



Interaction of Pb^{2+} and Cd^{2+} with gum kondagogu (*Cochlospermum gossypium*): A natural carbohydrate polymer with biosorbent properties

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ABSTRACT

Gum kondagogu (*Cochlospermum gossypium*), an exudates tree gum from India was explored for its potential to decontaminate toxic metals (Pb^{2+} and Cd^{2+}). Optimum biosorption of metals were determined by investigating the contact time, pH, initial concentration of metal ions and biosorbent dose at $25 \pm 2^\circ\text{C}$. The maximum metal biosorption capacity for gum kondagogu was observed for Pb^{2+} (48.52 mg g^{-1}) and Cd^{2+} (47.48 mg g^{-1}) as calculated by Langmuir isotherm model. Kinetic studies showed that the biosorption rates could be described by pseudo-second-order expression. The metal interactions with biopolymer were assessed by FT-IR, SEM-EDXA and XPS analysis. Results based on these techniques suggest that mechanism of metal binding by the biopolymer involves micro-precipitation, ion-exchange and metal complexation.

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1. Introduction

Heavy metals are discharged from various industries as effluents and these have deleterious effects on human, animal and plant health and cause distress to the environmental balance. Lead and cadmium are used as industrial raw materials in the manufacture of storage batteries, pigments, leaded glass, fuels, photographic materials, matches, explosives, painting and in ceramic industries. Lead and cadmium are extremely toxic metals and their accumulation in the living organisms cause severe damage to nerves system, liver, kidneys, bones and at metabolic level blocks the functional group of vital enzymes (Carson, Ellis, & McCann, 1986). The US Environmental Protection Agency (EPA) strictly suggested that lead and cadmium in drinking water should not exceed 0.015 ppm and 0.005 ppm, respectively.

Biosorption is a process that utilizes inexpensive dead biomass to sequester toxic heavy metals and is particularly useful for the removal of contaminants from industrial effluents. Compared with conventional methods of removing toxic metals from industrial effluents such as precipitation, ion-exchange and electrochemical process, the biosorption process offers the advantages of low operating cost, minimization of the volume of chemical and/or biolog-

ical sludge to be disposed. Different types of biomass have been used for the clean up of industrial wastes such as Fly ash, silica gel, zeolites, lignin, wool wastes, agricultural wastes, algae, bacteria, fungi, yeasts, crosslinked chitin, chitosan and plant polysaccharides (Trimukhe & Varma, 2008; Varma, Deshpande, & Kennedy, 2004; Volesky, 2007). This process is highly effective in detoxifying very dilute effluents, eliminates the problem of toxicity and the economics of nutrient supply and culture maintenance required for live microbial-based methods (Davis, Volesky, & Mucci, 2003; Kratochvil & Volesky, 1998). The use of dead biomass is of particular economic interest, because the biomaterials are used in the same way as synthetic adsorbents or ion exchangers (Klimmek, Stan, Wilke, Bunke, & Buchholz, 2001). Various metal binding mechanisms are thought to be involved in the biosorption process including ion-exchange, surface adsorption, chemisorptions, complexation and adsorption-complexation (Matheickal, Yu, & Woodburn, 1999). There is a continued interest in identifying newer biosorbents that are capable of reducing toxic metal concentrations to environmentally acceptable levels at affordable cost.

Gum kondagogu (*Cochlospermum gossypium*) tree is a plant naturally growing in the forests of India. The exudate gum of this tree has the potential application as a cheap source of biosorbent. In the recent past, the morphological, physicochemical, structural and rheological properties of gum kondagogu has been extensively studied by us and the primary structure of this biopolymer was

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established to contain 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 characterization, the probable structural feature assigned to gum kondagogu was (1 → 2) β-D-Gal p, (1 → 6)-β-D-Gal p, (1 → 4) β-D-Glc p A, 4-O-Me-α-D-Glc p A, (1 → 2) α-L-Rha and (1 → 4) α-D-Gal p A (Janaki & Sashidhar, 1998; Vinod, Sashidhar, Sarma et al., 2008; Vinod et al., 2008). The toxicological evaluation of gum kondagogu had established that, this gum was non-toxic and has potential application food additive (Janaki & Sashidhar, 2000). The novel polyelectrolyte complex of gum kondagogu–chitosan was prepared and its application as drug carrier in pharmaceutical was evaluated recently (Naidu et al., 2009). Non-food applications of gum kondagogu are yet to be explored as a natural biosorbents. Even though, many plant-derived materials have earlier been explored as biosorbents, while the natural exudate gums are yet to be evaluated for their potential application in the biosorption of toxic heavy metals. Gum kondagogu is an acidic gum with high content 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 (Janaki & Sashidhar, 1998; Vinod, Sashidhar, Sarma et al., 2008; Vinod et al., 2008). Previously, it was reported that the major binding groups responsible for metal biosorption are hydroxyl, carboxyl, carbonyl, thiol, amine, phosphonate and phosphodiester (Volesky, 2007). Interestingly, gum kondagogu fulfils the requirements as a biosorbents as it contains many of the functional groups identified earlier that are involved in metal binding. Thus, this gum has a potential application as a matrix for toxic metal biosorption from aqueous media.

The aim of the present experimental study was to investigate and explore the potential application of gum kondagogu as a novel biosorbent for removal of the industrially relevant toxic heavy metals such as lead and cadmium. This communication describes the ability of gum kondagogu to bind toxic heavy metals and its quantitative evaluation and kinetic study. The metal adsorption was assessed based on Langmuir and Freundlich adsorption isotherm model. The interaction of gum with toxic metal was established by Fourier transform infrared spectroscopy (FT-IR), scanning electron micrographs-energy dispersive X-ray analysis (SEM-EDXA), and X-ray photoelectron spectroscopy (XPS) analysis.

2. Experimental

2.1. Materials

Gum kondagogu samples were collected from Girijan Co-operative Corporation, Hyderabad, Government of Andhra Pradesh Undertaking, Hyderabad, India, and *gratis* samples were provided by M/s D.K. Enterprises, Hyderabad, India. Gum kondagogu (Grade-1, hand picked, fresh, clean with no extraneous material), was used in the experimental analysis. Gum samples collected were stored in airtight polypropylene jars in desiccated condition.

2.2. Processing of gum specimen

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 tem-

perature and gently stirred over night. Later, the gum solution was allowed to stand at room temperature (30 °C) for 12 h, so as to separate any undissolved 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.

2.3. Metal solutions

The standard stock solutions of lead and cadmium (1.0 g/L) were prepared by dissolving appropriate amounts of Pb(NO₃)₂ and Cd(NO₃)₂·4H₂O in de-ionized (Milli Q) water. The pH of the metal solution was adjusted to a desired value with 0.1 M sodium hydroxide and 0.1 M hydrochloric acid. All the metal reagents were purchased from Merck (Mumbai, India). The concentration of each metal ion before and after biosorption was determined by using an atomic absorption spectrophotometer (AAnalyst 300, Perkin Elmer, FL, USA). The data given are the mean ± SD value of three separate experiments. Any metal ion bound to the glass surface was also evaluated, while calculating the residual metal ions present in the supernatant, so as to nullify any losses due to the metal ion interaction with the glass surface.

2.4. Biosorption experiments

Contact time, optimum pH, initial metal ion concentration, sorbent dose and batch sorption experiments were performed at room temperature (25 ± 2 °C). Batch sorption experiments were performed in 250 mL Erlenmeyer flasks. Hundred milliliters each of Pb²⁺ and Cd²⁺ (100 mg/L) individual solutions were transferred into a 250 mL stoppered Erlenmeyer flask, respectively. The mixtures were shaken on an orbital shaker (Innova-43, New Brunswick Scientific Co. Ltd., NJ, USA) at 200 rpm, 25 ± 2 °C for 2 h. The residual concentrations of metal ions in the supernatant was analyzed after the separation of metal bound biosorbent by centrifugation at 10,242g for 15 min, by atomic absorption spectrophotometer (AAS). Based on the AAS data, the amount of metal ion biosorbed per unit mass of biosorbent (mg metal/g dry biosorbent) was determined. The effect of biosorbent–biosorbate contact time was varied from 30 min to 180 min. The influence of pH on metal ion biosorption was also determined in the pH range of 2–6. Adsorption isotherm studies were conducted at a metal ion concentration in the range of 10–300 mg/L. The gum was added in concentration 1.0–5 g/L to determine the optimum biosorption ratio.

2.5. Adsorption isotherm model

In order to optimize the biosorption process parameter, both Langmuir and Freundlich isotherm models were tested on experimental results. Langmuir adsorption isotherm model was used to characterize the interactions of metal ions with the biopolymer. The Langmuir model is based on the assumption that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption being a constant and there is no migration of adsorbate molecules in the surface plane. This is indicated by the following equation.

$$q_e = q_{\max} b C_e / (1 + b C_e) \quad (1)$$

where q_e and q_{\max} are the equilibrium and maximum uptake capacities (mg g⁻¹ biosorbent), C_e the equilibrium concentration (mg/L), b is the Langmuir constant.

Freundlich model is given by the equation:

$$q_e = k_f C_e^{1/n} \quad (2)$$

where k_F and n are Freundlich's constants relating to the adsorption capacity and adsorption intensity of the adsorbent characteristics of the system and k and n can be determined from the linear plot of $\log q_e$ vs $\log C_e$.

2.6. Metal biosorption kinetics

Kinetics of biosorption is one of the most important characteristics to describe the solute sorption rate that in turn controls the residence time of biomass sorption at the solid–solution interface. In order to investigate the mechanism of adsorption at different initial concentrations, characteristic adsorption rate constants were determined by using a pseudo-first-order equation of Lagergren based on solid capacity, and pseudo-second-order equation based on solid phase adsorption (Baysal, Cinar, Bulut, Alkan, & Dogru, 2009).

2.7. Characterization metal binding to biopolymer

A qualitative and preliminary analysis of the main functional groups that might be involved in metal binding was assessed by FT-IR. The native gum kondagogu before and after adsorption of heavy metal ions (Pb^{2+} and Cd^{2+}) were recorded with a FT-IR spectrometer (Model-420, Jasco, Tokyo, Japan).

The surface structure of biopolymer before and after biosorption 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 a resolution of 3.5 nm for tungsten filament and 2.5 nm for LaB6 filament and EDX detector resolution is 133 eV EDXA (INCA, Oxford, UK). The native and metal-loaded gum kondagogu samples were mounted on a stainless steel stub with double stick tape with a thin layer of gold in a high vacuum condition.

X-ray photoelectron spectroscopy (XPS) analysis of powder samples of gum kondagogu before and after heavy metal (Pb and Cd) adsorption were performed on Kratos AXIS 165 instrument (Kratos XPS system, AXIS HIS-165 Ultra, Shimadzu, Kyoto, Japan) to determine the interactions between the organic functional groups in the biomass and the adsorbed metals. The functional groups were characterized by the binding energy peaks obtained from C 1s. In addition, the metal ions adsorbed on these functional groups were analyzed through XPS spectra acquired by applying Mg K α (1253.6 eV) energy source of monochromatic radiation operating at 15 kV and 10 mA. The residual pressure in the analysis chamber was 5×10^{-10} Torr. Survey scans were recorded in the binding energy range 0–1100 eV with pass energy of 80 eV. High-resolution narrow scans were scanned for the elements Pb and Cd in the corresponding energy ranges with pass energy of 40 eV. The spectra were decoded using the curve-fitting program, after subtracting the Shirley background and the ratio of Gaussian (0%) to Lorentzian (100%). For calibration purposes, the binding energy of the spectra was standardized with the C 1s peak at 284.6 eV. When comparing the results with the reference, peaks were identified as the same if the difference of the peak position was within 0.5 eV.

3. Results and discussion

3.1. Effect of contact time on metal biosorption

The effect of contact time of the biopolymer, which was varied from 30 min to 180 min on metal sorption [Pb^{2+} and Cd^{2+} ions]. In this study the parameters such as metal ion concentrations [100 (mg/L) each for Pb^{2+} and Cd^{2+}], volume of the metal ion solution (100 mL), gum kondagogu quantity (1.0 g/L), and pH (5.0 ± 0.1)

were kept constant. It was observed that uptake of metal sorption equilibrium was attained after 2 h. The amount of metal ions adsorbed ($mg\ g^{-1}$) increased with increase in contact time and initial concentration. After this equilibrium period the amount of adsorbed metal ions did not change significantly with contact time ($p > 0.05$). Similar types of results were observed in the case of other biosorbents attaining equilibrium while interacting with metals (Saeed, Iqbal, & Akhtar, 2005). The fast adsorption of metals [Pb^{2+} and Cd^{2+}] may be attributed to its highly porous and amorphous structures of gum kondagogu.

3.2. Effect of pH on metal biosorption

The influence of pH on the biosorption capacity for the Pb^{2+} and Cd^{2+} on heavy metal biosorption showed that pH was an important factor affecting the biosorption process. The interaction of metal ions with the electron-rich functional groups located on the biopolymer may be strongly sensitive to the pH values of the environment. At very low pH values (pH 1–2) metal biosorption was found to be negligible (Saeed et al., 2005). In the present investigation, the optimum initial pH values for biosorption of Pb^{2+} and Cd^{2+} ions were determined as 5.0 ± 0.1 . Further, the pH of the adsorption matrix also affects the solubility of metal ions and the ionization state of the functional groups on the surface of biosorbent. The biosorption capacity of metal cations strongly depends on pH value and electrostatic attraction to negatively charged functional groups might be one of the specific biosorption mechanisms and at pH 4.5–5.0, phosphate, carboxyl and sulphate groups are active (Yin, Yu, Jin, & Ling, 1999). The pH value of solution strongly influences not only the site dissociation of the biomass surface, but also the solution chemistry of the heavy metals. Biosorption of the heavy metals involve hydrolysis, complexation by organic or inorganic ligands, redox reactions, precipitation and the speciation (Zhou, Zhang, Zhou, & Guo, 2004). The biosorption capacity of metal cations increases with increasing pH of the sorption system, but not in a linear relationship. At lower pH values, biomass functional groups (sites of interaction) would be closely associated with the hydronium ions (H_3O^+) and restrict access to binding sites by metal cations as a result of repulsive forces (Akar, Tunali, & Kiran, 2005). On the other hand, too high pH value can cause precipitation of metal as metal complexes. In the present study, the carboxyl and hydroxyl groups present in gum kondagogu are responsible for metal biosorption. Gum kondagogu is an acidic gum that consists of high uronic acid content and the major functional groups identified in the gum are hydroxyl, acetyl, carbonyl and carboxylic groups and contains tannin, fibers, amino acids and fatty acids. The Zeta potential of the native gum was determined as -23.4 mV, which indicates the presence of negatively charged groups. Earlier, it has been reported that high uronic acid content is correlated to the bioremediation of toxic heavy metals in *Sargassum* algal tissue (Volesky, 2007). Additionally, the pH of gum kondagogu in aqueous solution was determined to be 4.9–5.0 (Janaki & Sashidhar, 1998; Vinod, Sashidhar, Sarma et al., 2008; Vinod et al., 2008). At low pH value most of the carboxylic groups present in gum kondagogu are less protonated to give negatively charged species to interact with divalent cations. With increasing pH ($pH\ 5.0 \pm 0.1$), these groups get deprotonated and thus result in negatively charged sites that enhance the metal biosorption. Similar pH value ($pH\ 5.0 \pm 0.1$) was observed for maximum biosorption of lead and cadmium by cellulose/chitin and black gram husk (Saeed et al., 2005; Zhou, Zhang, & Guo, 2005).

3.3. Effect of initial metal ion concentration

The initial metal ion concentrations provide an important driving force to overcome all mass transfer resistance of metal ion

between the aqueous and solid phases. The relation between the equilibrium adsorption of metal ions (q_e) and its initial concentration using different concentrations of gum kondagogu biopolymer in the range of 1–5 g/L are depicted in Fig. 1. The parameters such as contact time (120 min), volume of solution (100 mL), and pH (5.0 ± 0.1) of the metal solution were kept constant. Earlier, it has been suggested that, the metal uptake mechanism is particularly dependent on the initial metal ion concentration at low concentration of metals; they are adsorbed by specific sites. However, by increasing the metal concentration, the specific sites are saturated and later the exchange sites are occupied (Saeed et al., 2005). Bio-sorption capacity of gum kondagogu was found to increase with increasing metal ion concentration in the medium. The observed enhancement of metal biosorption could be due to an increase in electrostatic interactions (relative to covalent interactions) that involves sites of progressively lower affinity for metal ions. The present experimental results suggest that metal biosorption (Pb^{2+} and Cd^{2+}) by gum kondagogu to be higher as compared to many of the other low cost natural biosorbents reported in the literature, such as *Ficus religiosa* leaves, black gram husk, chitin (Benguella & Benaissa, 2002; Klimmek et al., 2001; Qaiser, Saleemi, & Ahmad, 2007).

3.4. Effect of biopolymer dose

The effect of gum kondagogu dose on the adsorption of Pb^{2+} and Cd^{2+} from aqueous solutions was investigated using different adsorbent concentrations in the range of 1.0–5.0 g/L and different initial concentration (10–300 mg/L) of metal ions. The relationship between the varied quantity of gum kondagogu (1.0–5.0 g/L) and metal biosorption was investigated by keeping fixed amounts of metal ion concentration, at an optimum pH (5.0 ± 0.1), with a shaker speed of 200 rpm, at a temperature of ($25 \pm 2^\circ\text{C}$) so as to assess the optimum concentration of biopolymer needed for maximum biosorption. The results are presented in Fig. 2, which indicate that the equilibrium concentration of Pb^{2+} and Cd^{2+} ions decreases with increasing gum kondagogu concentration for a given initial metal ion concentrations (Pb^{2+} and Cd^{2+}). Similar, metal biosorption results have been reported earlier by Saeed et al. (2005) and Sangi (Sangi, Shahmoradi, Zolgharnein, Azimi, & Ghorbandost, 2008) using black gram husk and *Ulmas carpinifolia* and *Fraxinus excelsior* tree leaves and suggests that the increase of efficiency of removal with increase of adsorbent dose is due to the increase in the of adsorption sites and the decrease in unit adsorption is basically due to the biosorption sites that remain unsaturated during adsorption reaction.

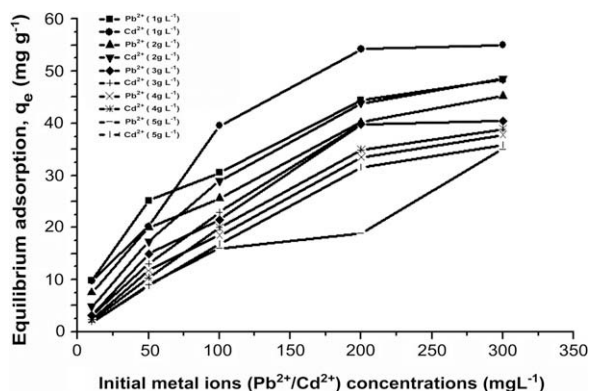


Fig. 1. The relation between the amount of Pb^{2+} and Cd^{2+} adsorbed at equilibrium (q_e) and its initial concentration using different doses of gum kondagogu at pH 5.0 ± 0.1 , shaking at 200 rpm at $25 \pm 2^\circ\text{C}$ during 120 min contact time.

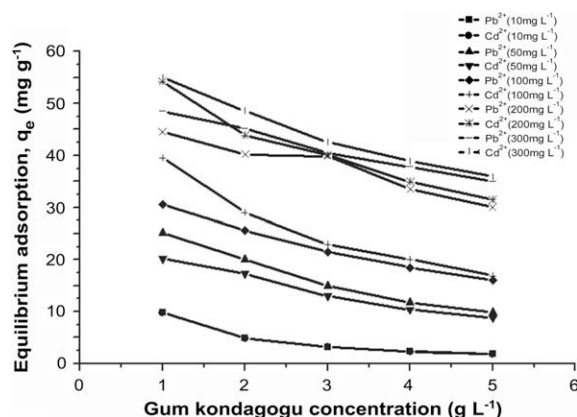


Fig. 2. The effect of different concentrations of gum kondagogu on Pb^{2+} and Cd^{2+} adsorption at equilibrium (q_e); initial concentration (10–300 mg/L); agitator speed 200 rpm; temperature $25 \pm 2^\circ\text{C}$; and contact time 120 min.

3.5. Biosorption isotherms

The basic assumption in Langmuir isotherm is that the adsorbed layer is one molecule thick and that all sites are equal, thereby resulting in equal energies and enthalpies of adsorption. Once a sorbate occupies a site, no further sorption can take place at this site (Akar, & Tunali, 2005; Aksu & Gonen, 2004; Pardo, Herguedas, & Barrado, 2003). The Langmuir and Freundlich adsorption constants evaluated from the isotherms with the correlation coefficients are presented in Table 1. The maximum monolayer capacity obtained from the Langmuir isotherm was 48.5 mg g^{-1} for Pb^{2+} and 47.48 mg g^{-1} for Cd^{2+} , respectively. Values of coefficients of correlation R^2 (0.996 for Pb^{2+} and 0.999 for Cd^{2+}) show that the Langmuir isotherm model fitted best to the experimental data compared to Freundlich isotherm model. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogenous distribution of active sites onto adsorbent surface. The adsorption mechanisms of heavy metals by gum kondagogu mainly involve complexation between heavy metal ions and gum, adsorption, surface micro-precipitation and ion-exchange. The extent of adsorption was calculated based on the difference of metal ion concentration in the aqueous solution before and after adsorption. The Freundlich model was chosen to estimate the adsorption intensity of the Pb^{2+} and Cd^{2+} on the gum kondagogu biopolymer based on adsorption heterogeneous energetic distribution of active sites accompanied by interactions between adsorbed molecules. The Freundlich isotherm parameters are presented in Table 1. The correlation coefficient obtained for gum kondagogu is 0.998 for Pb^{2+} and 0.983 for Cd^{2+} , respectively. The n values for Pb^{2+} (1.93) and Cd^{2+} (1.68) are higher than 1.0, indicating that Pb^{2+} and Cd^{2+} are favourably adsorbed by gum kondagogu at $25 \pm 2^\circ\text{C}$. The Freundlich constant (K_F) for Pb^{2+} and Cd^{2+} are 3.489 and 3.258, respectively.

Table 1

Comparison of q_{max} obtained from Langmuir and Freundlich adsorption isotherms for Pb^{2+} and Cd^{2+} biosorption by gum kondagogu at pH 5.0 ± 0.1 , temperature, $25 \pm 2^\circ\text{C}$, agitator speed: 200 rpm, initial metal ions concentration: 100 mg/L, gum kondagogu concentration: 1 g/L.

Metal ions	Langmuir parameters			Freundlich parameters		
	q_{max} (mg g^{-1})	b (L mg^{-1})	R^2	k	n	R^2
Pb^{2+}	48.52	0.023	0.996	3.489	1.93	0.998
Cd^{2+}	47.48	0.037	0.999	3.258	1.68	0.983

Table 2

Comparison of the pseudo-first- and -second-order adsorption rate constants and calculated and experimental q_e values for different initial concentrations of Pb^{2+} and Cd^{2+} on gum kondagogu; conditions: pH 5.0 ± 0.1 , temperature; $25 \pm 2^\circ\text{C}$, agitator speed; 200 rpm, gum kondagogu concentration; 1 g/L.

Metal ions	Initial concentrations (mg/L)	q_e (experimental) (mg g ⁻¹)	First-order kinetic model			Second-order kinetic model		
			k_1 (min ⁻¹)	q_e (calculated) (mg g ⁻¹)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	q_e (calculated) (mg g ⁻¹)	R^2
Pb^{2+}	10	9.85	0.0037	1.43	0.991	0.0189	10.13	0.999
	50	25.24	0.079	13.40	0.966	0.0078	26.45	0.998
	100	30.50	0.024	9.02	0.966	0.0005	31.84	0.999
	200	44.84	0.041	21.14	0.987	0.0035	47.08	0.999
	300	48.50	0.075	25.38	0.967	0.0064	50.15	0.999
Cd^{2+}	10	9.80	0.0713	7.718	0.962	0.0205	10.76	0.994
	50	20.24	0.0673	13.73	0.996	0.0040	22.43	0.997
	100	39.55	0.0265	13.67	0.988	0.0017	43.51	0.999
	200	54.25	0.0200	14.0	0.990	0.0008	59.70	0.991
	300	55.00	0.0310	14.21	0.981	0.0012	59.63	0.995

3.6. Biosorption kinetics

Kinetics of biosorption is one of the most important characteristics to describe the solute sorption rate that in turn controls the residence time of metal as a function of biopolymer sorption at the solid–solution interface. Pseudo-first-order equation of Lagergren based on solid capacity and pseudo-second-order rate equation based on solid phase adsorption was applied to the experimental data so as to predict the biosorption kinetics. The amount of Pb^{2+} and Cd^{2+} adsorbed at equilibrium (q_e), the equilibrium rate constants of pseudo-first-order (k_1) and pseudo-second-order (k_2), the correlation coefficient (R^2), are presented in Table 2. The kinetic analysis suggests that the pseudo-second-order kinetic model provided a good correlation for the biosorption of Pb^{2+} and Cd^{2+} onto biopolymer (gum kondagogu) at different initial concentrations of the metal ions. The value of q_e and k_2 was determined from the slope and intercept of the plot (t/q_t vs t), respectively. These theoretical values were close to the experimental values (q_e), with a correlation coefficient of $R^2 > 0.99$, indicating that the pseudo-second-order equation fitted well with the experimental data (figure is not shown).

3.7. Metal ion biosorption mechanism

3.7.1. FT-IR analysis

The FT-IR spectra of the gum kondagogu and metal-loaded gum kondagogu (Pb^{2+} and Cd^{2+}) are shown in Fig. 3. The FT-IR spectroscopic analysis indicated broad bands at 3400 cm^{-1} , representing bonded $-\text{OH}$ and $-\text{NH}$ groups. The bands observed at about 2930 cm^{-1} , could be assigned to the $-\text{CH}$ stretch. The carboxylate ions gave rise to two bands, a strong asymmetrical stretching band at 1623 and 1643 cm^{-1} , respectively, and a weaker symmetrical stretching band at 1421 and 1418 cm^{-1} , respectively. The bands at 1125 cm^{-1} and 1127 cm^{-1} were due to the $-\text{C}-\text{O}$ stretching of ether groups. The bands at 1072 cm^{-1} and 1062 cm^{-1} were assigned to the $-\text{C}-\text{O}$ stretching of alcoholic groups. The peaks around 1455 cm^{-1} and 1280 cm^{-1} gradually disappeared with increase of Pb^{2+} ions concentration in solution, while the peak around 1380 cm^{-1} became higher. The shift of peak at 1455 cm^{-1} transposing to lower frequencies up to disappearance is due to the complexation of amino and hydroxyl groups with Pb^{2+} . Another shift was observed at 1280 cm^{-1} to higher frequencies corresponding to complexation of oxygen from the carbonyl $-\text{C}-\text{O}$ bond. These band changes result in the absorbance band at 1380 cm^{-1} became stronger. The $\text{C}=\text{C}$ stretching in aromatic ring at 1610 cm^{-1} shifts to 1601 cm^{-1} after Cd^{2+} biosorption. The $-\text{OH}$ and $(-\text{COO})$ groups in gum kondagogu were involved in

Cd^{2+} biosorption. The functional groups involved in bivalent metal biosorption included hydroxyl carboxyl, ether and alcoholic groups. A comparison of the spectra for native gum kondagogu with that of lead-loaded gum reveals characteristic changes of the hydroxyl groups and the acetyl groups, which shift from 3415 cm^{-1} ($-\text{OH}$), amide (1654 cm^{-1}) before lead adsorption to 3427 cm^{-1} ($-\text{OH}$) and amide (1649 cm^{-1}) after lead adsorption. These observations were in agreement with Pb^{2+} and Cd^{2+} biosorption by cellulose/chitin beads and neem leaf powder (Sharma & Bhattacharyya, 2005; Zhou et al., 2005).

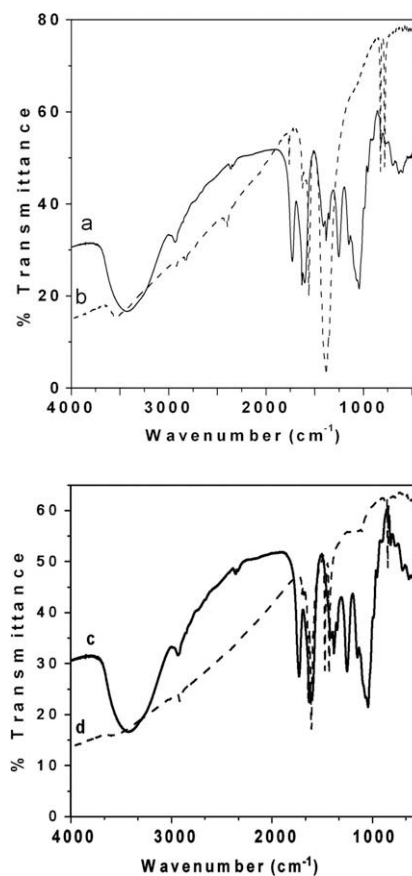


Fig. 3. FT-IR analysis of gum kondagogu (a and c) before metals (Pb^{2+} and Cd^{2+} biosorption); (b) after Pb^{2+} biosorption, (d) after Cd^{2+} biosorption, indicating the involvement of various functional groups in biosorption of metals.

3.7.2. SEM–EDXA analysis

Scanning electron microscopic examination of gum kondagogu before and after metal biosorption (Pb^{2+} and Cd^{2+}) was undertaken in order to locate the active sorptive sites of the gum kondagogu. The scanning electron microscopic (SEM) micrographs and the X-ray energy dispersion analysis (EDXA) of gum kondagogu before and after equilibration with lead and cadmium metal solutions are shown in Fig. 4(a)–(f). Scanning electron microscopy is an extremely useful tool for visual conformation of surface morphology and the physical state of the surface. SEM coupled with energy dispersive analysis of X-rays (EDXA) was used to determine the metal uptake mechanism on gum kondagogu which is a complex phenomenon involving nodule formation on the polymer surface, ion adsorption and ion absorption. SEM pictures of the gum kondagogu without metal binding show a flowery flakes appearance with high porous structure on the surface [Fig. 4(a)]. After lead and cadmium biosorption the gum kondagogu surface appears littered with nodules [Fig. 4(c)]. The EDXA analysis conclusively identified the bound material as Pb^{2+} and Cd^{2+} , respectively [Fig. 4(d) and (f)]. The experimental result confirms that the sorption of Pb^{2+} and Cd^{2+} on gum kondagogu is apparently located on the biopolymer

surface. This clearly shows that Pb^{2+} and Cd^{2+} biosorption on the surface of gum kondagogu probably due to micro-precipitations. The biosorption of metals by this kind of material might be due to the presence of carboxyl, hydroxyl, sulphate, phosphate and amino group that can bind metal ions. Similar metal binding observations were made with chitin, chitosan and grape stalk waste (Benguella & Benaissa, 2002; Martínez et al. 2006). The appearance and disappearances of Na^+ , Mg^{2+} , and Ca^{2+} peaks in EDXA spectrum indicated that biosorption process also included ion-exchange mechanism for the removal of both metal ions by gum kondagogu [Fig. 4(b), (d) and (f)].

3.7.3. XPS analysis

XPS technique is a useful tool in characterizing ligand effect in transition metal complexes (electron-donating ligands will lower the binding energy (BE) of the core-level electrons and electron-withdrawing ligands will increase their BE) and is also used to identify the existence of a particular element in a material and distinguish the different oxidation states of the same element. The XPS spectra of gum kondagogu before and after metal adsorption of lead (Pb^{2+}) and cadmium (Cd^{2+}) are shown in Fig. 5(a)–(c). As

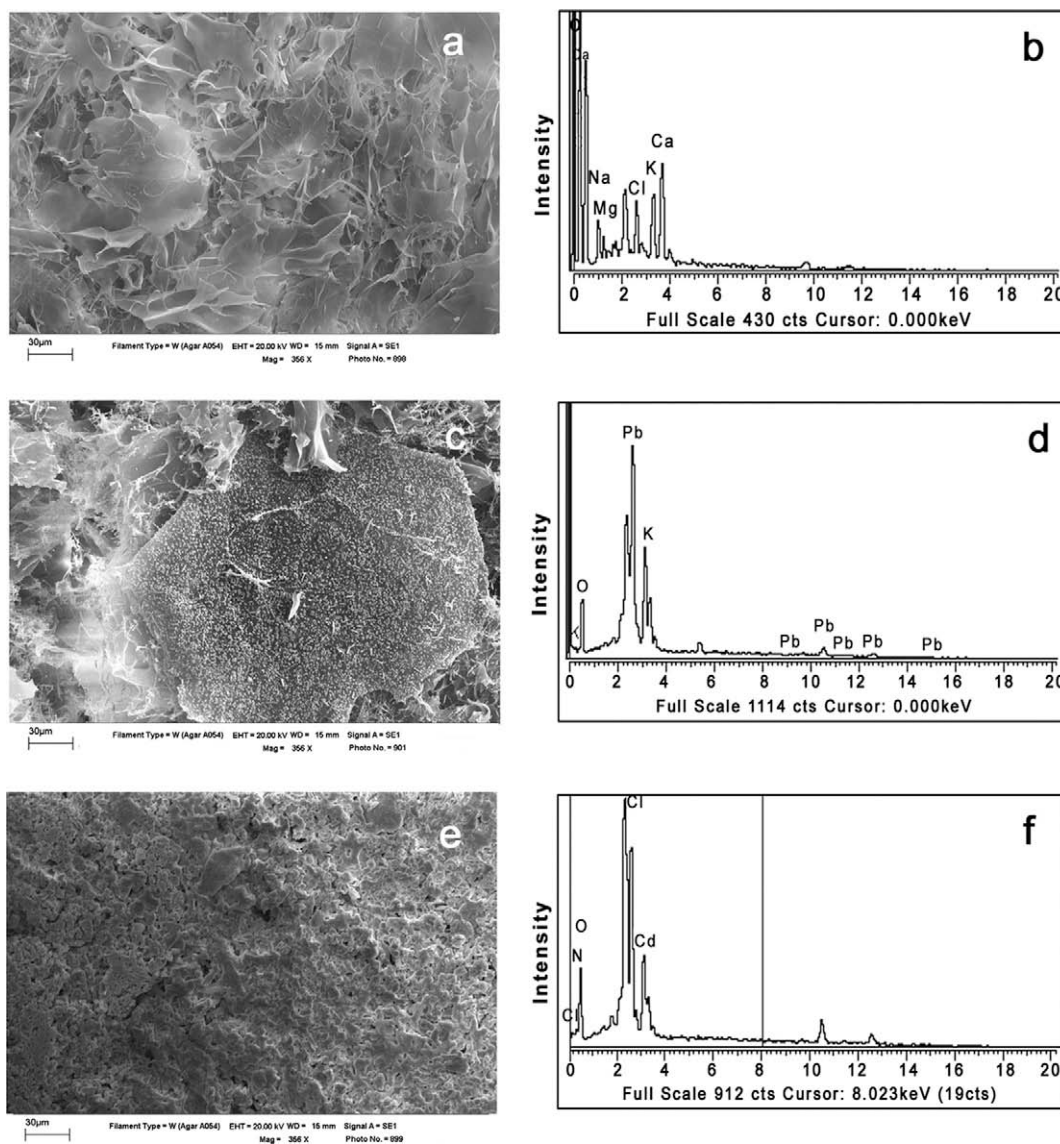


Fig. 4. SEM–EDXA spectra of gum kondagogu (a and b) before metals loaded; (c and d) after Pb^{2+} loaded; (e and f) after Cd^{2+} loaded.

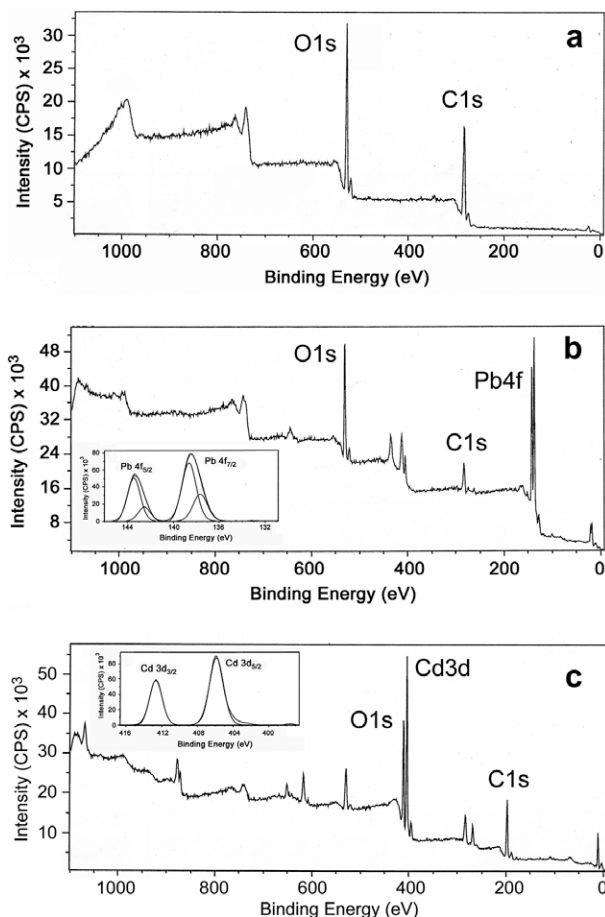


Fig. 5. XPS survey scanning spectra of the gum kondagogu (a) before metals adsorption (b) after Pb^{2+} adsorption (c) after Cd^{2+} adsorption. Inset figure shows the XPS spectra of (C 1s) of gum kondagogu biosorbed with (b) Pb^{2+} and (c) Cd^{2+} metal ions.

can be seen from the spectra, the XPS survey scans of pure gum kondagogu shows binding energy peaks characteristic of carbon and oxygen only. The spectrum of metal adsorbed gum kondagogu on the other hand indicates the presence of lead and cadmium on the surface of gum kondagogu, obviously after metals biosorption in addition to carbon and oxygen [Fig. 5(b) and (c)]. High-resolution narrow scans of C 1s core-level spectra of gum kondagogu samples before and after metal adsorption comprise of three peaks corresponding to binding energies of 284.59, 286.36, and 288.29 eV that were identified *via* the deconvolution. The changes in the binding energies of C 1s before and after metal adsorption and their area ratios are summarized in Table 3. The observed C 1s binding energy peaks that are assigned due to C–C, C–O and C=O functional groups present in gum kondagogu are in consonance with the observations made by FT-IR. The peaks C–O and C=O can be assigned to hydroxyl and carboxylate groups present in the biopolymer. The O 1s high-resolution narrow scans could be deconvoluted into binding energy peaks at 531.8 eV and 532.7 eV which can be assigned to the O in the C=O and alcoholic C–O groups. The C=O group may be in them due to the carboxylate groups present in the gum kondagogu. The metal ions adsorbed on gum kondagogu were also analyzed by XPS to know the presence of the metals and their oxidation states. The high-resolution narrow scan of Cd 3d Fig. 5(c), shows binding energy peaks at 405.89 and 412.70 eV that are assigned due to Cd 3d_{5/2} and Cd 3d_{3/2}, respectively, which are characteristic due to the formation of $(-COO)_2 Cd$ sorption species. Fig. 5(c) shows the high-resolution

Table 3

Summary of binding energies and peak ratios of C 1s spectra for gum kondagogu before and after heavy metal (Pb^{2+} and Cd^{2+}) adsorption, based on XPS analysis.

Fresh gum kondagogu		Cd^{2+} adsorbed gum kondagogu		Pb^{2+} adsorbed gum kondagogu	
Peak (eV)	Peak ratio (%)	Peak (eV)	Peak ratio (%)	Peak (eV)	Peak ratio (%)
284.59	60.2	284.58	55.3	284.61	43.1
286.35	31.1	286.28	30.2	285.90	30.6
288.29	8.7	288.54	14.5	287.42	26.2

narrow scan of Pd 4f shows two peaks at 138 and 143 eV characteristic of $Pb\ 4f_{7/2}$ and $Pb\ 4f_{5/2}$, respectively. These observations could be deconvoluted into two peaks each, 137.64 and 138.65 and 142.56 and 143.46 eV, respectively, which clearly indicates the presence of Pb in two different forms, namely Pb^{2+} and Pb^{2+} ion bonded to carboxylate group in the adsorbed gum kondagogu. Similar spectra of Pb^{2+} and Cd^{2+} were observed in the uptake of these metals by calcium-alginate based ion-exchange resin, marine algal biomass, chemically modified chitosan and aerobic granules (Chen, Hong, Wu, & Wang, 2002; Sheng, Ting, Chen, & Hong, 2004; Wang & Wang, 2008; Xu & Lu, 2008). The information provided by the XPS analysis and the characterizations of the oxidation state are of great importance in evaluating the stability of the sorbent as well as predicting the behavior of the gum kondagogu.

4. Conclusions

The experimental investigations conclude the capacity of a natural biopolymer in toxic metal biosorption. The biosorption of Pb^{2+} and Cd^{2+} by gum is influenced by contact time, pH of the medium, initial concentration of the metal ions and biopolymer content. The experimental data turn out good fits with Langmuir isotherm ($R^2 > 0.99$). The kinetic studies proved that pseudo-second-order kinetic was the applicable model. The FT-IR analysis indicates that the involvement of hydroxyl, carbonyl, ether and acetyl groups in the binding of Pb^{2+} and Cd^{2+} metal ions. The SEM–EDXA, analysis suggests micro-precipitation of metal ions along with ion-exchange process as Na^+ , Ca^{+2} and Mg^{+2} ions were simultaneously exchanged for toxic metals by the biopolymer. XPS analysis demonstrates that metal ion interaction with gum involves various changes in the metal oxidation state, as well as in the chemical state of the reactive sites of the biopolymer. It further substantiates the results of FT-IR analysis, indicating that metal sorption occurs on hydroxyl, carbonyl and carboxyl groups. The experimental results contribute to a better understanding of the biosorption phenomena and aid in the development of potential new biosorbent using locally derived natural product. The biopolymer being biodegradable can be complimentary for environmental defensive.

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