

Preparation and Evaluation of the Chitin Derivatives for Wastewater Treatments

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ABSTRACT: The chitin thiocarbonate–Fe(II)–H₂O₂ redox system was investigated as the initiator for the graft copolymerization of acrylonitrile and acrylic acid monomers onto chitin powder. The reaction with vinyl monomers onto chitin was carried out under various parameters of the graft copolymerization reaction to elucidate the polymerization behavior in terms of graft yield. Reactions of chitin–acrylonitrile graft copolymer with hydroxyl amine hydrochloride, as well as, sodium hydroxide were conducted in order to obtain chitin–(amidoxime-co-acrylonitrile) and chitin–(acrylate-co-acrylamide) graft copolymers, respectively. The reaction efficiency depends upon the alkali concentration, time, temperature, and on the reactant concentrations. The prepared chitin derivatives were evaluated for use in the wastewater treatments for adsorption and desorption of heavy metal ions as well as acid and basic dyes. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1939–1946, 1997

Key words: chitin; wastewater treatment; graft copolymerization; heavy metals removal; dye removal

INTRODUCTION

Modification of the natural polymers like cellulose, starch, and lignin by graft copolymerization has been extensively studied.^{1–6} Chitin is one of the most abundant organic materials that can be easily obtained in nature. The natural source of chitin is the shell of crustaceans (lobsters, shrimps, etc.) or the broth from industrial fungal processes (e.g., citric acid). Chitin is similar in its chemical structure to cellulose, but its uses and applications have not yet been studied as much as those of cellulosic materials.^{7,8} In recent years

various researches on the use of chitin have drawn attention, especially for wastewater treatments.^{9,10} Effluent from textile dyeing processes contains various products of decomposed dye and unused intact dyes that often contain heavy metals. Therefore, free ionic metals and complexed metals as well as decomposed products of the dye could be present in the effluent. Thus, the objective of this work was to prepare a series of chitin derivatives that have the ability to adsorb and desorb heavy metal ions, acidic, and basic dyes. The goal was achieved by the graft copolymerization of vinyl monomers, such as acrylonitrile and acrylic acid onto chitin powder using chitin thiocarbonate–Fe(II)–H₂O₂ redox system. Further chemical modifications for chitin–acrylonitrile graft copolymer with hydroxylamine and metha-

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nolic sodium hydroxide were undertaken for this purposes.

EXPERIMENTAL

Materials

The chitin used was a commercial product obtained from Sigma Chemical Company. High purity acrylic acid (AA) and acrylonitrile (AN) were used without purification. Other chemicals used were analytical grade.

Thiocarbonation of Chitin Powder

The chitin powder was placed in stoppered glass vessel containing the thiocarbonation solution (1% NaOH, W/V; 1% CS₂, V/V). The material-to-liquor ratio was 1 : 50, and the temperature of solution was kept at 30°C. The contents of the vessel were in continuous shaking through the thiocarbonation reaction. After 6 h, the solution was drained and the powder thoroughly washed with distilled water until the pH of the washing liquor was 7. The chitin powder after thiocarbonation reaction will be referred to as chitin thiocarbonate.

Grafting Procedure^{3,11}

The chitin thiocarbonate was pretreated by immersing in ferrous ammonium sulfate solution kept at 40°C for 30 min with continuous shaking. After impregnation, the sample was washed repeatedly with distilled water and filtered before introducing into the polymerization solution. The sample was placed in a glass vessel containing the polymerization solution consisting of specific concentration of both H₂O₂ and the monomer at the chosen pH. The material to liquor ratio was 1 : 20. The glass vessel was kept in a thermostatic water bath at definite temperature and time. The sample was under continuous shaking during the polymerization reaction. After the graft polymerization, the sample was filtered and repeatedly extracted with a proper solvent, depending on the nature of the homopolymer to be removed. The percent polymer add-on was calculated from the difference between the original weight and the weight after the extraction. The percent of the graft yield for chitin-acrylic acid (chAA) graft copolymer was calculated from the "capacity" values

(mmol COOH/100 g sample of the copolymer) obtained by titration.¹²

Preparation of Chitin-(acrylate-co-acrylamide) (chAA-co-Am) Graft Copolymer¹³

The sample of chitin-acrylonitrile (chAN) graft copolymer was pretreated with methanolic sodium hydroxide solution for a given time and temperature. At the end of the reaction, the chitin powder was washed several times with acidified water/methanol mixture and methanol solution, and dried at room temperature.

Preparation of Chitin-(amidoxime-co-acrylonitrile) (chAm-co-AN) Graft Copolymer

The powder of chAN graft copolymer was treated with neutralized hydroxylamine in methanol solution for 6 h at 75°C. At the end of the reaction, the powder was washed several times with methanol and dried at room temperature.

Adsorption of Metal Ions

Aqueous metal ion solutions were prepared from CoCl₂, FeCl₃, CrCl₃, and CuSO₄. The pH of the solutions was kept constant at 3. One gram of chitin powder derivatives was put into a glass bottle containing 50 mL of the metal ion solutions. The mixture was left for a predetermined time for adsorption, then the adsorbent was filtered off. The concentration of cations in the original solution and in the filtrate was determined by atomic absorption spectroscopy (AAS, Z-6100, Hitachi). The adsorbed cation concentration (A) was calculated from the following equation:

$$A(\%) = \frac{X - X'}{X} \times 100$$

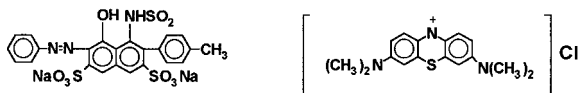
where, X and X' are the concentration (ppm) of the cations before and after treatment, respectively.

Desorption of Metal Ions

One gram of chitin derivatives with adsorbed metal ions was stirred in 50 mL of 0.1 *N* hydrochloric acid for 5 h at room temperature and then filtered. The metal ions in the filtrate were determined by atomic absorption analysis.

Adsorption of Acidic and Basic Dyes

The dyes used in this research were C.I. Acid Red 106 (18110) and methylene blue.



C. I. Acid Red 106 (18110), $\lambda_{\max} = 533.0$

Methylene Blue, $\lambda_{\max} = 664.8$

All concentrations of dyes were determined by measuring absorbance at λ_{\max} . The chitin powder derivatives were treated with 100 mL of various dye solutions for predetermined time. The amounts of the dyes adsorbed were determined from the difference in dye concentration between the initial and final filtrates using the spectrophotometer (Perkin–Elmer Model Lambda 16).

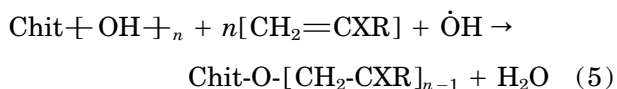
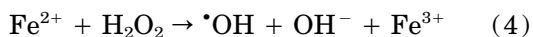
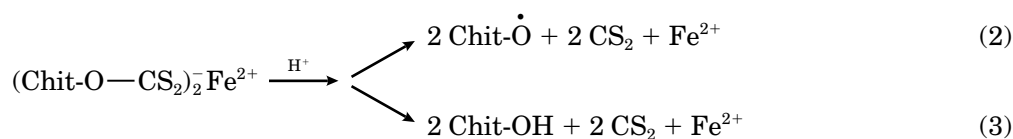
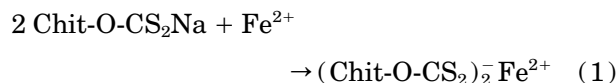
FTIR Analysis

IR spectra were recorded on a Perkin–Elmer Model 1760X Fourier Transformer Infra-Red (FTIR) spectrometer with the KBr technique to confirm the structure of chitin derivatives.

RESULTS AND DISCUSSION

Previous reports¹⁴ have shown the mechanism of the cellulose thiocarbonate– H_2O_2 redox system

for graft polymerization of cellulose, and in the other previous work,¹⁵ it was suggested that the OH free radical formed by the reaction of hydrogen peroxide with ferrous ion is responsible for the initiation of the graft polymerization of cellulose. By taking these considerations, chitin thiocarbonate was treated with ferrous ions [eq. (1)]. Ferrous ion was released through the disintegration and oxidation of thiocarbonate group [eqs. (2) and (3)]. The released ferrous ion was oxidized with hydrogen peroxide to generate OH free radical [eq. (4)]. The created OH free radical produces chitin macroradical via the direct abstraction of hydrogen atom from the hydroxyl groups of the chitin molecules. In the presence of vinyl monomer, the chitin macroradical is added to the double bond of the vinyl monomer resulting in a covalent bond between the monomer and the chitin and then the creation of a free radical on the monomer (i.e., a chain) is initiated. Subsequent addition of monomer molecules to the initiated chain propagates grafting onto chitin [eq. (5)]. This mechanism was proved by Merz¹⁶ and Hebeish et al.¹⁷ onto cellulose.



where X is H: and R is CN in AN and COOH in AA.

The effects of reaction conditions such as time, temperature, pH, and the concentration of Fe^{2+} , H_2O_2 , and monomer on the graft copolymerization of AN and AA with chitin using the chitin thiocarbonate– Fe^{2+} – H_2O_2 redox system were studied. The effects of Fe^{2+} concentration on the graft yield are shown in Table I, which shows that Fe^{2+} increased the percent graft yield for both monomers AA and AN until the concentration of Fe^{2+}

reached 0.15%, and it had adverse effects when the concentration of Fe^{2+} was higher than 0.15%. The significant increase of graft yield could be due to the creation of OH free radical species according to the reaction suggested by eq. (4). A decrease in the graft yield at higher than 0.15% of Fe^{2+} concentration could be due to the consumption of the OH free radical [eq. (6)].

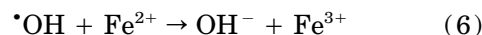


Table I also shows the effect of H_2O_2 concentration on the graft yield that was determined by calculating the increase of sample weight and the carboxyl content when AN and AA were used, respectively. The graft yield slightly increases until

Table I Effect of Reaction Conditions on the Graft Yield of chAN and chAA

Reaction Conditions	Graft Yield (%)		Remarks
	chAN	chAA	
[Fe ²⁺] (g/100 mL)			
0	21	14	
0.05	62	22	[H ₂ O ₂] = 0.3% pH = 3
0.1	81	40	
0.15	85	42	
0.2	79	38	
[H ₂ O ₂] (%)			
0.07	79	24	[Fe ²⁺] = 0.15 g pH = 3
0.15	84	39	
0.3	85	41	
0.45	64	28	
pH			
1	44		[H ₂ O ₂] = 0.3% [Fe ²⁺] = 0.15 g
2	63	—	
3	85		
5	34		

Chitin powder, 1 g; monomer concentration, 200%; time, 90 min; temperature, 60°C.

the concentration of H₂O₂ reached to 0.3%, then decreases thereafter. The decrease of graft yield above 0.3% H₂O₂ was explained in a view of the radical termination. Namely, a lot of free radicals formed above the concentration of 0.3% contributed mainly to the termination between growing chains and oligomeric vinyl radicals. The maximum graft yield was obtained at pH 3 (Table I). This could be interpreted in terms of an accelerated oxidation/reduction reaction at lower pH. At the same time the fast disintegration and oxidation processes of chitin–thiocarbonate lead to the destruction of the OH free radical by ferrous ions.

It is apparent from Table II that the increase of the monomer concentration led to an increase of the graft yield. The effect of temperature on the graft yield are also shown in Table II. The optimum temperature for the maximum graft yield was 70°C. Further increase in temperature reduced the percentage of grafting. At higher temperatures the radical initiate the homopolymerization rather than the graft copolymerization, thereby showing a decrease of graft yield. Table II also shows the effect of polymerization time on the graft yield. The increase of polymerization time up to 120 min increased the graft yield; thereafter, it leveled off. Leveling off could be attributed to a drop of monomer and initiator con-

Table II Effect of Monomer Concentration, Time, and Temperature on Graft Yield

Time (min)	Temperature (°C)	[Monomer] ^a (%)	Graft Yield (%)	
			AN	AA
120	60	100	43	32
120	60	200	89	44
120	60	300	92	56
120	60	400	101	59
30	60	200	43	27
60	60	200	79	39
180	60	200	89	44
120	40	200	28	16
120	70	200	89	46
120	80	200	86	41

Chitin, 1 g; material-to-liquor ratio, 1 : 40; [Fe²⁺], 0.15 g 100 mL; [H₂O₂], 0.3%; pH, 3.

^a Monomer % is the monomer weight/chitin weight × 100.

centration as well as to a decrease of the available active grafting sites on the chitin backbone.

Sodium acrylate and acrylamide units are formed by the alkaline hydrolysis of polyacrylonitrile. During the hydrolysis the interchain cross-

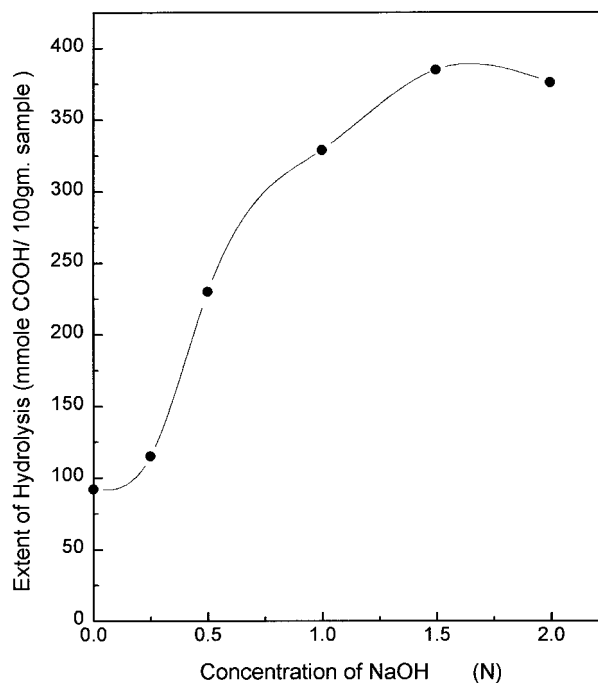


Figure 1 Effect of NaOH concentration on the hydrolysis of the chAN graft copolymer: temperature, 70°C; time, 6 h; material-to-liquor ratio, 1 : 20.

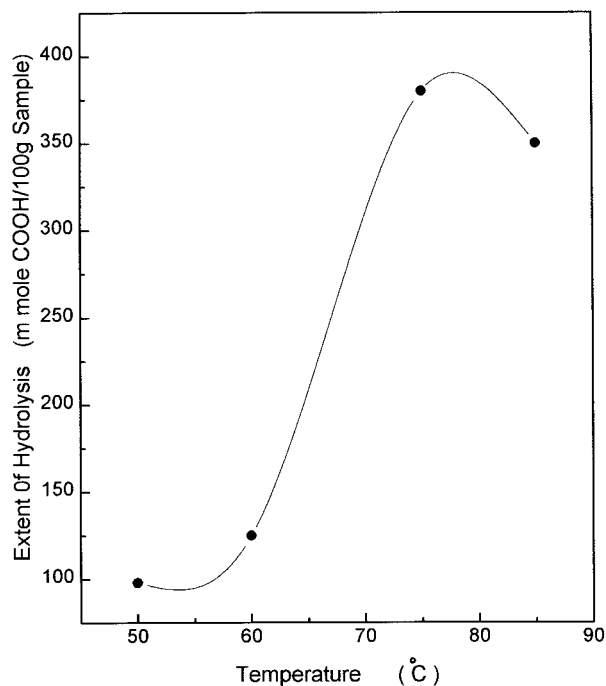


Figure 2 Effect of temperature on the extent of hydrolysis of the chAN graft copolymer: [NaOH], 1.5 *N*; time, 6 h; material-to-liquor ratio, 1 : 20.

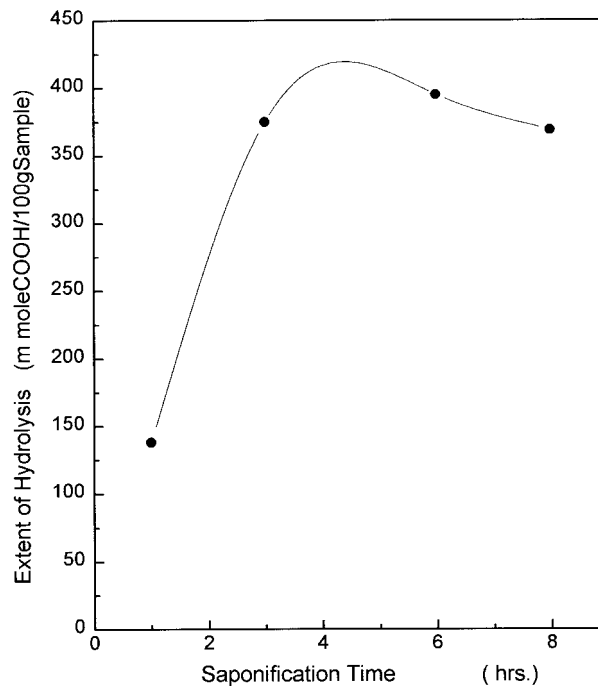


Figure 3 Effect of saponification time on the hydrolysis extent of the ChAN graft copolymer: [NaOH], 1.5 *N*; temperature, 85°C; material-to-liquor ratio, 1 : 20.

linking bonds are formed, which prevents the grafted compound from solubilization.¹³ Figure 1 shows the extent of hydrolysis, expressed by mmole COOH/100 g sample versus the concentration of NaOH in methanolic water mixture for chAN graft copolymer. We note that the extent of hydrolysis increased markedly with the increase of sodium hydroxide concentration up to 1.5*N*.

After that, it decreased. The increase of hydrolysis extent is ascribed to the cleavage of some interchain crosslinking bonds and the formation of ionic groups. NaOH higher than 1.5*N* leads to a decrease of hydrolysis extent due to an increase of the solubilizing chains.

Figure 2 shows the extent of hydrolysis vs. the temperature. The extent of hydrolysis increased

Table III Effect of Hydroxylamine Concentration, Time, and Temperature on the Extent of Amidoximation in chAN Graft Copolymer

Hydroxylamine (g)	Time (h)	Temperature (°C)	Extent of Amidoximation	
			mmol COOH/100 g Sample	<i>N</i> %
0	—	—	90	9.9
0.5	6	65	130	10.5
1	6	65	175	11.1
1.5	6	65	215	11.6
1.5	6	50	143	10.9
1.5	6	75	205	11.4
1.5	1	85	189	11.6
1.5	3	85	260	12.4
1.5	5	85	210	11.5
1.5	6	85	198	11.3

ChAN, 1 g; H₂O/methanol, 1/4 (v/v); material-to-liquor ratio, 1 : 20.

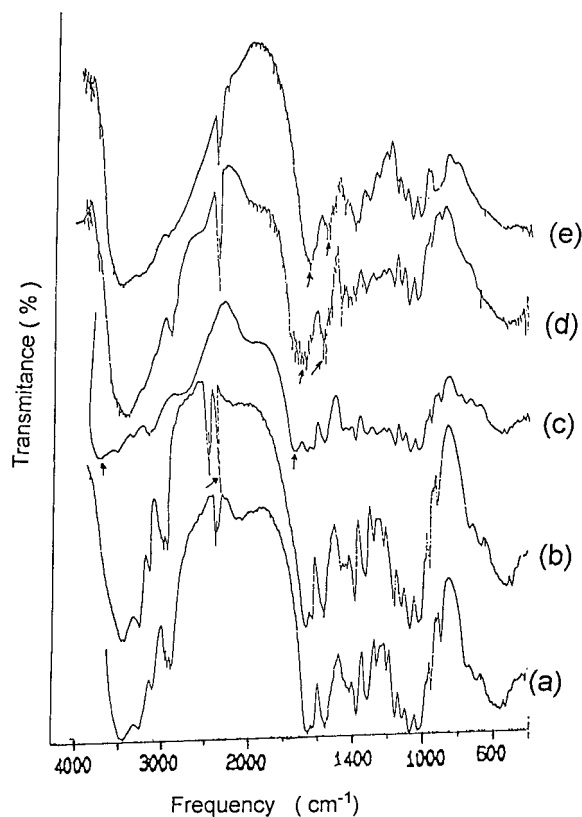


Figure 4 FT-IR spectra of (a) chitin, (b) chAN, (c) chAA, (d) chAA-co-Am, and (e) chAm-co-AN.

by increasing the bath temperature within the range of 60–80°C. At lower temperature less than 60°C the extent of hydrolysis was low and it could be due to the presence of conjugated double bonds and so the intercrosslinking chains are still present. But the decrease of the hydrolysis extent at temperature higher than 80°C is referred to the presence of solubilized ionic chain and the capability of the decarboxylation of ionic group.

Figure 3 represents the extent of hydrolysis vs. the saponification time. It is shown that the hy-

Table V Adsorption Amounts of the Metal Cations on 1 g of Chitin Derivatives

Type of Substrate	Adsorption Amount (PPM)			
	Cu ²⁺	Cd ²⁺	Cr ³⁺	Fe ³⁺
Type II	617	398	1980	181
Type III	1430	418	2210	420
Type IV	600	359	1270	57

pH, 3.5; volume of metal solution, 50 mL; temp, 25°C; time, 24 h.

drolysis of chAN graft copolymer depends also on the saponification time. The hydrolyzed group increases with the saponification time up to 4 h; after that, it decreases. The decrease of hydrolysis extent could be associated with both the depletion of sodium hydroxide concentration as the reaction proceeds and the decarboxylation reaction.

Table III shows the effect of neutralized hydroxylamine concentration, time, and temperature on the amidoximation extent of chAN graft copolymer. The nitrogen percentage increased with the increase of the hydroxylamine concentration. The high extent of amidoximation was achieved at 85°C for 3 h or at 65°C for 6 h. This means that both the temperature and time affected highly on the extent of amidoximation. The decrease of amidoximation extent may be due to the solubilization of ionic functional group and/or to the cleavage of N—C group.

IR spectra of the resulting chitin derivatives were shown in Figure 4. The curves a, b, c, d, and e are the IR spectra of the chitin, chAN, chAA, chAA-co-Am, and chAm-co-AN graft copolymers, respectively.

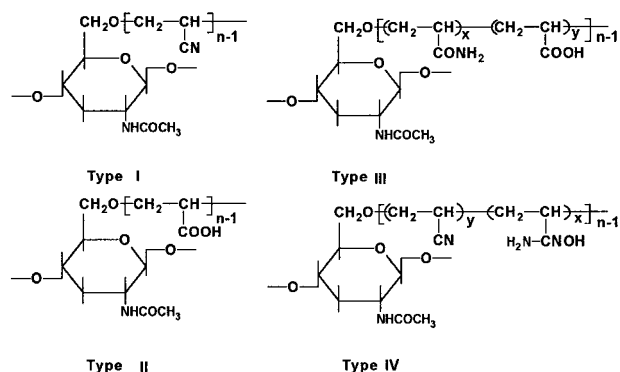
In curve b we can confirm the grafting of acrylonitrile on chitin by the additional sharp peak at 2250 cm⁻¹ corresponding to the CN group. In

Table IV Functional Group Contents of Chitin Derivatives

Chitin Derivatives	Functional Group Content
ChAN graft copolymer (Type I)	N% = 9.9 mmol COOH/100 g, sample = 90 graft yield = 48%
ChAA graft copolymer (Type II)	N% = 5.8
ChAA-co-Am graft copolymer (Type III)	mmol COOH/100 g, sample = 368
ChAm-co-AN graft copolymer (Type IV)	N% = 11 mmol COOH/100 g, sample = 189

curve c, it is found that the two additional peaks at 1750 cm^{-1} and 3450 cm^{-1} corresponding to the ester carboxyl group and OH group appear. The peak at 2250 cm^{-1} corresponding to nitrile group completely disappears in curves c and d and is weakened in curve e. In curve d, the peak at 1537 cm^{-1} corresponding to carboxylate group appears and the sharp peak near 1600 cm^{-1} corresponding to the bending vibration of $-\text{NH}_2$ appears. In curve e the peak at 2250 cm^{-1} does not completely disappear, and the new peaks at 1637 cm^{-1} and also 1540 cm^{-1} appear due to the presence of $-\text{C}=\text{N}-$ and $-\text{N}-\text{H}$ bonds, respectively.

The chemical analysis data of the chitin derivatives such as functional group content (mmol COOH/100 g sample), nitrogen content, and the graft yield are listed in table IV, and their chemical structural are shown as follows:



Three types of chitin derivatives were prepared and their ability of removing metal ions were evaluated. ChAA graft copolymers containing numerous carboxylic acid groups in the side chains were prepared by grafting chitin powder with acrylic acid (type II). The other products, type III and IV, were prepared by reacting the chAN graft copolymer with methanolic sodium hydroxide and hydroxylamine, respectively.

Table V shows the adsorption amounts of metal

Table VI Desorption Content of Metal Ions Adsorbed by the Chitin Derivatives

Type of Substrate	Desorption (%)			
	Cu^{2+}	Cd^{2+}	Cr^{3+}	Fe^{3+}
Type II	90	86	83	81
Type III	87	85	80	72
Type IV	83	72	74	65

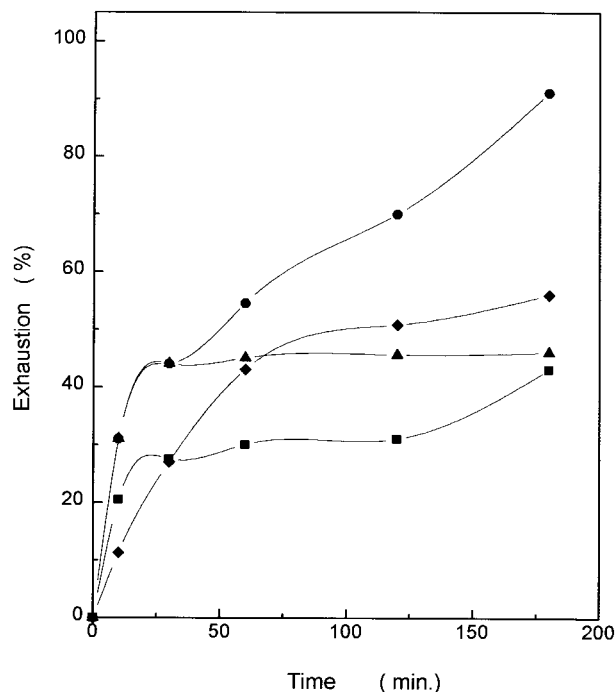


Figure 5 Exhaustion of acidic dye on chitin derivatives: (●) type I; (■) type II; (▲) type III; (◆) type IV.

cations of Cu^{2+} , Cd^{2+} , Cr^{3+} , and Fe^{3+} on the prepared chitin derivatives. All prepared products have high adsorption amounts for metal cations; therefore, those products can be applied for the treatment of wastewater containing heavy metal ions. In addition, among those three types of products, the product with $-\text{NH}_2$ and $-\text{COONa}$ groups, type III, showed higher adsorption amounts for metal cations, which is attributed not only to the adsorption capacity of the functional groups, but also to the hydrophilicity of the main chain and the pendant of coordination sites which form chelate rings with metal ions.

The desorption percent of metal ions adsorbed by chitin derivatives in 1 N HCl solutions is shown in Table VI.

In all derivative products, high desorption percent of metal cations was confirmed. The amount of cations desorbed under this condition was 65–90% of cations originally adsorbed. Type II achieved high desorption percent, and type IV showed the lowest desorption percent.

0.4 grams of four types of chitin derivatives were used to determine their acidic and basic dye adsorption characteristics from aqueous solutions. Figure 5 shows the rate of the acid dye exhaustion in the chitin derivatives. It is clear that

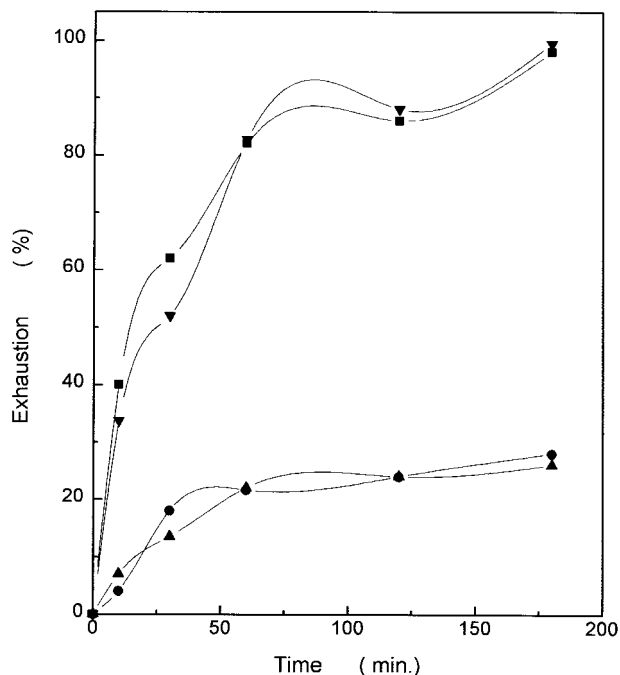


Figure 6 Exhaustion of basic dye on chitin derivatives: (●) type I; (▼) type II; (■) type III; (▲) type IV.

regardless of chitin derivatives the percent exhaustion increased substantially by increasing the treatment time. Figure 5 also shows that the type I has the highest exhaustion percent and type II exhibits the lowest. The possible explanation for the difference in the percent exhaustion of the acid dye in different types of chitin derivative could be ascribed to the accessibility of the substrate. For the type I the acrylonitrile group has high desorption of dye due to the breakdown of the crystallinity in chitin structure. Hence, the extent of acid dye removal, as determined by the results of acid dye exhaustion, was the following order: type I > type II > type III > type IV.

Figure 6 shows the exhaustion percent of basic dye for different types of chitin derivatives. From Figure 6 we notes that the exhaustion percent increases with the increase of the treatment time up to 60 min; further prolongation of the treatment time resulted in the lower rates of exhaus-

tion. In addition, types II and III have the higher ability of dye absorption rather than types I and IV. This is due to the carboxylic acid groups present in the chitin derivatives of types II and III.

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