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Synthesis, characterization and mercury (II) removal using poly(vinylacetate) grafted guar gum

Vandana Singh*, Angela Singh, Preeti, Sneha Joshi, Tulika Malviya

Department of Chemistry, University of Allahabad, Allahabad 211002, India

*Corresponding author: Tel: (+91) 9415310942, (+91) 8127598952; E-mail: singhvandanasingh@rediffmail.com

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ABSTRACT

Guar gum-*graft*-poly(vinylacetate) (GG-g-PVA) has been synthesized and evaluated for Hg(II) removal from synthetic Hg(II) solution. The optimum performance GG-g-PVA sample (G_1) was synthesized using 0.25 g guar gum, 1.0×10^{-2} M $K_2S_2O_8$, 2.3×10^{-2} M ascorbic acid, 0.46 M vinyl acetate (VA), total reaction volume 25 mL, grafting time 1 h, and reaction temperature 35±0.5 °C. G_1 has been extensively characterized using FTIR, SEM, TGA, and DSC studies. pH drift experiments have shown that G_1 has pH_{zpc} of 2.8 and it was most efficient in removing Hg(II) at pH 6. The kinetic studies indicated that the removal involved chemisorption in the rate determining step and the sorption equilibrium was attained in 4 h. High Q_{max} (100 mg g^{-1}) of the copolymer indicated its suitability as a versatile and sustainable adsorbent for exceptionally high mercury recovery. Copyright © 2016 VBRI Press.

Keywords: Guar gum; grafting; poly(vinylacetate); mercury; adsorption.

Introduction

Synthetic polymer can be grafted onto natural biopolymers to obtain macromolecular materials of industrial significance **[1, 2]**. The structure diversity and multifunctional nature **[3]** of polysaccharides are the two important parameters which offer flexibility in designing new materials. Such materials have been exploited in water remediation **[4]**, drug delivery **[5]**, sensors **[6]**, and biomedical applications **[7]**. Vinyl modification **[8]** is a well established procedure that can transform a polysaccharide to a much conducive macromolecular material for biomedical **[9]** applications. The grafting leads to novel materials which not only retain the usefulness of native polysaccharides but also develop new properties of associated graft chains **[10]**. Considerable attention has been given to the chemical modification of polysaccharides where hydrophilic and hydrophobic vinyl monomers **[11]** are grafted through free radical graft copolymerization. These biodegradable and low cost graft copolymers with new properties find use in textiles, paper industry, agriculture, environmental remediation, and medical treatment.

Guar gum is a hydrophilic galactomannan polysaccharide. Its properties have been severely diversified by chemical derivatization, grafting, and network formation for a wide spectrum of end-uses. Graft copolymers based on guar gum and poly(N-vinyl-2-pyrrolidone) are reported for Fe^{2+} and Cr^{+6} removal **[12]**. Poly(methylacrylate) grafted guar gum **[13]** has been used for efficient capture Cr(VI) ions from aqueous solution. Guar gum based hydrogel **[14]** is known for Cu^{2+}sorption from aqueous solutions. Guar gum-graft-poly(acrylamide) copolymer has been used for the sorption of hexavalent chromium ion **[15]**. Vinyl acetate has been grafted on starch using persulfate/acetone sodium bisulphate **[16]**, and cobalt-60 irradiation **[17]**, while guar gum has been modified with polyvinyl acetate **[18]** using Ce(IV) as radical initiator. In general, vinyl grafting is known to change the solubility behavior of the seed gums.

The contamination of water resources due to the disposal of heavy metals from industries is of much concern over the world. Mercury is one of the most toxic metals among the heavy metals found in the environment **[19]**. It is desired to remove Hg(II) from wastewaters before it is transported and recycled in the ecosystem. Conventionally Hg(II) is removed by sulphide precipitation, ion exchange, alum/iron coagulation, and adsorption on activated carbon **[20]**. Among these methods, adsorption is considered to be most effective and economical method for the Hg(II) removal from wastewaters. High cost of activated carbon necessitates the design and development of low cost effective adsorbents.

In the present work, we aim to design Hg(II) sorbent from guar gum through its vinyl acetate modification. Guar gum is an abundant polysaccharide which contains metal chelating cis hydroxyl groups but its water solubility and easy biodegradation make it unsuitable for adsorption applications. The previously reported method of vinyl acetate grafting at guar gum used Ce(IV) initiation. The method required 4 h grafting time and resulted into low percentage grafting. Thus the method is not very attractive in view of high cost of Ce(IV), and the specific pH requirement of the reaction medium to achieve good grafting yield. Moreover, industrial use of Ce(IV) may lead to undesirable toxicity.

In view of reported good performance of persulfate-ascorbic acid redox system **[21]**, in the present study we have attempted to graft vinyl acetate onto guar gum using $K_2S_2O_8$/ascorbic redox initiator and optimized the grafting conditions while focusing Hg(II) removal by the copolymer. To understand the adsorption behavior of the copolymer, the kinetic and adsorption studies have also been carried out.

Experimental

Materials and measurements

Guar gum (GG), mercury (II) chloride (G.R), potassium iodide (G.R), potassium hydrogen phthalate (G.R), $K_2S_2O_8$ and ascorbic acid were all purchased from Merck, India. Rhodamine 6G, vinyl acetate (for synthesis) were purchased from Loba Chemie Pvt Ltd., Mumbai, India. Sodium thiosulphate (A.R) and gelatin (bacteriological) were purchased from central drug house (P) Ltd. India and Qualigens fine chemicals respectively. Double distilled water was used in all the procedures. The pH values were adjusted by the addition of 5 M HCl (G.R, Merck, India, 35%); or 1 M NaOH (Merck, India). EUTECH Instruments pH meter (model 510) was used for the pH measurements. Scanning Electron Microscopy (SEM) was employed to observe microscopic morphology of the copolymer using FEI ESEM QUANTA 200 instrument with an accelerating voltage of 25 kV. The samples were gold coated to avoid charging. FTIR was done on Perkin Elmer Infrared version 10.03.06 spectrophotometer. UV/Vis Spectrophotometer UV 100, Cyber lab, USA was used to determine mercury concentrations in the solution. TGA was done using SETARAM TGA analyzer (model SETSYS Evolution 2400). About 15 mg samples were heated at the rate of 10 ºC min^{-1} in Pt basket 170 µl crucible from 25 ºC-600 ºC using Ar as carrier gas.

Grafting procedure

The copolymer samples of different % G were synthesized by thermal grafting method for which known volumes of vinyl acetate and ascorbic acid were added to 25 mL of guar gum aqueous solutions of known concentrations in different sets of experiments. These reaction mixtures were thermostated on a thermostatic water bath at 35 ± 0.2 ºC. After 30 min a calculated amount of $K_2S_2O_8$ was added to the reaction mixtures and this time of persulfate addition was considered as zero time. Graft copolymerization in each reaction set was allowed for 1 h. Grafted samples of different % grafting were separated from the different sets of experiments by pouring the respective reaction mixtures to excess of acetone. The copolymer samples thus obtained were finally extracted with acetone in a soxhlet apparatus for 4 h to dissolve all the homopolymer and the copolymers were finally dried under vacuum at 50 °C for >24 h to a constant weight.

The degree of the grafting was determined by the equation (1).

$$\text{Percentage of grafting (\%G)} = \frac{W_g - W_0}{W_0} \times 100 \qquad (1)$$

Various reaction parameters such as vinyl acetate concentration, persulfate concentration, ascorbic acid concentration, and guar gum were varied to obtain different copolymeric products having different % G and different performance in removing mercury from Hg(II) aqueous solution.

Hg(II) removal

Hg(II) adsorption by the GG-g-PVA was studied using batch adsorption method. The stock solution of Hg(II) (1000 mg L^{-1}) was prepared by dissolving an appropriate amount of $HgCl_2$ in deionized double-distilled water. Batch adsorption experiments were carried out using the copolymer as adsorbent on a temperature-controlled incubator shaker set at 100 rpm (the rpm variation showed optimum result at 100 rpm; rpm optimization is not shown) and maintained at 30 °C. The adsorbent (50 mg) was left in an incubator shaker with 20 mL of 100 mg L^{-1}solution for a desired time period, and then filtered through a Whatman 0.45 mm filter paper. After suitable dilution, the remaining Hg(II) was estimated spectrophotometrically (at λ575 nm) using Rhodamine 6G dye in the presence of iodine buffer **[22]**. The amount of metal ions adsorbed per gram of the copolymer was calculated by the difference between the initial and final Hg(II) concentrations using the equation (2).

$$q_e\,(\text{mg g}^{-1}) = \frac{C_0 - C_e\ (\text{mg L}^{-1}) \times \text{V (L)}}{\text{W (g)}} \qquad (2)$$

where, q_e is the amount of the metal ion adsorbed (mg g^{-1}), C_0 is the initial concentration of the metal ion (mg L^{-1}), C_e the equilibrium concentration of the metal in solution (in mg L^{-1}), V the volume of the solution used (L), and W the weight of the copolymer used as adsorbent. All the adsorption experiments were performed in triplicates and the results presented are the average of three readings.

To optimize the sorption, different processes parameters were varied, one at a time while keeping the others fixed. pH variation (pH 1 to pH 8) was done for 100 mg L^{-1}Hg(II) solutions using 50 mg copolymer as adsorbent at 100 rpm, 30°C temperature, and 4 h contact time, while adsorbent (copolymer) doses of 20-100 mg were contacted for 4 h with 20 mL of 100 mg L^{-1} Hg(II) solutions at 100 rpm, 30°C and pH 6. Adsorption at various initial Hg(II) concentrations, ranging from 25 to 350 mg L^{-1} was studied at pH 6, 50 mg copolymer dose, 4 h contact time, and 100 rpm at 30 and 40 ºC. The kinetic study was performed at 150 and 200 mgL^{-1} initial Hg(II) concentrations, using 50 mg of copolymer dose, pH 6, rpm 100, and temperature 30°C.

Zero-point charge determination

All the synthesized copolymer samples were screened for the Hg(II) adsorption at 30 ºC, using 100 rpm, pH - 6, contact time = 4 hours, adsorbent dose = 50 mg. pH_{zpc} of optimum performance sample (G_1) was determined (**Table 1**). To carry out pH drift experiments, 500 mL of 0.005 M solution of $CaCl_2$ was made CO_2 free by 30 min boiling.The solution was cooled to room temperature and its small aliquots (20 mL) were adjusted to different pH values, ranging from pH 2 to pH 10 (using either 2.5 M HCl or 5 M NaOH). Each of these pH adjusted $CaCl_2$

aliquots were separately equilibrated with 50 mg of the copolymer for 48 h in capped vials. The final pH of these solutions were measured and plotted against their respective initial pH values. The pH at which this curve crosses the $pH_{initial} = pH_{final}$ line was taken as pH_{zpc} **[23]**.

Table 1. Optimization of Grafting by considering the Hg(II) uptake capacity of the copolymer samples at fixed total reaction volume 25 mL, grafting time 1 h, and temperature 35ºC; Hg(II) adsorption of the copolymer samples was monitored at 30 ºC, 100 rpm, pH-6, contact time = 4 h, adsorbent dose =50mg.

Sample	GG (g)	VAC (M)	$K_2S_2O_8$ (M)	AA (M)	%G	% Hg(II) removal
G_1	0.25	0.46	1.0×10^{-2}	2.3×10^{-2}	66	98.62
G_2	0.25	0.46	1.2×10^{-2}	2.3×10^{-2}	70	88.26
G_3	0.25	0.46	1.4×10^{-2}	2.3×10^{-2}	76	87.71
G_4	0.25	0.46	1.6×10^{-2}	2.3×10^{-2}	78	86.64
G_5	0.25	0.46	1.8×10^{-2}	2.3×10^{-2}	78.5	86.42
G_6	0.25	0.46	1.0×10^{-2}	1.3×10^{-2}	84	51.66
G_7	0.25	0.46	1.0×10^{-2}	3.3×10^{-2}	36	96.62
G_8	0.25	0.46	1.0×10^{-2}	4.3×10^{-2}	32	95.02
G_9	0.25	0.65	1.0×10^{-2}	2.3×10^{-2}	57	88.26
G_{10}	0.25	0.86	1.0×10^{-2}	2.3×10^{-2}	78	90.4
G_{11}	0.20	0.54	1.0×10^{-2}	2.3×10^{-2}	42.5	88.26
G_{12}	0.15	0.54	1.0×10^{-2}	2.3×10^{-2}	80.6	73.1
G_{13}	0.15	0.54	1.0×10^{-2}	2.3×10^{-2}	90	70.1

Results and discussion

Different grades of copolymer samples (G_1-G_{13}) having different % G and performance in terms of mercury uptake were synthesized by varying the grafting process parameters such as [$K_2S_2O_8$], [Ascorbic acid], [VA], and [guar gum] (**Table 1**). Persulfate/ascorbic acid redox system proved very efficient in grafting vinyl acetate onto guar gum yielding copolymer sample (G_{10}) having % grafting as high as 90 %, and the grafting did not require any inert atmosphere. However, the copolymer sample (G_1) which had moderate % G (66%) showed optimum performance in mercury removal from synthetic mercury solutions **(Table 1).** This observation indicated that the hydroxyls groups of guar gum are mainly responsible for the mercury binding and not the vinyl grafts. The sample having 90 % grafting is less efficient as it has poly(vinyl)acetate graft chains at most of the hydroxyls site at the guar gum. This assumption is in conformity with the results from the pH drift experiments. The pH_{zpc} of G_1 has been calulated to be 2.8 (**Fig. 1S**). Thus at pH < 2.8 the material has a positive surface charge, while at pH higher than this the copolymer's surface charge is negative, and at pH 2.8, the surface of G_1 is electrically neutral. On the basis of the stability constant calculations it has been revealed **[24]** that in the presence of $Cl,^-$ the predominant Hg species **[25]** at pH > 4 are the nonionic species such as $Hg(OH)_2$ and HgClOH while at pH < 4:0 it is $HgCl_{2.}$ At the pH of mercury removal (pH 6) in the present study, the surface charge of G_1 is likely to be negative, while mercury species are nonionic. Thus involvement of electrostatic forces in mercury uptake is unlikely rather the adsorption of the mercury species through hydrogen bonding interactions between the hydroxyl group at the ungrafted segment of guar gum and hydroxyl species of mercury can be assumed in the present study.

Characterization

Fourier transform infrared spectroscopy**:** FTIR spectrum of guar gum (**Fig. 1**(**A**)):IR (KBr): ν = 3395 (s) (O-H stretch primary hydroxyl group at the polysaccharide sugar units); ν_{sym}= 2926 (w) (C-H), ν_{asym} = 2853 (w) (C-H); ν = 1633 (s) (ring stretch.) **[26]**; ν = 1200-900 (fingerprint carbohydrates) **[27]**; ν = 771, 1217, and 1403 cm^{-1}, (CH_2bendings); ν = 1085 (s) C-O str.); ν = 668 (s) cm^{-1} (C-OH out of plane bending)

The FTIR spectrum of G_1 indicated that the grafting has taken place at guar gum's hydroxyl groups. **Fig. 1(B)** ν = 3366 (s) (O-H stretch.), ν = 1736 (s) (C=O Ester str) is seen masked with ring stretching vibration ν = 1631 cm^{-1} ν_{sym} = 769 (s) cm^{-1} (CH_2 bending at guar gum and at PVA grafts present at guar gum backbone).

FTIR spectrum of mercury loaded G_1 show significant shifting of O-H stretching which indicated its involvement in the binding: peaks are seen at ν = 3405 (s) (O-H stretch), ν = 1736 (s) (C=O Ester str), ring stretching vibration ν = 1631 cm^{-1} ν_{sym} = 769 (s) cm^{-1} (CH_2 bending).

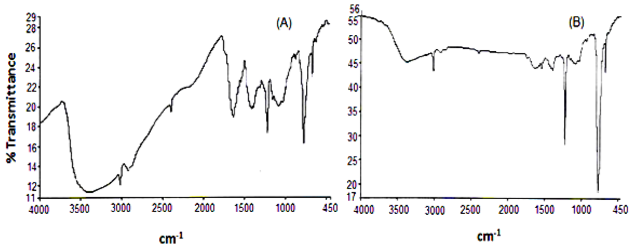

Fig. 1. FTIR of GG (A); and G_1(B).

Scanning electron microscopy

SEM picture of GG has been compared with the SEM picture of G_1 in **Fig. 2(A)**. The surface topology of GG is quite different than that of G_1 **Fig. 2(B)**. GG has slightly elongated scattered bulk particles, while the G_1 showed a stiff surface with somewhat scaly appearance. Deposition of Hg(II) at guar-graft-poly(vinylacetate) is evident in the SEM picture of Hg(II) loaded copolymer sample G_1-Hg **(Fig. 2(C)**, where deposited mercury is clearly visible at the surface of the copolymer.

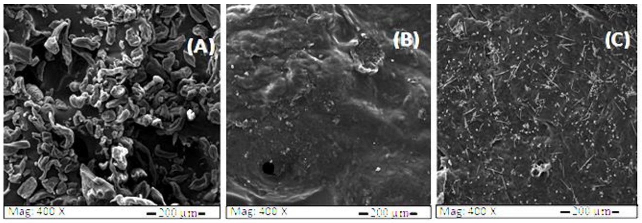

Fig. 2. SEM picture of (A) GG; (B) G_1, (C) G_1-Hg(II).

Thermo gravimetric analysis (TGA) of G_1

The thermal analysis of G_1 has been done in comparison with the GG and G_1-Hg. TGA-DTG curves of the samples are shown in **Fig. 3**, which evidenced the grafting very clearly. The thermo gravimetric analysis of GG **Fig. 3(A)** showed a weight loss of 13 % corresponding to a peak observed at 84°C in DTG curve, while another peak at 294ºC corresponded to a weight loss of 62%, where the degradation might have involved dehydration, and chain scissions. The first weight loss can be attributed to the loss of adhered moisture while second loss is due to thermal degradation of the GG.

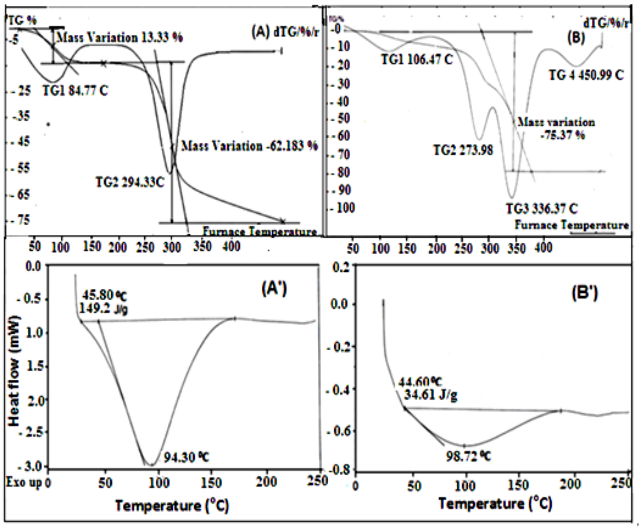

Fig. 3. TGA/DTG curves of GG (A) and G_1(B); DSC curves of GG (A'), G_1 (B').

G_1 (**Fig. 3(B)**) showed three stage thermogram, the first 12 % weight loss corresponded to a peak at 106 °C, which can be attributed to the loss of moisture and residual solvent (used for precipitation of G_1). A second peak at 273 ºC can be assigned to the loss of the GG back bone while third peak may be due to the loss of poly(vinyl)acetate (PVA) grafts. A total weight loss of 75 % takes place in the organic region. A small peak at 450 ºC corresponds to 18 % loss which may be attributed to the cross linked copolymer.

Differential scanning calorimetry (DSC)

The DSC thermograms of GG and G_1 are given in **Fig. 3(A')** and **3(B')** respectively. GG showed one endothermic peak at 94ºC, which corresponded to vaporization of water contents. While G_1 showed corresponding endothermic peak at 98 ºC, indicating that the grafting of GG increased the vaporization temperature. It is clear that the grafting increased the peak temperature of endothermic peak. Compared to the sharp curve of GG, the peak of G_1 became broader; the widening of peak depicts the delay in degradation of grafted guar gum **[28]**. The Hg(II) loading at $G_1$was further established by DSC thermogram which show endothermic peaks at 43 ºC, 81ºC and 228 ºC, it is evident that mercury loading sharpened and shifted the endothermic peak at 94 ºC of guar to 81 ºC. Other two peaks may be related to change in state of mercury species **(Fig. 2S)**.

DSC study revealed that the T_g of GG is higher (45 ºC) than the G_1(44ºC), this can be attributed to more flexibility of the vinyl acetate grafts as compared to GG, so the G_1 need less energy to pass from glassy state to rubbery state **[29, 30]**. On mercury loading, T_g of the G_1 shifted to 35 ºC **(Fig. 2S)**.

Adsorption kinetics

The kinetic study indicated an initial rapid Hg(II) adsorption by G_1which slowly decreased. In first 30 min > 70 % adsorption was completed. A state of equilibrium was reached within 4 h and no further uptake was observed up to 6 h. The initial rapid phase may be attributed to the higher availability of vacant sites at the initial stage which resulted in to an increased concentration gradient between adsorbate in solution and adsorbate at the adsorbent **[31]**. Initial rapid adsorption is characteristics of surface reaction process, which eventually slowed down as the available adsorption site gradually decreased. Kinetic data have been modeled **[32]** by the first order Lagergren equation, pseudo-second-order equation and the second order equation shown below as equations. (3) – (5), respectively **(Fig. 4)**.

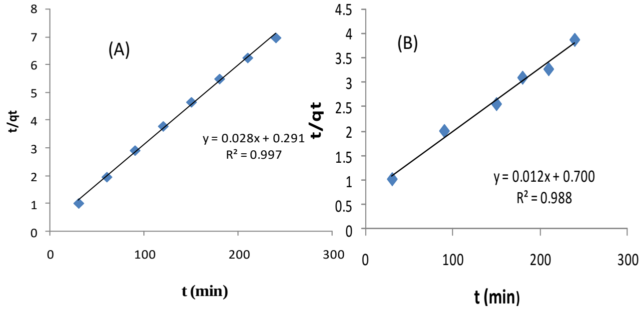

Fig. 4. Pseudo second order kinetic models for the adsorption at 100 mg L^{-1} (A) and (B) 200 mg L^{-1}initial Hg(II) concentration, adsorbent dose 50 mg, contact volume 20 mL, rpm 100, pH 6, contact time 4 h, temperature 30 ºC.

$$\text{Log}\ (q_e\text{-}q_t) = \text{Log}\ q_e - k_L \times t/2.303 \quad (3)$$

$$t/q_t = 1/k'\, q_e^2 + t/q_e \quad (4)$$

$$1/q_t = 1/q_e + k_2 t \quad (5)$$

where, K_L is the Lagergren rate constant of adsorption (min^{-1}); k' the pseudo-second-order rate constant ($gmg^{-1}min^{-1}$) of adsorption, and k_2 the second order rate constant ($g\ mg^{-1}\ min^{-1}$); q_e and q_t are the amounts of metal ion adsorbed ($mg\ g^{-1}$) at equilibrium and at time t, respectively. The kinetic data of Hg(II) sorption fitted best in to pseudo second order kinetic equation, where linear plot of t/q_t vs t was obtained. The correlation coefficient (R^2) and the rate constant at 100 mg L^{-1} initial Hg(II) concentration were computed to be 0.997 and 2.6×10^{-3} g mg^{-1} min^{-1} respectively. While rate constants at 200 mg L^{-1} initial Hg (II) concentration was 2.0 x 10^{-4} (R2 = 0.988). The equilibrium rate constant of pseudo second-order model ($k^{'}$) decreased with the increase in initial concentrations of Hg (II), similar observation was previously made by Bash and Murti **[33].** The decrease in the k' with increasing Hg (II) concentrations may be explained as below. The eq. (3) can be changed into equation (6) expressed as:

$$k' = \frac{F}{q_e(1\text{-}F)t} \quad (6)$$

where, F is the fraction of q_t/q_e, and t is the time to reach q_t, so k' can be expressed as a function of uptake fraction F (q_t/q_e) and t. Equation (5) indicates that k' is inversely related to t, and therefore, the decrease of k' with increasing initial concentrations of mercury only suggests that a longer time will be needed to realize the specific uptake fraction of mercury at higher concentrations, while the adsorption rate (dq_t/d_t) at contact time t still increased as the initial concentration of mercury increased.

Optimization of adsorption

Effect of pH: The Hg(II) sorption by G_1 was studied in the pH range of pH 2 to pH 7. The sorption of Hg(II) was low (12%) at pH 2. It sharply increased (88 %) as the pH was raised to pH 3, thereafter the increase was slow and 97% Hg(II) removal was possible at pH 6. Further increase in pH decreased the adsorption (**Fig. 5(A)**). This can be well explained by the surface charge of the copolymer. pH drift experiments revealed that the pH_{zpc} of the G_1 is 2.8 **(Fig. 2S)**. Its surface will be positively charged below this pH and it will acquire negative charge at pH > 2.8. At pH 2, the copolymer surface is likely to have positive surface. The major mercury species is also positively charged (Hg^{2+} at pH 2), and therefore the adsorption was significantly low, however as the pH was raised to pH 3, the copolymer surface acquires negative charge which attracts the Hg^{2+} so the adsorption was enhanced significantly. At pH > 4, the adsorption did not seem to govern by electrostatic attraction as now major mercury species is $Hg(OH_2)$. It appears that hydrogen bonding with the copolymer's surface hydroxyls becomes the major factor which now controls the adsorption, though $Hg(OH)^+$ species also exist in small amount which is electrostatically held at the negative surface of the copolymer. Thus slow increase in adsorption after pH 4 is explainable.

Effect of adsorbent dose

The effect of copolymer(G_1) dose on the adsorption was studied in the range of 25 to 100 mg at 100 mg L^{-1} initial Hg(II) concentration,100 rpm, pH 6, and temperature 30 ºC **(Fig. 5(B))**. The adsorption increased with the increase in adsorbent dose due to the availability of extra binding sites at higher doses. 50 mg adsorbent dose was selected for further optimization and kinetic studies as there was only nominal increase (in adsorption) beyond 50 mg adsorbent dose.

Effect of initial Hg(II) concentration

The increase in initial Hg(II) concentration from 25 to 350 mg L^{-1} increased the adsorption from 10 mg L^{-1} to 62 mg L^{-1} respectively **(Fig.5 (C))**. This increase may be attributed to the availability of extra Hg(II) species at higher concentrations. However, with increase in Hg(II) concentration, % adsorption decreased (slowly up to 200 mgL^{-1}, sharply afterwards) due to decrease in ratio of adsorbent to adsorbate.

Adsorption isotherms

Adsorption equilibrium data were fitted to the linear forms of Langmuir and Freundlich adsorption isotherms **[34]**, that may be expressed as equation (7) and equation (8) respectively.

$$C_e/q_e = 1/bQ_o + Ce/Q_o \tag{7}$$

$$\text{In } q_e = \text{In } K_f + 1/n \text{ In } C_e \tag{8}$$

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. K_f indicates adsorption capacity and n an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. The greater the values of the 1/n, better is the favorability of the adsorption. The higher fractional value of 1/n ($0<1/n<1$) signifies that the surface of the adsorbent is heterogeneous in nature.

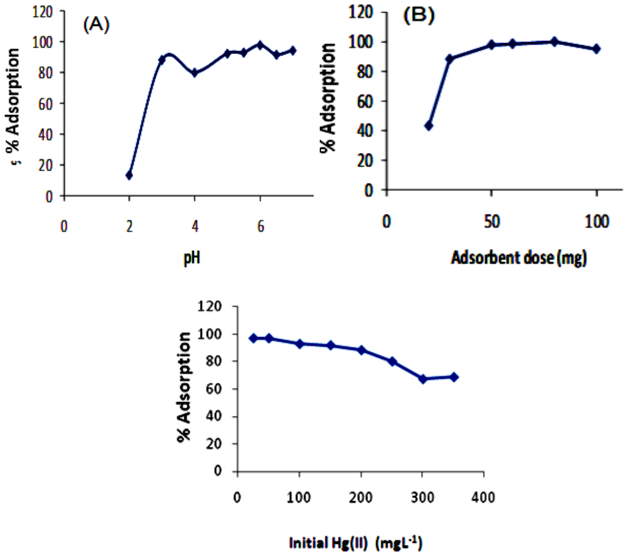

Fig. 5. Optimization of the adsorption conditions.

R_L, the essential feature of the Langmuir adsorption is a dimensionless constant which is referred as separation factor or equilibrium parameter for predicting whether an adsorption system is favorable or unfavorable. R_L can be calculated using the equation (9).

$$R_L = 1/(1+ bC_0) \tag{9}$$

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 equilibrium data better conformed to Langmuir model than the Freundlich model which indicated surface homogeneity of the adsorbent and unilayer adsorption. From Langmuir isotherm Q^0 was calculated to be 100 mg g^{-1} indicating that the adsorbent had a significantly high capacity to remove Hg(II) ions **(Fig. 3S)**. The values of Langmuir constant (b) at 30 ºC and 40 ºC were calculated to be 0.1190 and 0.1388 respectively that indicated the adsorption process was endothermic in nature.

At 100 mg L^{-1}Hg(II) at 30ºC, R_L was calculated to be 0.0775, indicative of the adsorption as being favorable.

Table 1. Langmuir and Freundlich constants at 30 ºC and 40 ºC at pH 6, rpm 100, G_1dose 50 mg, contact volume 20 mL, contact time 4 h.

Temperature	**Langmuir isotherm**			**Freundlich isotherm**		
(^{0}C)	Q_{max}	b **(Lmg^{-1})**	**R^2**	n	K_f	**R^2**
30	100	0.1190	0.985	2.390	15.38	0.935
10	41.66	0.1388	0.957	5.263	15.63	0.730

Conclusion

The persulfate/ascorbic acid redox initiator proved very useful in grafting vinyl acetate onto guar gum where good % G (90%) could be achieved in 1h grafting time. The grafting could be done in air and afforded much superior yield than the previously reported Ce (IV) initiated grafting which requires 4 h to complete. The copolymer sample having 60 % G showed very good ability to capture Hg(II) from synthetic mercury solutions, where the adsorption equilibrium could be achieved in just 4 h time and maximum adsorption capacity of the copolymer was found to be 100 mg g^{-1}. However, the copolymer samples of 90% G were less efficient as the metal chelating hydroxyls are less available due to the presence of poly(vinyl acetate) grafts at these sites. The adsorption followed a pseudo second kinetics with a rate constant of 2.6 × 10^{-3} g mg^{-1}min^{-1}at 100 mgL^{-1} initial Hg(II) concentration. At the optimum pH (pH 6), the involvement of only physical forces is indicated for the adsorption process.

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Author’s contributions

Conceived the plan: V S; Performed the expeirments: AS, SJ; Data analysis: V S, A S; Preeti, TM, Wrote the paper: VS, AS, TM. Authors have no competing financial interests.

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Supporting information

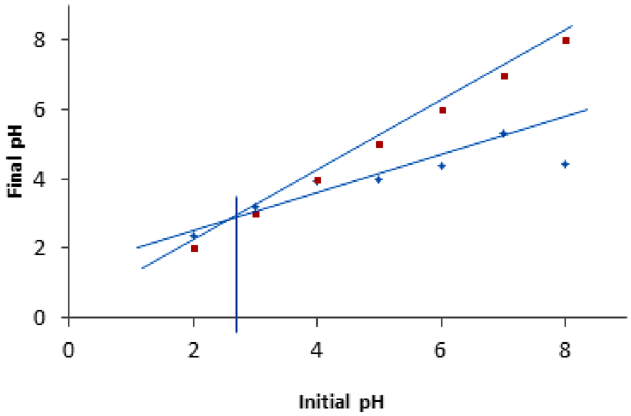

Fig. 1S. Determination of zero-point charge of the G_1.

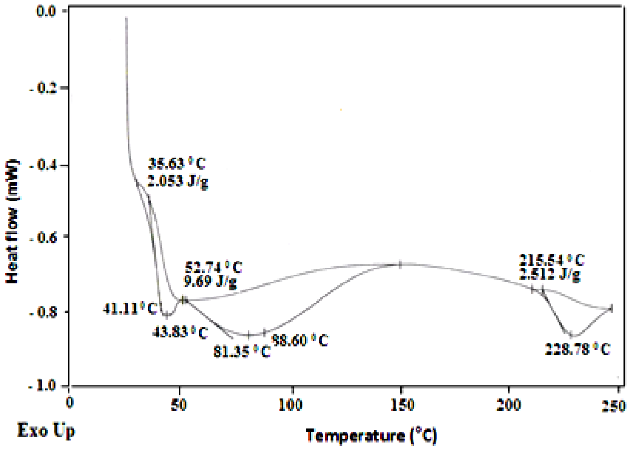

Fig 2S. DSC of G_1-Hg(II).

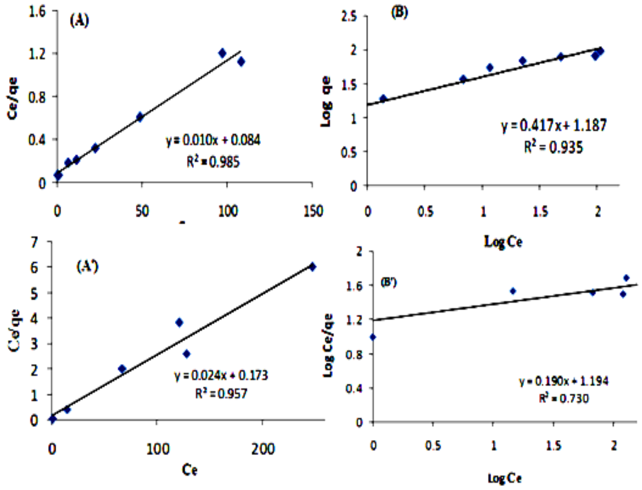

Fig. 3S. Langmuir (A) and Freundlich (B) isotherms at 30 ºC; Langmuir (A') and Freundlich (B') isotherms at 40ºC.