content of uronic acid and the major functional groups identified in the gum are hydroxyl, acetyl, carbonyl and carboxylic groups. The *zeta* potential of native gum was determined to be –23.4 mv, indicating that it contains negatively charged groups[9-11]. The toxicological evaluation of gum kondagogu had established that, this gum was non-toxic and has potential application as food additive[12]. With regard to their role as a biosorbent in the process of bioremediation of toxic metals, it is necessary to know the binding sites for the metals on the surface of gum kondagogu. Interestingly, gum kondagogu fulfils the requirements as a biosorbent as it contains many of the functional groups recognized earlier of having involvement in metal binding. Thus, this gum has an impending application as a matrix for toxic metal bioremediation from industrial effluents.

The aim of the present experimental study was to investigate and explore the potential application of gum kondagogu as a novel biosorbent for the removal of the industrially relevant toxic heavy metals (Cd^{2+}, $Cu^{2+,}$ Fe^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+} & total Cr) from effluents. This communication describes the competitive ability of gum kondagogu to remove mixture of toxic heavy metals from industrial effluents.

Materials and Methods

Biosorbent

Gum kondagogu samples (Grade 1, hand picked fresh, clean with no extraneous material) were procured from Girijan Co-operative Corporation, Government of Andhra Pradesh Undertaking, Hyderabad, India, and used in the experimental analysis. Moreover, M/s D K Enterprises, Hyderabad, also provided gratis samples of the gum.

Metal Solutions

All the chemicals used were of analytical grade. Experiments were performed using synthetic stock solutions. 1 g $L^{-1}$of Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+} and Cr were prepared in Milli-Q water using corresponding chlorides or nitrate salts. All the working solutions were prepared by diluting the stock solution in Milli-Q water.

Industrial Effluents Collection

The industrial effluent samples were collected from 5 different industrial locations (Nacharam, Cherlapally, Tank bund, Balanagar & Kattedan) in the city zone of Hyderabad. Three independent samples were collected (1 L) at each location and later transferred into clean polypropylene containers and transported to laboratory for analysis.

Biosorbent Preparation

Gum kondagogu was powdered in a high-speed mechanical blender, (Philips, Mumbai, India) and later sieved using a bin (mesh size, 250 μm), so as to obtain a fine and uniform sample. Gum kondagogu powder (2 g) was accurately weighed, and dispensed into a clean glass beaker containing 1 L of de-ionized water. The whole gum solution was kept on a magnetic stirrer at room temperature and gently stirred over night. Later, the gum solution was allowed to stand at room temperature (30^{o}C) for 12 h to separate any suspended matter. The gum solution was filtered through a sintered glass funnel (#G-2 followed by #G-4). The clear solution so obtained was freeze-dried and stored, until further use. Lyophilized gum kondagogu was powdered by using ceramic mortar and pestle. Later the powder was sieved to select particles in the range of 200-350 μm for to be used as a biosorbent in batch adsorption studies. The analysis was carried out using a particle size distribution analyzer (Malvern Zetasizer, Nanosyatem, Worcestershine, UK).

Biosorption Studies

In a typical experiment, 0.1 g of biosorbent was added into 100 mL of industrial effluent solution and *p*H 5 was maintained by 0.1 *M* HCl and 0.1 *M* NaOH. An optimal *p*H 5 was selected on the basis of earlier

report where maximum biosorption of metal ions cadmium, lead and nickel by gum kondagogu was achieved at this *p*H[7,8]. The samples were kept for 2 h at 25°C in an orbital shaker at 200 rpm (Innova-43, New Brunswick Scientific Co. Ltd, NJ, USA). The contents were then centrifuged for 300 sec at 10,000× *g*. The supernatants were collected and later filtered through a 0.45 µm micro-filter. Subsequently, all the adsorption experiments were corrected by blank tests, in which no adsorbent was added into the mixed metal solutions. The biosorption (%) and the amount of metals adsorbed per unit mass of the biosorbent (mg g^{-1}), i.e., adsorption capacity, were calculated by using the following equations.

$$\text{Biosorption } (\%) = \frac{C_i - C_f}{C_i} \times 100$$

Where, C_i and C_f are the initial and final metal ion concentrations, respectively.

$$q_e = \frac{[(C_i - C_e)V]}{m}$$

Where, 'q_e' is the adsorption capacity (mg g^{-1}); 'C_i' and 'C_e' are the concentration of the heavy metal in the initial, equilibrium solution (mg L^{-1}) and after biosorption, respectively; 'V' is the volume of the aqueous phase (liter); and 'm' is the amount of the biomass (g). All adsorption and desorption experiments were done thrice and all values are presented as mean ±S.D.

Determination of Heavy Metals in Industrial Effluent Samples by ICP-MS

Samples of gum kondagogu (0.1 g) were mixed with 100 mL volume of industrial effluent sample taken in 250 mL clean glass Erlenmeyer flask. The *p*H of the test samples was adjusted to value 5 by adding 0.1 *M* NaOH or 0.1 *M* HCl, using a digital *p*H meter. The samples were kept for 2 h at 25°C in an orbital shaker at 200 rpm (Innova-43, New Brunswick scientific Co. LTD, NJ, USA). The contents were later centrifuged for 5 min at 10,000× g and supernatants were collected and subsequently filtered through a 0.45 µm micro-filter. The metal ions, namely Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+} and total Cr were analyzed by using ICP-MS. The concentrations of the above metals in original effluent (before treatment with gum) were also analyzed by ICP-MS. A control assay was also run under similar experimental conditions with the effluent samples to determine the metal ion profile before biosorption. Supernatants were acidified with nitric acid before the samples were introduced into ICP-MS.

Langmuir Isotherm Experiments

The isotherms were derived at the optimum *p*H 5 and kept in an orbital shaker at 200 rpm for 2 h at 25°C. The gum kondagogu (1 g) was mixed with varying concentrations of individual metal ion (between 25 to 300 mg L^{-1}), in a volume of 1 L.

Desorption and Regeneration Experiments

For desorption studies, 0.1 g of gum kondagogu was loaded into 100 mL volume of industrial effluent sample taken in 250 mL clean glass Erlenmeyer flask. The *p*H of the test samples was adjusted to value 5 by adding 0.1 *M* NaOH or 0.1 *M* HCl, using a digital *p*H meter. The agitation rate was fixed at 200 rpm. Toxic metals loaded gum kondagogu biopolymer matrix was collected gently washed with Milli-Q water so as to remove any un-adsorbed metal ions. Later, the biopolymer was agitated with 100 mL of various leaching agents, such as, EDTA, HCl and HNO_3 (0.1 *M* each). The final concentrations of metal ions in the aqueous phase were determined by ICP-MS. The desorption (%) of metal ions from the gum kondagogu polymer was calculated. The regeneration of the biopolymer was tested by its adsorption-desorption in 3 cycles, each time using the same biopolymer.

ICP-MS Instrumentation and Calibration

ICP-MS (ELAN DRC 11, Perkin-Elmer SCIEX, Toronto, Canada) was used to carry out the elemental analysis. The sample introduction system consisted of a standard Meinhard nebulizer with a cyclonic spray chamber. All measurements were performed using instrumental software. In order to check the instrumental errors, high purity multi-element standards of 1 and 200 ng mL^{-1}, obtained from Perkin-Elmer (SCIEX, Toronto, Canada), were used respectively for mass calibration and for external calibration during semi-quantitative analysis.

Statistical Analysis

All experiments were carried out in triplicates and results are reported as mean±SD. The significance of differences among the values was determined at $p < 0.05$ using analysis of variance (ANOVA).

SEM-EDX Analysis

The surface structure of biosorbent was analyzed by scanning electron microscope coupled with energy dispersive X-ray analysis (SEM-EDXA) [SEM-LEO S1430 VP from M/S LEO Electron Microscopy Ltd, Cambridge, England (UK) with Resolution of 3.5 nm for Tungsten filament & 2.5 nm for LaB6 filament and EDX detector resolution is 133 eV; EDXA (INCA, Oxford, UK)]. The gum kondagogu samples were mounted on a stainless steel stab with double stick tape with a thin layer of gold in high vacuum conditions.

FT-IR Analysis

FT-IR spectra were obtained using a spectrophotometer (420, Jasco, Tokyo, Japan). In order to collect the spectra, small amounts of freeze-dried metal-gum kondagogu complex were mixed with KBr and compressed to form pellets. IR spectra of gum kondagogu and gum kondagogu-metal complexes were obtained in the spectral region of 4000-400 cm^{-1} using resolutions of 4 cm^{-1} and 64 co-added scans.

Results and Discussion

Biosorption Studies

The industrial effluents collected from 5 different industrial locations (Hyderabad, India) were used for the determination of metal biosorption capacity of gum kondagogu at *p*H 5. The biosorption (%) and adsorption capacity (mg g^{-1}) of metals by gum kondagogu are presented in Table 1. Biosorption studies confirmed that the optimum conditions for metal ions biosorption were *p*H 5, minimum contact time 2 h and temperature 25°C. The per cent biosorption of metals ions (Pb, Cd, Ni, Zn, Cu, Fe, Hg and total Cr) by gum kondagogu from the mixed metal solutions occurred at *p*H 5. The biosorption (%) and adsorption capacity (mg g^{-1}) of the metals in the test samples as determined by ICP-MS indicated the following pattern in decreasing order: $Cd^{2+} > Cu^{2+} > Fe^{2+} > Pb^{2+} > Hg^{2+} >$ total Cr > $Ni^{2+} > Zn^{2+}$, and $Fe^{2+} > Cu^{2+} > Cd^{2+} > Pb^{2+} > Zn^{2+} > Ni^{2+} >$ total Cr > Hg^{2+}, respectively. Among the metals, maximum % biosorption was observed for Cd^{2+} (97%) and the least for Zn^{2+} (34%) in the samples tested. The maximum adsorption capacity of metals by gum kondagogu varied in the range of 31-37 mg g^{-1} for Fe^{2+} and minimum of 5.5-9.3 mg g^{-1} for Hg^{2+} (Table 1).

Previous, studies on heavy metal biosorption has shown that *p*H is an important factor affecting the biosorption process. The interactions of metal ions with the electron-rich functional groups located on the biopolymer are strongly influenced by the *p*H of the surrounding environment. At very low *p*H values (*p*H 1-2), metal uptake has been found negligible. In the present investigation, the optimum values for bioremediation of industrial effluents were determined at initial *p*H 5. At higher (*p*H >5) the metal ions might be undergoing hydrolysis and form metal hydroxides, which promote a reduction in the adsorption capacity of the gum. At *p*H (4.5-5), phosphate, carboxyl and sulphate groups were active. Further, the *p*H value of solution strongly influences not only the site dissociation of the biomass surface but also the solution chemistry of the heavy metals such as, hydrolysis, complexation by organic or inorganic ligands, redox reactions, precipitation, the speciation and the biosorption availability of the heavy metals[13].

Table 1—Heavy metal biosorption (%) and adsorption capacity (mg g^{-1}) by gum kondagogu as determined by ICP-MS from industrial effluent samples (Conditions: Metal ions concentration, 5-35 mg L^{-1}; biosorbent dosage, 0.1 g/100 mL; *p*H 5.0; agitation speed, 200 rpm; temperature, 25°C)

Metal ions	Sample 1[a]		Sample 2[b]		Sample 3[c]		Sample 4[d]		Sample 5[e]	
	% B	q_e	%B	q_e	% B	q_e	% B	q_e	% B	q_e
Cd^{2+}	97.4±0.34[f]	17.7±0.02	97.9±0.12	15.4±0.02	97.0±0.09	17.7±0.02	97.2±0.00	19.9±0.05	97.1±0.08	23.6±0.04
Cu^{2+}	93.7±0.08	19.3±0.05	94.8±0.09	21.1±0.02	94.0±0.08	25.8±0.06	94.4±0.08	24.1±0.08	94.8±0.05	27.5±0.04
Fe^{2+}	87.1± 0.09	35.4±0.10	87.9±0.08	37.3±0.08	87.8±0.02	31.2±0.06	87.6±0.05	33.7±0.08	87.9±0.02	35.9±0.09
Pb^{2+}	75.1±0.22	15.4±0.02	74.8±0.08	16.9±0.04	75.5±0.04	18.6±0.04	75.4±0.04	19.6±0.04	75.6±0.04	25.1±0.05
Hg^{2+}	71.7±0.08	6.1±0.02	70.8±0.06	6.3±0.02	70.6±0.04	5.5±0.02	71.2±0.08	7.7±0.02	70.4±0.05	8.1±0.02
Cr (Total)	52.0±0.08	6.5±0.06	51.9±0.04	6.8±0.02	51.3±0.04	7.6±0.03	51.6±0.08	9.3±0.04	51.9±0.05	10.5±0.03
Ni^{2+}	39.1± 0.08	6.6±0.02	40.0±0.05	7.5±0.03	40.2±0.03	8.2±0.03	39.4±0.09	8.5±0.02	39.8±0.05	10.2±0.06
Zn^{2+}	34.1±0.08	11.0±0.09	34.2±0.08	8.8±0.05	34.8±0.05	7.7±0.04	34.8±0.04	8.1±0.04	34.9±0.03	9.3±0.03

Samples collected from Industrial area of [a]Nacharam ; [b]Cherlapally ; [c]Tank bund; [d]Balanagar ; [e]Kattedan

[f] = All values are mean±S.D, n = 3; % B = Biosorption (%); q_e = Adsorption capacity (mg metal ion g^{-1} dry biosorbent)

Equilibrium Sorption Isotherms

The isotherms of Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+} and total Cr ions biosorbed by the gum kondagogu are comparatively illustrated in Fig. 1. The amount of metal ions biosorbed per g of gum kondagogu at equilibrium is represented as a function of the equilibrium metal ion concentration (Fig. 1). The biosorption of metal ions by gum kondagogu varied in the order of $Cd^{2+} > Cu^{2+} > Fe^{2+} > Pb^{2+} > Hg^{2+}$ > total Cr > $Ni^{2+} > Zn^{2+}$ over the whole range of metal initial.

The Langmuir model for adsorption equilibrium was applied to the experimental data obtained for the biosorption of metal ions (Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+} and total Cr) by the gum kondagogu. Fig. 2

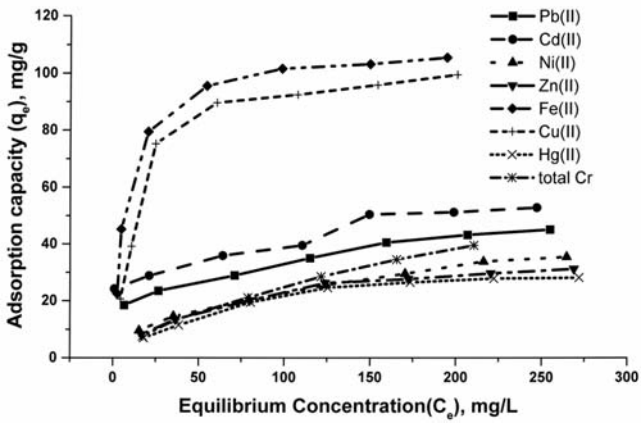

Fig. 1—Equilibrium isotherms of metal ions (Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+} and total Cr) and gum kondagogu interaction. Conditions: Initial metal ions concentrations, 25-300 mg L^{-1}; gum kondagogu dose, 1 mg mL^{-1}; *p*H 5; temperature, 25°C; time of contact, 2 h.

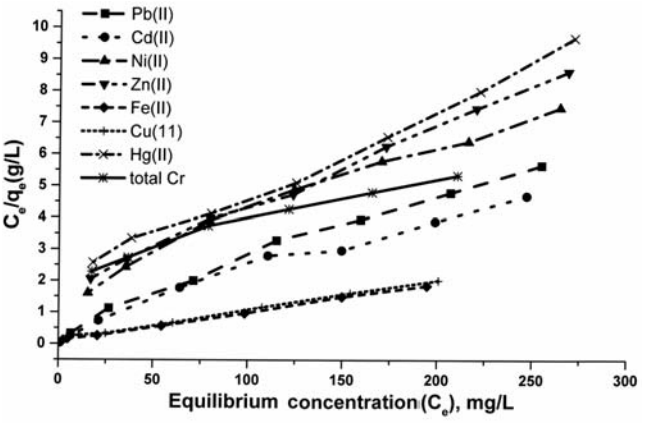

Fig. 2—Langmuir plots for metal ions (Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, $Hg^{2+}$and total Cr) biosorption by gum kondagogu. Conditions: Initial metal ions concentrations, 25-300 mg L^{-1}; gum kondagogu dose, 1 mg mL^{-1}; *p*H 5; temperature, 25°C; time of contact, 2 h.

shows the ability of the Langmuir model to describe the experimental data represented for all of the investigated systems. Good agreements between the predicted and experimental values were found over the range of initial concentrations (25-300 mg L^{-1}) used, as substantiated by high correlation coefficients ($R^2 > 0.99$). The maximum adsorption capacity was obtained for Fe^{2+} ions and least for Hg^{2+} ions. Based on the Langmuir adsorption model, the following maximum biosorption capacity of metals was observed in decreasing order $Fe^{2+} > Cu^{2+}$ > total Cr > $Cd^{2+} > Pb^{2+} > Zn^{2+} > Ni^{2+} > Hg^{2+}$. A high value of *K* is indicative of a high affinity between active sites of the biomass and metals. The present investigation reflects on the high value of *K* for Fe^{2+}(0.103) and least for total Cr (0.006). The comparative *p*H for maximum adsorption capacities (q_{max}) of metal ions by gum kondagogu and other adsorbents reported in literature[14-18] are given in Table 2. The multi-metal ion removal capacity of gum kondagogu was found closely resembling to that of chitosan at *p*H 5-6. The added advantage of gum kondagogu is that the biopolymer has a native *p*H value of 5 due to its acidic nature.

Desorption and Regeneration Characteristics

Biosortpion studies should be complemented with desorption studies as it is important to recover the metal and then retain and reuse the biomass in subsequent loading and unloading cycles. In order to apply biosorbent to real industrial situations, desorption process of toxic metal ions is essential. Various factors are involved in determining the rate of metal ion interaction with polymer microstructure. One of the important factors that probably play a major role is the binding strength of metal ion[19]. The mineral acids, such as, HCl and HNO_3, and EDTA (0.1 *M* each) were evaluated as potential eluants for the recovery of metal ions biosorbed by the

Table 2—Comparison of various adsorbents used in biosorption of toxic metals from industrial effluents

Biosorbent	Toxic metals removed	*p*H	Reference
Chitosan	Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2} Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} Pb^{2+}	5-6	14
Rice straw	Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}	5.0	15
Activated sludge	Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+} Pb^{2+}	4-5	16
Filamentous fungus (*Phanerochete chrysosporium*)	Cd^{2+}, Pb^{2+}, Cu^{2+}	6.0	17
Saw dust	Zn^{2+}, Cd^{2+}	5.0	18
Neem bark	Zn^{2+}, Cd^{2+}	5.0	18
Gum kondagogu	Fe^{2+}, Ni^{2}, Cu^{2+}, Zn^{2+} Cd^{2+}, Hg^{2+}, Pb^{2+}, total Cr	5.0	Present Study

biopolymer. Among the mineral acids used, 0.1 *M* HCl was observed to be very effective eluant as compared to HNO_3 and EDTA. The desorptions of metal ions by using 0.1 *M* HCl is presented in Table 3. The desorption of metal ions was maximum for Cd^{2+} ions and least for total Cr. The overall desorption of metal ions (Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+} and total Cr) was in the range of 34 to 97.9% with a contact time of 2 h. The release of metal ions from the biopolymer active sites by acid suggests an ion-exchange mechanism. In order to establish the reusability of gum kondagogu biopolymer, sequential adsorption-desorption cycles were repeated thrice on the same matrix. The recycled biopolymer shows a re-adsorption capacity of 90% at the end of 3rd adsorption-desorption cycle. Regeneration aspect of gum kondagogu affirms its cost effectiveness, as the biopolymer can be recycled for multiple reuses.

Scanning Electron Microscopy/Energy Dispersive X-ray Analysis (SEM-EDXA)

SEM micrographs of the gum kondagogu biopolymer used for adsorption studies are shown in Fig. 3(a). It shows that the adsorbents had an irregular and porous surface. The corresponding EDXA spectrum of gum kondagogu is depicted in Fig. 3(b). The EDX spectrum showed the presence of alkali (Na^+, K^+) and alkaline earth metals (Ca^{2+}, Mg^{2+}), indicating that biosorption process by gum kondagogu also included ion-exchange mechanism for the removal of metal ions.

FT-IR Characterization

The FT-IR spectra of native gum kondagogu and its metal complexes are presented in Fig. 4. The gum kondagogu biopolymer possesses functional groups, which can adsorb heavy metals. The major functional groups include carboxylate anion (-COO), hydroxyl cation (-OH) and others (-C-N, -C-O, -C-H, -C=O, -NH; Fig. 4a). The FTIR spectra (Fig. 4b) of metals loaded gum kondagogu was scanned in region of 400-4000 cm^{-1} to specifically identify the functional groups that are responsible for the metal biosorption. The functional groups involved in bivalent metal biosorption included hydroxyl, carboxyl, ether

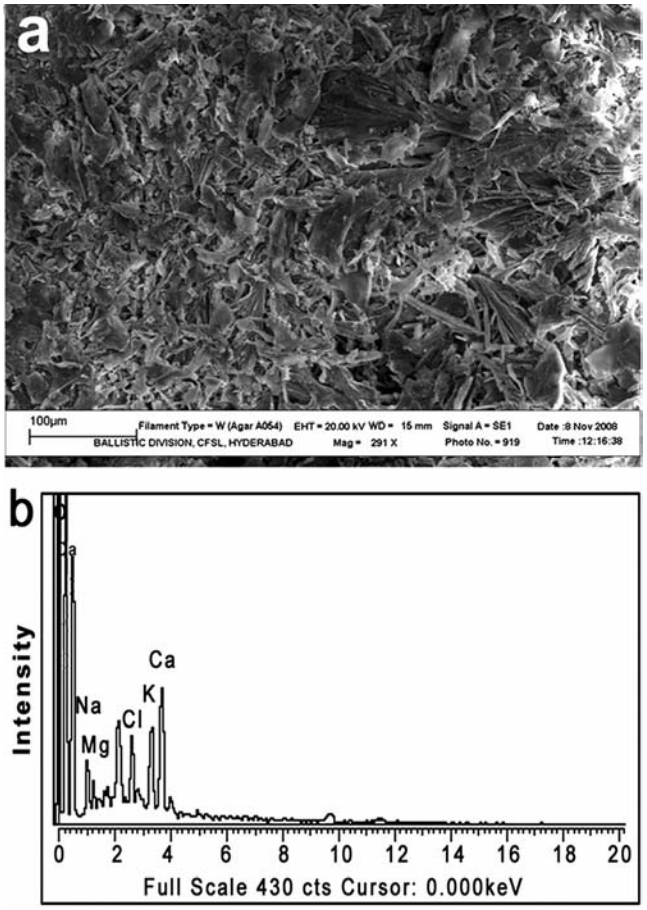

Fig. 3(a & b)—SEM micrograph of gum kondagogu before metal biosorption (a); EDXA spectrum of gum kondagogu before biosorption indicating various alkali and alkaline earth metals present (b).

Table 3—Desorption (%) of toxic metals from gum kondagogu by using 0.1 *M* HCl
(Conditions: Metal ion concentration, 5-35 mg L^{-1}; biosorbent dosage, 0.1 g/100 mL; agitation speed, 200 rpm; temperature, 25°C)

Metal ions	Sample 1[a] %D	Sample 2[b] %D	Sample 3[c] %D	Sample 4[d] %D	Sample 5[e] %D
Cd^{2+}	97.1±0.28[f]	97.0±0.21	96.1±0.15	96.1±0.18	95.8±0.15
Cu^{2+}	65.4±0.51	65.2±0.45	64.2±0.20	62.8±0.14	61.8±0.24
Fe^{2+}	82.4± 0.15	81.9±0.14	81.2±0.04	80.8±0.24	79.4±0.15
Pb^{2+}	65.4±0.18	63.8±0.15	62.8±0.25	61.2±0.14	60.8±0.12
Hg^{2+}	68.2±0.12	67.2±0.45	67.1±0.15	68.9±0.18	67.1±0.14
Cr (Total)	28.5±0.10	27.2±0.15	25.2±0.14	24.2±0.19	23.8±0.16
Ni^{2+}	38.2± 0.05	39.1±0.02	38.9±0.25	37.8±0.21	37.1±0.14
Zn^{2+}	32.5±0.05	32.9±0.08	32.1±0.15	31.9±0.12	30.8±0.14

Samples collected from Industrial area of, [a]Nacharam ; [b]Cherlapally ; [c]Tank bund; [d]Balanagar ; [e]Kattedan
% D = Desorption (%); [g] = All values are mean±S.D, n = 3

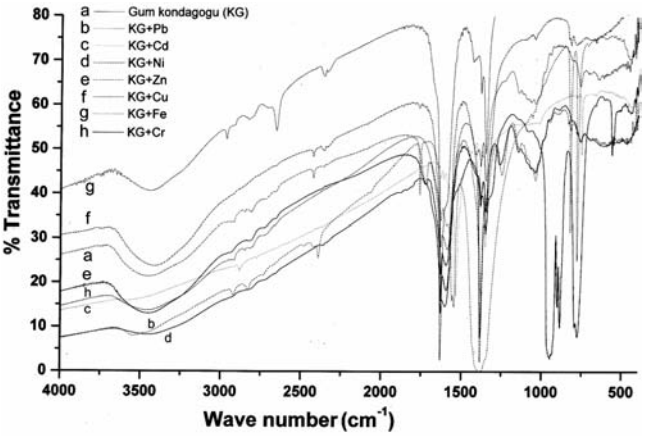

Fig. 4—FT-IR spectra of gum kondagogu before metal biosorption (a), Pb^{2+} loaded (b), Cd^{2+} loaded (c), Ni^{2+} loaded (d), Zn^{2+} loaded (e), Cu^{2+} loaded (f), Fe^{2+} loaded (g) and Cr loaded (h).

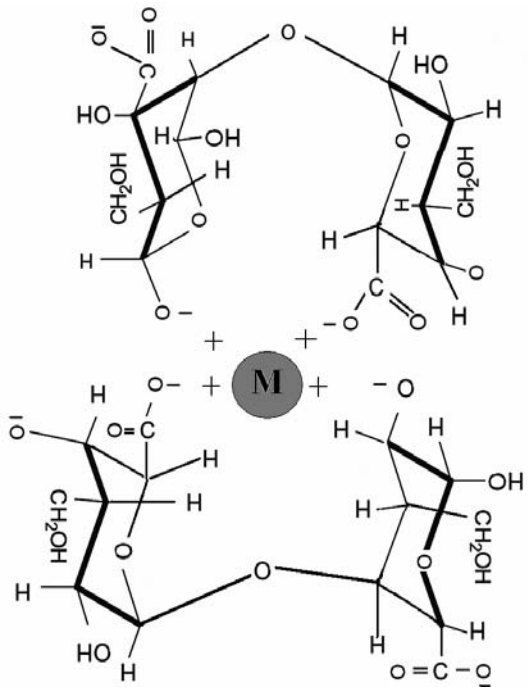

Fig. 5—Schematic diagram showing the cross-linking of a metal cation within gum kondagogu matrix (M^+ = Cd^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, $Hg^{2+}$and total Cr).

and alcoholic groups. The experimental result of the present study indicated that biosorption of metals ions (Cd^{2+}, $Cu^{2+,}$ Fe^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+} and total Cr) by gum kondagogu occurs as a result of electrostatic interaction and complexation with hydroxyl, carboxylic, carbonyl, alcoholic, ester, amino, uronic acid and acetyl groups present in the biopolymer that are amenable for the interaction with metal ions at *p*H 5[20]. Fig. 5 depicts the nature of interaction of metal ion (M^+) with the biopolymer.

Conclusion

Present experimental evidence suggests that gum kondagogu, a carbohydrate biopolymer, was capable of biosorbing 8 metal ions competitively from the samples of industrial effluents tested. The efficiency observed was in the following order, $Cd^{2+} > Cu^{2+} > Fe^{2+} > Pb^{2+} > Hg^{2+} >$ total Cr $> Ni^{2+} > Zn^{2+}$. A similar trend was observed earlier wherein gum kondagogu biosorbed 10 metal ions ($Cd2^+ > Cu^{2+} > Fe^{2+} > Se^{+2} > Pb^{2+} >$ total Cr $> Ni^{2+} > Zn^{2+} > Co^{2+} > As^{2+}$) present in the synthetically prepared metal ion mixture dissolved in deionized water[36]. Further, the adsorption capacity (mg g^{-1}) of the metals by gum kondagogu determined by ICP-MS indicated the following trend in decreasing order: $Fe^{2+} > Cu^{2+} > Cd^{2+} > Pb^{2+} > Zn^{2+} > Ni^{2+} >$ total Cr $> Hg^2$. The competitive biosorption capacity of gum kondagogu for removal of metal ions was best effective at *p*H 5. Among the metals, maximum % biosorption by gum kondagogu was observed for Cd^{2+} (97%) and the least for Zn^{2+} (34%) in the samples tested. The maximum adsorption capacity of metals by gum kondagogu varied in the range of 31-37 mg g^{-1} for Fe^{2+} and the minimum of 5.5-9.3 mg g^{-1} for Hg^{2+}. The interactions between metal ions (Cd^{2+}, $Cu^{2+,}$ Fe^{2+}, Pb^{2+}, Ni^{2+}, $Zn^{2+,}$ Hg^{2+} & total Cr) and functional groups on the gum kondagogu were confirmed by FTIR analysis. The FT-IR results indicate that the bioremediation of metal ions by gum kondagogu occurred as a result of electrostatic interaction as well as complexation with hydroxyl, carboxylic, carbonyl, alcoholic, ester, amino, acetyl groups, and the high amount of uronic acid of the biopolymer. Based on the desorption studies, it is inferred that the overall desorption (%) of metal ions (Cd^{2+}, $Cu^{2+,}$ Fe^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+} and total Cr) was in the range of 34 to 97.9%. Further, the reusability of gum kondagogu biopolymer was established by sequential adsorption-desorption cycles, wherein a re-adsorption capacity of 90% was observed at the end of 3rd adsorption-desorption cycle.

It is demonstrated in the present study that bioremediation of metals from industrial effluent using gum kondagogu biopolymer is a viable and cost-effective technology that could be included in the process of commercial evaluations. The combination of biodegradability, high biosorption capacity, various functional groups and high uronic acid content contributes to make this biopolymer a suitable matrix for toxic heavy metal bioremediation.

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