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Microwave induced poly(acrylic acid) modification of *Cassia javanica* seed gum for efficient Hg(II) removal from solution

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ABSTRACT

Microwave induced poly(acrylic acid) modification of *Cassia javanica* (CJ) seed gum furnished an efficient Hg(II) sorbent. Copolymer samples of different performances in terms of Hg(II) binding were synthesized by changing acrylic acid concentration at fixed microwave power and exposure time. The optimum sample has been characterized using FTIR spectroscopy, X-Ray diffraction, BET and SEM analysis and using this sample adsorption of mercury (II) was studied as a function of pH, sorbent dose, initial Hg(II) concentration, % grafting, temperature and ionic strength. Equilibrium isotherm data were analyzed using the Langmuir and Freundlich isotherms. The Langmuir model yielded a much better fit than the Freundlich model indicating unilayer sorption. Isotherms have also been used to obtain the thermodynamic parameters such as free energy, enthalpy, and entropy of sorption. The maximum sorption capacity was 135 mg g^{-1} at 30 °C. In order to investigate the mechanism of sorption, kinetic data were modeled using the first order Lagergren, pseudo-second-order and intra-particle diffusion model where intra-particle diffusion and chemical reaction both seem relatively significant in the rate controlling step. The regeneration experiments revealed that the CJ-graft-poly(acylic acid) can be successfully reused for six cycles without any significant loss in the sorption capacity.

1. Introduction

Mercury (Hg) as one of the most toxic heavy metal is commonly found in the global environment. Its toxicity is related to the capacity of its compounds to bioconcentrate in organisms and to biomagnify through food chain [1]. The toxicity of mercury depends strongly on its redox state [2]. The most toxic form of mercury is the highly reactive Hg^{2+} which binds to the amino acid ‘cysteine’ in proteins. In contrast, the danger of elemental mercury and organo-mercury compounds lies in their transport routes. Hg contamination can be much more widespread than that observed for other metals due to atmospheric transport [3,4] or to biomagnification through the food chain, reaching fish and humans [5]. Removal of mercury ions from water and wastewater is very important and different technologies are available such as chemical precipitation, coagulation, ion exchange, membrane technologies, adsorption, etc. The latter is by far the most versatile and widely used and activated carbon is the most commonly used sorbent. However, the use of activated carbon is expensive, so there has been increased interest in the use of other adsorbent materials, particularly low-cost adsorbents [6] derived from natural polymers, in particular chemically and physically modified polysaccharides [7] e.g. poly(acrylonitrile) and poly(acrylic acid) grafted cellulose [8,9] is reported to remove cadmium, copper and lead ions where the amount of metal ion adsorbed was dependent on metal type and the nature and level of the incorporated grafts in the polymer. Similarly poly(acrylic acid) grafted cotton cellulose [10], starch-g-poly(acrylic) acid copolymers [11] and poly(methylmethacrylate) grafted *Cassia grandis* seed gum [12] effectively removed heavy metal ions from the solutions. There has been recent interest in using microwave irradiation in the copolymer synthesis [13] as its use not only saves chemicals and reaction time but also furnishes copolymer samples that are more efficient sorbent materials than the conventionally synthesized ones.

Cassia plants are non-conventional source of seed gums having structural resemblance with industrial gums like guar and locust bean gums. Non-conventional *Cassia* seed gums are galactomannans [14] and their mannose to galactose ratio and molecular weights vary from species to species. Thus they are renewable reservoir for obtaining polysaccharide materials that can be modified to functional copolymers through vinyl grafting. Since primary structures and molecular weights of these *Cassia* seed gums are different from guar gum, on vinyl modification they are likely to furnish graft copolymers that are different from vinyl modified guar gum in terms of properties and performance.

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Native to the tropical regions of Asia, *Cassis javanica* is distributed naturally from India to Malaysia, Sumatra, Indonesia, Southern China, and the Phillipines. *Cassia javanica* is a fast-growing, semideciduous tree up to 25 m in height and 35 cm d.b.h. *C. javanica* as other *Cassia* plants has been reported to furnish seed gum (yield = 26%). The intrinsic viscosity and viscosity average molecular weight for the seed gum is reported to be $[\eta] = 11.3\ \mathrm{dL\,g^{-1}}$ (at 25 °C) and $M_v = 1.5 \times 10^6$ respectively. *C. javanica* [15] seeds are rich source of seed gum that contains galactose and mannose in the molar ratio of 1.02: 3.20. The seed polysaccharide has been graft copolymerized with methylmethacrylate [16] for obtaining functional copolymer that can be commercially exploited.

In the present study, an efficient mercury sorbent has been crafted by poly(acrylic acid) grafting onto *C. javanica* seed gum under microwave irradiation. Varying the reaction conditions, graftcopolymer samples of different %G have been synthesized. To evaluate the adsorption capability and to determine the regeneration feasibility of the adsorbent, batch adsorption experiments were carried out using the optimum sample.

2. Materials and methods

All the reagents used were of analytical grade. A stock Hg(II)) solution ($1000\ \mathrm{mg\,L^{-1}}$) was prepared in deionized water using $HgCl_2$ (Merck) and all the working solutions were prepared by diluting this stock solution with deionized water. Seeds of *C. javanica* were supplied by Himani Seed Stores, Deheradun. Acrylic acid (SRL, India), $K_2S_2O_8$ (Merck) and Ascorbic acid (Merck) were used. Shimadzu electronic balance-model-AUY-220 was used for weighing. An unmodified Kenstar domestic microwave oven, model-OM-34 ECR having 2450 MHz microwave frequency and a power output from 0 to 800 W with continuous adjustment has been used for the adsorbent synthesis. Surface area of the adsorbent was determined using surface area analyzer Model: SMART SORB 92, Make – Smart Instruments Company (P) Ltd. The concentration of mercury ion was determined photometrically using Rhodamine-6G (Merck) at $\lambda = 575$ nm using Systronics single beam visible Spectrophotometer model 105. Systronics Digital pH meter model 335 was used for pH measurement. The pH values are adjusted by the addition of 5N HCl or 5N NaOH. FTIR spectra were recorded on a Perkin–Elmer Infrared Spectrophotometer using KBr pellets. X-ray diffraction (XRD) was carried out on Rigaku D/MAX-2200 using Mo/k-d1 target (λ 0.7107 Å). TGA analysis was done on Pyris diamond TG/DTA, model-8. SEM analysis was done on EDAX, FEI Quanta 200 machine

2.1. Isolation and purification of Cassia javanica seed gum

Seeds (1 kg) of *C. javanica* were exhaustively extracted with light petroleum followed by EtOH to remove fatty and coloring materials respectively and then suspended in 1% aqueous acetic acid overnight. The filtrate of the 1% solution was precipitated with 95% EtOH and this was repeated three times to obtain a white amorphous crude gum that was collected, washed with ethanol and dried. The pure seed gum was a non-reducing, white, fibrous material.

2.2. Adsorbent synthesis

2.2.1. Grafting under microwave irradiation in aqueous medium

An open necked flask (150 mL) containing calculated amount of the *C. javanica* seed gum solution and acrylic acid (AA) was exposed to a definite microwave power for a definite time period in an unmodified domestic microwave oven. Poly(acrylic acid) grafted *C. javanica* seed gum samples of different % grafting were separated from the respective reaction mixtures by pouring them to excess of methanol: water (8:2). The grafted samples were finally extracted with methanol: water (8:2) in soxhlet apparatus for 4 h to dissolve all the homopolymer. The colorless graft copolymer samples (CJ-g-PAA) were dried under vacuum at 50 °C for >24 h to a constant weight and the results were recorded in Table 1. At optimum microwave power and exposure time, concentrations of the acrylic acid ($20–32 \times 10^{-2}$ M) and *C. javanica* (50–250 mg/25 mL) were varied one at a time, keeping the other fixed and the results are summarized in Tables 2 and 3.

Table 1
Optimization of microwave power and exposure time at fixed monomer concentration (26×10^{-2} M); CJ (100 mg), total reaction volume 25 mL.

S.No.	Microwave power (%)	Exposure time (s)	Yield (mg)	% G	%E
1.	20	15	118	18	3
		30	127	27	5
		40	132	32	6
		50	153	53	11
		60	168	68	14
2.	40	15	148	48	10
		30	164	63	13
		40	172	72	15
		50	191	90	19
		60	185	84	17
3.	60	15	183	82	17
		30	205	104	22
		40	213	112	23
		50	218	118	25
		60	208	108	22
4.	80	15	194	94	19
		30	216	115	24
		40	231	130	27
		50	216	115	24
		60	219	118	25
5.	100	15	206	105	22
		30	191	90	19
		40	183	82	17
		50	166	65	13
		60	154	54	11

Table 2
%G and %E with change in monomer concentration, CJ (100 mg), total reaction volume 25 mL at 80% microwave power, 40 s exposure time.

S.No.	Monomer in M	Yield (mg)	%G	%E
1.	20×10^{-2}	165	65	17
2.	23×10^{-2}	205	105	25
3.	26×10^{-2}	231	130	27
4.	29×10^{-2}	227	126	24
5.	32×10^{-2}	224	124	21

2.2.2. Thermal grafting using $K_2S_2O_8$/ascorbic acid redox pair

To an aqueous solution of *C. javanica* seed gum (100 mg/25 mL) taken in a 150 mL reaction flask, acrylic acid (26×10^{-2} M), and ascorbic acid (3.7×10^{-2} M) were added and thermostated on water bath at 35 ± .2 °C. After 30 min $K_2S_2O_8$ (30×10^{-3} M) was added and this time of addition of persulfate was taken as zero time. Graft

Table 3
%G and %E with change in Gum concentration, monomer (26×10^{-2} M), total reaction volume 25 mL at 80% microwave power, 40 s exposure time.

S.No.	Gum/25 mL	Yield (mg)	%G	%E
1.	50	94	89	18
2.	100	231	130	27
3.	150	290	93	19
4.	200	415	107	22
5.	250	530	112	23

copolymerization was allowed for 1 h. Then the reaction product was precipitated in methanol: water (8:2) as described above and %G and %E were calculated to be 110.5% and 22.93% respectively.

2.2.3. Determination of pH_{ZPC}

A solution of 0.005 M $CaCl_2$ was boiled to remove the dissolved CO_2 and then cooled to room temperature. The pH was adjusted to a value between 2 and 10 using 2.5 M HCl or 5 M NaOH. The copolymer (0.03 g) was added into 20 mL of the pH adjusted solution in a capped vial and equilibrated for 24 h. The final pH was measured and plotted against the initial pH. The pH at which the curve crosses the pH initial/pH final line is taken as pH $_{PZC.}$

2.3. Hg(II) adsorption batch experiment

Poly(acrylic acid) (PAA) modified CJ seed gum (synthesized under microwave irradiation) having 130%G was evaluated for Hg(II) removal from synthetic solution. The operating variables studied were pH, sorbent dosage, initial metal ion concentration, %G in the sorbent, ionic strength and temperature.

Stock solutions of $1000\,mg\,L^{-1}$ each of standardized Hg(II) were prepared from mercury chloride in double distilled-deionized water. Experiments were carried out on a temperature controlled incubator shaker set at 120 rpm and maintained at 30 ± 2 °C for 4 h in 50 mL conical flasks. After the flasks were shaken for the desired time, the suspensions were filtered using Whatman 0.45 mm filter paper and the filtrates after suitable dilutions were analyzed for Hg(II) concentration spectrophotometrically at 575 nm wavelength by developing light pink colour with Rhodamine 6G in acidic medium. The solutions of Hg(II) chloride, buffered potassium iodide and Rhodamine 6G were prepared as described elsewhere [17].

To make spectrophotometric determination, a suitable aliquot (up to 10 mL) of the sample solution containing not more than 25 g of mercury was transferred to a 25 mL volumetric flask and to it 5 mL of the buffered potassium iodide and 5 mL of the rhodamine 6G solution were added followed by 1 mL of 1% (w/v) gelatin solution (which was prepared in the usual way). Diluted the solution to the mark with distilled water, and measured the absorbance at 575 nm against a reagent blank. A calibration curve was prepared for 5–25 μg of mercury.

Control experiments showed that no sorption occurred on either glassware or filtration systems. The amount of metal ions adsorbed [18] per gram of the adsorbent was calculated by the difference between the initial and the final readings using the following equation.

$$q_e(mg\,g^{-1}) = C_0 - C_e(mg\,L^{-1}) \times V(L)/W(g) \tag{1}$$

where q_e is the amount of the mercury adsorbed ($mg\,g^{-1}$) on the adsorbent, C_0, the initial concentration of Hg(II) ($mg\,L^{-1}$), C_e, the equilibrium concentration of Hg(II) in solution ($mg\,L^{-1}$), V, the volume of the solution used (L), and W, the weight of the adsorbent used in g.

Keeping the other parameters fixed, one parameter was varied at a time. For pH studies, 20 mL solutions of $100\,mg\,L^{-1}$ metal ion were adjusted to various pHs ranging from 1 to 10. Different adsorbent doses ranging from 20 to 100 mg were used to study the effect of adsorbent on the removal of Hg(II) at $100\,mg\,L^{-1}$ initial Hg(II) concentration. The range for different initial concentrations of mercury was 50–700 $mg\,L.^{-1}$ Copolymer samples of different % grafting were used to study the effect of % grafting on the Hg(II) removal under the optimum adsorption conditions. All the batch experiments were carried out in triplicate and the values reported are average of three readings.

2.4. Desorption studies

The copolymers loaded with mercury were placed in the 0.05N H_2SO_4 and stirred at 120 rpm for 4 h at 30 °C and the final Hg(II) concentration was determined. For sorption–desorption cycles 250 mg sorbent dose and $500\,mg\,L^{-1}$ initial Hg(II) concentration were used to avoid practical difficulty in handling the small quantities. After each cycle, the used copolymer was washed with distilled water and used in the succeeding cycle. The amount desorbed was calculated from the amount of metal ions loaded on the copolymer and the final mercury concentration in the stripping medium. For the quantitative stripping, 4 h of equilibration was required.

2.5. Cation exchange capacity (CEC) measurements

For CEC measurement [19], H^+ form of the adsorbent was obtained by stirring 0.5 g of the sorbent in 100 mL 0.05N HNO_3 in a orbital shaker for 4 h at 30 °C and 120 rpm. The resulting H^+ form of the sorbent was now filtered and washed with deionized water and dried. Its 0.1 g was taken in 50 mL of 1 M salt solution ($NaNO_3$, KCl and $MgCl_2$ separately) and stirred in orbital shaker for 4 h at 30 °C and 120 rpm. The material was then filtered and the filtrate was titrated with 0.1 M standard NaOH solution to know the concentration of H^+ ions released in the solution after exchange with the respective cation.

3. Results and discussions

C. javanica seed gum-graft-poly(acrylic acid) (CJ-g-PAA) was synthesized efficiently both by persulfate/ascorbic initiated thermal grafting method and by microwave induced grafting method; however at same monomer concentration, higher %G copolymer sample was obtained in microwave method due to incorporation of higher number/larger PAA grafts [13]. The optimum %G was obtained when a reaction mixture (25 mL) containing 26×10^{-2} M AA and 0.1 g CJ gum was exposed to 640 W microwave power for 40 s. The dried copolymer was crushed to 1.0–1.5 mm flakes before use. The material was water insoluble at neutral and alkaline pH however it dissolves at pH <1 or on overnight stirring at pH 1. The BET surface area of the material was $0.342\,m^2/g$ and cation exchange capacity for potassium, sodium and magnesium ions

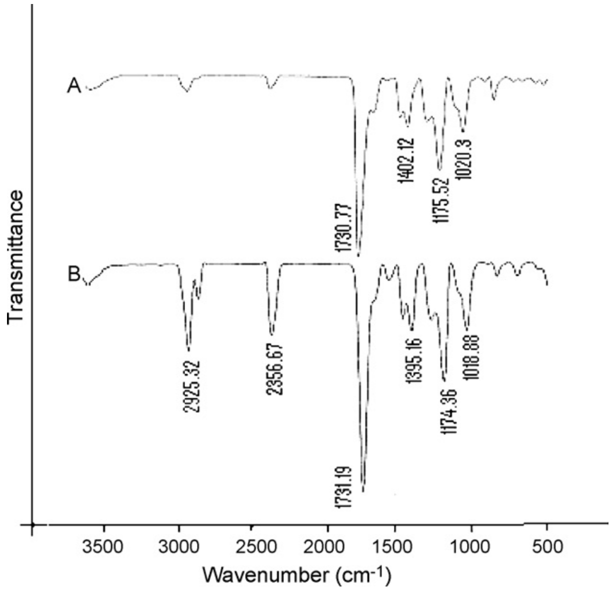


Fig. 1. IR spectrum of CJ-g-PAA (A) and loaded CJ-g-PAA (B).

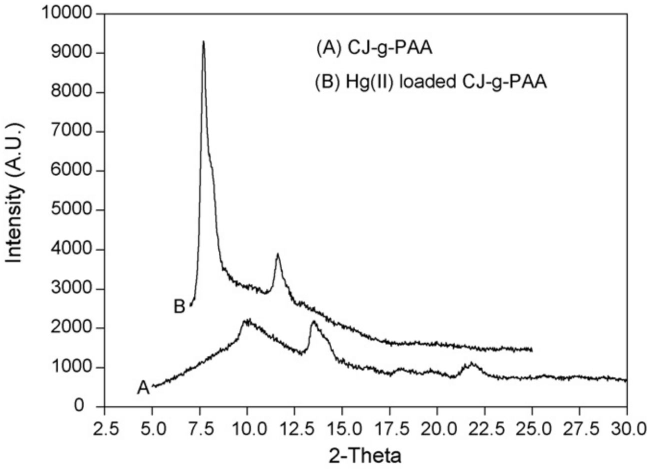


Fig. 2. XRD pattern of the CJ-g-PAA (A) and loaded CJ-g-PAA (B).

were 7.6 meq g^{-1}, 5.4 meq g^{-1} and 3.8 meq g^{-1} respectively. The representative sample (sample having maximum %G) of CJ-g-PAA and mercury loaded copolymer (CJ-g-PAA-Hg) were characterized using FTIR, XRD, SEM and BET analyzes.

3.1. Charcterization of the adsorbent

3.1.1. Fourier transform infrared spectroscopy

IR spectrum of pure CJ gum (spectra not shown) has a broad strong band at 3440 cm^{-1} due to O–H stretching and at 2928 cm^{-1} due to C–H linkages while IR spectrum of CJ-g-PAA (Fig. 1A) had O–H stretching peak of very low intensity at 3595 cm^{-1} indicating the copolymer is highly cross linked and O–H groups available on ungrafted portion lose hydrogen bonding due to change in secondary structure of the gum on cross linking. Acid carbonyl group stretching and C–H stretching peaks of $-CH_2$ and –CH– groups are seen at 1730 cm^{-1}, 2958 cm^{-1} and 2870 cm^{-1} respectively.

On mercury loading (CJ-g-PAA-Hg), significant shift (from 2958 to 2925 cm^{-1}) of C–H stretching peaks to lower wave number is observed (Fig. 1B) indicating their role in binding mercury species. Further on mercury loading, O–H stretching is seen in low inten-

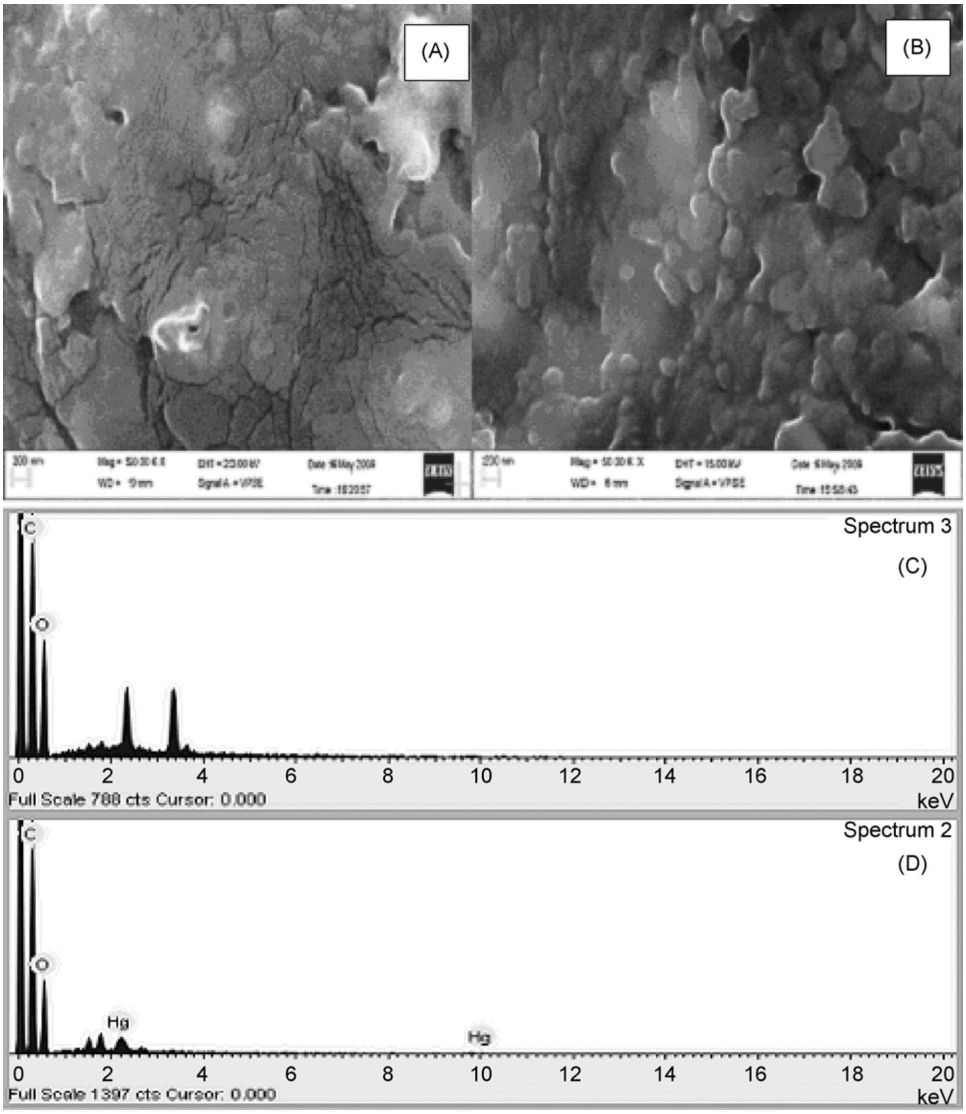


Fig. 3. SEM picture of CJ-g-PAA (A), Hg(II) loaded CJ-g-PAA (B) and EDX spectra of CJ-g-PAA (C), Hg(II) loaded CJ-g-PAA (D).

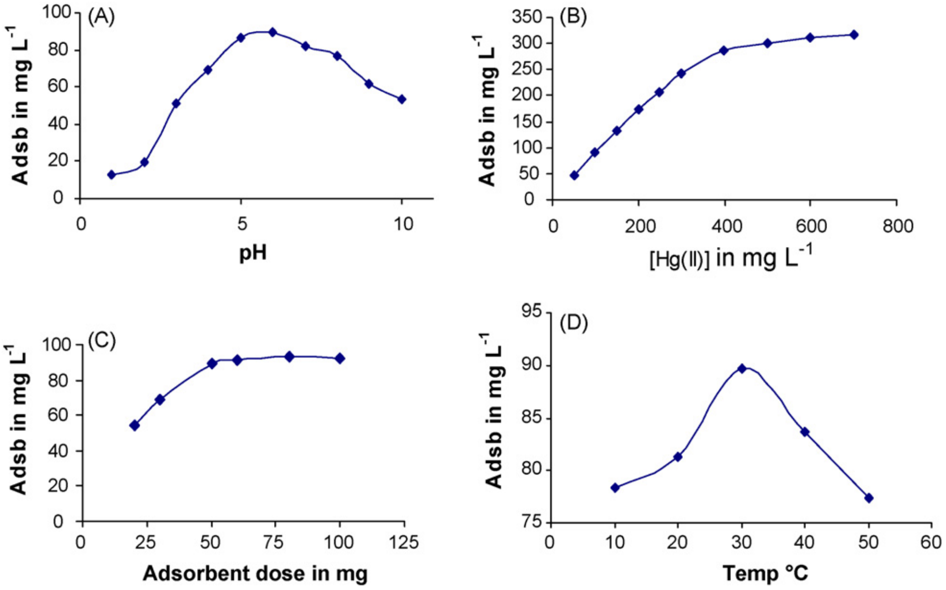


Fig. 4. Optimization of adsorption conditions (A) Adsorption at various pH at 100 mg L^{-1} initial Hg(II), adsorbent dose 50 mg, contact time 4 h at 303 K (B) Adsorption at various initial Hg(II) concentration,adsorbent dose 50 mg, pH 6, contact time 4 h at 303 K (C) Adsorption at various adsorbent dose at 100 mg L^{-1} initial Hg(II), pH 6, contact time 4 h at 303 K (D) Adsorption at various temperature, 100 mg L^{-1} initial Hg(II), adsorbent dose 50 mg, pH 6, contact time 4 h.

sity at 3620 cm^{-1} (due to non bonded free hydroxyl groups present in the ungrafted portion of CJ seed gum). It appears that besides complexation, there is significant contribution of nonelectrostatic interaction in the binding where the methylene groups at the graft chain play important role. Mercury species are held in between highly crosslinked grafted chains which interrupt the secondary interactions across the chains. Other peaks show only mild shift; >C=O stretching from 1730 to 1731 cm^{-1}, C–O stretching from 1020 to 1018 cm^{-1} O–H bending shifts 1402–1395 cm^{-1}. CJ-g-PAA-Hg showed significantly different spectrum in the range of 500–1000 cm^{-1} due to incorporation of mercury species.

3.1.2. *X-ray diffraction analysis*

The XRD spectrum (Fig. 2) of the CJ-g-PAA showed two prominent peaks at 2θ 10.05° (d = 4.0571, particle size (2.66 nm) (broad) and at 2θ 13.5° (d = 3.0212, particle size 4.69 nm) (a sharp crystalline peak) while other small broad peaks are visible at 2θ 18.1°, 19.6° and 21.8° (interplaner spacing being (d) = 2.2546, 2.0815 and 1.8783, particle size 10.3 nm, 5.28 nm and 3.93 nm) respectively. The appearance of broad peaks and small edges are due to lack of long-range crystallographic order of finite size effect. While in the mercury loaded sorbent, only two crystalline sharp peaks are visible at 2θ 7.6° (d = 5.3625, particle size 7.88 nm) and 2θ 11.62° (d = 3.5464, particle size 13.3 nm) while other peaks, originally present in the sorbent are lost that confirmed the loading of metal ion. It appears that on mercury sorption the overall crystallinity of the sorbent decreases while new crystalline peaks appear due to loaded mercury species.

3.1.3. *Scanning electron microscopy*

SEM picture of the CJ-g-PAA showed that it has flattened flaky appearance; however the graftcopolymer after mercury loading clearly shows small deposition of mercury species at the copolymer's surface. Mercury deposition on the surface of graftcopolymer was further evidenced by energy dispersive X-ray (EDX) spectrum (Fig. 3) where two peaks for mercury species are observed at 2.2 and 10 keV besides other peaks (for carbon oxygen and the standard used).

3.2. *Optimization of Hg(II) removal*

3.2.1. *Effect of pH on Hg(II) adsorption*

The effect of pH on Hg(II) removal by CJ-g-PAA was studied in the range of pH 1–10 (Fig. 4A) where maximum sorption was observed at pH 6.0. The removal increased up to pH 6.0 and then decreased. At 100 mg L^{-1} initial Hg(II) concentration, Hg(II) sorp-

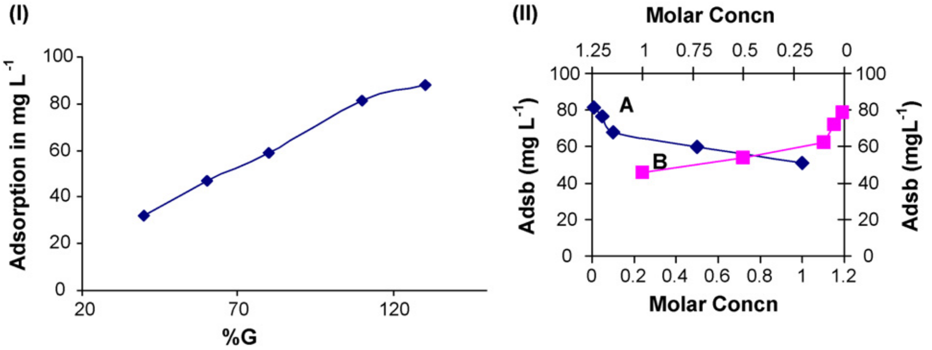


Fig. 5. (I) Effect of %G on the adsorption; (II): Effect of electrolytes ((A) NaCl; (B) Na_2SO_4) on the mercury adsorption at 100 mg L^{-1} initial Hg(II), pH 6, 120 rpm, 50 mg adsorbent dose, contact volume 20 mL, contact time 4 h, temperature 303 K.

tion increased from 12.83% to 89.73% on increasing the pH from 1 to 6, further increase in pH decreased mercury sorption and at pH 10 only 53.69% Hg(II) was sorbed. There are other biopolymeric material with carboxylic acid functionality which show maximum removal at pH 6 e.g. poly(γ-glutamic acid [20]. The variation in the removal of mercury by CJ-g-PAA with respect to pH can be elucidated by considering the surface charge of the sorbent material and the speciation of mercury (II). From the pH drift experiments, the PZC of the sorbent was found to be 4.9. Thus the surface charge of copolymer is positive at pH <4.9, is neutral at pH 4.9, and is negative at pH >4.9. At low pH values (<4.9), the number of negatively charged surface sites decreased and the number of positively charged sites increased, which did not favor the sorption of positively charged metal ions (Hg^{2+} and $Hg(OH)^+$)due to electrostatic repulsion. The increase in Hg(II) sorption in the pH range 2–6 is due to an increase in concentration of $Hg(OH)^+$ species, and to the fact that the solution pH influences the sorbent surface charge. At pH 6, deprotonation of –COOH groups at PAA grafts and increased formation of $Hg(OH)^+$ species facilitate an exchange of H^+ from –COOH groups of CJ-g-PAA over mercury species (Scheme 1).

3.2.2. *Effect of initial concentration of Hg(II)*

With the increase in the initial concentration of Hg(II) from 50–700 mg L^{-1} the removal of Hg(II) decreased from 96.42% to 45.22% at 0.05 g/20 mL adsorbent dose (Fig. 4B). Initially on increasing the initial Hg(II) concentration, due to availability of extra Hg(II) species, adsorption increased which on saturation of the adsorption sites gradually stagnates.

3.2.3. *Effect of adsorbent dose*

The percentage removal of Hg(II) increased from 53.89% to 92.36% on increasing the adsorbent dose from 20 mg to 100 mg in 20 mL of 100 mg L^{-1} Hg(II) solution at 30 °C, rpm 120 and 4 h contact time (Fig. 4C). This increase is because at higher dose of sorbent more binding sites are available for the binding.

3.2.4. *Effect of temperature*

The effect of temperature on the adsorption was studied in the range of 10–50 °C. Initial increase in the adsorption with the increase in the temperature (up to 30 °C), indicates that adsorption is endothermic nature. However at temperature >30 °C, a nominal decrease in adsorption was observed (Fig. 4D), which indicates some desorption is taking place at high temperatures.

3.2.5. *Effect of %G*

With increase in % grafting (in the sorbent sample) from 40% to 130%, the adsorption increased from 32.79% to 88.92% at fixed copolymer dose 0.05 g, pH 6.0, initial Hg(II) 100 mg L^{-1} temperature 30 °C, rpm 120 and 4 h contact time (Fig. 5I). Up to 80%G, the graft copolymer samples were partially water soluble at room temperature and neutral pH and hence their efficiency in mercury removal was quite low. The increase in the removal with increase in grafting ratio is due to increase in binding sites.

3.3. *Effect of electrolyte*

The presence of salts may interfere with the mercury adsorption. To understand the effect of electrolytes ions on Hg(II) binding, NaCl and Na_2SO_4 were added to the aqueous synthetic solution of mercury. With increase in concentration of both NaCl and Na_2SO_4 from 0.01 M to 1.0 M, removal decreased from 81.38 mg L^{-1} to 51.03 mg L^{-1} and from 78.57 mg L^{-1} to 45.71 mg L^{-1} respectively (Fig. 5(II)). The decrease in the removal on increasing the electrolyte concentration is due to competition between mercury species and ionic species furnished by electrolytes.

3.4. *Adsorption isotherm studies*

Adsorption data were fitted to the Langmuir and Freundlich isotherms [21]. The Langmuir isotherm is valid for monolayer sorption due to a surface of a finite number of identical sites and expressed in the linear form as under

$$C_e/q_e = b/Q_o + C_e/Q_o \tag{2}$$

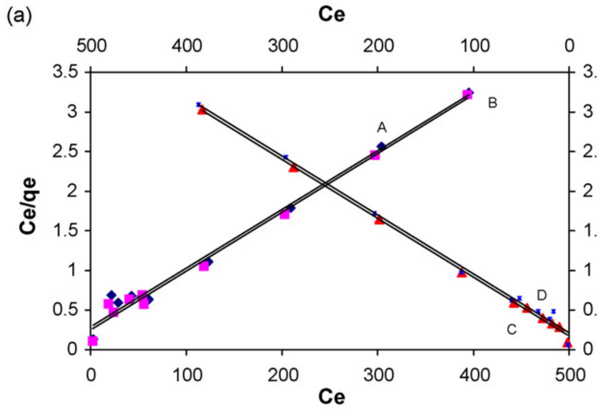
where C_e is the equilibrium concentration (mg L^{-1}) and q_e the amount adsorbed at equilibrium (mg g^{-1}). The Langmuir constants Q_o(mg g^{-1}) represent the monolayer adsorption capacity and b (L mg^{-1}) relates the heat of adsorption. The essential feature of the Langmuir adsorption can be expressed by means of R_L, a dimensionless constant referred to as separation factor or equilibrium parameter for predicting whether an adsorption system is favorable or unfavorable. R_L is calculated using the following equation

$$R_L = 1/(1 + bC_0) \tag{3}$$

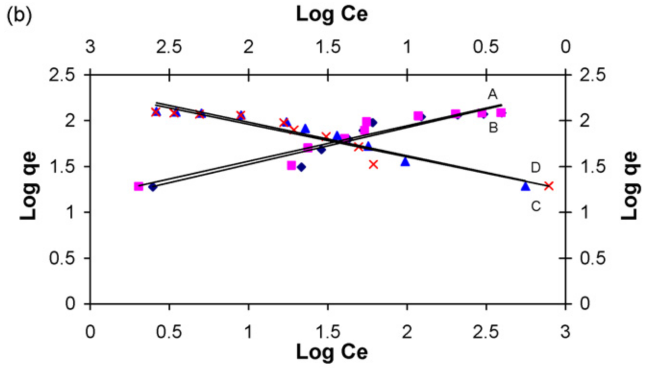
where C_0 is the initial Hg(II) concentration (mg L^{-1}). If R_L values lies between 0 and 1, the adsorption is favorable. The Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as:

$$\text{Ln}\, q_e = \text{Ln}\, K_f + 1/n\, \text{Ln}\, C_e \tag{4}$$

where K_f indicates adsorption capacity (mg g^{-1}) and n an empirical parameter related to the intensity of adsorption, which varies with



(A) $y = 0.0074x + 0.294$ $R^2 = 0.9863$ (B) $y = 0.0074x + 0.2517$ $R^2 = 0.99$ (C) $y = 0.0074x + 0.1712$ $R^2 = 0.9984$ (D)$y = 0.0074x + 0.2146$ $R^2 = 0.9933$



(A) $y = 0.404x + 1.1206$ $R^2 = 0.8995$ (B) $y = 0.388x + 1.1696$ $R^2 = 0.9095$ (C) $y = 0.3658x + 1.2524$ $R^2 = 0.94$ (D) $y = 0.3567x + 1.2473$ $R^2 = 0.9237$

Fig. 6. (a) Langmuir isotherms models for Hg(II) adsorption on CJ-g-PAA at different temperatures (A) 283 K (B) 293 K (C) 303 K (D) 313 K. (b) Freundlich isotherms for Hg(II) adsorption on CJ-g-PAA at different temperatures (A) 283 K (B) 293 K (C) 303 K (D) 313 K.

Table 4
Langmuir and Freundlich constants for the adsorption of Hg(II) by CJ-g-PAA.

Temperature (K)	Langmuir isotherm			Freundlich isotherm		
	$Q_{\max}$ (mg g^{-1})	b (L mg^{-1})	R^2	n	K_f (mg g^{-1})	R^2
283	135.14	0.0251	0.9863	2.48	13.20	0.8995
293	135.14	0.0293	0.9900	2.58	14.77	0.9095
303	135.14	0.0432	0.9984	2.73	17.88	0.9400
313	135.14	0.0345	0.9933	2.80	17.67	0.9237

the heterogeneity of the adsorbent. The greater the values of the $1/n$, better is the favorability of the adsorption.

Adsorption of Hg(II) by CJ-g-PAA was modeled by Langmuir (Fig. 6a) and Freundlich adsorption (Fig. 6b) models (Table 4) where the data fitted better to Langmuir isotherm indicating unilayer adsorption. Some of the reported mercury adsorbents have been compared with the present sorbent in Table 5. Present sorbent proved more efficient than most of the previously reported ones.

3.5. Sorption kinetics

% Removal of Hg(II) at a fixed adsorbent dose was monitored with time. The kinetics of Hg(II) removal by CJ-g-PAA indicated rapid binding of Hg(II) to the sorbent during first few minutes, followed by a slow increase until a state of equilibrium at 4 h was reached. No change in the uptake capacity was observed with further increase in equilibration time up to 4.5 h. The initial rapid phase may be due to increased number of vacant sites available at the initial stage, as a result there was an increased concentration gradient between adsorbate in solution and adsorbate in the adsorbent [22]. Generally, when adsorption involves a surface reaction process, the initial adsorption is rapid. Then, a slower adsorption would follow as the available adsorption sites gradually decrease. Kinetics [23] of sorption was modeled by the first order Lagergren equation and the pseudo-second-order equation at three different initial Hg(II) concentrations (100, 150 and 200 mg L^{-1}) using Eqs. (5)–(6). Because the above two equations cannot give definite mechanisms, another simplified model intra-particle diffusion model is tested using Eq. (7). The initial rates of intra-particle diffusion [24] can be obtained by linearization of the curve q_t vs $t^{1/2}$

$$\mathrm{Log}(q_e - q_t) = \mathrm{Log}\, q_e - k_L \times t/2.303 \quad (5)$$

$$t/q_t = 1/k' q_e^2 + t/q_e \quad (6)$$

$$q_t = k_{id} = t_{0.5} \quad (7)$$

where $k_{L,}$ k' and k_{id} are Lagergren rate constant (min^{-1}), pseudo-second-order rate constant of adsorption (g mg^{-1} min^{-1}) and intra-particle diffusion rate constant (mg g^{-1} min$^{0.5}$) respectively. q_e and q_t are the amounts of metal ion sorbed (mg g^{-1}) at equilibrium and at time t, respectively.

The data fit satisfactorily well both in pseudo-second-order model (where linear plots of t vs. t/q_t) and intra-particle diffusion model (where plots of q_t vs. $t^{0.5}$ yielded straight lines passing through the origin and the slope gives the rate constant K_{id}) up to 3 h after that data do not satisfy intra-particle diffusion model, indicating that adsorption in the beginning is diffusion controlled (Fig. 7). Pseudo-second-order rate constants were found to decrease from

Table 5
Comparison of Hg(II) adsorption capacity of CJ-g-PAA with other sorbents.

S.No.	Biosorbent	$Q_{\max}$ (mg g^{-1})	Reference
1.	Activated carbon from Ceiba pentandra hulls	25.88	[28]
2.	Fruit shell of *Terminalia catappa*	94.43	[29]
3.	Eucalyptus bark	33.11	[30]
4.	Extracellular biopolymer poly(γ-glutamic acid)	96.79	[31]
5.	Sago waste carbon	55.6	[32]
5.	Bicarbonate treated pea nut hull carbon	110	[33]
5.	*Cassia javanica* seed gum-graft-poly(acrylic acid)	135	Present study

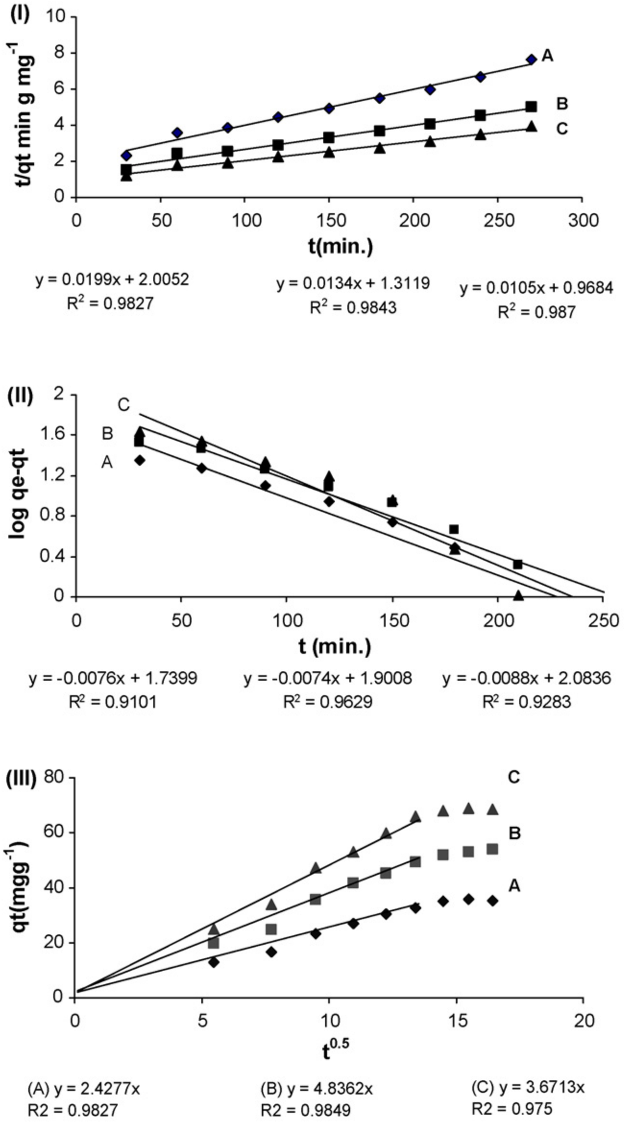


Fig. 7. Pseudo-second-order (I), Lagergren first order (II) and Intra-particle diffusion model (III) for the adsorption at 100 mg L^{-1}(A), 150 mg L^{-1} (B) and 200 mg L^{-1} (C) initial Hg(II) concentrations using 50 mg adsorbent dose, pH 6, temperature 303 K, rpm 120.

Table 6
Constants of kinetic models for Hg(II) adsorption on CJ-g-PAA at different Hg(II) concentration, pH 6, temperature 30 °C, rpm 120.

Hg(II) (mg L^{-1})	Lagergren R^2	k_L (min^{-1})	Pseudo-second-order R^2	k'(g mg^{-1} min^{-1})	q_e (mg g^{-1})	Intra-particle diffusion model R^2	k_{id}(mg g^{-1} $min)^{0.5}$
100	0.9101	4.4×10^{-4}	0.9827	1.97×10^{-4}	50.25	0.9827	2.4277
150	0.9629	2.3×10^{-4}	0.9843	1.36×10^{-4}	74.62	0.9725	3.6712
200	0.9283	2.3×10^{-4}	0.9870	1.36×10^{-4}	95.23	0.9849	4.8632

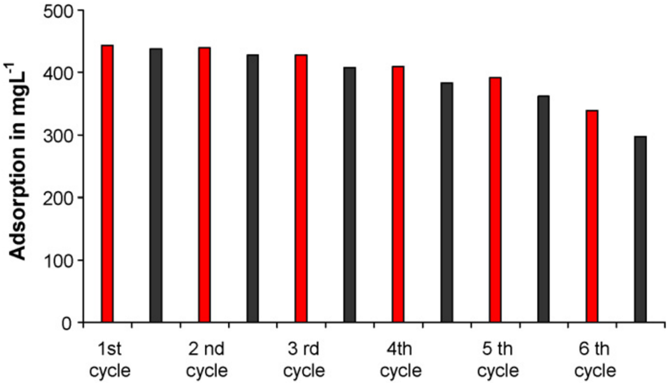


Fig. 8. Adsorption desorption cycles.

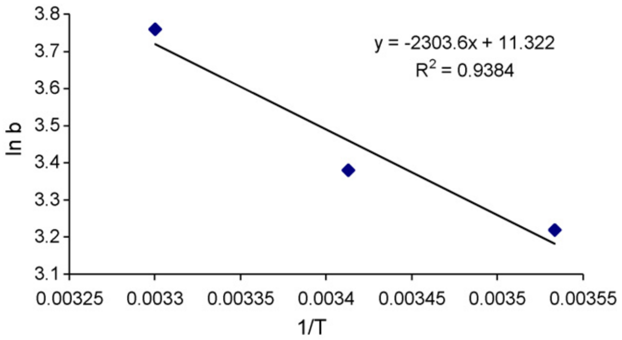


Fig. 9. Thermodynamic simulation of the adsorption of Hg(II) by CJ-g-PAA.

1.97×10^{-4} to 1.36×10^{-4} g mg^{-1} min^{-1}, for an initial increase in concentration from 100 mg L^{-1} to 200 mg L.$^{-1}$ Plot of q_t against $t^{0.5}$ reveals the extent of intra-particle diffusion influence in the sorption mechanism. Since diffusion is an endothermic process [25], the rate of sorption increases with increased solution temperature when intra-particle transport (pore diffusion) is the rate-limiting step.

The correlation coefficients (R^2) and the rate constants for CJ-g-PAA are summarized in Table 6 These results suggest in the beginning (up to 3 h) the adsorption is intra-particle diffusion controlled and there after adsorption kinetics of the Hg(II) is not diffusion controlled, but chemisorption. A good correlation of the kinetic data in this model justified the adsorption mechanism [26].

3.6. Desorption studies

Hg(II) loaded copolymer sample was stirred with 0.05N H_2SO_4 for 4 h (for the desorption) and was reused in the next cycle and adsorption desorption cycles were repeated for six times at 500 mg L^{-1} Hg(II) concentration, adsorbent dose 250 mg, pH 6, 120 rpm, contact time 4 h. It was observed that even in 6th cycle the adsorbent could adsorbed 67.88% Hg(II). Only 21% loss in adsorption ability of the copolymer was observed up to 6th cycle (Fig. 8).

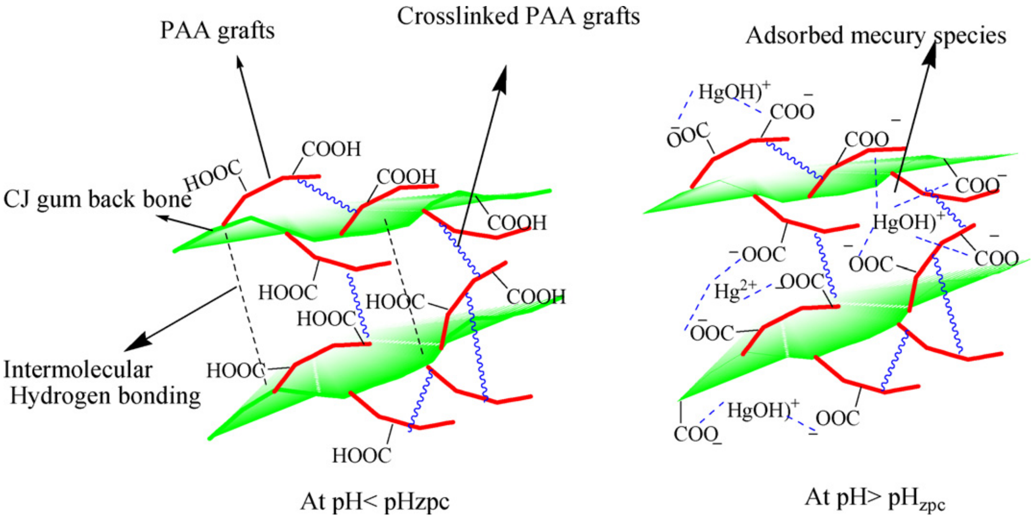
3.7. Adsorption thermodynamics

The values of thermodynamic parameters are relevant for the practical application of adsorption process [27]. Isotherm data related to adsorption of Hg(II) onto the CJ-g-PAA at various temperatures ranging from 10 to 30 °C were analyzed to obtain the values of thermodynamic parameters. The values of thermodynamic function ΔS and ΔH were evaluated using Vant Hoff's equation [28] which is given by:

$$\ln b = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{RT}\right) \tag{8}$$

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

where ΔG change in Gibbs free energy (J mol^{-1}), R universal gas constant (8.314 J K^{-1} mol^{-1}), T temperature (Kelvin), ΔH change in



Scheme 1. Schematic diagram of mercury sorption by the CJ-g-PAA at pH >pHzpc.

Table 7
Thermodynamic parameters of the adsorption by CJ-g-PAA.

Temp (K)	ΔG^0 (KJ mol^{-1})	ΔH^0 (KJ mol^{-1})	ΔS^0 (KJ mol^{-1})
283 10	−7.58	+19.15	+0.094
293 20	−8.23		
303 30	−9.48		
313 40	−9.20		

enthalpy (J mol^{-1}), b is Langmuir constant at temperature T, ΔS change in entropy (J mol^{-1} K^{-1}).

Ln b was plotted with $1/T$ (Fig. 9) and ΔS and ΔH were calculated from the intercept and slope respectively.

Negative values of ΔG indicated that the adsorption process was favorable and spontaneous in nature. It may be noted that with the increase in temperature from 10 to 30 °C the magnitude of ΔG increased from −7.58 to −9.48 kJ mol^{-1} (Table 7) implying an increased degree of spontaneity at a higher temperature.

Thus adsorption of Hg(II) onto the CJ-g-PAA was increased at higher temperature. The positive value of enthalpy change (ΔH) confirmed the endothermic nature of the adsorption process. Positive values of ΔS suggested good affinity of the metal ion toward the adsorbent and increased randomness at the solid-solution interface during the fixation of the metal ion on the active site of the adsorbent.

4. Conclusions

Microwave induced synthesis of CJ-g-PAA has been optimized by changing the various reaction parameters such as AA concentration, microwave power and microwave exposure time. The optimum CJ-g-PAA sample proved to be an efficient mercury ion sorbent. The sorption by the copolymer was pH dependent and pH 6 was found most suitable for the sorption. The sorption followed pseudo-second-order kinetic model which in the beginning was diffusion controlled. Adsorption isotherm and thermodynamic studies indicated unilayer and endothermic adsorption by the copolymer. The sorbent could be successfully recycled for six consecutive cycles without much loss in its sorbing capacity.

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