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Preparation and application of chitosan/poly(methacrylic acid) graft copolymer

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Abstract

2,2-Azobis(2-methylpropionitrile) (AMPN) was investigated as initiator for the graft copolymerization of methacrylic acid (MAA) onto chitosan. A number of variables in the grafting reaction were investigated, including AMPN and monomer concentration, material to liquor ratio, duration, and temperature of polymerization reaction. The graft copolymers were evaluated in terms of graft yield, homopolymer, monomer conversion percent, and grafting efficiency. The apparent viscosity of the resultant polymerization product was measured at different rates of shear. The optimum conditions for grafting of MAA onto chitosan are: AMPN; 0.125%, material-to-liquor ratio 1:30, and reaction temperature; 80 °C. The resultant product was used for preparation of crosslinked chitosan/poly(MAA) graft copolymer (CCPMAAGC) by its reaction with epichlorohydrin in alkaline medium. The result obtained reflects the feasibility for using CCPMAAGC as adsorbent for both Cu^{2+} ions and hepatit A virus.

Keywords: Chitosan; Methacrylic acid; Grafting; Copolymer; Copper removal

1. Introduction

Chitin is an abundant naturally occurring polysaccharide with annual production very near the levels of cellulose. Chitin consists mainly of β-(1-4)-2-acetamido-2-deoxy-D-glucose units (Wongpanit et al., 2005). Despite much recent research into its utilization, its strong intermolecular hydrogen bonding and poor solubility in common organic solvents have so far prevented widespread utilization of chitin (Kurita, Sugita, Kodaira, Hirakawa, & Yang, 2005; Peng, Weng, Li, & Gu, 2005; Sashiwa & Aiba, 2003). Chitosan is the N-deacetylated form of chitin that is obtained by alkaline treatment of chitin (NaOH) at high temperature. Chitosan and its derivatives have become useful polysaccharides in the biomedical area because of their biocompatible, biodegradable, and non-toxic properties (Park, Park, & Kim, 2006; Yun, Jiang, Chan, & Chen, 2005). Chitosan is abundant, available, renewable sources for valuable polymeric starting blocks and that the development of new routes to produce valuable products is an important research task (Abou-Aiad, Abd-El-Nour, Hakim, & Elsabee, 2006; Ahmad, Nawawi, & So, 2005; Singh, Tiwari, Tripathi, & Sanghi, 2006).

Chitosan is well known sorbent for metal ions in diluted effluent (Qian Guibal, Touraud, & Roussy, 2005; Li, Bai, & Liu, 2005). The adsorption capacity for metal ions depends on the amine group concentration of the chitosan (Wang et al., 2005; Yun & choi et al., 2005). It should be emphasized, however, that it is not the total concentration but the concentration of the accessible amine groups that is important, since these are the ones available for complex formation. A grafting of specific functional groups onto chitosan backbone allows sorption performance to be improved due to the appearance of new sorbing functions and by improvement in the diffusion property (Wan, Wang, & Qian, 2002).

Graft copolymerization of chitosan with hydroxyethyl methacrylate (MMA) using azobisisobutronitrile (AIBN)

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(Bayramoglu, Yilmaz, & Arica, 2003), methyl methacrylate using Fenton's reagent as redox initiator (Lagos & Reyes, 1988), dimethylamino ethyl methacrylate, and *N*,*N*-dimethyl-*N*-methacryloxyethyl-*N*-(3-sulfopropyl) ammonium using ceric(IV) salt as redox initiator (Liang, Ni, Zhang, & Yu, 2004; Zhang, Yuan, Shen, & Lin, 2003) and *N*-isopropylacrylamide by γ-irradiation method have been reported in the literature (Cai, Zhang, Sun, Zhang, & He, 2005).

Currently, we studied the modification of chitosan by graft copolymerization with methacrylic acid (MAA) using AMPN in order to investigate eventual changes produced in the properties of products and to compare this with that unmodified chitosan. Moreover, the main parameters affecting the grafting process were studied systematically. Utilization of the unmodified chitosan and the grafted chitosan as ionic exchanger for the removal of Cu^{2+} ions and hepatit A virus from their solutions.

2. Experimental part

2.1. Materials

Chitosan was kindly supplied by Pronova Biopolymer, Inc. (USA), degree of deacetylation and molecular weights are 85% and 127,000, respectively. Methacrylic acid (MAA), 2,2-azobis(2-methylpropionitrile), formic acid, potassium bromate, potassium bromide, and potassium iodide were all purchased from Aldrich and was used without any further purification.

2.2. Grafting process

The graft copolymerization of methacrylic acid onto chitosan was carried out in a homogenous solution. This was achieved by dissolving chitosan in a definite amount of water, having equivalent amount of formic acid in a close glass vessel. Using a mechanical stirrer, the mixture was subjected to continuous stirring till complete dissolution of chitosan. To control the reaction temperature (50–80 °C), the glass vessel was placed in a thermostatic water bath. When the reaction temperature is attained, 0.275–1.1 g MAA/1 g chitosan was added in the reaction medium. Variable amounts of AMPN (0.05–0.15%) was then added to initiate the polymerization. The reactants were subjected to continuous stirring for 2 h.

2.3. Preparation of crosslinked chitosan/poly(MAA) graft copolymer

Preparation of crosslinked chitosan/poly(MAA) graft copolmer (CCPMAAGC) was carried out by adding one mole of the grafted chitosan powder to a definite amount of water containing 2-mol sodium hydroxide. The suspension solution was subjected to continuous stirring in an ice bath under reflux, and then epichlorohydrin (1–4 mol/mol chitosan) was added dropwise. The reaction vessel was heated up to 50 °C for 2 h. The product was decanted in distilled water and filtered through a sintered glass filter and dried.

2.4. Heavy metal adsorption

To a glass-stoppered bottle containing 0.1 g chitosan derivative in the sodium form, 40 ml of 0.5 mol acetic acid/0.5 mol sodium acetate (pH 5.8–6.5) and 10 ml of 0.05 mol metal ion solution were added. The mixture was occasionally shaken at room temperature for different period of time. The adsorbed metal ion was calculated from metal ion concentration before and after treatment with chitosan derivative using standard EDTA solution.

2.5. Virus adsorption

Five liters of tap water were dechlorinated by the addition of sodium thiosulfate (2 g/L) and incubated with Hepatite A Virus (HAV) to a final concentration of 1.2×10^3 PFU/L. One liter of HAV-seed water was passed through 1 g of each adsorbent in a 2-cm diameter glass column. The filtrates were assayed for virus counts. The collected samples are decontaminated by treating it with chloroform and extracted with *n*-pentane.

2.6. Testing and analysis

At the end of the polymerization reaction, the monomer conversion percent (M.C. %) was calculated via quantitative estimation of the free double bonds of MAA before and after the polymerization process according to a method reported by (Wallace & Young (1966)). The grafted chitosan samples were separated by neutralization of formic acid with sodium hydroxide solution, filtered, then washed with distilled water till pH 7 and finally dried at 50 °C. The graft yield was calculated via determining the decrement in the nitrogen content of the grafted samples according to the procedure described by Kjeldal (Vogel, 1966). The homopolymer percent and grafting efficiency were determined by mathematical calculation based on the monomer conversion percent and graft yield percent.

The infrared spectra of chitosan and chitosan grafted poly(MAA) samples were recorded by Fourier transform IR (FTIR) spectrophotometer using KBr disk technique.

The metal adsorption capacity of crosslinked chitosan grafted copolymer for Cu^{2+} ions was calculated via determining the metal ion content by titration against standard EDTA solution (Vorlicek & Vydra, 1965).

The evaluation of crosslinked chitosan graft copolymer for removal of hepatit A Virus from the drinking water based on their titration by Plaque assay (Borovec & Uren, 1997) to count the included viruses. The adsorption efficiency was determined as the percentage of the difference of the total seeded virus recovered in filtrates.

3. Results and discussion

As already indicated, the present work is concerned with polymerization of MAA with chitosan using AMPN as a redox initiation system. The polymerization reaction was carried out under different reaction conditions including concentrations of AMPN and MAA, reaction temperature and material-to-liquor ratio. However, before going into detailed investigation of these parameters, it seems logical to shed insight on the mechanism involved in the polymerization reaction using the said initiation system.

3.1. AMPN concentration

Preparation of chitosan grafted poly(MAA) was carried out by graft copolymerization of MAA onto chitosan in a homogenous system using AMPN as a redox system. AMPN plays a dual function during the polymerization process, AMPN acts as a free radical generator and oxidant generator. The conditions of the polymerization reaction determine which route is going AMPN to work. Fig. 1 shows the dependence of the polymer yield percent including percentages of the graft yield (G.Y. %), homopolymer (H.P. %), monomer conversion (M.C. %), and grafting efficiency (G.E. %) on the AMPN concentration (0.05–0.15%) at the end of the polymerization reaction.

Obviously, all these criteria with the exception of homopolymer % increase as AMPN increases up to 0.125%, then decrease with further increase beyond this concentration. Enhancement of the redox process with subsequent abundance of free radical species capable of initiating MAA polymerization, may account for the increment in the monomer conversion, graft yield, and graft efficiency % as the AMPN concentration increases up to 0.125%. Above this concentration, decomposition products of AMPN in termination reaction prevail. These adverse effects resulting from using higher AMPN concentration certainly would lead to decreased M.C. %, G.Y. %, and G.E. %. On the other hand, the behavior of homoplymer as the AMPN concentration increases is logical consequence as it is a reversible competitive behavior for the grafting efficiency.

Fig. 2 shows the effect of AMPN concentration used during the polymerization reaction on the apparent viscosity of the resultant products measured at different shear rates. It is seen that, regardless of the concentration AMPN used the apparent viscosity decreases by increasing the shear rates up to 1032 S^{-1}, and then leveled off beyond this limit. It is also clear that the apparent viscosity of the resultant products is significantly lower than that the ungrafted chitosan solution. Also the apparent viscosity of the polymerization products decreases considerably by increasing AMPN concentration within the range studied. The decrement in the apparent viscosity could be associated with (a) molecular degradation of chitosan under the influence of the decomposition products of AMPN, (b) the higher rate of termination which leads to shorter polymer side chains.

3.2. Effect of reaction temperature

Fig. 3 summarize the graft copolymerization of MAA onto chitosan at different reaction temperatures (50–80 °C), when the polymerization reaction was carried out using AMPN, 0.125%; MAA, 0.55 g/1 g chitosan, and material to liquor ratio, 1:25 for 2 h. It was observed that the polymer yield %, except G.E %, is increase by raising the reaction temperature from 50 to 80 °C. The above finds imply that raising the polymerization temperature acts in favor of polymerization of MAA with chitosan. Raising the temperature within this the range seems to cause (a) greater molecular collision among reactants through decreasing the viscosity of the polymerization medium along with higher mobility of the so made "energetic" molecules, that is monomer and chitosan macroradicals, (b) speeding up the rate of initiation and propagation

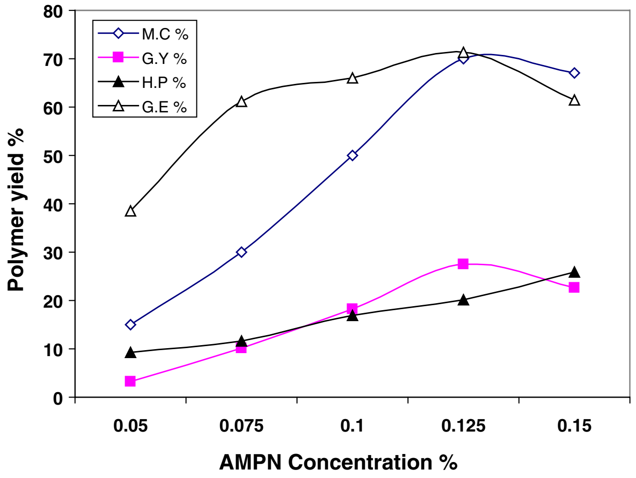

Fig. 1. Effect of AMPN concentration on the polymer yield %. Chitosan 4 g, formic acid; 1.2 g, M/L ratio 1:25, temperature 60 °C, MAA; 0.55 g/g chitosan.

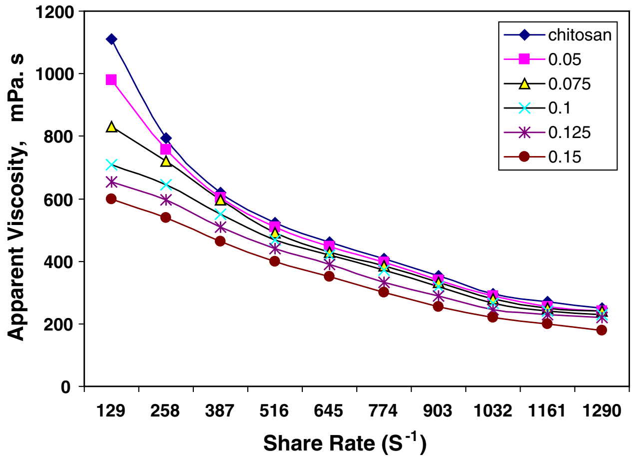

Fig. 2. Effect of AMPN concentration on the apparent viscosity of the grafted polyblend. Chitosan 4 g, formic acid; 1.2 g, M/L ratio 1:25, temperature 60 °C, MAA; 0.55 g/g chitosan.

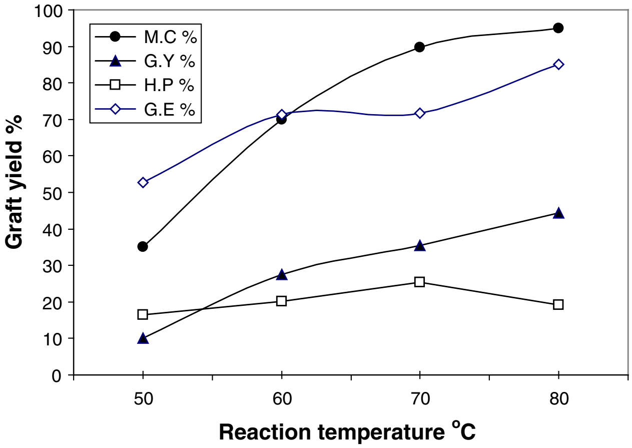

Fig. 3. Effect of reaction temperature on the polymer yield percent. AMPN, 0.125%; formic acid, 0.4 g/1 g chitosan g; M/L ratio 1:25, time; 2 h, [MAA]; and 0.55 g/g chitosan.

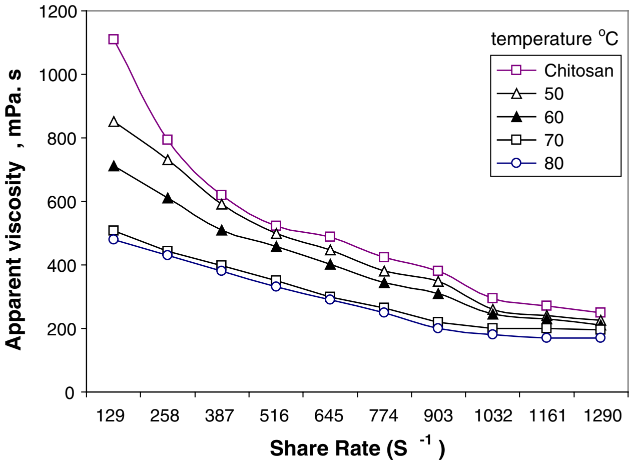

Fig. 4. Effect of reaction temperature on the apparent viscosity of grafted polyblends AMPN, 0.125%; formic acid, 0.4 g/g chitosan g; M/L ratio 1:25, MAA, 0.55 g/g chitosan, time, 2 h.

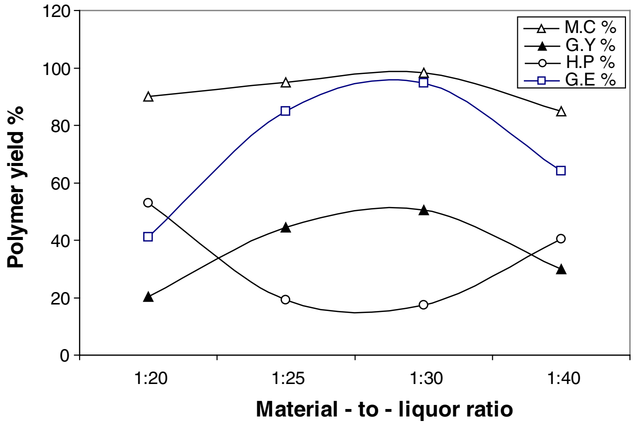

Fig. 5. Effect of material-to-liquor ratio on the polymer yield % AMPN; 0.125%, (formic acid) 0.4 g/g chitosan, reaction temperature; 80 °C, MAA; 0.55 g/g chitosan; time, 2 h.

of grafted/poly(MAA) growing chains as well as homopoly(MAA) chain radicals by virtue of enhancing the initiation efficiency of the redox system, and (c) higher rate of AMPN decomposition and consequently increase the number of free radical sites in the polymerization medium.

Fig. 4 shows the dependence of the apparent viscosity of resultant polymerization products on the polymerization temperature. It is evident that the apparent viscosity decreases by raising the reaction temperature from 50 to 80 °C. The decrement in the apparent viscosity may be attributed to the oxidative and termination actions that reflect the higher rate of AMPN decomposition at higher temperature.

3.3. Effect of material to liquor ratio

Fig. 5 shows the extent of polymerization, expresses as M.C. %, G.Y. %, H.P. %, and G.E. %, when the polymerization was conducted using different liquor ratios. It is obvious that the optimum material-to-liquor ratio (M/L) is 1:30. Decreasing the M/L ratio below 1:30 is accompanied by a decrement in the M.C. %, G.Y. %, and G.E. %, such decrease may be attributed to the high viscosity of the polymerization medium and thereby lower movability of the reactant molecules and accessibility of chitosan macroradicals. While increasing M/L ratio above 1:30 is accompanied by dilution of the reactants and lesser molecular collision.

Fig. 6 shows the effect of material-to-liquor ratio of the resulting polymerization products on the apparent viscosity. The data indicate that the apparent viscosity depends on the M/L ratio and follow the order: 1:30 > 1:40 > 1:25 > 1:20. This behavior is expected and reflects the data given in Fig. 5 which indicate that the highest M.C. %, G.Y. %, and G.E. % are obtained on using M/L ratio 1:30. The higher apparent viscosity on using M/L- ratio 1:30 is rather interesting. It suggested that, the M/L ratio 1:30 would help established rapid combination between chitosan macroradicals Ch-X$^{\bullet}$ and poly(MAA) radicals (PMAA$^{\bullet}$)

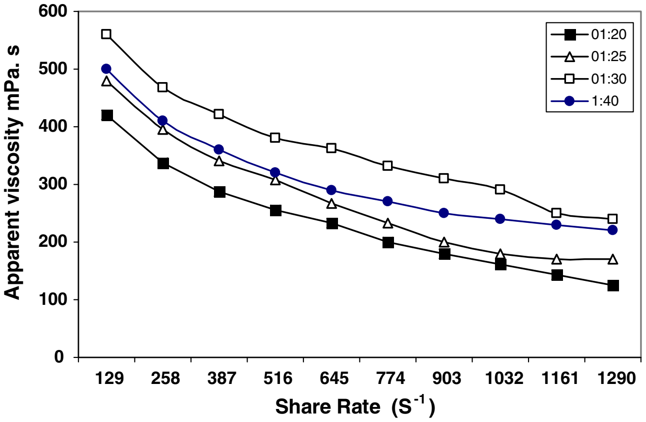

Fig. 6. Effect of material-to-liquor ratio on the apparent viscosity of the grafted polyblends. AMPN, 0.125%; formic acid, 0.4 g/g chitosan; temperature, 80 °C; MAA, 0.55 g/g chitosan; time, 2 h.

$$\text{Ch-X}^{\bullet} + \text{Ch-X}^{\bullet} \rightarrow \text{Ch-X-X-Ch}$$

$$\text{PMAA}^{\bullet} + \text{PMAA}^{\bullet} \rightarrow \text{PMAA-PMAA}$$

$$\text{Ch-X}^{\bullet} + \text{PMAA}^{\bullet} \rightarrow \text{Ch-X-PMAA}$$

That is, termination via combination of growing polymers chain radicals seems to be responsible for the observed increment in the apparent viscosity of the resultant products.

3.4. Effect of methacrylic acid concentration

Fig. 7 shows the effect of MAA concentration (0.275–1.1 g/1 g chitosan) on the polymer yield percent. The polymerization reaction was carried out using 0.125% of AMPN, M/L-ratio 1:30 at 80 °C. The percentages of G.Y, H.P, and G.E increase by increasing MAA concentration within the range studied. On the other hand, the M.C. % marginally increases by increasing MAA concentration from 0.275 to 0.55 g /1 g chitosan, further increase above this limit leads to a significant decrement in the M.C. %. The enhancement in the polymerization reaction by increasing MAA in the polymerization medium could be associated with (a) decreasing the pH of the polymerization medium and consequently faster decomposition of AMPN, (b) enhancement of the redox process as a whole, (c) abundance of primary free radical species which contribute in initiation of grafting and homopolymerization, (d) greater solubility and compatibility of chitosan with the reaction ingredients, and (e) the higher concentration of MAA in the polymerization system provides opportunity for greater availability of MAA molecules to be present in the proximity of immobile chitosan macroradicals, thus increasing the grafting reaction. The decrement in M.C. % on using MAA higher than 0.55 g/1 g chitosan may be attributed to shortage of the active species which is needed to initiate such amount of monomer.

Fig. 8 depicts the influence of amount of MAA incorporated in the polymerization medium on the apparent viscosity of the resultant polymerization products. It is evident that the apparent viscosity of the resultant polymerization products, regardless of the rate shear, follows the order: 1.1 > 0.828 > 0.55 > 0.275. It is clear also from the data (Fig. 8) that the apparent viscosity increases by increasing the amount of MAA incorporated in the polymerization medium. The increase in the apparent viscosity by increasing MAA concentration may be ascribed to (a) higher rate of free radical formation due to higher AMPN decomposition, (b) the consumption of AMPN decomposition product in the polymerization reaction (homopolymer and grafting) rather than oxidative degradation reaction Fig. 9.

3.5. Evidence of grafting: IR-spectra

On comparing the infrared (IR) spectra of chitosan and chitosan/grafted Poly(MAA), the absorption bands corresponding to the carbonyl groups were observed in the spectra of chitosan/grafted poly(MAA), whereas these absorption band were absent in the spectra of chitosan. A strong band at 1654 cm^{-1} due to carbonyl band of carboxylate anion is present.

4. Utilization of crosslinked chitosan/poly(MAA) graft copolymer in the adsorption of Cu^{2+} ion and hepatit A virus from it is effluents

4.1. Adsorption of Cu^{2+} ion onto CCPMAGC

In this section experiments were designed to study the overall adsorption capacity as a function of the properties of the crosslinked chitosan/poly(MAA) graft copolymer (CCPMAAGC). The latter was prepared as recorded in the experimental part using chitosan/Poly (MAA) with 65% graft yield and 1 mol epichlorohydrin/mol chitosan copolymer. Results obtained along with their appropriate discussion are given below.

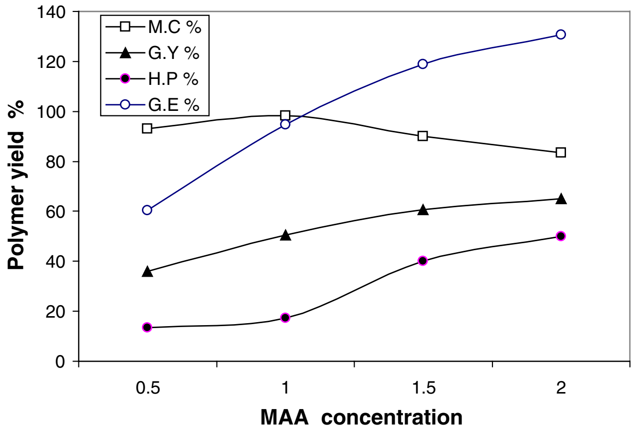

Fig. 7. Effect of MAA concentration on the polymer yield percent AMPN, 0.125%; formic acid, 0.4 g/g chitosan, temperature, 80 °C; M/L-ratio; 1:30, time 2 h.

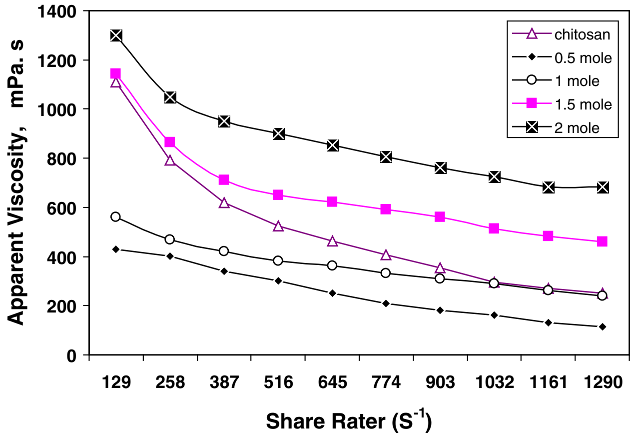

Fig. 8. Effect of MAA concentration on the apparent viscosity of the grafted polyblends. AMPN, 0.125%; formic acid, 0.4 g/g chitosan, temperature, 80 °C; M/L ratio, 1:30; time, 2 h.

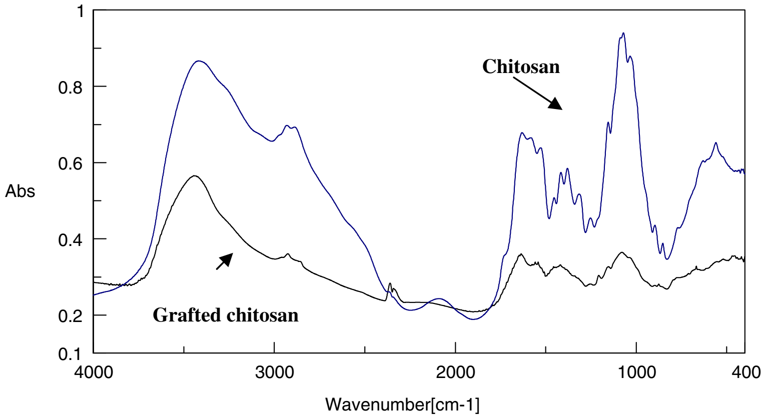

Fig. 9. The FTIR spectra of the unmodified chitosan and grafted samples.

Figs. 10 and 11 show the effect of duration and amount of CCPMAAGC on the exhaustion percent and adsorption capacity expressed in mg copper/1 g CCPMAAGC. It is seen (Fig. 10) that, regardless of the amount of CCPMAAGC incorporated in the copper acetate solutions, the percent exhaustion of Cu^{2+} ion increases by increasing the duration of adsorption. Also, as expected it is might be found that increasing the amount of CCPMAAGC incorporated in a fixed volume and concentration of the Cu^{2+} ion solutions is accompanied by higher rate of exhaustion percent. This suggested that increasing the amount of CCPMAAGC provided higher surface area for better metal uptake.

Fig. 11 shows the effect of the amount of CCPMAAGC on the adsorption capacity expressed by mg Cu^{2+} ions/g CCPMAAGC. It was found that, increasing the amount of CCPMAAGC incorporated in the adsorption medium is accompanied by significant decrease in the adsorption capacity for Cu^{2+} ions.

Taking in consideration the fixed volume of the copper acetate solution and its fixed concentration therein one would realize that most, if not all the Cu^{2+} ions were taken up by certain amount of CCPMAAGC. Thereafter incorporation of further amount of CCPMAAGC would not contribute much in Cu^{2+} ions adsorption.

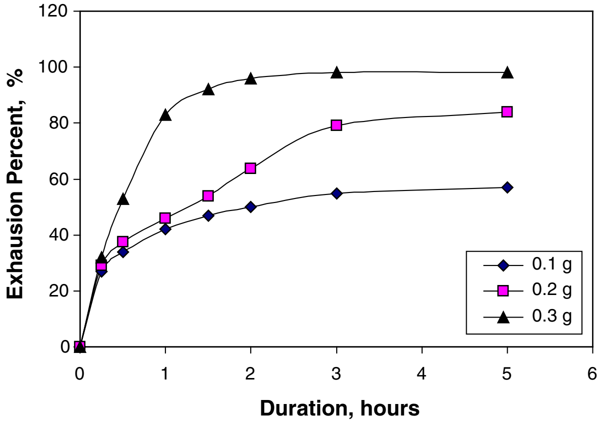

Fig. 10. Effect of duration and amount of CCPMAAGC on the exhaustion percent of Cu^{2+} ions temperature 25 °C, G.Y. % of CCPMAAGC, 65%.

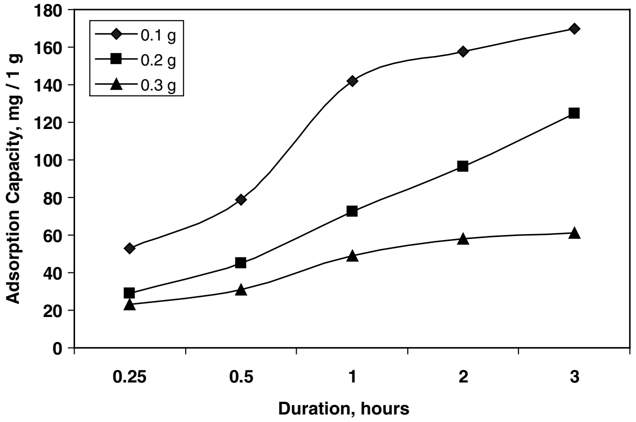

Fig. 11. Effect of duration and amount of CCPMAAGC on the adsorption capacity of Cu^{2+}ions.

The increment in the amount of CCPMAAGC in a fixed volume and concentration of copper acetate leads to increment in the number of active sites per unit volume and simultaneously a decrement in the available Cu^{2+} ions per unit weight of CCPMAAGC.

4.2. Adsorption of HAV onto CCPMAGC

Crosslinked chitosan/poly(MAA) graft copolymer was evaluated as adsorbent for the hepatit A virus from drinking water.

Fig. 12 shows the effect of graft yield percent, having two different degree of crosslinking, on the adsorption percent of hepatit A virus when 1 L of HAV-seed water was passed through 1 gm of each adsorbent in a 2-cm diameter glass column.

Fig. 12 summarizes also, the effect of the graft yield percent of crosslinked chitosan/poly(MAA) graft copolymer (CCPMAAGC) on the adsorption percent of the hepatit

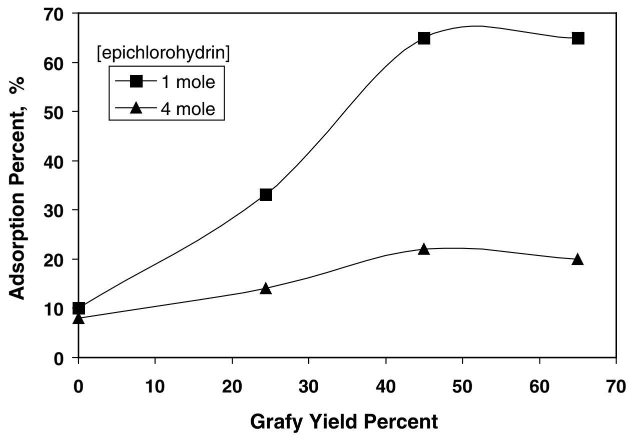

Fig. 12. Effect of graft yield percent of CCPMAAGC on the adsorption percent of hepatit A virus.

A viruses (HAV) from the drinking water. It is clear from the data that, the adsorption percent of HAV increases by increasing the graft yield percent up to 45% and then leveled off. It is understandable that the increment in the adsorption percent by using variable graft yield of CCPMAAGC and the same amount of crosslinking agent is may be attributed to the increase in the number of available active sites as well as the presence of hydrophilic groups appears to play an important role in the ability to adsorb viruses.

Fig. 12 also, shows that the effect of the degree of crosslinking during the crosslinking step using 1 and 4 mol epichlorohydrin/mole chitosan/poly(MAA) copolymer, on the adsorption percent of viruses. The results indicate that the CCPMAAGC with low degree of crosslinking "using 1 mol epichlorohydrin" has higher adsorption percent for HAV than CCPMAAGC with higher degree of crosslinking "using 4 mol epichlorohydrin". The increase in the adsorption percent of HAV was attributed to the low levels of crosslinking that prevent the formation of closely packed chain arrangement without any great reduction in the swelling capacity. Whereas, the decrement in the adsorption percent at high levels of crosslinking may be due to the lower swelling capacity of the CCPMAAGC and hence lower accessibility.

5. Conclusion

Chitosan/poly(MAA) graft copolymer was prepared by polymerization of MAA with chitosan using AMPN initiation system. The systematic studies of the factors affecting the polymerization reaction indicated that the optimum conditions for grafting of MAA onto chitosan are: AMPN; 0.125%, material-to-liquor ratio 1:30, and reaction temperature; 80 °C. The resultant product was used for preparation of crosslinked chitosan/poly(MAA) graft copolymer (CCPMAAGC) by it is reaction with epichlorohydrin in alkaline medium. The result obtained reflects the feasibility for using CCPMAAGC as adsorbent for both Cu^{2+} ions and hepatit A virus.

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