

Synthesis and characterization of acrylic acid grafted gum tragacanth and its effect in Fe²⁺ removal

Zohreh Didar¹

¹ Department of Food Sciences and Technology, Neyshabur Branch, Islamic Azad University, Neyshabur, Iran

Original Article

Abstract

In this paper, grafting of acrylic acid monomer on Gum tragacanth was performed. Variable of experiment included concentration of initiators and monomer, time, and temperature. Grafting efficiency was measured in the term of percentage of grafting (%G) and percentage of grafting efficiency (%E). Effectiveness of grafted gum in ferrous ion removal at different condition was assessed. According to this study, grafting was influenced by different concentration of initiators. The best result obtained at 5×10^{-3} mol/dm³ [Fe²⁺], 1.35×10^{-3} mol/dm³ [H⁺], 4×10^{-3} mol/dm³ potassium monopersulfate and monomer concentration = 5×10^{-2} mol/dm³. Amount of added gum was restricted to 0.25 g, addition of more gum resulted to abrupt decrease of both parameters. Time and temperature affected grafting reaction and the best condition for grafting was 25 °C, 90 min. Finally, the ability of resultant grafted gum for removal of ferrous ion from aqueous media was assessed. The maximum removal of ferrous ion took place at pH = 6, grafted gum = 150 mg and contact time 60 min.

KEYWORDS: Tragacanth, Acrylic acid, Grafting, Fe²⁺

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Introduction

Heavy metals are one of the major pollutants in water and wastewater that their removal imposes high costs to different industries. Tendency to accumulate in living organs, is the main reason for controlling these contaminants.¹ Since the strict environmental legislations, elimination of these contaminants from wastewaters has received much attention in recent years.² Different traditional and novel technologies and processes have been applied for treatment of wastewater. Flocculation is one of the most common approaches for treatment of wastewater because of good efficacy and economic reasons. Polysaccharides are one alternative for synthetic flocculant.³

Gum tragacanth is secreted from a plant namely Astragalus genus (Astragalus sp.) which wildy grows in the dry deserts and mountainous regions of South West Asia, from Pakistan to Greece, and in particular, in Iran and Turkey.⁴ World market for gum tragacanth of Iran is estimated to be about 500 t/year.⁵ Gum tragacanth is known as stabilizing, viscosity enhancing agent in food emulsions and confer high viscosity to food products. Gum tragacanth is comprised of two fractions named tragacanthin and bassorin which are soluble and insoluble in water, respectively. When water is added to gum tragacanth, tragacanthin, dissolves and gives a colloidal hydrosol whereas bassorin swells to a gel.⁴ Gum tragacanth is a high molecular weight carbohydrate biopolymer (840,000 g/mol) and has complex chemical structure that includes acidic branched hetero-polysaccharides containing D-galacturonic acid. D-galactose, L-

Corresponding Author:

Zohreh Didar

Email: Z_didar57@yahoo.com

fructose (6-deoxy-L-galactose), D-xylose, and L-arabinose are products of hydrolysis.⁶ Figure 1 shows chemical structure of gum tragacanth.

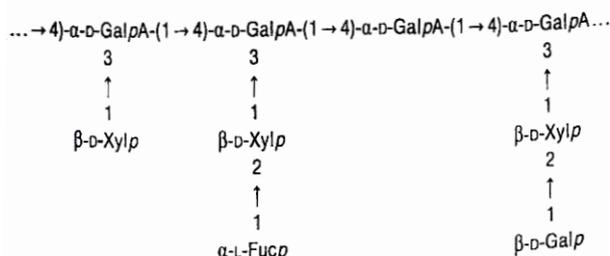


Figure 1. Structure of gum tragacanth

Purification, grafting, hydrolysis and cationization are useful methods for increasing effectiveness of natural flocculants. Chemical grafting is one approach for changing structure and properties of gums. Grafting offer more availability of pollutant particles to polyacrylamide chains on rigid polysaccharide backbone,³ so it receives great deal of interest recently. Numerous studies are focused on grafting different gums like gum ghatti,⁷ gum Arabic,⁸ locust bean gum,⁹ carrageenan,¹⁰ cellulose and its commercial derivatives.¹¹ To perform grafting reaction, various initiators, copolymer and gums could be used such as ceric and acrylonitrile,¹² Fe²⁺/H₂O₂ and methacrylic acid,¹³ Potassium Persulfate and methacrylic acid,¹⁴ manganese (IV)-nitric acid, and acrylonitrile.¹⁵

Fe²⁺ is one pollutant in water and wastewater that could induce color and other negative changes. Removal of Fe²⁺ is difficult because of its solubility in water.¹⁶ This study is directed toward assessing influence of different parameters on efficacy of grafting acrylic acid on gum tragacanth structure as well as investigation of ability of resultant grafted gum in ferrous ion removal from aqueous solution.

Materials and Methods

All chemical material in this study was purchased from Merck. Gum tragacanth prepared from local markets.

For each experiment, gum tragacanth solution was prepared by adding a given amount of gum in triple distilled water (Table 1). The reaction was done under nitrogen atmosphere at constant temperature. Thereafter, calculated amount of acrylic acid, sulfuric acid [H⁺], and ferrous sulfate solutions [Fe²⁺] (Table 2) were added to the known amount of gum solution. For starting the reaction, a known amount of potassium monopersulfate (PMS) solution was added (Table 2). After desired intervals of time, the reaction was ceased by letting air into the reactor. The grafted sample was precipitated by pouring the reaction mixture into a methanol/water mixture and kept overnight. The sediment was filtered, dried, and weighted.¹⁷

Table 1. Descriptive statistic of reaction conditions on grafting parameters

Parameters	Time (min)	Percentage	Gum tragacanth		Temperature (°C)	[Acrylic acid]		
			(g/dm ³)	Percentage		(×10 ⁻³ mol/dm ³)	Percentage	
Percentage of grafting (%G)	30	90.0 ± 1.00 ^(a)	0.25	111.0 ± 3.21 ^(d)	25	101.0 ± 1.00 ^(d)	3.5	109.0 ± 1.52 ^(b)
	60	95.3 ± 2.52 ^(b)	0.50	84.3 ± 1.52 ^(c)	35	84.7 ± 4.16 ^(c)	5.0	115.0 ± 0 ^(c)
	90	105.0 ± 3.51 ^(c)	0.75	71.7 ± 1.52 ^(b)	45	78.0 ± 1.73 ^(b)	6.5	111.0 ± 1.00 ^(b)
	120	105.0 ± 3.51 ^(c)	1.00	39.0 ± 1.00 ^(a)	55	64.7 ± 3.05 ^(a)	8.0	79.0 ± 2.00 ^(a)
Percentage of grafting efficiency (%E)	30	24.9 ± 0.27 ^(a)	0.25	30.8 ± 0.88 ^(d)	25	27.9 ± 0.27 ^(d)	3.5	30.1 ± 0.42 ^(b)
	60	26.4 ± 0.69 ^(b)	0.50	23.3 ± 0.42 ^(c)	35	23.4 ± 1.15 ^(c)	5.0	31.8 ± 0 ^(c)
	90	29.0 ± 0.97 ^(c)	0.75	19.8 ± 0.42 ^(b)	45	21.6 ± 0.47 ^(b)	6.5	30.7 ± 0.27 ^(b)
	120	29.0 ± 0.97 ^(c)	1.00	10.8 ± 0.27 ^(a)	55	17.9 ± 0.48 ^(a)	8.0	21.9 ± 0.55 ^(a)
F		19.778		676.076		89.286		444.773
P		< 0.001		< 0.001		< 0.001		< 0.001

Means, within each column, followed by the same letter(s) are not significantly different at the 0.05 probability; level using Duncan's Multiple Range Test

Table 2. Descriptive statistic of initiator concentration on grafting parameters

Parameters	[Fe ²⁺] (×10 ⁻³ mol/dm ³)		[H ⁺] (×10 ⁻³ mol/dm ³)		[PMS] (×10 ⁻³ mol/dm ³)	
		Percentage		Percentage		Percentage
Percentage of grafting (%G)	2.0	84.0 ± 1.00 ^(b)	1.35	111.0 ± 1.15 ^(d)	2.5	94.7 ± 2.51 ^(b)
	3.5	93.8 ± 4.50 ^(c)	1.80	88.3 ± 1.15 ^(c)	4.0	113.0 ± 1.52 ^(c)
	5.0	102.0 ± 0.57 ^(d)	2.25	75.3 ± 2.08 ^(b)	5.5	113.0 ± 1.52 ^(c)
	6.5	66.0 ± 4.00 ^(a)	2.70	42.7 ± 3.00 ^(a)	7.0	78.7 ± 0.57 ^(a)
Percentage of grafting efficiency (%E)	2.0	23.2 ± 0.15 ^(b)	1.35	30.8 ± 0.31 ^(d)	2.5	26.2 ± 0.69 ^(b)
	3.5	26.0 ± 1.25 ^(c)	1.80	24.4 ± 0.31 ^(c)	4.0	31.4 ± 0.42 ^(c)
	5.0	28.1 ± 0.15 ^(d)	2.25	20.8 ± 0.57 ^(b)	5.5	31.4 ± 0.42 ^(c)
	6.5	18.3 ± 1.10 ^(a)	2.70	11.8 ± 0.84 ^(a)	7.0	21.8 ± 0.15 ^(a)
F		74.927		603.776		296.157
P		< 0.001		< 0.001		< 0.001

Means, within each column, followed by the same letter(s) are not significantly different at the 0.05 probability; level using Duncan's Multiple Range Test.

Grafting parameters including percentage of grafting (%G) and grafting efficiency (%E) were calculated according to Maia et al.¹⁸

$$\%G = \frac{W_g - W_p}{W_p} \times 100$$

$$\%E = \frac{W_g - W_p}{W_m} \times 100$$

Where W_g , W_p , and W_m are the weights of graft copolymer, gum, and acrylic monomer, respectively.

IR spectra were measured on a Perkin-Elmer model Spectroma2 FT-IR using KBr pellets in a range of 400–4000 cm⁻¹ and DSC analyses were performed using Mettler Toledo model DSC822 equipment. Test conditions included: 2.229 mg samples, alumina sealed pans, nitrogen stream: 50 ml.min⁻¹, heating rate of 10 °C min⁻¹ and temperature range between ambient and 450 °C.¹⁸

Isoelectric point of grafted copolymer was measured according to method outlined by Singh et al.¹⁹ in which 500 ml of CaCl₂ (0.005 M) was boiled for 30 min and then cooled to reach room temperature. Several aliquots (20 ml) of this solution were adjusted to different pH values, ranging from pH 2 to pH 10. Each of them mixed with 0.05 g grafted copolymer for 48 h. Thereafter, final pH was measured and plotted against their corresponded initial values.¹⁹ Isoelectric point of grafted copolymer was measured at pH = 3.

For sorption experiment, 0.02 g (20 mg) of grafted gum added to 10 ml of given

concentration of ferrous ion solution (10 mg.l⁻¹) and keeping it undisturbed for 24 h, at pH = 9. Thereafter, the strength of unabsorbed metal ion was determined by standard method.²⁰ Removal percent was calculated using the following expressions.²¹

$$\% \text{removal} = \frac{C_0 - C_e}{C_0} \times 100$$

Where C_0 = the initial concentration of the metal ions and C_e = the residual concentration of the metal ions in the solution (filtrate).

All data were treated in replicates and the mean values were taken. Data were tested by one-way analysis of variance (ANOVA) using STATISTICA software (version 12.5.192.7 Enterprise, Stat Soft, Tulsa, OK, USA). A significance level of $P < 0.05$ was used. All experiments were performed in triplicate.

Results and Discussion

Optimization grafting parameters

Several factors could influence the grafting efficacy such as initiators concentrations, dosage of monomer and gum, time and temperature of the reaction, so optimization of these factors is notably important. Results of the effect of different factors on grafting parameters are summarized at tables 1 and 2.

Effect of PMS concentration

Effect of PMS concentration was examined at the range of 2.5–7 × 10⁻³ mol/dm³. As shown in table 2, increase concentration of PMS to some extent (5 × 10⁻³ mol/dm³) resulted in increase of

either percentage of grafting and percentage of grafting efficiency. Further increase in amount of added PMS, caused decline in both two grafting parameters. Present result is in agreement with Pandey et al.¹⁷ that reported amount of PMS that can be added for grafting xanthan gum is limited. PMS has a key role in free radical production, so starting the reaction is related to its concentration.

Effect of Fe²⁺ concentration

Examined concentration of Fe²⁺ was between $2-6.5 \times 10^{-3} \text{ mol/dm}^3$. Fe²⁺ stimulatory resulted to PMS at different concentration that could be attributed to similar role in the reaction. Fe²⁺ is known as a retarding component in radical polymerization. This could explain decrease in grafting parameters at high concentration of Fe²⁺. Pandey et al. underlined similar effect of Fe²⁺ on graft copolymerization of acrylic acid onto xanthan gum with a maximum value of grafting (%G = 192.3) at Fe²⁺ ion concentration of $5.0 \times 10^{-3} \text{ mol/l}$.¹⁷ In the present work, maximum value of grafting in the same concentration of Fe²⁺ ion, reached to 101.67%. Difference in maximum grafting value could be ascribed to different gum structures.

Effect of hydrogen ion concentration

Acidic condition has negative effect on grafting reaction and grafting parameters are diminished at high concentration of H⁺. Negative result of high acid concentration on grafting is mentioned by other authors.¹⁷ By virtue of H⁺ ability to complex with HSO₅⁻, inverse effect of high concentration of H⁺ could be obvious.

Effect of acrylic acid concentration

Acrylic acid concentration has obvious effect on %G and %E (Table 1). The effect of monomer concentration on grafting reaction was stipulated by other authors. This effect ascribed to the phenomenon called "gel effect" that is particularly pronounced in the case of grafting with methyl methacrylate, methyl acrylate, and acrylic acid at various concentrations. It occurs also with other monomers, such as styrene and vinyl acetate,

but for these monomers the effect is less pronounced. Increase of acrylic acid concentration at the first of the reaction causes increase of grafting percentage and grafting efficiency that is due to high concentration of monomer and low concentration of polymer. In this condition, low viscosity confers desirable access of monomer to polymer chain.²² High viscosity resulted from polymer formation, restrict grafting reaction.

Effect of gum tragacanth concentration

Table 2 demonstrates the negative effect of gum on grafting. Higher amount of added gum causes less reaction parameters. High viscosity resist availability of monomer to polymer chain, so higher gum exhibits opposite effect on grafting parameters. Mohamadnia et al.²³ reported increase in gum concentration causes increase in grafting value but this effect was restricted to 1.25 g gum. Further increase in the substrate concentration, caused an increase in the reaction medium viscosity that restricts movements of macro radicals, thereby leads to decreasing the grafting ratio value.²³

Effect of time

Grafting rate accelerated over the time (Table 2). Such observation was in line with that of Behari et al.²⁴ which showed that extended period time causes increase of grafting ratio in the case of grafting of acrylamide onto xanthan gum.²⁴ The maximum magnitude of grafting percent and efficiency occurred at reaction time of 120 minutes.

Effect of temperature

Increase in temperature, conversely affect grafting reaction. This phenomenon could be result of decomposition of free radicals at higher temperature.

Mechanism

The interaction of Fe²⁺ and KHSO₅ produces OH and SO₄²⁻ free radicals, which abstracts hydrogen atoms from gum tragacanth, resulting in the formation of a gum tragacanth macroradical.

gum tragacanth except absorption band at 1584 cm⁻¹ (Table 4) that implies to ester group formation and confirm grafting of the gum.²⁵

Differential scanning calorimetry (DSC)

To discern thermal properties of native and grafted gum tragacanth, differential scanning calorimetry was conducted using Mettler Toledo model DSC 822 equipment and test conditions were: 2.229 mg samples, alumina sealed pans, 50 ml.min⁻¹ nitrogen atmosphere, heating rate of 10 °C min⁻¹, and temperature range between ambient and 450 °C.

In DSC curves, while the major thermal decomposition of gum tragacanth was presented at 348 °C, grafted copolymer exhibited an intensive exothermic peak around 410 °C (Figure 4). Accordingly, it is concluded that grafting confers a higher thermal stability to gum tragacanth as is well recognized in the literature.²³

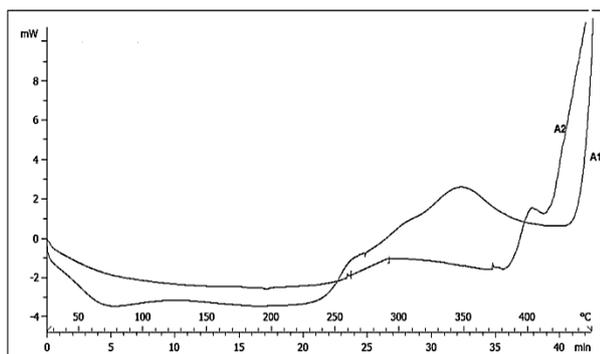


Figure 4. Differential scanning calorimetry of gum tragacanth (A1) and grafted gum tragacanth (A2)

Optimization of adsorption of ferrous ion

To find the best condition for percentage of ferrous ion removal in aqueous media (10 mg.l⁻¹), effect of pH, adsorbent dose (grafted gum tragacanth) and contact time was assessed.

Effect of pH

Ability of grafted gum in elimination of ferrous ion was measured at pH rang = 2-8. As can be seen in figure 5, the lowest removal occurred at pH = 2. With increase in pH

value, adsorption percent gradually increased and the highest adsorption was at pH = 6-8. At pH 6-8, the magnitude of adsorption was steady. According to isoelectric point determination test, isoelectric point of grafted copolymer is about 3. At pH lower than isoelectric point, copolymer surface has positive charge and at pH > 3, copolymer surface likely to be negative. Regarding to positive charge of Fe²⁺, more adsorption could be seen at pH > 3. This behavior is reported by Singh et al.¹⁹ in the case of Hg²⁺ adsorption of poly (vinyl acetate) grafted guar gum.

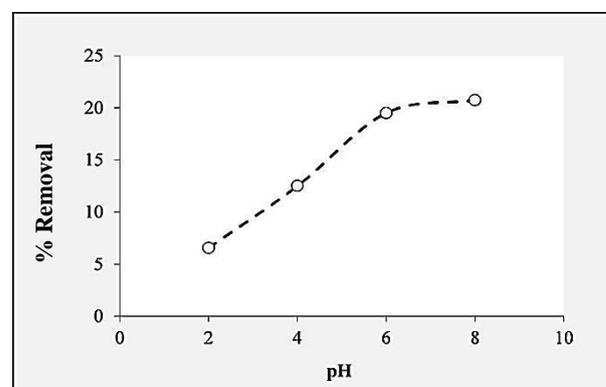


Figure 5. Effect of pH on ferrous ion removal

Effect of grafted gum dose

The effect of grafted gum dose on ferrous ion removal was studied at the range of 50-250 mg of ferrous ion, pH = 6, and contact time 60 min. As could be expected, increase in the amount of grafted gum caused more removal. Possible explanation of it is more availability of adsorbent at higher dose (Figure 6).

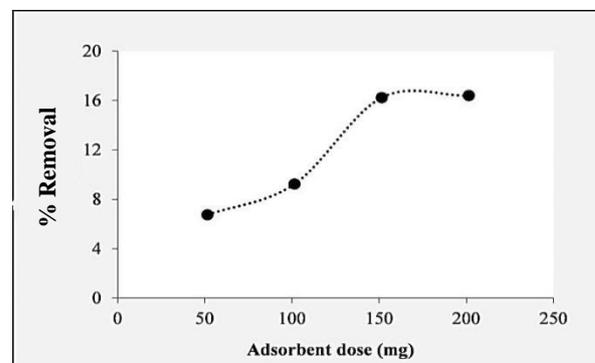


Figure 6. Effect of grafted gum on ferrous ion removal

Effect of contact time

The most adsorption was observed at the first time of reaction (up to 60 min). Thereafter, no significant change in adsorption was taken placed (Figure 7).

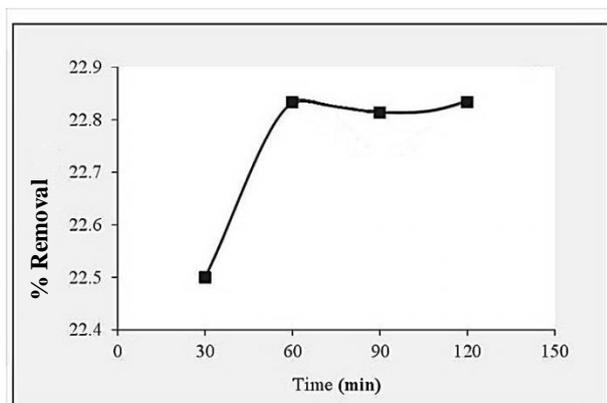


Figure 7. Effect of contact time on ferrous ion removal

Conclusion

In the present study, gum tragacanth was successfully grafted by acrylic acid using PMS and Fe²⁺ as initiators. Different reaction conditions such as temperature, time, initiator concentration, and monomer concentration were optimized. The best circumstance for reaching the maximum grafting parameters was 5×10^{-3} mol/dm³ [Fe²⁺], 1.35×10^{-3} mol/dm³ [H⁺], 4×10^{-3} mol/dm³ potassium monopersulfate. Monomer concentration also, at 5×10^{-2} mol/dm³ showed the best result. Amount of added gum was restricted to 0.25 g. Resultant grafted gum was tested for removal of metal pollution from water. In this respect, effectiveness of grafted gum in reduction of ferrous ion concentration (10 mg/l) was examined and the best result obtained at pH = 6, grafted gum: 150 mg and contact time = 60 min.

Conflict of Interests

Authors have no conflict of interests.

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