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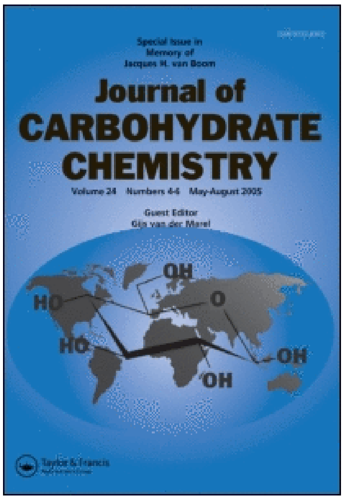

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GRAFTING OF SOME CARBOHYDRATES WITH MULTI-GROUP CHELATING MONOMER[1]

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ABSTRACT

Graft copolymerization reactions onto some polysaccarides were carried out using acryloylcyanoacetohydrazide (ACAH) as chelating monomer. Different grafting variables onto chitin were studied, namely time, temperature, concentrations of monomer and initiator. Grafting by the prementioned chelating monomer was also carried out on chitosan and bagasse raw materials for different periods. The grafting parameters obtained were compared with those values of PACAH-grafted chitin and polyacrylonitrile-grafted polysaccharides. FTIR-spectra of the grafted polysaccharides were also studied to evidence the grafting. The PACAH- and PAN-grafted carbohydrates with the same range as molecular substitution (M.S. 0.8- 1.2) were compared their ability to chelate some metal ions, namely Cu (II), Mn(II), Fe(III) and Cr(III). The adsorption ability of metals onto the grafted polysaccharides was also compared with that obtained from previously examined modified polysaccharides, under nearly the same adsorption conditions.

INTRODUCTION

Chitin is a polysaccharide constituted of repeating β-(1 → 4)-2-acetamido-2-deoxy-D-glucose units, some of which are deacetylated. This natural polymer can be considered a derivative of cellulose wherein the C-2 hydroxyl groups have been replaced by acetamido groups. Chitin is the second most abundant polysaccharide occurring in nature, after cellulose.[2] Chitin was expected to yield better performances than cellulose and some substituted celluloses in chromatographic separation of metal ions by chelation, this view having been espoused because the nitrogen percent of chitin is theoretically high, 6.89 %, compared to about 1.5–3.8[3,4] for most artificially substituted celluloses, e.g. diethylaminohydroxypropyl cellulose.

However, because of the highly crystalline nature of chitin it has a lower surface activity and is less accessible to penetration by water and other reagents, limiting the practical usefulness of chitin, especially in its ability to extract heavy metal ions from aqueous media.[5–9] One of the earliest attempts to improve the affinity of metal ions to chitin was to first convert it to chitosan, by *N*-deacetylation under alkaline conditions.[10]

Graft copolymerization reactions of vinyl monomers on polysaccharides, using a redox initiator or by a photoinduced method, have recently been explored as an interesting alternative chemical modification to develop natural /synthetic polymer hybrid materials. These graft polysaccharides are of importance in view of industrial applications such as water absorbents, ion exchangers, flocculants, membranes, and principally, chelating agents.[11-15] A considerable number of studies concerned with graft copolymerization on cellulose, starch, cotton, wool and agricultural wastes have been carried out,[16-22] but the literature of the graft copolymerization on natural nitrogen-containing polysaccharides, e.g, chitin and chitosan are limited.[15,23] It appears that, modified polysaccharides can adsorb metal ions from solutions to a much greater extent than can the natural polysaccharides. Therefore, a number of grafting procedures have been employed to introduce multiple functional groups onto the backbone of polysaccharides. [24-28]

This study was undertaken to introduce multifunctional groups onto chitin through grafting with acryloylcyanoacetohydrazide (ACAH) monomer. Moreover, the ability of PACAH-grafted chitin to chelate divalent and trivalent metal ions such as Cu(II), Mn(II), Fe(III) and Cr(III) was also studied and compared with the chelating ability of PACAH-grafted chitosan, PACAH-grafted bagasse and polyacrylonitrile-grafted polysaccharides. Choosing bagasse as an example of a cellulosic material was deemed important as bagasse produces the most abundant lignocellulosic waste in Egypt, where its dry amount is ~ 1.2 million ton /year.

EXPERIMENTAL

a. Materials. Chitin from crab shells ($M_r \sim 400{,}000$, crystallinity index[29,30] 1.14244) and chitosan (medium molecular weight, $M_r \sim 400{,}000$, degree of deacetylation[31] 72.1% and crystallinity index[29,30] 1.05) purchased from Fluka were used without further purification and powdered (200 mesh) before use. Raw bagasse was supplied from the Kom-Ombo Mill of the Sugar-Cane Co., Upper Egypt, and powdered (200 mesh) before use. The chemical constituents of bagasse are: 42.68 % α-cellulose[32], 27.60 % pentosans[33] and 20.92 % lignin.[34] The crystallinity index of bagasse is 1.174.[29,30] Acryloylcyanoacetohydrazide (ACAH) monomer (mp 195 °C) was prepared according to the method described by Mikhael.[35] All other chemicals were of analytical grade.

b. Graft-copolymerization of ACAH onto chitin. Chitin powder (1.0 g) was dispersed in distilled water, followed by adding an aqueous solution (5 mL) ammonium persulfate (0.05 mol/L) as a free radical initiator and grafting ACAH monomer (1 g in 30 mL of water), The final water to chitin ratio (wt/wt) was 60 /1. The mixture was left for 2 h at 60 °C in a nitrogen atmosphere under continuous stirring, and then the reaction was terminated by pouring the reaction mixture into a large volume of ethanol. The precipitate was filtered and washed several times with ethanol and ethanol and water mixture (1:1), and then dried at 60 °C to constant weight. Purification of the graft copolymer was done by extraction of the homopolymer with dimethylformamide for 72 h in a Soxhlet apparatus. The solid obtained was filtered and dried at 60 °C to constant weight. The grafting parameters (% of polymerization, % grafting yield and % grafting efficiency) and molecular substitution (M.S.) were calculated from the increment in the nitrogen content of grafted sample compared to the nitrogen content of chitin treated under the same conditions of grafting, but without monomer. The nitrogen content was determined by the Kjeldahl method. The molecular substitution (M.S.) is the average number of moles of monomer that become attached to each acetylglucosamine unit in chitin.

Different variables were applied in the grafting experiments namely monomer to chitin ratio (0.5 – 4), concentration of initiator (0.01 – 0.1 mol /L) , temperature (40 - 80 °C) and time (1- 5 h).

c. Graft-copolymerization of ACAH and acrylonitrile (AN) onto some polysaccharide. Chitosan and raw bagasse were used in this study as were other polysaccharides materials, in comparison with chitin. The preparation of PACAH- and

PAN-grafted polysaccharide were done according to the described method but for different reaction periods (1- 5 h). The baseline copolymerization conditions were 2 /1 monomer to polysaccharide ratio, 0.05 M /L ammonium persulfate, and 60 /1 water to polysaccharide ratio, at 60 °C.

d. IR-Spectra. FTIR spectral analysis was used to elucidate the structure of the grafted polymeric ACAH wastes. The spectra of all examined samples were recorded in an Insco FT /IR-300E Fourier Transform infrared Spectrophotometer at 4000 –200 cm^{-1} wavelength, using samples in the form of KBr tablets.

e. Binding ability of grafted polysaccharides to metal ions. Aqueous solutions of bidistilled water containing 0.44 mmol of divalent and trivalent metal chlorides, such as $CuCl_2$, $MnCl_2$, $FeCl_3$ and $CrCl_3$ were prepared. The PACAH- and PAN- grafted polysaccharides (200 mg), having nearly the same M.S. (~ 0.81 – 1.3), were put into plastic bottles containing 50 mL of the metal chloride solution (pH ~ 5.5). The mixtures were gently stirred for 24 h at room temperature (~ 25 °C). Grafted polysaccharide-metal products were removed by filtration, and residual metal ion amounts in the filtrate determined from atomic absorption measurements. Adsorbed metal ion amounts were then calculated based upon original metal ion concentrations. For comparison, the same experiments were carried out on the unmodified polysaccharides.

RESULTS AND DISCUSSION

1. Graft copolymerization of acryloylcyanoacetohydrazide onto chitin

Effect of chelating monomer to chitin ratio. To trace the influence of the degree of grafting on the polysaccharides, different ratios of monomer to polysaccharide (wt/wt) were used: 0.5/1, 1/1 , 2/1, 3/1 and 4/1. The other experimental conditions were : 0.05 mol/L ammonium persulfate and a 60/1 water to chitin ratio, for 2 h at 60 °C . The results obtained are shown in **Figure 1.** It is clear that increasing the monomer to chitin ratio from 0.5/1 to 4 /1, gradually increases the percentage of polymerization with maxima for the grafting yield and molecular substitution (M.S) at monomer to chitin ratio 2/1 – 3 /1. For the grafting efficiency, the maximum value is shown at monomer to chitin ratio 1/1. The increase in the grafting yield, and consequently the M.S., on increasing the monomer concentration (from 0.5/1 to 3/1), is related to the increase in the number of monomer

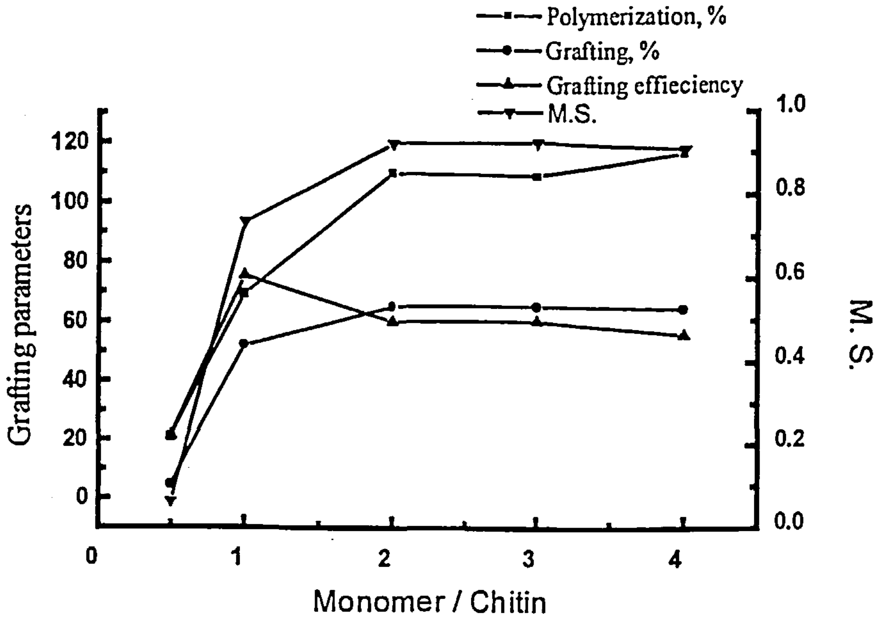

Figure 1. Effect of ACAH to chitin ratio on grafting degree of chitin.

molecules which bond with initiated sites on the chitin chains. However, the unexpected decrease in the grafting yield on further increasing the monomer to chitin ratio (4 :1), may be related to further increase of radicals created on monomers than accessible hydroxyl groups of chitin. This enhances the rate of termination through coupling of polymer radicals to form homopolymers rather than enhancing the rate of propagation of chitin radicals.

From these results it is clear that the monomer to chitin ratio (1/1) plays a role on grafting efficiency. Therefore, to study the effects of concentration of initiator, temperature and time of copolymerization reaction, the monomer to chitin ratio used was 1/1.

Effect of the concentration of initiator. Grafting reactions using different concentrations of ammonium persulfate, APS (0.01– 0.1 mol / L) as a free-radical initiator were carried out at 60 °C, for 2 h and water to chitin ratio 60 /1. From **Figure 2** it is clear that, the maxima of the percentages of polymerization, grafting yield, and molecular substitution occur at initiator concentration 0.03 mol /L, while grafting efficiency occurs at a concentration of 0.05 mol/L.

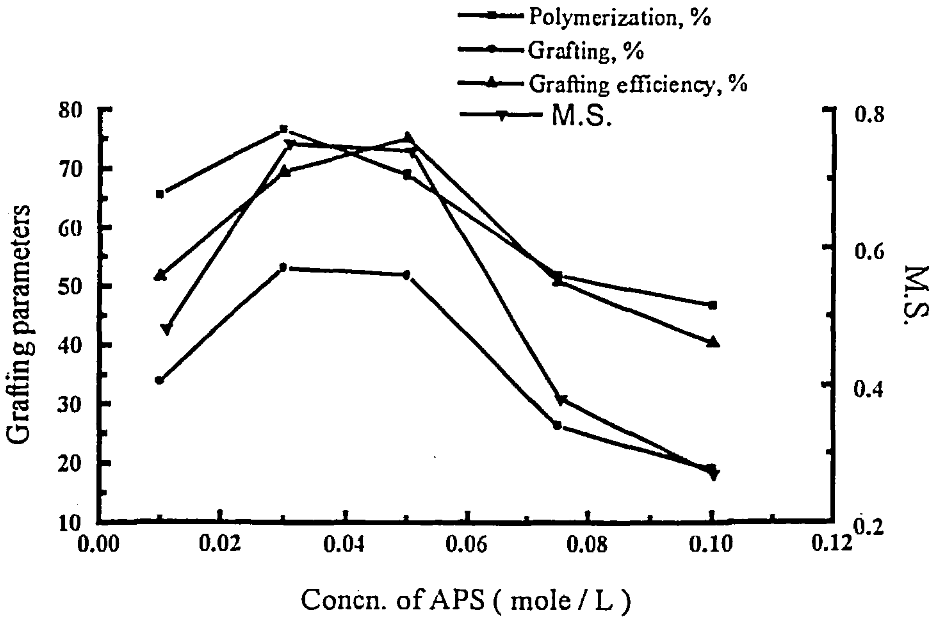

Figure 2. Effect of concentration of initiator on grafting degree of chitin.

The increase of the grafting yield upon increasing the APS concentration to a maximum followed by a decrease in grafting yield, may be related to an increase in the number of free radicals, which affects the increased grafting yields. The further increase in the number of free radicals may cause termination reactions through coupling with other polymer radicals. This view is supported by the increased amount of extracted homopolymer.

Effect of reaction temperature. Grafting reactions using 1/1 chitin to monomer ratio, 0.05 mol/L APS initiator and a 60:1 water to chitin ratio were carried out at temperatures between 40 °C - 80 °C, for 2 h. The variation of the grafting parameters and molecular substitution as a function of temperature are shown in **Figure 3**. It is clear that the grafting parameters and molecular substitution (M.S.) at relatively high reaction temperatures are higher than at lower ones. This may be due to increased penetration of the grafting medium throughout the macrostructure of chitin with increase in temperature, and consequently creating a greater number of grafting sites, which increases the rate of initiation and decreases the rate of termination of the growing polymer chain.

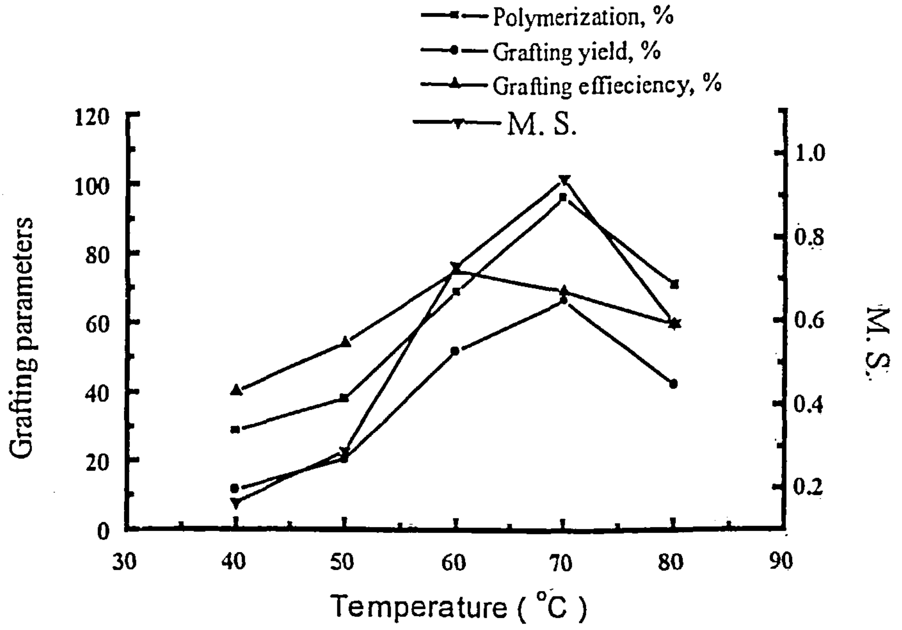

Figure 3. Effect of grafting temperature on grafting degree of chitin.

The observed maximum grafting efficiency at a reaction temperature of 60 °C indicates that the ceiling temperature for the polymerization reaction of acryloylcyanoacetohydrazide that uses the free radical polymerization method is 60 °C. The ceiling temperature T_c of the polymerization is defined as the temperature at which the rate of the addition (propagation) reaction is equal to the rate of the elimination (depropagation) reaction for a given system.[36] One of the basic reactions that free radicals undergo is the unimolecular elimination of the monomer from the radical end group of a given polymer chain. This reaction is the reverse of the propagation or addition reaction and is termed depropagation or depolymerization. The equilibrium involved in the reaction of a monomer-derived radical with the monomer is shown in the equation below.[36] Increasing the temperature of the reaction

$$M^{\cdot} + M \underset{k_{-p}}{\overset{k_p}{\rightleftarrows}} MM^{\cdot}$$

has a greater effect on increasing k_p than k_{-p}. At a ceiling temperature $k_p = k_{-p}$. Therefore, the temperature of copolymerization reaction over the ceiling temperature (> 60 °C) leads to a faster rate of termination than propagation, and consequently leads to an increase in the percentages of extracted homopolymers.

Effect of reaction time. In this study, the grafting reactions were carried out under the same experimental conditions described in the previous method but for different periods between 1 h to 5 h, at 60 °C. The results obtained are illustrated graphically in **Figure 4**. It is shown that there the percentages of polymerization and grafting yield, in addition to the molecular substitution at 3- 4 h are at a maximum. However, at reaction time 2 h maximum grafting efficiency still occurs, indicating that after a reaction time of 2 h the formation of homopolymer predominates.

The initial increase in the percentages of polymerization and grafting yield, and consequently M.S., with increase in reaction time from 1 h to ~ 4 h may be due to the availability of grafting sites for a longer period as the reaction proceeds. However, the decrease in the rate of grafting with prolonged reaction time can be attributed to decrease in concentration of both the monomer and the initiator as well as a reduction in the available number of active sites on the polysaccharide accessible for grafting.[37,38]

From all the foregoing results it can be concluded that optimum grafting yield and M.S. of graft copolymerization of ACAH onto chitin occur at monomer to chitin ratio 2/1 **(Figure 1)**, or at a reaction temperature 70 °C **(Figure 3)**, whereas the grafting yields and molecular substitution are 65 % and 66.5 % and 2.7 and 2.8, respectively. Because of the undesirable relative decrease in the nitrogen content of chitin from 6.74 to 6.3 after reaction at 70 °C without monomer and since the main interest was improving binding ability of chitin to metal ions in comparison to chitosan and cellulosic materials, a further study was applied. In this study the graft-copolymerization reactions of ACAH and acrylonitrile (as another chelating monomer with a pendant nitrile group) onto chitin, chitosan and raw bagasse were examined.

2. Graft copolymerization of chelating monomers onto other polysaccharides.

Grafting reactions were carried out using 2/1 monomer to polysaccharide ratio, 0.05 mol/L ammonium persulfate and water to polysaccharide ratio 60/1, for different periods (1- 5 h) at 60 °C.

When ACAH was used as a chelating monomer for grafting onto chitin, chitosan and raw bagasse, **Figure 5** shows that, generally there are maxima for the grafting

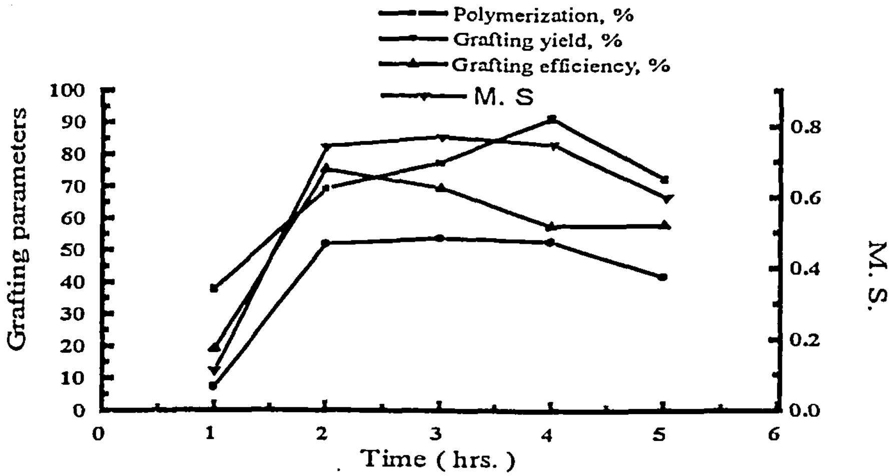

Figure 4. Effect of concentration of initiator on grafting degree of chitin.

parameters and molecular substitution. The extent and the rate of copolymerization reaction depends upon the type of polysaccharide used. The grafting yields and M.S. for the copolymerization of ACAH onto chitosan showed relatively higher values than those obtained for the copolymerization onto chitin; while the grafting yields of PACAH-grafted bagasse lies in between. The relatively lower grafting yields of PACAH-grafted chitin compare to PACAH-grafted bagasse and PACAH-grafted chitosan are probably related to the higher order structure of chitin resulting from a network of hydrogen bonds between the NH and C=O groups in neighboring molecules,[39] i.e., less accessible groups are available to graft reaction.

On using acrylonitrile as chelating monomer for grafting onto the prementioned carbohydrates, **Figure 6** shows that, as was the case of graft copolymerization using ACAH monomer, the relative grafting yield and M.S. are as follows: PAN-grafted chitosan > PAN-grafted bagasse > PAN-grafted chitin. The increase in the grafting yield is more noticable at relatively shorter reaction time (1- 3 h) than longer ones (4 –5 h). It is clear also that, especially in the case of grafting onto chitin, in spite of the molecular substitutions using acrylonitrile are higher than using ACAH, the grafting efficiencies using ACAH monomer are higher than AN monomer, i.e., less homopolymer is formed. This means that the rate of propagation for ACAH is higher than AN, i.e., the reactivity of ACAH is higher than AN.

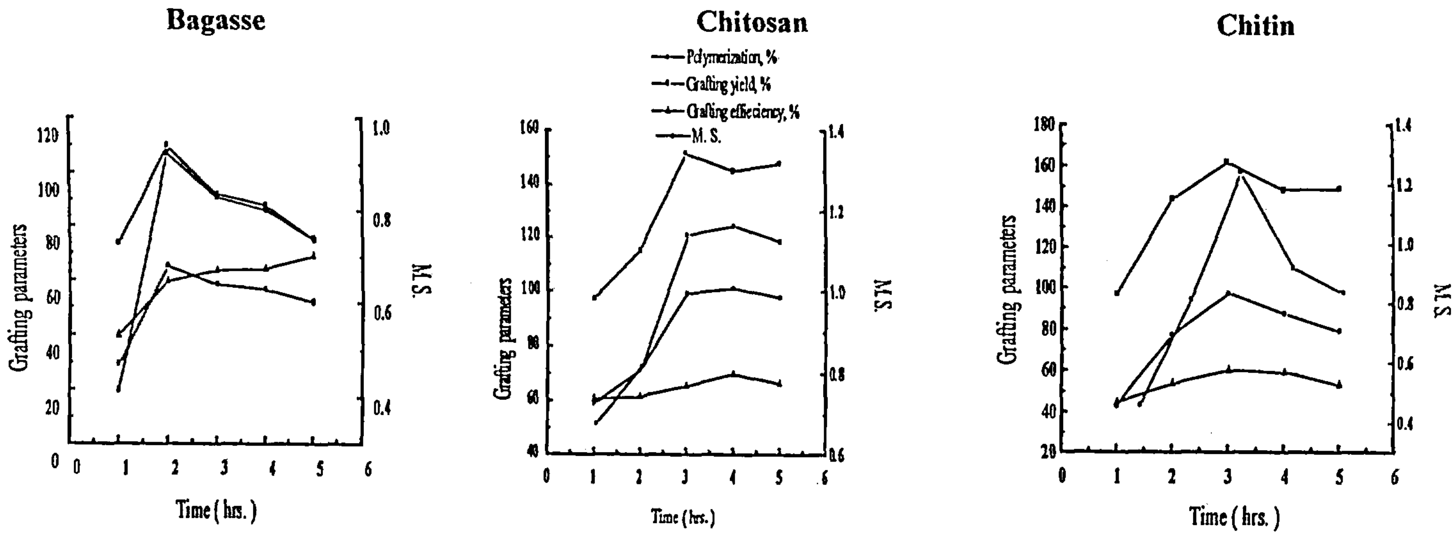

Figure 5. Effect of the time of graft copolymerization of acryloylcyanohydrazide onto polysaccharides on grafting degree.

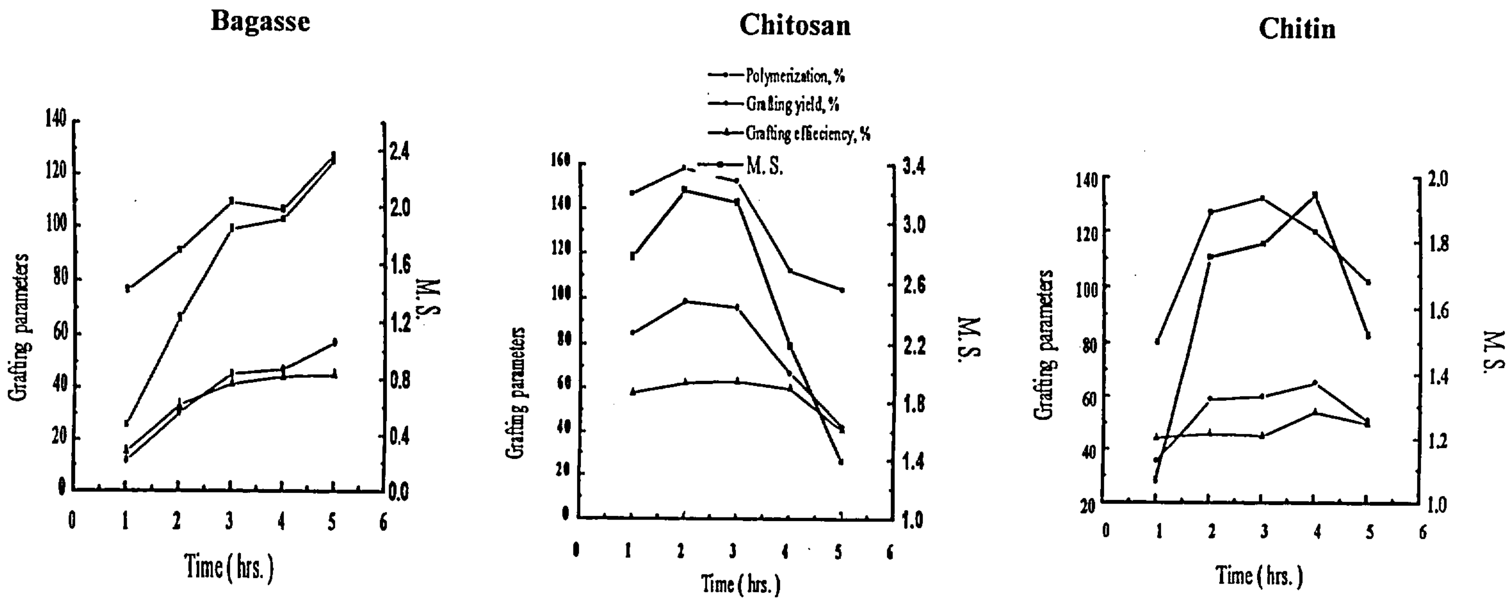

Figure 6. Effect of the time of graft copolymerization of acrylonitrile onto polysaccharides on grafting degree.

3. FTIR-spectra.

To prove the addition of ACAH and the graft copolymerization of ACAH and AN onto the three polysaccharides FTIR spectra of monomer, unmodified and grafted carbohydrates were recorded. The examined PACAH- and PAN-grafted carbohydrates have nearly the same M.S , ~ 0.8 – 1.3 (see **Figures 1, 5 and 6**).

Table 1 lists the main IR frequency bands of the prepared ACH□AH monomer and Table 2 lists the relative absorbancies of the grafted polysaccharides in comparison with ungrafted ones. The relative absorbance, E, is the ratio of the absorbance of the investigated band to that of the band at 1160 cm^{-1} which corresponds to C-O of the glucopyranose ring (nearly constant for all samples).

From Table 2 it is clear that unmodified chitin has a characteristic bands at 3450, 2960, 1657, 1627, 1559, and 670 cm^{-1}. The bands at 3450, 1559 and 670 cm^{-1} are due to XH (X = N or O) stretching vibration inplane, XH bending, and out-of-plane XH-bending, respectively, for the acetamido groups.When X = O, XH = OH, there isn't an OH function in an acetamido groups clarify. The broadening of the bands in the region of wave-numbers 4000- 3000 cm^{-1} and the appearance of more than one shoulder indicates a difference in hydrogen bonding from residual OH and NH functions. This view is emphasized by the appearance of two absorption bands in the 1700-1600 cm^{-1} region, at 1657 cm^{-1} and 1627 cm^{-1}. Darmon and Rudall[41] assigned the frequency 1660 cm^{-1} to the stretching vibration of C=O hydrogen bonded to an –NH group and the frequency at 1625 cm^{-1} to C=O stretching when C=O is hydrogen bonded to an OH group. On graft copolymerization of ACAH or AN onto chitin, the bands due to C≡N group at 2260 cm^{-1} appear. Its relative absorbance, E, in the case of PAN-grafted chitin is relatively higher than that of PACAH-grafted chitin. This indicates that the relative absorbencies of the bands corresponding to C=O at 1675 and 1627 cm^{-1} increase compared with ungrafted chitin. On grafting the maximum band position corresponding to the NH and OH stretching vibration (~ 3450 cm^{-1}) is shifted to lower wave numbers. The extent of the shift in the case of PAN-grafted chitin is higher than PACAH-grafted chitin. Spectra of un- and grafted-chitosan samples showed the same trend for chitin samples.

For the effect of graft-copolymerization onto raw bagasse using monomers ACAH and AN, the spectra (Table 2) show that in addition to the shift in the position of band maxima corresponding to the stretching vibration of the OH group and the

Table 1. Main IR- frequency bands of acryloyl- cyanoacetohydrazide.

Band Cm^{-1}	Assignment
3199	N-H stretching
3047	N-H stretching
2972	CH stretching of methylene group.
2933	" " " " "
2260	C ≡ N stretching vibration
1686	C = O stretching
1641	C = O stretching
1599	C = C stretching
1487	C-H bending of methylene group.
1394	C- H deformation (symmetric)
1221	N- H deformation
997	CH_2- rocking vibration

appearance of the C≡N stretching vibration band at 2260 cm^{-1} or 2243 cm^{-1}, a new band at 1546 cm^{-1} appeared in the spectrum of PACAH-grafted bagasse, with increased relative absorbancies of the bands at 1724 cm^{-1} and 1605 cm^{-1} corresponding to the C=O stretching frequecy of aldehydic groups and C=C of lignin, respectively.

The presence of the band in the 2200-2300 cm^{-1} region corresponds to the stretching frequency of C≡N groups and is accompanied by new carbonyl bands confirming the blocking of the free OH groups of polysaccharide with PACAH or PAN.

4. Adsorption of metal ions.

The binding abilities of ungrafted and grafted polysaccharides having nearly the same molecular substitution (~ 0.8 – 1.3), to some metal ions are shown in Table 3. The adsorption experiments were usually carried out in an aqueous solution at pH ~5.5.

From Table 3 it can be concluded that the ability of natural nitrogen-containing polysaccharides (chitin and chitosan) to chelate the metal ions is greater than raw bagasse. The amount of the adsorbed metal ions (mM / 1 g adsorbent) is as follows: chitosan > chitin > bagasse. This observation is related to the presence of the non bonding nitrogen electrons present in the amino and acetylamino group of chitosan and chitin, respectively.[42] The observed relatively low ability of chitin to chelate metal ions,

Table 2. Main IR-frequency bands of ungrafted and grafted polysaccharides

Chitin Samples						Chitosan Samples						Bagasse Samples					
Chitin		PACAH-chitin		PAN-Chitin		Chitosan		PACAH-chitosan		PAN-chitosan		Bagasse		PACAH-bagasse		PAN-bagasse	
cm^{-1}	E	cm^{-1}	E	cm^{-1}	E	cm^{-1}	E	cm^{-1}	E	cm^{-1}	E	cm^{-1}	E	cm^{-1}	E	cm^{-1}	E
3450	1.631	3448	1.597	3432	1.401	3452	1.588	3433	1.569	3433	1.396	3436	1.421	3430	1.423	3425	1.346
3270	sh.	3260	sh.	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3100	Sh.	3100	Sh.	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2960	Sh.	2960	Sh.	-	-	-	-	-	-	-	-	-	-	2960	sh.	-	-
2920	1.034	2920	1.262	2920	1.160	2920	0.910	2920	1.227	2920	1.031	2920	0.986	2920	1.197	2925	1.057
-	-	2880	sh.	-	-	-	-	-	-	-	-	-	-	2880	sh.	-	-
-	-	2262	0.856	2260	1.120	-	-	2260	0.923	2243	0.713	-	-	2260	0.8852	2243	0.781
1657	1.074	1675	1.143	1657	0.915	1657	0.887	1654	1.077	1657	0.908	1724	0.851	1658	1.092	1724	0.778
1627	1.044	1627	1.139	1630	0.986	-	-	-	-	-	-	1605	0.822	1604	1.095	1648	0.885
1559	1.011	1560	1.082	1600	0.984	1600	0.471	1545	0.907	1550	0.541	-	-	1546	1.150	-	-
1417	0.883	1417	0.967	1417	0.918	1430	0.819	1407	0.970	1407	0.926	1430	0.832	1430	0.930	1430	0.897
1380	1.027	1379	0.973	1380	0.953	1381	0.840	1381	0.984	1380	0.933	1381	0.908	1380	0.871	1381	0.800
1310	0.954	1320	0.933	1320	0.919	1320	0.947	1320	0.739	1320	0.863	1325	0.884	1325	0.957	1325	0.845
1260	0.904	1260	0.838	1250	0.969	1255	0.891	1250	0.775	1250	0.863	1250	0.953	1250	0.875	1260	0.916
1157	1.00	1157	1.00	1157	1.00	1159	1.00	1158	1.00	1159	1.00	1159	1.00	1159	1.00	1159	1.00
1076	1.040	1074	1.077	1049	1.062	1080	1.199	1080	1.029	1072	1.020	1049	1.128	1049	1.049	1074	1.047
947	0.862	950	0.953	895	0.781	-	-	-	-	-	-	900	0.709	900	0.879	900	0.708
895	0.769	897	0.789	830	0.737	895	0.780	895	0.798	895	0.774	830	0.659	835	0.760	830	0.679
670	0.900	669	0.883	669	0.830	-	-	-	-	-	-	669	0.803	557	0.943	557	0.970

Table 3. Affinity of divalent and trivalent metal ions to grafted polysaccharides

Adsorbent Sample	M.S.	Adsorbed metal ions (mM / 1g adsorbent X 10^2)				
		Cu(II)	Mn(II)	Fe(III)	Fe(III)*	Cr(III)
Chitin	-	7.372	1.561	6.959	-	3.580
PACAH-grafted chitin	3.0	10.865	3.815	~ 11.000	17.965	10.242
PAN-grafted chitin	3.3	10.146	1.682	8.122	-	7.987
Chitosan	-	9.274	2.488	7.779	-	4.542
PACAH-grafted chitosan	2.8	10.897	4.490	~ 11.000	19.678	10.475
PAN-grafted chitosan	3.2	10.904	2.826	9.266	-	10.120
Bagasse	-	1.693	0	3.592	-	0.177
PACAH-grafted bagasse	3.5	9.276	1.561	8.623	-	1.518
PAN-grafted bagasse	3.7	4.825	0.406	6.209	-	0.251

Adsorption conditions: 200 mg adsorbent and 0.44 mM /L metal ion, for 24 h, at pH 5.5.
* Original conc. of Fe(III) = 0.88 mM /L

is related to the network of intermolecular hydrogen bonds between the NH and C=O groups in neighboring chitin molecules.[35] This limits the availability and nonbonding nitrogen and oxygen electrons of the acetamido groups to chelate with metal ions.

From Table 3 we also learn that modification of the polysaccharides by graft copolymerization using two different chelating monomers diminishes the difference in the amount of adsorbed metal ions as a function of the polysaccharide employed. PACAH-grafted polysaccharides have a relatively higher binding ability than PAN-grafted polysaccharides. For most examined samples the binding ability of unmodified and modified polysaccharides to Cu(II), Fe(III) and Cr(II) metal ions is relatively higher when compared with Mn(II).

By comparing the adsorption ability of the investigated grafted-polysaccharides to metal ions with that obtained from other modified polysaccharides as adsorbents[42-45] (Table 4) it is clear that bagasse graft copolymerized with a multichelating groups monomer has a relatively higher binding ability to adsorb Cu(II) and Fe(III) ions than does diethylaminoethyl cellulose (DEAEC) or p-aminobenzyl cellulose (PABC). The reverse is noticed in case of adsorption ability of Mn(II) and Cr(III).[41] Furthermore,

Table 4. Affinity of metal ions to other modified polysaccharides[42-45]

Modified Polysaccharide	Adsorbed metal ions (mM / 1g adsorbent X 10^2)			
	Cu(II)	Mn(II)	Fe(III)	Cr(III)
DEAEC [(a)]	8.904	3.630	7.810	7.150
PABC [(a)]	1.319	1.650	2.090	3.300
AmAC [(b)]	0.445	-	-	-
Chitosan-CPECH [(c)]	2.203	-	-	-
Crosslinked chitin [(d)]	22.500	-	-	-

Adsorption conditions:

a) 200 mg adsorbent and 0.44mM /L metal ion, for 24 h, at pH 5.5.
b) 100 mg adsorbent and 1 mM /L metal ion, for 24 h, at pH 5.28.
c) 100 mg adsorbent, 0.32 mM /L metal ions for 2 hr, at pH 5.0.
d) 50 mg adsorbent, 0.5 mM /L metal ion, for 72 h,at pH ~ 4.5.

aminoalkyl cellulose[42] (AmAC) has a lower adsorption ability for Cu (II) than does grafted bagasse.

Finally, modified grafted chitosan and chitin (Table 3) have higher adsorption ability for Cu(II) ions than does chitosan-pyridoxal-epichlorohydrine (CPECH), Table 4, but the amount of adsorbed Cu(II) ion on crosslinking water soluble chitin (CLWSC) is considerably higher than PACAH- or PAN- grafted chitin.[44, 45]

CONCLUSIONS

The main observations from this work can be summarized as follows :

Maximum grafting yield and molecular substitution (M.S.) of graft copolymerization of ACAH onto chitin, were obtained at 2 /1 monomer to chitin ratio, 0.05 mol/L APS initiator and 60/1 liquor ratio, for 2 h at 60 °C.

Grafting copolymerization of ACAH onto chitosan produces higher grafting characteristics than grafting onto chitin; while the grafting characteristics of PACAH-grafted bagasse are in the middle.

The degrees of grafting of three examined polysaccharide samples using acrylonitrile as the chelating monomer are higher than using the ACAH monomer.

However, the percentages of the grafting efficiency in the former case are lower than in the later case.

The affinity of metal ions to the examined polysaccharides was as follows: following chitosan > chitin > bagasse. Modification of the polysaccharides by grafting with two different chelating monomers diminishes the difference in the percentages of adsorbed metal ions as a function of the type of polysaccharide employed. PACAH-grafted polysaccharides have a higher binding ability than PAN-grafted polysaccharides.

The adsorption ability of investigated PACAH-grafted polysaccharides for Fe(III), and/or Cu(II) ions are higher than that obtained using other modified natural polymers previously mentioned in the literature as adsorbents. These include diethylaminoethyl cellulose (DEAEC), *p*-aminobenzyl cellulose (PABC), diethylaminoethyl cellulose (DEAEC) and chitosan-pyridoxal-epichlorohydrine (CPECH). However, the reverse trend was noticed in the case of adsorption ability of PACAH-grafted polysaccharides for Mn(II) and Cr(III) ions, and crosslinked soluble chitin (CLSC) for Cu(II) ions.

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