

Graft copolymerization of polyacrylic acid onto Acacia gum using erythrosine–thiourea as a visible light photoinitiator: application for dye removal

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Abstract Graft copolymerization of polyacrylic acid (PAA) onto Acacia gum (AG) using erythrosine dye (ERY) in aqueous media combined with thiourea (TU) as a reducing agent under visible light was studied. The optimal grafting parameters were examined in terms of irradiation time and the concentrations of ERY, TU, AA, and AG. Grafting factors such as grafting percentage (GP%), grafting efficiency (GE%), as well as homopolymerization (HP%) all were determined. Graft products of PAA-*g*-AG copolymers were characterized using FTIR spectroscopy, X-ray diffraction, and thermal analysis. The highest GP (310%) was obtained through optimization of the grafting variables. The optimized graft product was crosslinked and used as a potential candidate for removing of methylene blue dye from an aqueous system.

Keywords Acacia gum · Graft copolymerization · Acrylic acid · Photoinitiator · Methylene blue

Introduction

Acacia gum, also known as Arabic gum, is a highly branched polysaccharide composed of a linear core chain of $\beta(1,3)$ -linked galactose units with extensive branching at the C6 position. The branches involved in galactose and arabinose and terminate with rhamnose and glucuronic acid or methyl glucuronic acid [1]. The common advantages including renewability, biodegradability, nontoxicity, and

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biocompatibility make it found extensive applications as a commercial polymer in many areas such as food, suspending agents, and pharmaceutical and cosmetic industries [2, 3]. However, the performance and applicability of the raw gum are hindered due to its fixed structure and the limited functional groups. Graft copolymerization of natural gums with vinyl monomers is an effective technique to improve their properties and industrial application. The introduced groups or branch chains on the gum backbone may alter its charges, mobility, flexibility, hydrophilicity, molecular weight, viscosity, and thermal stability and this will open a new application for the grafted gum in industry [4]. Polyacrylic acid (PAA) is a common high reactive synthetic polymer that used in grafting onto various natural polymers, optimizing the viscosity of the graft copolymer for using as a thickener [5], flocculating agent [6] as well as for obtaining a super absorbent water retaining copolymer with the aid of crosslinking agent for agriculture uses [7] and in sand fixing purpose [8]. However, removing of the basic dye wastes originated from various industries, such as dyeing, textile, cosmetics, leather, food processing, and paper using polysaccharides graft synthetic copolymer, has gain much interest in the recent years. Dye adsorption using graft copolymers is considered as a preferred and effective technique due to its simplicity, high efficiency, easy recovery, and the reusability of the adsorbent [9]. The polysaccharides' graft copolymers were usually prepared in the form of hydrogels owing to their three-dimensional porous inner structure, readily swelling behavior and strong adsorption capacity of dyes.

Superabsorbent made from PAA grafted onto various polysaccharides such as cellulose and starch showed a high efficiency for removing of methylene blue (MB) from aqueous solutions [10–12]. In our study, optimized graft copolymers using photoinitiator based on (erythrosine coupled with thiourea) were used to prepare PAA-g-AG hydrogel for removing of MB from aqueous solutions.

Experimental

Materials

Acacia gum (A-gum, Acros, Belgium) and acrylic acid (AA, Sigma-Aldrich, United States) were purified by distillation under reduced pressure. Erythrosine (ERY, Prolabo, France), epichlorohydrin (ECH, Acros, Belgium), thiourea, acetone, xylene, and methanol were supplied by (LOBA, India) used as received, laboratory prepared distilled water was used through this study.

Methods

Graft copolymerization of PAA onto AG

Grafting reaction was carried out in closed Pyrex cells under photo inducing with visible light by placing the cells between two tubes of fluorescent lamps (40 W) for definite time periods [14]. AG (0.5 g) was dissolved in 10 ml distilled water with stirring until obtaining homogenous solution. After that, freshly prepared ERY and

TU solution (0.1 and 5×10^{-7} mol/l) was added with stirring for 10 min followed by monomer addition. The polymerization process was finally terminated by pouring the reaction in 1:3 (acetone–xylene) mixture for precipitation. The crude copolymer that obtained was dried to constant weight under vacuum at 40 °C. The dried product was extracted with 80% methanol for 48 h to remove the homopolymer (PAA). Obtained pure graft copolymer was dried under 40 °C until obtaining constant weight. Grafting percentage (GP%), grafting efficiency (GE%), and homopolymer percentage (HP%) were calculated according to the following expressions [13]:

$$\text{Grafting percentage (GP\%)} = \frac{A - B}{B} \times 100$$

$$\text{Grafting efficiency percentage (GE\%)} = \frac{A - B}{C} \times 100$$

$$\text{Homopolymer percentage (HP\%)} = \frac{\text{wt of homopolymer}}{C} \times 100$$

where A , B , C , and D are the weight of graft product, Acacia gum, monomer, and crude copolymer, respectively. Weight of homopolymer is $D - A$.

Preparation of PAA-g-AG hydrogel as an adsorbent for MB

Preparation of the graft hydrogel was done as follows [14]: 1 g of PAA-g-AG (310%) was dissolved in 30 ml water with stirring until obtaining a homogeneous viscous solution. 10 ml NaOH (2%) was added dropwise to reach an intensely alkaline environment. The crosslinking agent (ECH) 2.5 ml was then added dropwise under continuous stirring for 4 h at (60 – 65) °C. The hydrogel paste was then separated from the reaction by decantation and washed it with distilled water to remove unreacted chemicals followed by cutting into small discs then finally dried in an oven at 50 °C.

Physio-chemical behavior of crosslinked graft copolymer

Swelling behavior Dried hydrogels discs with constant weight (0.05 g) were left to swell in distilled water (30 ml) at room temperature. The swollen hydrogels were time intervals taken out (20 min–24 h) and superficially dried with filter paper for weighting. The hydrogels were then immersed again in the distilled water followed by drying and weighting again. This process was continued until obtaining a constant weight for each hydrogel sample [15]. The swelling ratio of the hydrogels was investigated using the following equation [15]:

$$\%S = \frac{M_t - M_0}{M_0} \times 100$$

where M_0 (g) is the initial mass of dry hydrogel, and M_t (g) is the mass of swollen hydrogel at time t (min).

Characterization

Chemical structure of the grafted products was examined by IR spectrometer (Perkin Elmer 1430) using KBr to prepare its disks. The thermal analysis of AG and graft copolymer was determined using thermal analyzers (Shimadzu DTA-50 and Shimadzu TGA-50H) under nitrogen atmosphere at a heating rate of 10 °C in min. Powder samples of some polymers were subjected to (X-ray diffraction - D8 advance X-ray diffractometer; Bruker AXS) using Cu K α radiation. The scattering angle 2θ was varied from 5° to 60°.

Application for dye removal

Adsorption of methylene blue

MB stock solution was prepared by dissolving 2 g of MB in 1000 ml distilled water to get 2000 ppm. The solution was suitably diluted to the desired initial concentration (200–1200) ppm. Batch mode experiments were conducted using (50–1000) ml capacity closed bottles. All effects studies were carried out using fixed weight of PAA-g-AG hydrogel (0.04 g) at room temperature and shaken time 4 h [16]. After equilibrium time, the bottles were then removed and amount of adsorbed MB was determined using UV spectrophotometer at 662 nm. The adsorption percentage (Ads.%) was calculated as follows [16]:

$$\text{Ads.}\% = \frac{C_i - C_f}{C_i} \times 100$$

where C_i is the initial concentration of MB and C_f is the final concentration of MB.

Desorption of methylene blue

Hydrogels at adsorption equilibrium were separated from the MB solution (200 ppm) by decantation. Then, the hydrogels were immersed into 50 ml of buffers prepared from (hydrochloric acid/potassium chloride) to obtain pH 1–2 and (Citric acid/Sodium citrate) to obtain pH 3–6 all under stirring at room temperature [16]. The amount of desorbed MB was determined by the UV spectrophotometer. Desorption percentage (Des.%) was calculated using the following equation [16]:

$$\text{Des.}\% = \frac{C_d}{C_a} \times 100$$

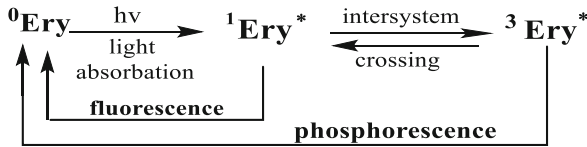
where C_d is the concentration of MB desorbed by buffers and C_a is the concentration of adsorbed MB using PAA-g-AG hydrogel.

Effects of the grafting parameters on GP%, GE%, and HP%

The reaction time

The data shown in Fig. 1a indicate that GP% and GE% increase with increasing time in the range of time used. This increase in grafting parameters may be due to the increase in the number of grafting sites with increasing time and this lead to more addition of monomer molecules to the growing grafted chain. The initial rate of grafting was determined to be 0.8%/min [17]. In addition, HP% decreases by increasing time [18, 19].

It has been reported [20, 21] that visible light absorbed by dyes (such as ERY) make its excitation to triplet state, and at this level, ERY becomes very active to accept electron from an electron donor (such as TU), which yields a semireduced form of the ERY—and then a protonated semireduced form HERY' (leuco form). This process is accompanied by the generation of an initiating thio radical. The HERY' radical disproportionates into ERY and ERYH₂ and scavenges the growing polymer radical. The mechanism can proceed as follows:



I—Generation of initiation radicals

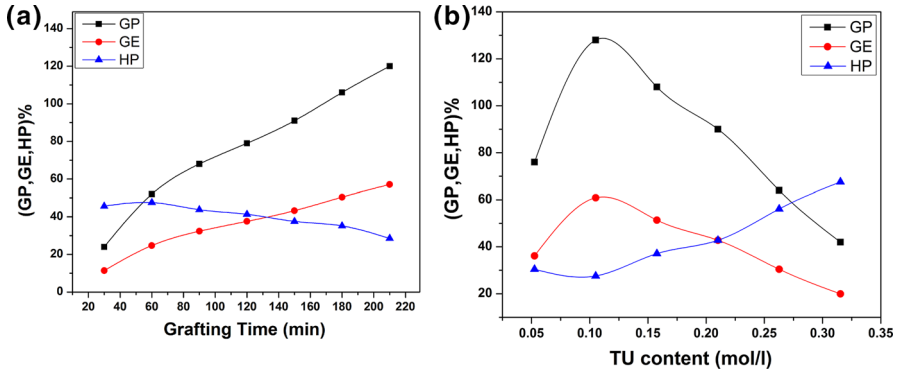
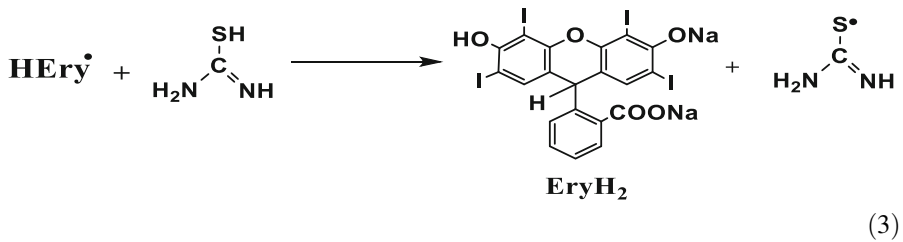
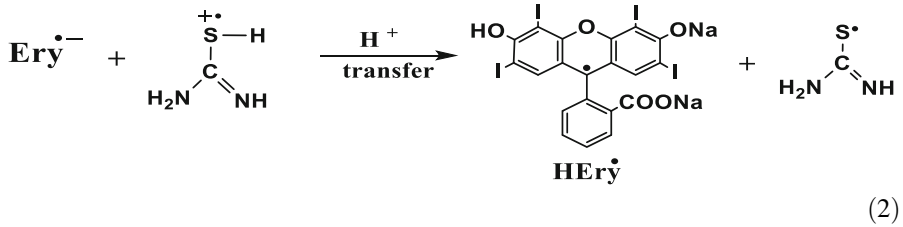
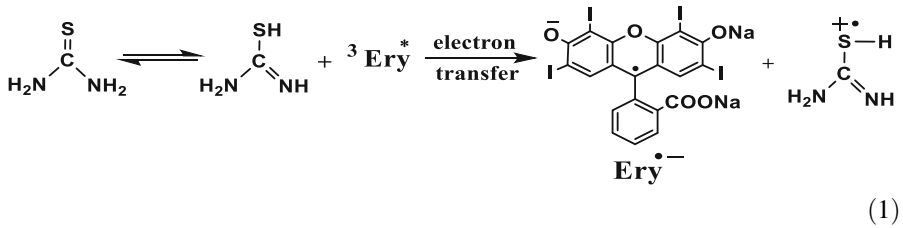


Fig. 1 **a** AG 100 g/l, AA 2.92 mol/l, ERY 5×10^{-7} mol/l, and TU 0.13 mol/l. **b** AG 100 g/l, ERY 5×10^{-7} mol/l, AA 2.92 mol/l, and time 210 min

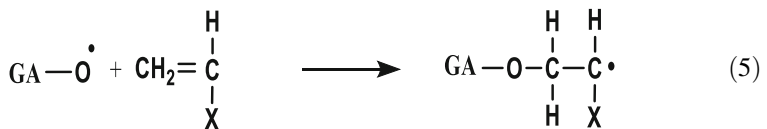


When free radical species ($R^{\cdot} = \text{HO}^{\cdot}$, $-\text{S}^{\cdot}$) are created, they generate AG macro-radicals

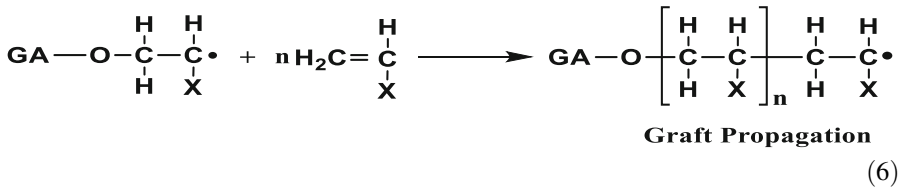


In the presence of vinyl monomer such as AA, the AG macro-radicals are reacted with the double bond of acrylic acid to create a free radical on the monomer, so a chain start initiated and then the initiated chain propagates grafting onto the AG as follows:

II—Chain initiation



III—Propagation of the initiated chain



Influence of TU content

From Fig. 1b, it is apparent that increase of TU concentration is accompanied by increasing the GP% and GE% until reaching to the optimum condition at TU concentration at 0.11 mol/l, then GP% and GE% decreased with a further increase in the TU content. This finding may be due to the chain transfer to monomer, which is accompanied by increasing homopolymer content as appearing from the increase of HP% values [17, 22] as follows:

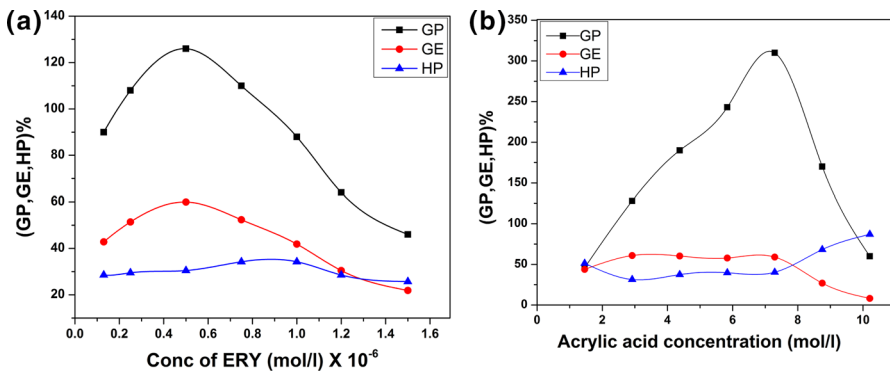
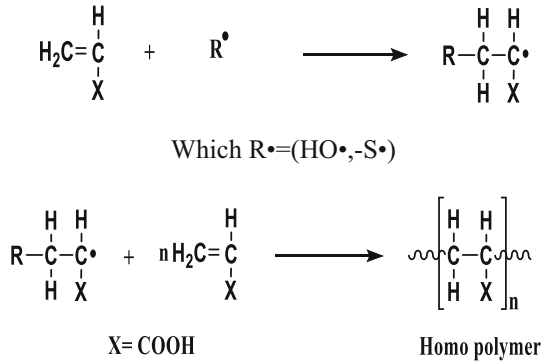
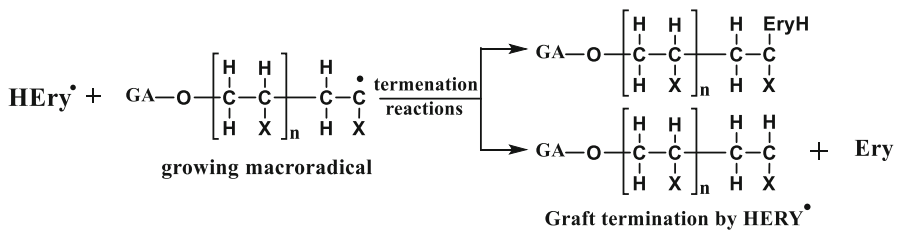


Fig. 2 a AG 100 g/l, TU 0.11 mol/l, AA 2.92 mol/l, and time 210 min. b AG 100 g/l, ERY 5×10^{-7} mol/l, TU 0.11 mol/l, and time 210 min

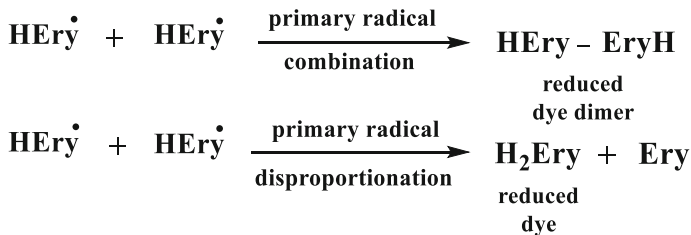
Influence of ERY content

The influence of variation of ERY concentrations on GP%, GE% and HP% is shown in Fig. 2a. The effect of ERY content was studied in the range 0.13×10^{-6} – 1.5×10^{-6} mol/l. The results show that values of GP% and GE% increase with increasing ERY content until 5×10^{-6} mol/l, and then, they will decrease with further increase in ERY content. Whereas HP% increases with increasing ERY content until 7.5×10^{-6} mol/l.

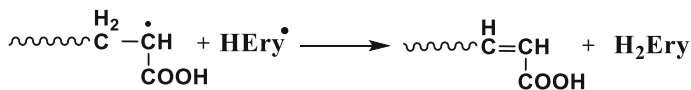
After that, HP%, GP%, and GE% values will decrease with a further increase of ERY content. This observation may be explained to participation of HERY' in the termination of the growing grafted chains as follows:



Or it may be converted to its reduced form as follows [21]:



In addition, HERY' can participate for termination of the growing PAA chains as follows:



Influence of monomer content

The effect of AA content in the range 1.46–10.46 mol/l on the grafting parameters and HP% was studied (Fig. 2b). The results indicate that the increase in AA content is accompanied by increasing in GP% and GE% until reaching up to a certain value (about 7.29 mol/l under the experimental conditions), and then, they decrease with a further increase in monomer content. This observation may be explained that at higher AA concentrations, the excess AA molecules could induce drastically more

chain transfer and termination reactions leading to more homopolymerization instead of graft copolymerization. This assumption was confirmed by the observed increase in HP% values, which initially rapidly decreases then finally increases with increasing monomer concentration. Moreover, once the PAA-g-AG copolymer is formed, the excess of AA may shield the graft copolymer, which may reduce the grafting rate [17, 23].

Influence of gum content

The influence of gum content in the range 40–200 (g/l) on the grafting parameters (GP, GE, and HP)% was studied at constant contents of initiator and monomer, as illustrated in Fig. 3. The results show that GP% and GE% decrease by increasing AG content. On the other hand, HP% increases with increasing gum content. These results can be attributed to the increase in the viscosity of the medium upon increasing the AG content, which consequently reduces the mobility of the macro-free radicals, and this result in a reduction in grafting and encouraging of homopolymer formation [17, 24].

Characterization techniques

FTIR spectroscopy

The IR spectrum of the AG in (Fig. 4a) shows that the main characteristic peaks of AG at 3400 cm^{-1} (O–H stretch), 2920 cm^{-1} (C–H stretch), and 1070 cm^{-1} (C–O–C stretch). For the spectrum of PAA-g-AG (Fig. 4b), in addition to the AG characteristic peaks, new peak at 1710 cm^{-1} is corresponded to the carbonyl group

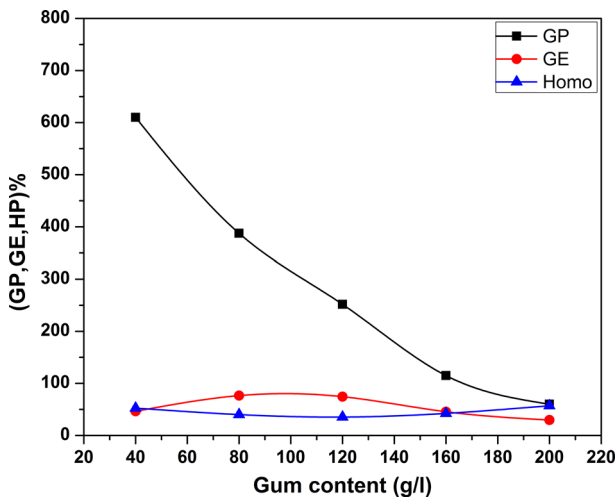


Fig. 3 AA 7.29 mol/l, ERY 5×10^{-7} mol/l, TU 0.13 mol/l, and time 210 min

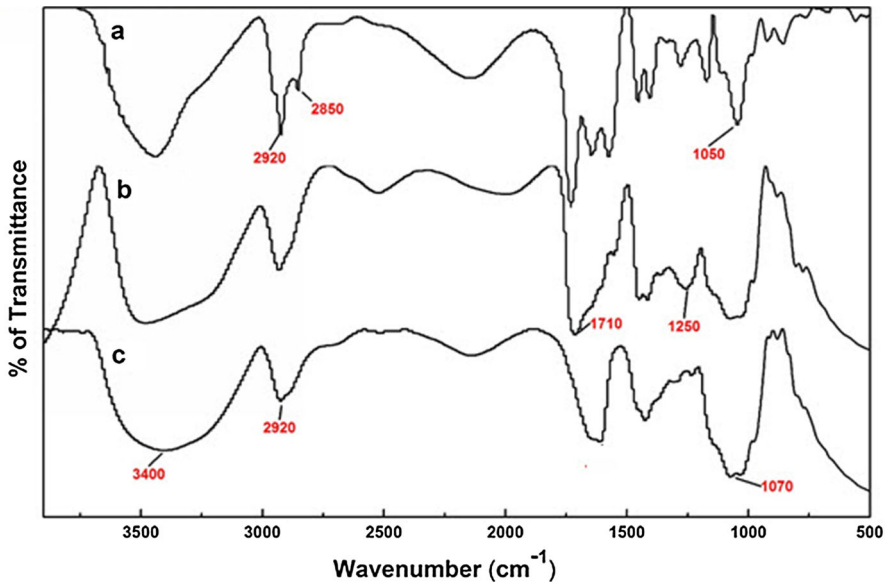


Fig. 4 FTIR spectra of *a* AG, *b* PAA-g-AG (GP 310%), and *c* crosslinked PAA-g-AG

absorption from grafted PAA and the band at 1250 cm^{-1} was characteristic absorption of C–O stretching [25]. These results indicate that PAA is successively grafted onto AG. Crosslinked PAA-g-AG (Fig. 4c) showed increasing in the intensity at 2920 cm^{-1} and appearance of new one at 2850 cm^{-1} is attributed to the more aliphatic methylene groups that introduced by ECH into the hydrogel structure. In addition, the presence of high sharp peak at 1050 cm^{-1} indicates more ether linkage (C–O–C) that may be due to crosslinking linkage [26].

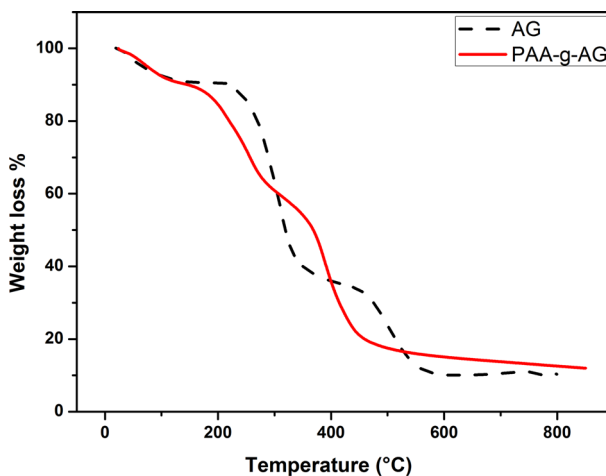


Fig. 5 TGA curve of AG and PAA-g-AG (193%)

Thermal analysis using TGA

In case of AG thermogram (Fig. 5) which shows that the decomposition of AG occurs in three stages as was reported [27]. Therefore, the first stage appears (~8%) weight loss up to 132 °C due to the loss of adhered and bound water, and then, a second sharp weight loss (~52%) which prolongs to 366 °C followed by a broad weight loss (~23.6%) up to 582.6 °C due to the loss of the polysaccharide. In general, the main decomposition of the polysaccharides starts above 200 °C.

On the other side, the weight loss in PAA-g-AG copolymers occurred in three main stages as in AG but at lower initial decomposition temperatures (IDTs) and final decomposition temperatures (FDTs). In case of PAA-g-AG (GP 193%), its first weight loss (9.1%) was up to 116 °C, the second was broad weight loss (26.9%) between 116 and 284.8 °C, and the third sharp weight loss (42.66%) was between 304.3 and 495.3 °C.

The polymer decomposition temperature indicated that grafting of acrylic acid lowers the initial decomposition temperature because of the formation of anhydride with the elimination of water from the two neighboring carboxylic groups of the grafted chains, as shown in the following steps [27]:

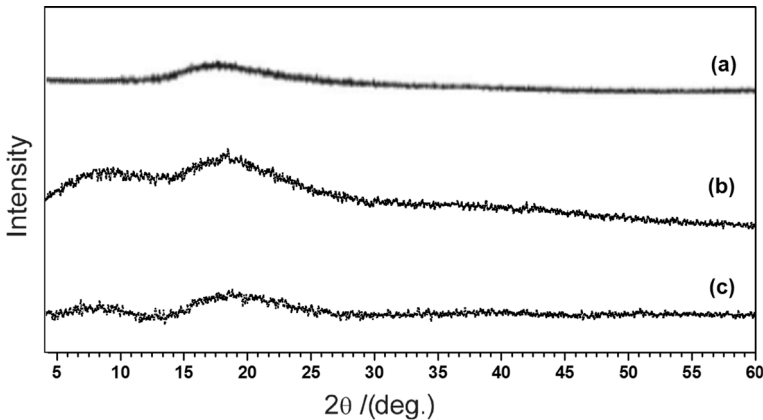
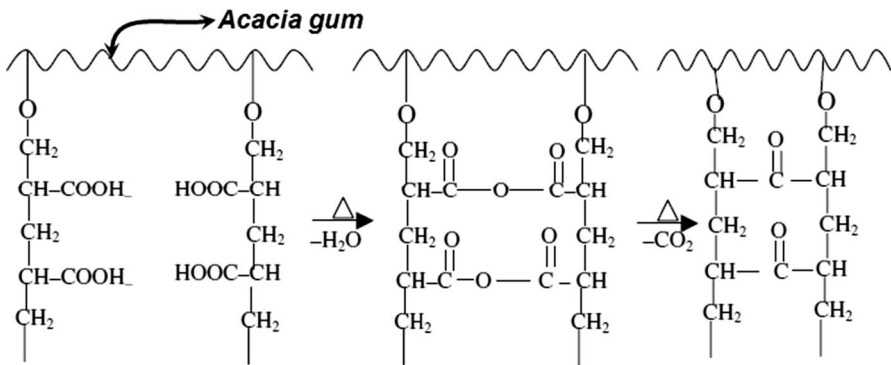


Fig. 6 XRD of *a* PAA, *b* AG, and *c* PAA-g-AG (310%)

X-ray diffraction

X-ray diffraction (XRD) analysis reveals the amorphous nature of PAA (Fig. 6a). On the other hand, AG shows two different broad halos at maximum $2\theta = 18.47^\circ$ and 7.92° indicating two distinct short ranges of ordering in specimen (Fig. 6b) [28]. In case of PAA-*g*-AG (GP = 193%), 2θ of AG was shifted to new position at 17.53° and 6.83° , respectively, with a decrease in intensity of the two haloes to be more broad and this indicates that grafting led to disruption in the original ordering of AG resulted in increasing the amorphous nature of the gum.

Physico-chemical properties of PAA-*g*-AG hydrogel

Swelling behavior with time

Figure 7 shows the time dependence of swelling ratio percentage (SR%) of PAA-*g*-AG hydrogel. After 1000 min \sim 16.5 h of immersion in distilled water, the hydrogel swells up to 50 times; i.e., it absorbs up to 50 g of water per 1 g of polymer. It is important to notice that the hydrogel exhibited water superabsorbent properties. This effect was attributed to the electrostatic repulsion among the carboxylic groups present in acrylate with each other and with glucuronic acid segments in AG that causes an expansion of the gel networks [29].

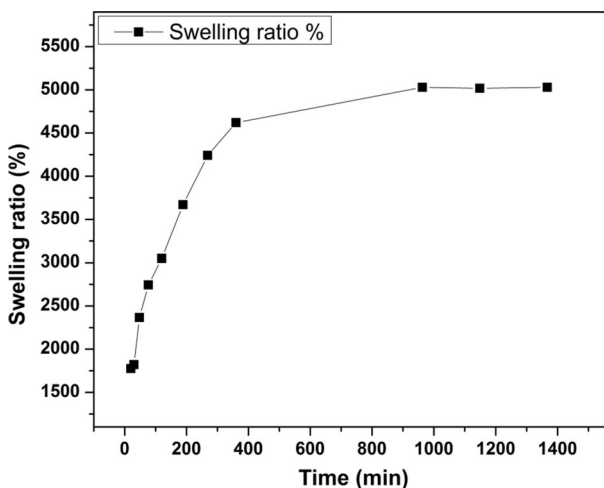


Fig. 7 Swelling curve of PAA-*g*-AG hydrogel (0.05 g/30 ml) in distilled water at room temperature

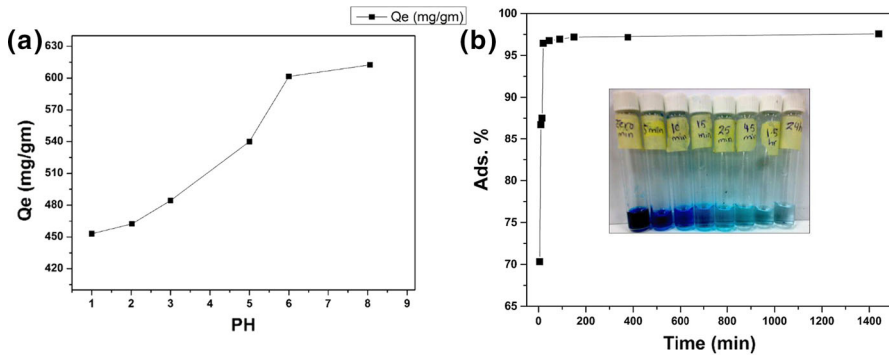


Fig. 8 **a** MB concentration 500 mg/l, adsorbent dose 40 mg/50 mL, and shaking time 4 h at room temperature. **b** MB concentration 200 mg/l and adsorbent dose 0.2 g/500 mL in distilled water at room temperature

Adsorption of MB using PAA-g-AG hydrogel

Effect of pH on MB adsorption

The effect of pH on the adsorption percentage (Ads.%) of MB using hydrogel is shown in Fig. 8a. The Ads.% of MB is significantly increased by varying pH from 1.0 to 6.0, while it slightly increased with pH range 6.0–10.6. It has been reported that pKa of AA is 4.3 [30]. A higher pH (above pKa) can cause the ionization of carboxyl acid groups and thus increase the interactions between negatively charged groups present in acrylate and glucuronic acid segments and dye cations. Moreover, at higher pH, increasing ionized groups leads to generate electrostatic repulsion forces between the adjacent ionized groups of polymer network. This produces an expansion network, which may also result in an increase of MB adsorption. At a lower pH (below pKa), the carboxyl acid groups of the hydrogel are protonated, and therefore, the competition of MB cations with H^+ for binding sites in adsorbents results in decrease of MB adsorption. Similar studies were also reported [31, 32].

Effect of contact time on MB adsorption

The time-dependent adsorption of MB on PAA-g-AG hydrogel is shown in Fig. 8b. The MB adsorption by PAA-g-AG hydrogel is rapidly increased in the first 150 min and then changes slightly until 400 min, after that no further adsorption occurs with prolonged time. Consequently, the equilibrium time reached at about 400 min. Similar results were also reported [31–33].

Effect of initial MB concentration

The effect of the initial MB concentration on the Ads.% using PAA-g-AG hydrogel was investigated by varying the initial concentration of MB between 200 and 1000 mg/l. The results in Fig. 9a indicate that Ads.% reduces from 99 to 69% when

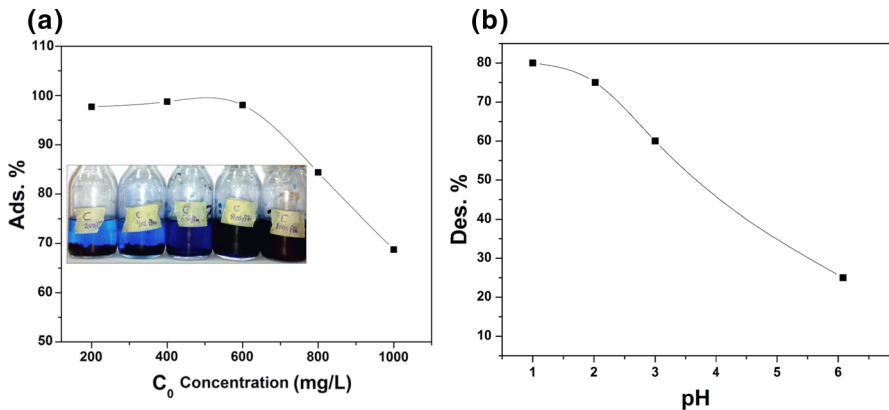


Fig. 9 a Adsorbent dose 40 mg/50 mL and shaking time 4 h in distilled water at room temperature. b MB concentration 200 mg/l, adsorbent dose 40 mg/50 mL, and shaken time 4 h at room temperature

the initial MB concentration varies from 400 to 1000 mg/l in distilled water, i.e., the adsorption decrease with increasing of initial dye concentration. The maximum Ads.% was 99% when using 400 mg/l of initial dye solution. From these results, it seems that the PAA-*g*-AG hydrogel would be an interesting and economic industrial adsorbent. Similar behavior was also reported [11].

Desorption behavior of PAA-*g*-AG hydrogel

Desorption studies can help for elucidating the mechanism of an adsorption process [11, 32, 33]. If the MB adsorbed onto the PAA-*g*-AG hydrogel can be desorbed by water, it can be concluded that the attachment of the dye onto the adsorbent is by weak bonds. If the strong acids, such as a buffer of pH 1, can desorb the dye, it can be concluded that the attachment of the dye onto the adsorbent is by ion exchange or electrostatic attraction. Therefore, the buffer aqueous solution with different pH 1, 2, 3, and 6 was used in the test; the effect of different buffers of pH on desorption capacity of MB by the PAA-*g*-AG hydrogel is shown in Fig. 9b. The results indicate that the desorption percentage (Des.%) increases from 25 to 80% with increasing of pH from 6.0 to 1.0, indicating that high acid concentration facilitates the desorption of MB from PAA-*g*-AG hydrogel. The relatively high desorption amount at pH 1 suggests that adsorption of MB onto PAA-*g*-AG hydrogel was carried out partially via electrostatic attraction, and was in accordance with the previous discussion of the effect of pH. The results also indicate that the hydrogel can be regenerated and reused after MB dye adsorption despite almost 25% dye remaining in the adsorbent in the case of pH 2.

Conclusion

In the present study, PAA was successfully grafted onto Acacia gum in air using a two-component photoinitiator system (ERY-TU) under visible-light irradiation. This method provides an easy procedure to incorporate a high percentage of PAA onto Acacia gum (310%) using a simple and low-cost technique. The prepared PAA-g-AG hydrogel showed a super-absorbent capacity of water (can absorb up to 50 times of its weight) indicating that hydrogel can be used in water saving materials. In addition, PAA-g-AG hydrogel showed a high efficiency for removing the cationic MB dye as it could absorb 99% of 400 mg/l of the initial dye solution indicating that hydrogel can be used as an ecofriendly material for removing of waste pollutants.

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