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Guar-Graft (Vinylacetate-Co-Ethylacrylate-Co-Acrylamide): A Potential Hg(II) Adsorbent

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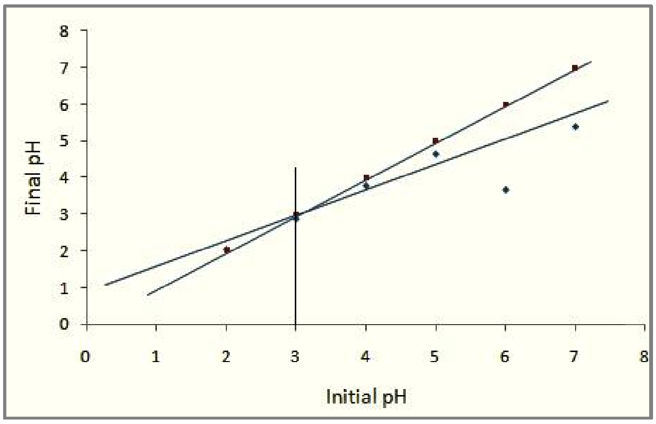
ABSTRACT

With the aim to explore new efficient, low-cost and environment-friendly adsorbent for water purification, a ternary graft copolymer(GG-g-poly-(VAC-co-EA-co-AAm) has been synthesized. Vinyl acetate and ethyl acrylate (VAC+EA) with comonomer acrylamide (AAm) were grafted onto guar gum using potassium persulfate/ascorbic acid (KPS/AA) redox initiator.The concentration of acrylamide was varied (from 0.08 to 0.2 M) at the pre-optimized conditions for binary grafting (vinyl acetate= 0.46 M, ethylacrylate=0.38 M, potassium persulfate=1.0x10^{-2} *M, ascorbic acid=2.3x0*$^{-2}$ *M, grafting time=1 h) at 35℃. The optimum ternary grafting percentage was obtained when the molar ratio of vinyl acetate, ethyl acrylate, and acrylamide was for 0.46: 0.38: 0.12. The synergistic effect of the ternary monomers(VAC+EA+AAm)were advantageous for achieving better % G(106%) as compared to % G for the unitary(VAC) and binary (VAC+EA) vinyl monomer/s. The graft copolymers were characterized by Fourier transform infrared spectroscopy (FTIR), Thermo gravimetric analysis (TGA) and Scanning electron microscopy (SEM).The ternary copolymer (GG-g-poly-(VAC-co-EA-co-AAm) was found efficient in Hg(II) uptake.*

Graphical Abstract



Determination of zero-point charge of the TC$_{3.}$

Keywords: Guar gum, Vinylacetate, Ethylacrylate, Acrylamide, Grafting, Hg(II) removal.

INTRODUCTION

Biopolymers find tremendous use in the development of new materials because of their greener and multifunctional nature. The natural polymers besides being renewable possess many unique properties such as non-toxicity [1], biodegradability, biocompatibility and multifunctionality[2, 3]. Nevertheless, the biopolymers in their native forms cannot cope with the diversity of materials required by the modern industry. Many biopolymers have been used for the ecological and environmental protection after suitable derivatization [4-7]. The presence of metal chelating hydroxyl groups in polysaccharides is responsible for their affinity for metal ions but this affinity does not guarantee for an effective removal of heavy metals as the metal adsorption processes may be influenced by several other factors, such as the number, accessibility, and the chemical nature of the active sites. This limitation can be alleviated by the suitable chemical modification of polysaccharides. Moreover, the thermo sensitivity and water solubility of the common polysaccharides can further limit their application as metal ion sorbent. The grafting of synthetic polymers can circumvent these limitations as it can induct specific required properties in polysaccharides [8-11], while still preserving the original properties of the native polysaccharide. Chemical grafting of selected monomers bearing metal binding moieties is another effective approach to improve the functional properties of a natural biopolymer and to boost their adsorption capacity. Out of various natural polysaccharides, guar gum is most popular because of its natural abundance, low cost, and biodegradability. It is bestowed with the abundant hydroxyl groups alongits chain and has emerged as an ideal raw material for the fabrication of absorbents for toxic ions.[12, 13] Comonomers and coagents are usually required for improving the grafting percentage and for minimizing the side reactions. Since the single monomer grafting does not satisfy the production requirements, multi-monomers graft copolymerization [14-16] have been attempted where higher grafting percentage and grafting degree were obtained in comparison to single-monomer graft copolymerization.

The modern civilization is facing severe challenges from toxic materials in water bodies [17-20] especially mercury [21-23] which is a serious water pollutant that enters human body through the food chain. Conventionally mercury can be removed through precipitation, ion exchange, solvent extraction and adsorption on activated carbon or synthetic polymers [24-28]. Among these, the adsorption [29, 30] is most attractive technique as it can be used without having any detrimental effect on the environment. It exhibits high efficiency even with low metal concentrations and this method of mercury remediation has low cost, easy operation, and good metal recovery.

Very recently, we prepared a new adsorbent by free radical grafting onto guar gum from the binary mixture of vinyl acetate (VAC) and ethyl acrylate (EA) [31]. The extent of vinyl acetate grafting increased in the presence of the ethyl acrylate (EA) comonomer. It was found that the maximum percentage grafting was obtained when the molar ratio of VAC to EA was approximately 0.46:0.38 M. On adding EA as a comonomer, EA-VAC copolymer was formed before the two monomers were grafted onto GG. The use of binary mixture for grafting could significantly enhance the VAC grafting degree besides suppressing the degradation of GG backbone.

As an extension to our previous work, in the present study we have modified the guar gum by the free radical graft copolymerization of vinyl acetate and ethyl acrylate (VAC+EA) with comonomer acrylamide (AAm) using KPS/AA as redox initiator. The prepared ternary chelating graft copolymer may behave as an efficient adsorbent for mercury removal due to its higher molecular weight and peculiar functional groups. The effect of acrylamide as a comonomer was studied in context with the % grafting and the optimum grafting copolymer has been evaluated as Hg(II) adsorbent.

MATERIALS AND METHODS

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), ethylacrylate (EA), and acrylamide (AAm), were purchased from Lobachemie 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 5 M NaOH (Merck, India).UV/Vis Spectrophotometer UV100, Cyber lab, USA was used to determine mercury concentrations in the solution. FTIR was done on KBr pellets using Perkin Elmer instrument (Version 10.0 3.06). TGA was done using SETARAM TGA analyzer (model SETSYS Evolution 2400). About 15 mg samples were heated at the rate of 10°C min^{-1} in Pt basket 170 μL crucible from 25°C-600°C using Aras carrier gas. SEM was recorded using a Nova Nano FE-SEM 450 (FEI) Field Emission Gun SEM.

Purification of the GG: The GG was purified through barium complexing method. The barium complex was formed by precipitating GG solution (2.5% (w/v)) with saturated solution of barium hydroxide. The complex was separated by centrifugation and suspended in 1 M CH_3COOH, stirred for 8 h, centrifuged, and precipitated with 90% EtOH. It was washed sequentially with 70, 80, 90 and 95% ethanol. The sample was finally purified by dialysis and filtration through millipore membranes. The purified seed gum was a non-reducing, white, and fibrous material.

Procedure for graft copolymerization: A known amount of vinyl acetate (VAC), ethyl acrylate (EA) and acrylamide (AAm) were added to 20 mL aqueous solution of guar gum (0.5 % w/v) and the reaction volume was made 25 mL by adding requisite amount of distilled water. This reaction mixture was thermostated on thermostatic water bath at 35 ± 0.2ºC. After a span of 30 min, a known amount of KPS was added to this reaction mixture. The time of addition of KPS was considered as zero time and the grafting was allowed for 1 h. The contents of the reaction mixture were poured to an excess of acetone in order to precipitate the ternary grafted copolymer. The adhered photopolymer if any was removed by extracting the copolymer with acetone in a soxhlet extraction apparatus for 5-6 h. The copolymer was finally dried in air in an oven at 50°C until a constant weight. The concentration of AAm was optimized for ternary grafting using 0.46 M VAC and 0.38 M EA (0.38 M) while keeping the time, amount of solvent, temperature, and initiator fixed as mentioned in table 1. The percentage grafting (%G) and percentage efficiency (%E) were calculated as perprocedure reported earlier [32].

Table 1. Optimization of the AAm concentration for ternary vinyl grafting on to guar gum (at fixed guar gum amount = 0.1 g, AA = 2.3 × 10^{-2} M, KPS = 1.0 × 10^{-2} KPS

Sample No.	Ternary Monomer Mixture	Time (min)	Temp. (°C)	%G	% E	Hg(II) adsorption (%)
TC_1	0.46+0.38+0.08	60	35	70	3.50	41
TC_2	0.46+0.38+0.10	60	35	76	3.70	55
TC_3	**0.46+0.38+0.12**	**60**	**35**	**106.4**	**5.21**	**87**
TC_4	0.46+0.38+0.14	60	35	51.2	2.40	69
TC_5	0.46+0.38+0.16	60	35	45.2	2.10	65
TC_6	0.46+0.38+0.18	60	35	24.2	1.13	85
TC_7	0.46+0.38+0.20	60	35	20.2	0.92	89

Hg(II) removal: Hg (II) adsorption was investigated in a batch adsorption experiment [33]for which the copolymer (50 mg) was agitated with 20 mL of 100 mg L^{-1} of $HgCl_2$solutionin an orbital shaker (set at 100 rpm and 30 ± 0.1°C temperature). After the equilibrium was attained, the copolymer adsorbent was separated by filtration using Whattman filter paper. The filtrate was analyzed for the concentration of remaining Hg(II) ions by adding Rhodamine 6G (in acidic medium). A pink colored complex (which absorbed at 575 nm) was formed after the addition of Rhodamine 6G whose intensity was proportional to Hg(II) concentration (mg L^{-1}) in solution. The color intensity of the solution was recorded spectrophotometrically and the sorption capacity of the copolymer (q_e in mg g^{-1}) was determined by using the following equation:

$$\frac{C_i - C_e}{W} XV = q_e \qquad \ldots 1$$

Where q_e is the amount of the mercury absorbed on the adsorbent in mg g^{-1}, C_o, the initial concentration of (mg L^{-1}), C_e, the equilibrium Hg(II) concentration in solution (mg L^{-1}), V, the volume of the solution used (L), and W, the weight of the copolymer used (g) as adsorbent.

pH_{zpc} Measurement: pH_{zpc} of optimum performance sample (TC_3) was determined. 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 was 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}.

RESULTS AND DISCUSSION

Influence of the monomer concentration: In our recent study [31]we reported that optimum monomer concentration for binary monomer grafting of VAC+EA were 0.46 M and 0.38 M respectively at 1.0×10^{-2} KPS and 2.3×10^{-2} M AA,1 h grafting time, and 35ºC temperature. The pH_{zpc} of the TC_3 has been determined by pH_{drift} experiments, since pH_{zpc} is an important parameter to understand the adsorption by any adsorbent. Ternary graft copolymer has been synthesized by grafting different concentrations of acrylamide (0.08 M to 0.2 M) at fixed binary monomer (VA+EA) concentration, 0.46 M+0.38 M respectively. %G increased as the concentration of AAm was increased since it was consumed in the formation and growth of the grafted chains onto guar gum. The increase in the monomer concentration gradually increased the monomer diffusion at the vicinity of GG. This increased the extent of reaction regions onto the GG backbone, and consequently increased the %G. However, when the concentration of AAm was increased >0.12 M, % G decreased because at higher monomer concentration there is a competition between the grafting reaction and the monomer self-polymerization. The homopolymer lumps which are formed simultaneously with the copolymer hindered the rate of monomer diffusion to the macroradicals. The extent of homopolymerization increased with high monomer concentration to increase the viscosity of the reaction medium. This further slowed down the monomer diffusion to the active sites of the GG. The grafted chains exerted steric hindrance which further retarded the rate of graft copolymerization as the monomer concentration was increased beyond a limit and this gradually decreased the graft efficiency and grafting percentage.

Characterization of the copolymer TC_3: A series of graft copolymer samples (from TC_1 to TC_7) were synthesized by varying the grafting reaction parameters. The copolymer sample TC_3 (Table 1) had highest % G and % E and was most efficient adsorbent for Hg(II) as revealed in a preliminary investigation therefore it was used for the characterization and the adsorption study (results not shown), therefore this sample was used for a detailed characterization.

pH_{zpc} Measurement: pH_{zpc} is an important parameter in deciding the adsorbent behaviour of an adsorbent. In the present study pH drift method was used for determining the pH_{zpc} of sample TC_3 which was found most efficient in adsorbing the Hg(II). The pH_{zpc} of TC_3 was found to be pH 3.0. Thus, the copolymer will have zero surface charge in the solution of pH 3.0, its surface will be positive at pH <3.0 and it will be negative at pH > 3.0 (Figure 1).

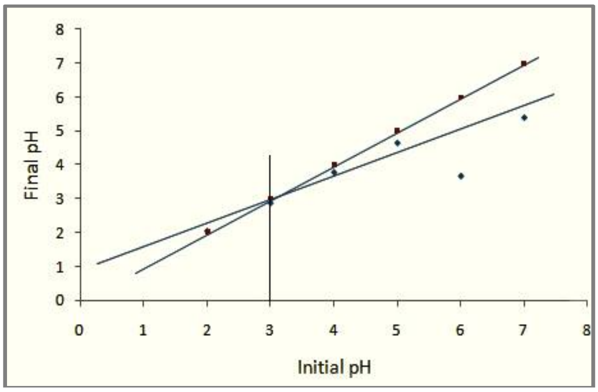


Figure 1. Determination of zero-point charge of the TC$_{3.}$

Fourier Transform Infrared Spectroscopy: The grafting was evidenced by comparing the FTIR spectrum of the guar gum (GG) with that of the grafted product TC$_3$. Figure 2 depicts the FTIR spectra of GG, TC$_3$ and mercury loaded TC$_3$ (TC$_3$-Hg). In FTIR spectrum of GG, the absorption peaks at 3308 cm^{-1}, 2915cm^{-1}, 1634 cm^{-1} and 1016 cm^{-1} can be attributed to the stretching vibrations of the hydrogen bonded hydroxyl groups (O-H),C-H stretching vibrations, the ring stretching and the C-O stretching vibrations of GG backbone respectively.

The formation of graft copolymer product was confirmed by the appearance of three new absorption peaks (at 3424 cm^{-1}, 1736 cm^{-1} and 1670 cm^{-1}) in the FTIR spectrum of TC$_{3.}$ The peak at 3424 cm^{-1} can be assigned as the combined overlapping peak due to the stretching vibrations of OH and NH$_2$ at the copolymer. The ester carbonyl group (>C=O), and C=O stretching of amide group (O=C-NH$_2$) of the grafted segments of PAM are visible at 1736 cm^{-1} and 1670 cm^{-1} respectively. Two sharp peaks at 1736 cm^{-1} and 1244cm^{-1} respectively are due to the carbonyl functional groups and ester linkages of poly (vinyl acetate) and poly (ethyl acrylate) graft regions respectively. The appearance of all these peaks confirmed the grafting of VAC, EA and AAm onto the GG. Other significant peaks that are visible are the methylde formation at 1377cm^{-1} and the C-O single bond stretching at 1019 cm^{-1}.

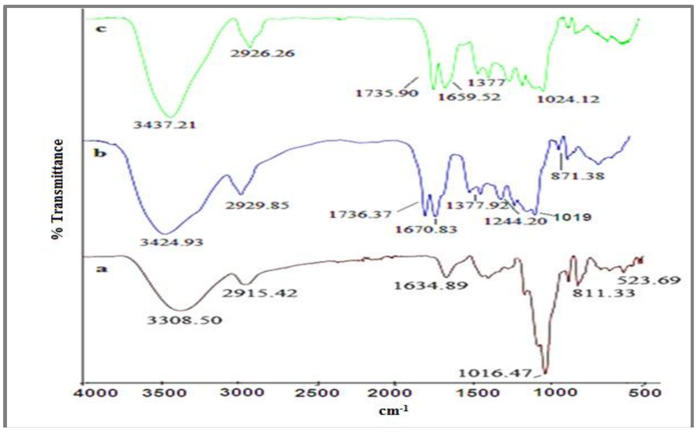


Figure 2. FTIR spectra of **(a)** GG **(b)** TC$_3$ **(c)** TC$_3$-Hg.

Moreover, in TC$_3$-Hg, new absorption peaks appeared at 3437 cm^{-1}, 1735cm^{-1} and 1659 cm^{-1} are due to the interaction between the Hg(II) species and functional groups of the graft copolymer. This interaction also increased the intensity of the hydroxyl absorption peak. At the same time, the intensity of the carbonyl stretching of ester was decreased by this interaction. This revealed that some of the hydroxyl and ester groups of the copolymer are definitely involved in adsorption of the mercury species.

Scanning Electron Microscopy: SEM pictures of GG, TC_3 and TC_3-Hgare seen in figure 3(A), figure 3(B) and figure 3(C) respectively. The picture shows that GG has a lamellar morphology which on grafting has acquired a flattened flaky surface with several interconnected pores inside. Mercury loaded copolymer sample TC_3 exhibited difference in the surface structure. It has wavy structure with surface containing agglomerated spherical particles which can be more clearly seen in figure 3(D) at 40000 x magnification.

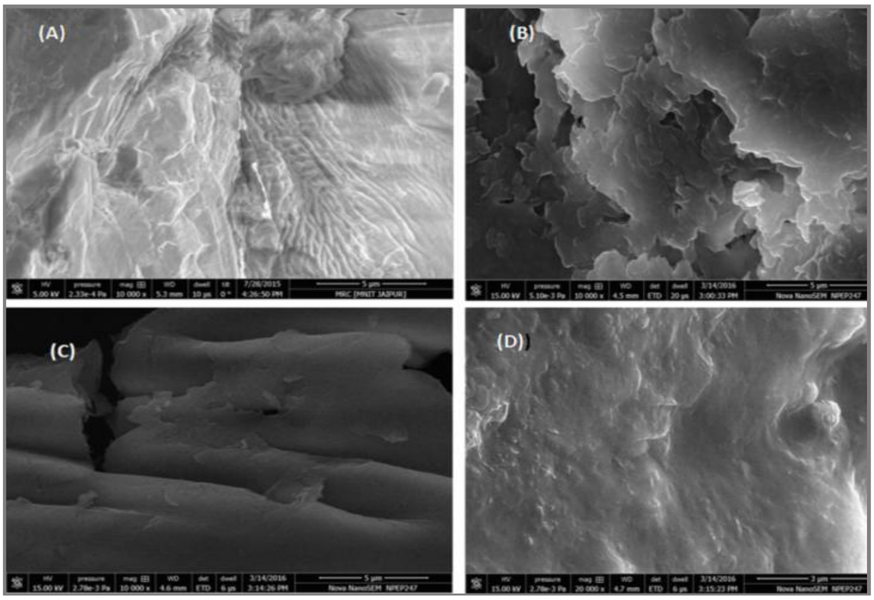


Figure 3. Scanning electron micrographs of; **(A)** GG **(B)** TC_3 **(C)** TC_3-Hg at 10000 x and **(D)** 40000 x magnification.

Thermogravimetric Analysis: TGA (A) and DTG (B) curves of TC_3 (Figure 4) revealed a three-stage weight loss. First 11% weight loss is seen between 26.83 to 125°C. This loss can be attributed to the loss of moisture and the solvent. The corresponding DTA peak is observed at 90°C. The second 28% weight loss is visible from 201 to 311°C, with corresponding DTA peak at 281°C. This weight

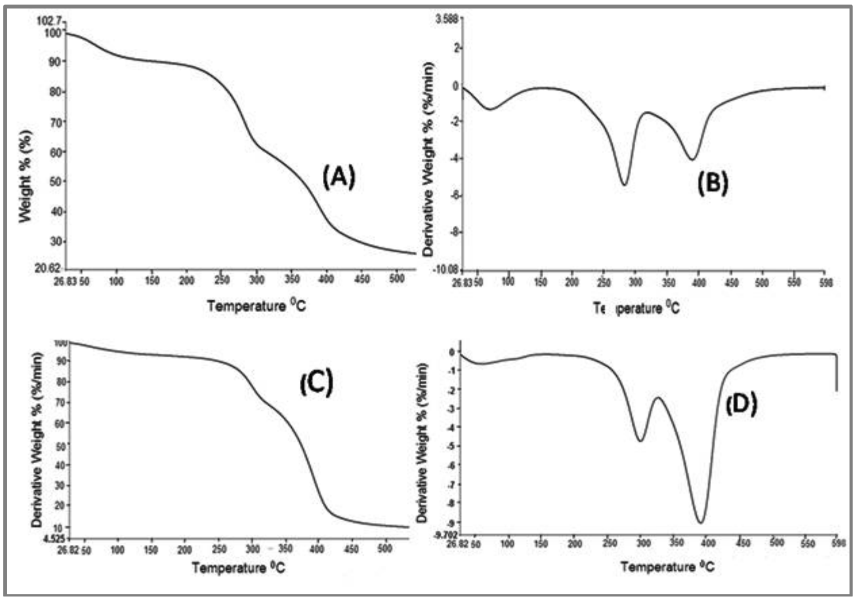


Figure 4. (A) TGA of copolymer, **(B)** DTA of copolymer, **(C)** TGA of mercury loaded copolymer,**(D)** DTG curve of the adsorbent after mercury loading.

loss may be attributed to the loss of poly (vinyl acetate) grafts. While third 22% weight loss extending from 325ºC to 424ºC is due to loss of poly (ethyl acrylate) and poly (acrylamide) grafts. The corresponding DTG peak is seen at 395°C. In Hg(II) loaded copolymer sample (TC_3-Hg), the DTG peak corresponding to first 8% weight loss is visible at 55ºC. The weight loss extended from 26.82 to 125ºC as that of TC_3 while the second peak is shifted to lower temperature (300ºC) and corresponded to 28% weight loss that extended from 228 to 348ºC. The shift of second DTG peak indicated the role of poly (vinyl acetate) in mercury complexation during the removal. The third DTG peak is visible at 395ºC, which corresponded to ~50% weight loss, this seems that some mercury species are also lost at this stage.

APPLICATION

Guar gum-based ternary graft copolymer (GG-g-poly-(VAC-co-EA-co-AAm) behaved as an efficient adsorbent for the removal of mercury (Hg(II))from its synthetic aqueous solution.

CONCLUSION

The graft copolymerization of the ternary vinyl monomer mixture on to GG was studied at the predetermined optimum conditions for the vinyl grafting for binary monomer mixture (VAC+EA). The synergistic effect of the ternary monomers (VAC+EA+AAm) significantly increased the % G (106%) as compared to %G (88%) for the binary vinyl monomers (VAC+EA). The optimum grafting ternary graft copolymer could remove 87% Hg(II) from 100 mg L^{-1} Hg(II) synthetic solution. Thus, the present study was a successful attempt for synthesizing potential mercury adsorbent in good yield using an easy grafting process that required environmental conditions only.

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