Graft Copolymerization of Acrylonitrile and its Amidoxime Derivative onto Chitosan

Riham Rashad Mohamed, Magdy Wadid Sabaa

Chemistry Department, Cairo University, Giza, Egypt

Received 18 November 2008; accepted 2 August 2009
DOI 10.1002/app.31254
Published online 1 December 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Acrylonitrile (AN) was investigated as an important monomer for the graft copolymerization onto chitosan. A number of variables in the grafting reaction were investigated, including initiator and monomer concentration, duration, and temperature of the polymerization reaction. The graft copolymers were evaluated in terms of graft yield, grafting efficiency and % homopolymer. Moreover, modification of grafted chitosan was done by changing the nitrile group (—CN) to the amidoxime group (—C=NOH). Certain characterization for both the grafted Chitosan (Ch-*g*-PAN) and its amidoxime derivative -as compared to the parent polymer- are measured including the swell ability property, dye uptake, surface morphology, and metal uptake property. The results obtained reflect the feasibility for using *Ch-g-PAN* as absorbent for both Ni^{2+} and Co^{2+} ions. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 413–421, 2010

Key words: Chitosan; grafting copolymerization; Swellability; amidoxime derivative; acrylonitrile; dye uptake; metal up take

INTRODUCTION

Chitosan is a natural polymer obtained by alkaline deacetylation of chitin, which is considered as second of the most abundant of all polysaccharides found in the natural environment after cellulose. The sea-food industry produces large amounts of chitin that originate from the external skeleton of many insects and crustaceans, e.g., crabs and prawns. Chitosan is exhibiting excellent biological properties[1] such as biodegradation in the human body, and immunological, antibacterial, and wound-healing activity. Chitosan has also been found to be a good candidate as a support material for gene delivery, cell culture packaging[2–4] and tissue engineering. However, practical use of chitosan has been mainly confined to the unmodified forms. As a revolution in the modification of chitosan via grafting with vinyl and acrylate monomers, a great benefit was reached to incorporate desirable properties into this biopolymer, which will enlarge the field of its potential applications. Free radical initiation by potassium persulphate (KPS) for the grafting process has been extensively used. KPS-initiated graft copolymerization of acrylonitrile (AN) onto chitosan was also reported by Prashanth et al.[5] The aim of this article is to graft AN and its amidoxime derivative onto Chitosan.

Correspondence to: M. W. Sabaa (mwsabaa@hotmail.com).

Journal of Applied Polymer Science, Vol. 116, 413–421 (2010)

Dyestuffs present in textile industry wastewater cause significant problems in treatment plants. Chemical and physical methods including adsorption, and electrochemical methods are very efficient in color removal,[6–10] but these methods are quite expensive. However, recent reports indicated the possibility of using some natural adsorbents as biopolymers graft for color removal.[11–14] Graft copolymerization of chitosan with hydroxyethyl methacrylate using azo-bis-isobutyronitrile,[15] methyl methacrylate using Fenton's reagent as redox initiator[16] and *N*-isopropylacrylamide by γ-irradiation method[17] have been reported in the literature.

The aim of the present work was to study the modification of chitosan by graft copolymerization with AN and to investigate eventual changes produced in the properties of the modified biopolymers in comparison with that of native chitosan.

Moreover, the main parameters affecting the grafting process were studied systematically. Utilization of the unmodified chitosan, the grafted one and its amidoxime derivative for adsorption of dyestuffs present in industry waste water and as also as chelating agent materials for the removal of Ni^{2+} and Co^{2+} ions was also investigated. As amidoxime groups were reported to be applied for the rare metal collection from sea water.[18–20] Grafting and amidoximation of the grafted polymer were elucidated by FTIR analysis and scanning electron microscope (SEM). Thermal properties of the grafted species were also studied using thermogravimetric analysis.

MATERIALS AND METHODS

Materials

Chitosan (code KB-002) was purchased from Funakoshi, Japan. Deacetylation content = 72%. AN was purchased from Kanto Chemical (Tokyo, Japan) and used without further purification.

Congo red dye (Acidic dye) and Maxilon Blue dye (cationic dye) was purchased from G. T. Gurr, London, S.W.6. Other reagents and solvents were of analytical grades and were used as received without further purification.

INSTRUMENTAL

Infrared spectroscopy

FTIR spectra were recorded in KBr discs on (FTIR model 8000) Testcan Shimadzu IR-Spectrometer under dry air at room temperature within the wave number range of 4000–600 cm^{-1}.

Scanning electron microscopy

The dry sample, spread on a double sided conducting adhesive tape, pasted on a metallic stub, was coated (100 μ) with gold in an ion sputter coating unit (JEOL S150A) for 2 min and observed in a JEOL-JXA-840A Electron probe microanalyzer at 20 KV.

Atomic absorption

Atomic absorption was done on AAnalyst 100 winlab- Perkin–Elmer to determine the amount of metal ions remaining in the graft liquor.

Colorimetric spectrophotometer

Colorimetric Spectrophotometry was done on Unico 1200 Spectrophotometer at λ_{max} 480 nm for Congo red dye and λ_{max} 580 nm for Maxilon blue dye.

Thermogravimetric analysis

It was done on TGA-50H Shimadzu thermogravimetric analyzer. Samples were heated from 0 to 500°C in a platinum pan with a heating rate 10°C/min, in N_2 atmosphere 25 mL/min.

EXPERIMENTAL METHODS

Graft copolymerization procedure

Chitosan (0.5 g) was placed in a flat bottomed three necked flask. The required amount of AN monomer (1–2 mol/L) dissolved in 25 mL distilled water was added firstly to chitosan drop wisely and the reaction temperature was adjusted as required at 50–60°C (using a thermostated water bath).

After 10 min, freshly prepared KPS solution as initiator in the range (10^{-3} – 10^{-2} mol/L) was added portion wise and the graft copolymerization reaction was conducted for the required time with continuous stirring. Nitrogen gas was allowed to pass into the system from the beginning till the end of the polymerization reaction. After the copolymerization time is elapsed, the reaction was stopped by rapid cooling and the product is filtered, as the grafting mixture is heterogeneous due to the insolubility of chitosan in water, then the product was washed thoroughly with water to get rid of unreacted monomer and any initiator residue. The product was then dried and weighed.

The grafted sample was then subjected to soxhlet extraction for 10 h using *N*,*N*-dimethyl formamide (DMF) to get rid of any homo polymer –if found- then the residue was reweighed after drying to constant weight. The graft yield, grafting efficiency (GE) and amount of homopolymer formed were calculated according to the following equations:

$$\text{Graft yield } (\%G) = [(W_1 - W_0)/W_0] \times 100$$

$$\text{Homo polymer } (\%H) = [(W_2 - W_1)/W_3] \times 100$$

$$\text{Grafting efficiency } (\%\text{GE}) = (W_1/W_2) \times 100$$

where W_0, W_1 are the weights of the initial matrix and grafted matrix (i.e., weight of product after extraction), respectively. Whereas W_2 is the crude product before extraction and W_3 is the weight of monomer.

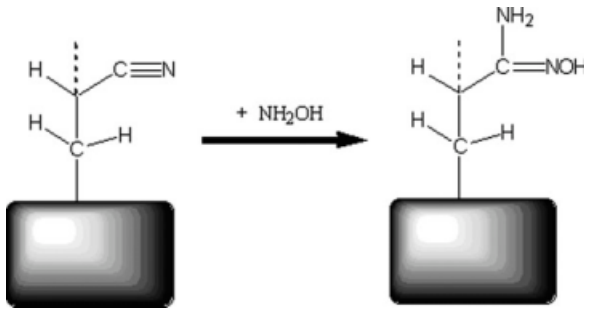
Amidoximation of polyacrylonitrile[20]

Treatment of the cyano group of the prepared Chitosan-*g*-PAN was done by addition of 3 (w/v) % hydroxylamine hydrochloride in methanol-water (1 : 1) mixture and the pH of the medium was adjusted to seven at by adding KOH solution. The reaction was then allowed to proceed at 80°C for 2 hrs to convert all the cyano groups of the grafted chains to amidoxime groups- as shown in Scheme 1.

The preparation of grafted amidoxime was proven by FTIR spectroscopy as the characteristic band for —CN in the Chitosan-*g*-PAN at 2245 cm^{-1} completely disappeared and a new band at 1777 cm^{-1} which is specific for —C=N— appeared.

Water uptake

Water uptake of Chitosan, Ch-*g*-PAN and its amidoxime derivative was studied at 30°C in a second



Scheme 1 Amidoximation of the PAN grafted on chitosan.

distilled water (pH 7) and in buffered solutions at different pH values; 4, 7, and 9. A known amount of pre-dried sample was placed into a flask with 25 mL water or buffer solution of a given pH and kept undisturbed in a thermo stated bath (at 30°C) until equilibrium swelling was reached. After certain time, the swollen sample was taken off and the surface was quickly wiped off by absorbent paper just to remove the droplets on the surface, then weighed.

$$\text{Water uptake percentage} = (W_s - W_o)/W_o \times 100$$

where, W_s, weight of wet sample; W_o, weight of dry sample.

The results obtained represent the average of three comparable experiments for each sample.

Dye uptake

Two types for dyes were used; Congo red (acidic dye) and Maxilon Blue (Cationic dye). 25 mL of the dye solution of a known concentration was added to 100 mg of the grafted copolymer in 100 mL flat bottomed flask and stirred continuously at room temperature for 24 hrs to reach equilibrium. After filteration, the concentration of the dye in the filterate was determined colourimetrically at 480 and 580 nm, for both dyes, respectively. The quantity of adsorbed dye was calculated according to the following equation[14]:

$$Q = (N_a - N_s)/W$$

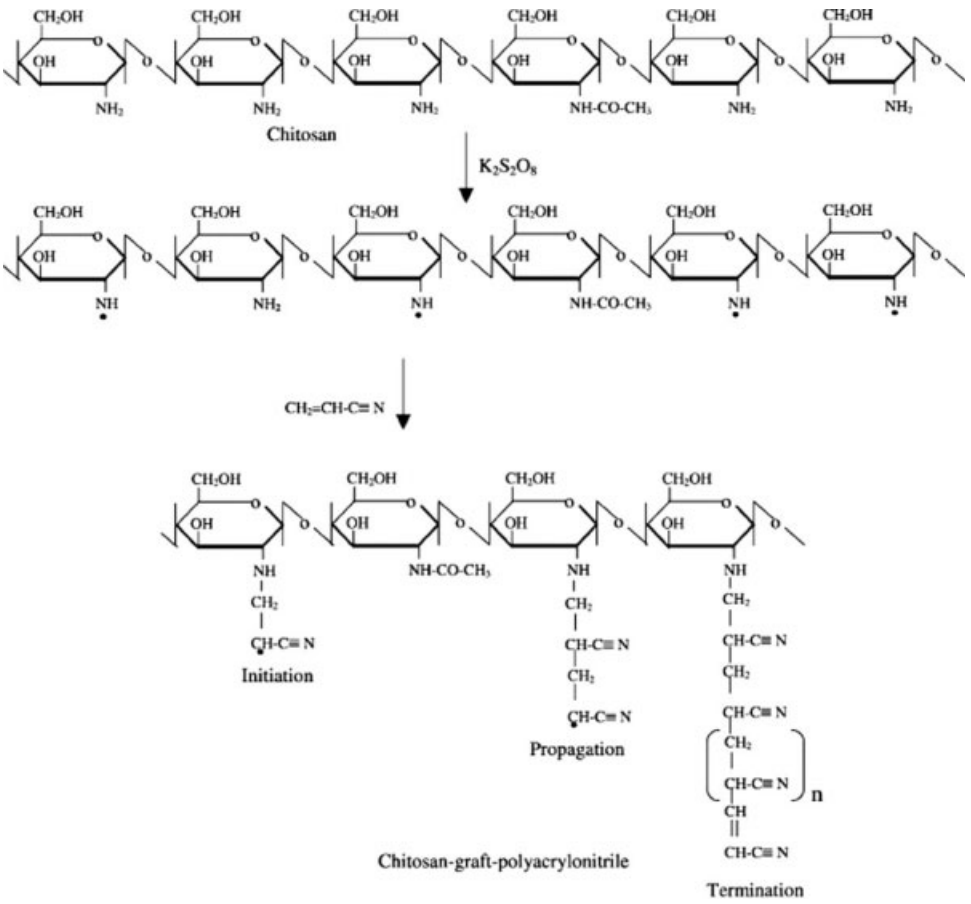
where, Q, Fixed quantity of dye (mg)/grafted chitosan (g); N_a, Quantity of original dye (mg); N_s, Quantity of remaining dye after adsorption (mg); W, Mass of grafted chitosan (g).

Adsorption of metal ions

Chloride salts of the heavy metal ions (Ni^{2+}, Co^{2+}) solutions of known concentrations were prepared (1.5 mmole/ Liter) then 100 mg of either ungrafted Chitosan, Chitosan-grafted polymer and its amidoxime derivative was added to 25 mL solution, stirred for 24 hrs at room temperature (equilibrium is attained after 6 hrs.). After filteration, the grafted

TABLE I
Effect of Various Copolymerization Reaction Parameters on the Graft Yield %, Graft Efficiency % and Homopolymer %

Copolymerization parameter	*G*%	GE%	*H*%
Effect of monomer conc. (mol/L)		[I] = 10^{-2} mole/L for 2 hrs at 65°C	
1	21	54	18
1.5	49	67	24
2	132	77	40
Effect of initiator conc. ($\times 10^{-2}$ mol/L)		[AN] = 1.5 mole/L for 2 hrs at 65 °C	
0.5	25	71	10
1	49	89	6
3	74	95	4
5	81	98	2
Effect of reaction temp. (°C)		[AN] = 1.5 mole/L, [I] = 10^{-2} mole/L for 2 hours	
50	29	69	13
55	49	85	9
60	83	94	5
65	86	97	2.5
Effect of reaction time (hr)		[AN] = 1.5 mole/L, [I] = 10^{-2} mole/L at 65 °C	
2	49	83	10
3	73	90	8
4	86	98	2



Scheme 2 Schematic representation of graft copolymerization of chitosan.

chitosan was estimated by using atomic absorption technique for the remaining metal solution after soaking to determine the amount of metal ions remaining and consequently the amount of adsorbed metal ions can be calculated by difference.

Solubility

Solubility test was done by dissolving a known weight of either the grafted samples or their amidoxime derivatives in a constant volume of solvent overnight and then observe their solubility.

RESULTS AND DISCUSSION

Polymer grafting reactions provide the potential for significantly altering the physical and mechanical properties of the starting materials. Polymer grafting is usually carried out by radical initiation.

The reactive C_2 amino group in Chitosan is important in several of the structural modifications targeted because the deprotonated amino group acts as a powerful nucleophile (pKa = 6.3) readily reacting with an electrophile. Even in free radical initiated copolymerization, $-NH_2$ groups of chitosan involve in macroradical formation. In the present work, potassium persulfate was used as a free radical initiator to induce grafting.

The effect of increasing the monomer concentration on the graft yield percent (*G*%), amount of homo polymer (*H*%) and GE% is illustrated in

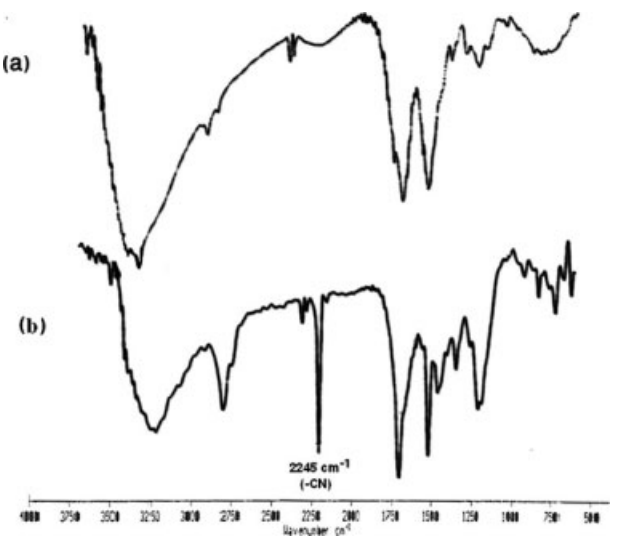


Figure 1 FTIR spectra of (a) Chitosan, (b) Ch-*g*-PAN (49%).

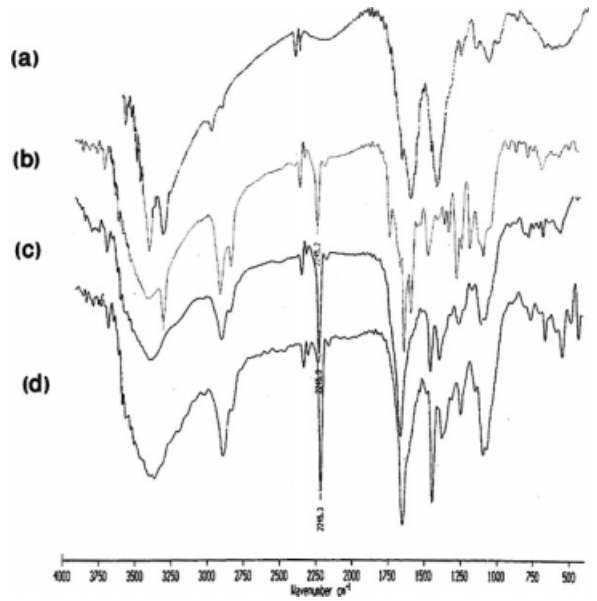


Figure 2 Changes of IR peak intensities of Ch-*g*-PAN copolymers of different grafting content. (a) Chitosan, (b) Ch-*g*-PAN (49%) (c) Ch-*g*-PAN (86%) (d) Ch-*g*-PAN (132%).

Table I. The data revealed the increase in the graft yield and consequently the increase in the GE as well as the increase in the amount of homo polymer with the increase of the AN concentration within the range studied (1–2 mol/L) keeping all the other parameters constant during the reaction. However, the increase in the % *G* is more pronounced than the amount of homo polymer formation and this is probably attributed to the sequence of addition of the reactants in the reaction vessel as the monomer solution was allowed to be adsorbed first on the polymer matrix (Chitosan) before adding the initiator (as the grafting reaction takes place in a heterogeneous system), which gives more chance for the grafting process to occur.

Table I also illustrates the effect of initiator concentration on the graft yield (*G*%), amount of homopolymer (*H*%) and the GE%. AN concentration was kept constant at 1.5 mole/L, while the polymerization reaction was conducted for 2 h at 65°C. The reported data clearly show the increase in the graft yield (*G*%) and consequently the increase of the GE% as a result of increasing the initiator concentration, while the (*H*%) is slightly decreased.

These results seem to be reasonable as increasing the initiator concentration will increase the amount of primary radicals on the polymer matrix and consequently more monomers will be consumed in the grafting process.

Moreover, the obtained results came to add a new support for the applied technique for the sequence of addition of the reactants during the graft copolymerization reaction.

Prior adsorption of the monomer onto the chitosan matrix before adding the initiator and the addition of the latter in portion wise gave much more chance for the grafting process on the expense of the homo polymer formation.

The dependence of the *G*%, GE%, and *H*% on the variation of the reaction temperature is illustrated in Table I. The monomer concentration was kept constant at 1.5 mole/L, while the initiator concentration was kept constant at 10^{-2} mole/L and the copolymerization reaction was conducted in all cases for 2 h. The results -as shown in Table I-clearly reveal as the temperature increases till it reaches the optimum condition around 65°C, both the % graft and the % GE increase consequently. On the other hand, increasing the polymerization temperature leads to a lowering in the amount of homopolymer formed. This result is partially due -once more- to the technique of graft copolymerization procedure as previously mentioned, and partially due to the possible coupling of the growing macro radicals formed in the medium with the graft macro radicals present on the chitosan matrix, as increasing the temperature will –with no doubt- increase the mobility of the macro radicals towards the grafted species. The effect of the reaction time on the *G*%, GE%, and *H*%

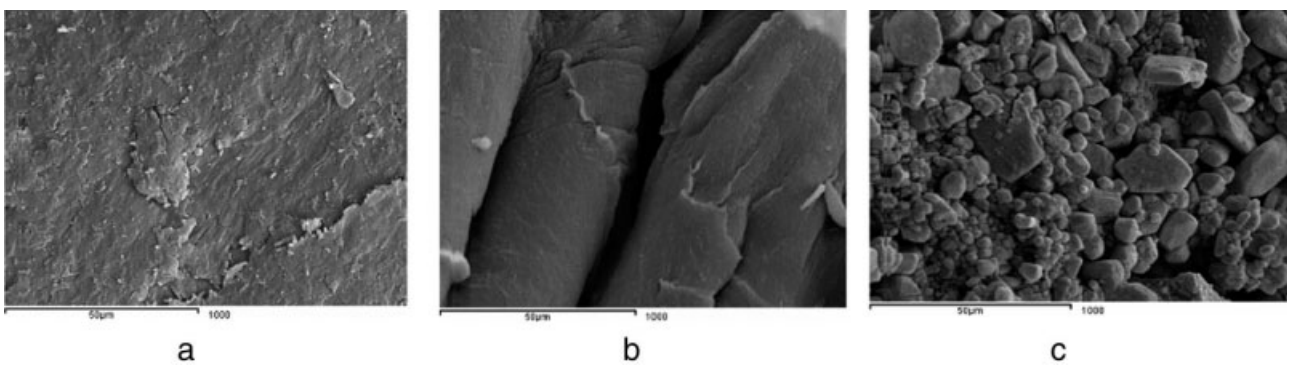


Figure 3 Scanning electron micrographs of Chitosan, Ch-*g*-PAN (49%) and its amidoxime. (a) Chitosan ungrafted, (b) Chitosan-*g*-PAN (49%), (c) Amidoxime of the graft (49%).

TABLE II
Thermo Gravimetric Data of Ungrafted Chitosan, Chitosan-*g*-PAN (86%) and its Amidoxime Derivative

T (°C)	Chitosan	Graft 86%	Amidoxime derivative
Initial decomposition temperature (IDT)	280°C	260°C	160°C
T (°C)	Wt. loss % of chitosan	Wt. loss % of graft 86%	Wt. loss % of amidoxime derivative
280	10	15	13
300	20	24	13
320	44	27	15
340	50	23	15
360	55	34	15
380	56	37	16
400	58	39	17

is illustrated in Table I. The results clearly reveal the increase in both the *G*% and GE% with the increase in the reaction time, while the % H is slightly lowered. The obtained results are quite reasonable as increasing the time of the polymerization reaction will give the opportunity of more monomer units to be added to the polymeric matrix via the formation of new graft chains. However, the lowering in the % H as a function of reaction time is again attributed to the possible coupling of the macro radicals formed in the medium with the macro radicals grafted onto chitosan especially at the later stages of polymerization.

EVIDENCE OF GRAFTING

IR-spectra

FTIR spectra of the grafted chitosan have proved that the initiation step for grafting was done on the amino group at C_2 –as shown in Scheme 2. This is well illustrated in Figure 1 by the transformation of the doublet bands at 3445 and 3422 cm^{-1} corresponding to the $-NH_2$ group to a singlet band at 3423 cm^{-1} for —NH group which indicates the abstraction of a H atom from the amino group by the KSO_4. radical derived from the decomposition of the KPS initiator, this result is also in accordance with that reported by Prashanth et al.[5] Moreover, as shown in Figure 2, the formation of a new absorption band at 2245 cm^{-1} corresponding to the —CN group specific for PAN moiety and its intensity increases as a function of the increasing in the % *G*, which gives an additional proof for the grafting reaction.

Scanning electron microscopy: (magnification ×1000)

The surface morphology of the native Chitosan, Ch-*g*-PAN (49% graft) –taken as an example for the least graft %—and its amidoxime derivative is illustrated in Figure 3. The SEM observation of native Chitosan reveals its fibrous as well as flaky nature. The fibrous nature of Chitosan was totally modified in the grafted samples. Thus, as for the grafted sample, the surface became more soft and porous, while as for the amidoxime derivative it became more rigid (rocks –like). This obvious change in the surface morphology of the modified chitosan gives an additional proof for both the grafting and amidoximation processes.

Solubility

The solubility characteristic of the material is another criterion for the grafting process, since native chitosan is soluble in acidic solutions (such as 1% solution of acetic acid) due to the presence of the amino group, whereas, the grafted chitosan –and its amidoxime- were found to be insoluble in acidic solutions and also are insoluble in DMF which is known to solublize the homo polyacrylonitrile (PAN). Solubility was done by dissolving a known

TABLE III
Water Uptake by Ungrafted Chitosan, Chitosan-*g*-Samples of Different % *G* and their Corresponding Amidoxime Derivatives in Buffered Solutions of Different pH Values

Water uptake (%)								
			Ch-*g*-PAN (*G* 49%)			Amidoximated Ch-*g*-PAN (*G* 49%)		
Chitosan (ungrafted)			pH 4	pH 7	pH 9	pH 4	pH 7	pH 9
pH 4	pH 7	pH 9	50	335	505	45	875	814
			Ch-*g*-PAN (*G* 86%)			Amidoximated Ch-*g*-PAN (*G* 86%)		
778	474	162	100	228	430	75	639	636
			Ch-*g*-PAN (*G* 132%)			Amidoximated Ch-*g*-PAN (*G* 132%)		
			150	112	239	100	549	336

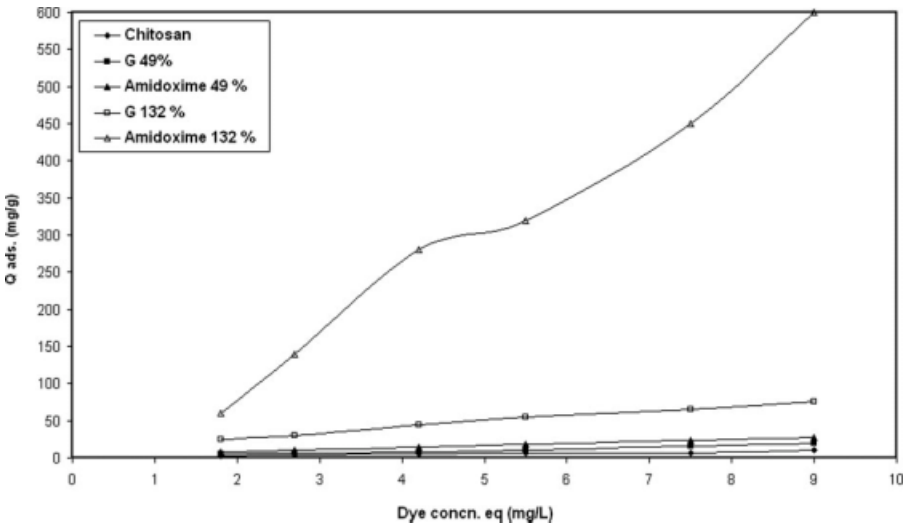


Figure 4 Variation of amount of congo red dye adsorbed by chitosan, *G* 49%, *G* 132% and their amidoxime derivatives.

weight of the graft or its amidoxime derivative in a constant volume of solvent.

Thermal behavior of modified Chitosan

Table II represents the TGA analysis of ungrafted Chitosan, Ch-*g*-PAN 86%—as an example for the intermediate % of graft—and its amidoxime derivative. The results showed that however the initial decomposition temperature (IDT) of ungrafted chitosan is 280°C which is higher by 20°C than the grafted sample (260°C), while the amidoxime derivative showed the least IDT being only 160°C, the thermal decomposition rate (the weight loss %) is faster in case of ungrafted chitosan than in case of the Ch-*g*-PAN and its amidoxime derivative. Thus, as shown in Table II, for example at 320°C, the weight loss in case of ungrafted chitosan is 44%, while in Ch-*g*-PAN the weight loss is 27%, and in case of its amidoxime derivative is only 15%. Also at 360°C, the ungrafted chitosan can keep almost 45% of its weight unlost, where as Ch-*g*-PAN can keep 66% of its weight unlost and its amidoxime derivative can keep 86% of its weight unlost. These results indicate that grafting chitosan by PAN and its amidoxime derivative may decrease its IDT especially for the amidoxime derivative, but it can improve to a great extent its thermal decomposition rate (thermal stability). This improvement in the thermal stability of grafted chitosan samples is mainly attributed to the nitrile groups of the acrylonitrlie units –grafted on Chitosan- which are known to undergo cyclic oligomerization with gradual heating[21] which will –with

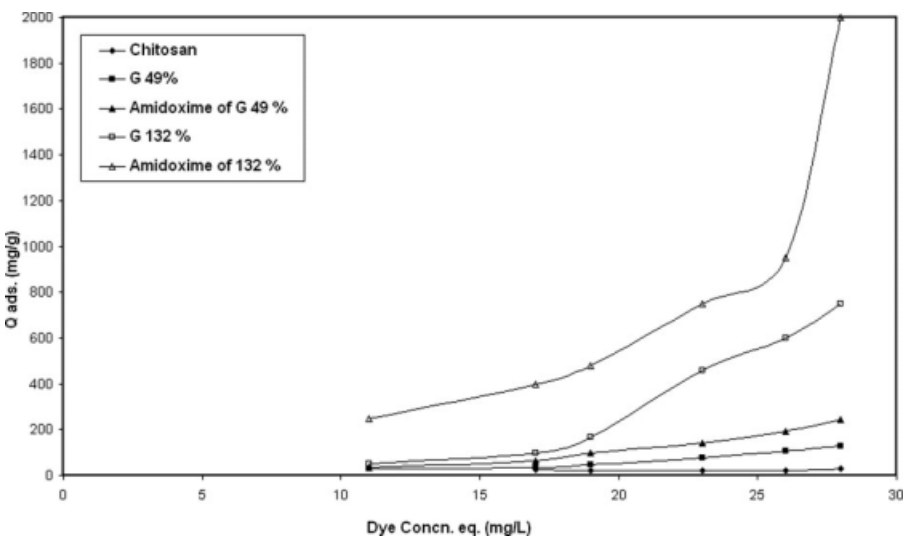


Figure 5 Variation of amount of Maxilon blue dye adsorbed by Chitosan, *G* 49%, *G* 132% and their amidoxime derivatives.

TABLE IV
Amounts of Adsorbed Metal Ions by Ungrafted Chitosan, Chitosan-*g*-PAN with Various % Grafts and their Corresponding Amidoxime Derivatives

	Metal ion uptake (%)						
Metal ions	Chitosan	Ch-*g*-PAN (*G* 49%)	Amidoximated Ch-*g*-PAN (*G* 49%)	Ch-*g*-PAN (*G* 86%)	Amidoximated Ch-*g*-PAN (*G* 86%)	Ch-*g*-PAN (*G* 132%)	Amidoximated Ch-*g*-PAN (*G* 132%)
Ni^{2+}	93.60	92.00	92.50	93.85	99.65	95.00	99.75
Co^{2+}	87.80	88.62	93.42	89.00	94.00	92.00	96.00

no doubt- leads to a delay in the degradation process.

APPLICATIONS OF THE CHITOSAN-*G*-PAN AND ITS AMIDOXIME DERIVATIVES:

Applications were done on three examples of Graft percentages: 49% as the least percentage, 86% as an intermediate percentage and 132% as a highest percentage to show the effect of variation of graft % on the characteristics of grafted Chitosan and the corresponding amidoxime derivative.

Water uptake

Chitosan swells much more in acidic medium (pH 4) than in basic medium (pH 9) due to the presence of the basic $-NH_2$ groups in chitosan chains, its swellability in neutral pH is intermediate- as shown in Table III.

As for the grafted chitosan samples, they swell much more in the basic medium than in both the neutral and acidic medium. As the graft % increases the swellability decreases in all pH values due to the high nonpolarity of the added —CN groups in the grafted samples. The Ch-*g*-PAN samples swell much more than Chitosan in basic medium.

As for the amidoxime derivatives, they swell much more in neutral medium due to the polarity of —C=N—OH groups. Amidoxime derivatives swell much more than chitosan and Ch-*g*-PAN samples in pH 7 and 9.

These data represented in Table III are the average of three comparable experiments.

Dye uptake

Colorimetric measurements were done to determine the amount of dye (Congo red and Maxilon blue) remained in Chitosan and the two examples of grafted chitosan (*G* 49% and *G* 132%) with their amidoxime filtrates. The results -as presented in Figures 4 and 5 clearly shows that as the % of graft increases and consequently more —CN groups are introduced into the chitosan matrix, in addition to the presence of some unaltered $-NH_2$ groups in Chitosan, the amount of dye (Congo red and Maxilon blue) adsorbed by Ch-*g*-PAN increases. Also, the amidoxime derivative adsorb more amount of dye than its corresponding graft as the —C=NOH group found in amidoxime derivative is much more polar than the —CN group found in graft. Moreover, the chitosan-grafted copolymers and their amidoxime derivatives adsorb much amount of Maxilon blue dye (Cationic dye) than the Congo red dye (acidic dye) as the basic $-NH_2$ group of chitosan starts to disappear by grafting and will be replaced by less basic groups like —CN (in grafted copolymers) and —C=NOH groups (in amidoxime derivatives). These data represented in Figures 4 and 5 are the average of three comparable experiments.

Metal uptake

Chitosan, grafted chitosan of different % *G* and their corresponding amidoxime derivatives were soaked into the metal ions solution overnight, then it was removed and the metal concentration remained was detected into the filterate. By increasing the graft %, the amount of metal ions (Ni^{2+} and Co^{2+}) adsorbed increases than that adsorbed by the ungrafted chitosan, as more —CN groups are present in the grafted chitosan that have the ability to chelate with more metal ions from their solutions, Table IV also shows that the amount of metal ions adsorbed by the amidoxime samples is much more than that adsorbed by the Ch-*g*-PAN and ungrafted Chitosan due to the great ability of the —C=NOH group for chelating and capturing more metal ions from the medium. These data represented in Table IV are the average of three comparable experiments.

CONCLUSIONS

The obtained results from this study revealed that the optimum conditions for grafting PAN onto chitosan were as follows: [M] is 2 mol/L, [I] is 5×10^{-2} mol/L, reaction temperature is 65°C and reaction time is 2 h. Great improvement of the water uptake behavior of chitosan in basic medium, as both the grafted chitosan and its corresponding amidoxime derivative swell more than the parent ungrafted chitosan and the swellability increased only for the amidoxime derivative in neutral medium more than

the chitosan itself. The improvement of dye uptake for both acidic and cationic dyes was achieved by increasing the % *G* of Ch-*g*-PAN and by their amidoxime derivatives. Also, the data revealed that the grafted chitosan and their amidoxime derivatives adsorb much amount of Maxilon blue dye (Cationic dye) than Congo red dye (acidic dye). The uptake of metal ions by chitosan is highly improved by grafting chitosan with PAN. Moreover, the improvement is highly pronounced when the nitrile groups in the grafted samples were converted into the more polar amidoxime groups. The results of the thermal stability of chitosan, Ch-*g*-PAN and its amidoxime derivative clearly show the lowering of the IDT of the modified chitosan as compared with the native one, whereas the rate of decomposition is highly improved through grafting and through amidoximation of the grafted samples.

References

1. Jayakumar, R.; Prabaharan, M.; Reis, R. L.; Mano, J. F. Carbohyd Polym 2005, 62, 142.
2. Zheng, L. Y.; Zhu, J. F. Carbohyd Polym 2003, 54, 527.
3. Chiou, M. S.; Li, H. Y. J Hazard Mater B 2002, 93, 233.
4. Singla, A. K.; Chawla, M. J. Pharm Pharmacol 2001, 53, 1047.
5. Harish, K. V.; Tharanathan, R. N. Carbohyd Polym 2003, 54, 343.
6. Selcuk, H. Dyes Pigm 2005, 64, 217.
7. Kim, T. H.; Park, C.; Shin, E. B.; Kim, S. Desalination 2004, 161, 49.
8. Daneshvar, N.; Sorkhabi, H. A.; Tizpar, A. Sep Purif Technol 2003, 31, 153.
9. Rathi, A.; Rajor, H. K.; Sharma, R. K. J. Hazard Mater 2003, 102, 231.
10. Bali, U.; Atalkaya, E. C.; Sengul, F. J. Hazard Mater 2004, 114, 159.
11. Kargi, F.; Ozmihci, S. Enzyme Microb Technol 2004, 35, 267.
12. Basibuyuk, M.; Forster, C. F. Proc Biochem 2003, 38, 1311.
13. Kapdan, I. K.; Kargi, F. Proc Biochem 2002, 37, 973.
14. Gregorio, C.; Frederic, G.; Capucine, R.; Bernard, M.; Olivier, A.; Nadia, M.; Francois, D.; Pierre-Marie, B. J Hazard Mater 2008, 153, 96.
15. Ketelsen, H.; Windel, M. S. Geoderma 1999, 90, 131.
16. Bayramoglu, Y. Arica Biochem Eng J 2003, 13, 35.
17. Borovec, S.; Uren, E. J Virol Methods 1997, 68, 81.
18. Cai, H.; Zhang, Z.h; Sun, P.; Zhang, Y.; He, B. Gaofenzi Xuebao 2005, 5, 709.
19. Khalid, S.; Sajjad, H.; Tae-Jin, O.; Soo-Young, P. J Membr Sci 2008, 322, 400.
20. Zohuriaan-Mehra, M. J.; Pourjavadib, A.; Salehi-Radb, M. React Funct Polym 2004, 61, 23.
21. Grassie, N. Developments in Polymer Degradation 1; Applied Science Publishers: London, 1977; Chapter 5, The Pyrolysis of Acrylonitrile Homopolymers and Copolymers. p 137.