

Preparation and Evaluation of Chitin Derivatives and Their Utilization For Wastewater Treatments

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ABSTRACT

The Chitin Thiocarbonate - Fe(II) - H₂O₂ redox initiator system was investigated for the graft copolymerization of acrylonitrile(AN) and acrylic acid(AA) monomers onto chitin powder. The reactions with vinyl monomers onto chitin were carried out under various the graft copolymerization conditions to elucidate the polymerization behavior in terms of graft yield. Reactions of chitin - acrylonitrile graft copolymer with hydroxyl amine hydrochloride and those with sodium hydroxide were conducted in order to obtain chitin - (amidoxime - co- acrylonitrile) and chitin- (acrylate - co - acrylamide) graft copolymers, respectively. The reaction efficiency was observed to depend on the alkali concentration, time, temperature, and the reactant concentrations. The prepared chitin derivatives were evaluated to find potential applications for use in wastewater treatments for adsorption and desorption of heavy metal ions as well as acidic and basic dyes.

INTRODUCTION

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, decomposition products of the dye could be present in the effluent. Thus, the objective of this work was to prepare a series of chitin derivatives which have the ability to adsorb and desorb heavy metal ions, acidic, and basic dyes. The goal was achieved by graft copolymerization of chitin powder with vinyl monomers, such as acrylonitrile and acrylic acid, using a chitin thio-carbonate-Fe(II)-H₂O₂ redox system.

EXPERIMENTAL

Materials

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

Grafting procedure

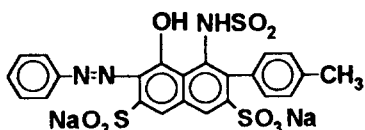
The thiocarbonate chitin was pretreated by immersing in ferrous ammonium sulfate solution in a bottle kept at 40°C for 30 minutes with continuous shaking. The sample was placed in a glass vessel containing the polymerization solution consisting of H₂O₂ and the monomer at predetermined pH. After the graft 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 in weight after extraction and before the graft reactions for chitin - AN. And the graft yield percent for chitin - AA was calculated from the “capacity” values (mmole of COOH/100g sample of the copolymer) obtained by titration.

Adsorption of metal ions

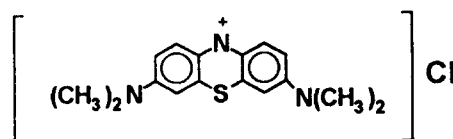
Aqueous metal ion solutions were prepared from metal solutions of CoCl₂, FeCl₃, CrCl₃, and CuSO₄. And the pH of the solutions was kept constant at 3. 1 g of chitin powder derivatives was put into a glass bottle containing 50 ml of the metal ion solutions. The mixture was left for a predetermined time for adsorption, then the adsorbent was filtered off. The concentration of cations in the original solution and the remaining in the filtrate was determined by atomic absorption spectroscopy.

Adsorption of acidic and basic dyes

The chemical structures of dyestuffs used in this research are listed below and they were as received.



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 desorbed were determined from the difference in dye concentration between the initial and final filtrates.

RESULTS AND DISCUSSION

Graft copolymerization of AN and AA onto chitin

The effects of reaction conditions such as time, temperature, pH, and the concentration of Fe²⁺, H₂O₂, and monomer on the graft copolymerization of AN and AA with chitin using the chitin thiocarbonate - Fe²⁺ - H₂O₂ redox system are studied. The effects of Fe²⁺ 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. A decrease in the graft yield could be due to the consumption of the OH free radical. And also an increase in Fe^{2+} concentration led to further increase in Fe^{3+} concentration which might participate in the termination process. And the free radicals produced on the backbone might be oxidized to produce the oxidation products. Table I clearly shows the effect of H_2O_2 concentration on the graft yield which was calculated by determination of the increase in weight and the carboxyl content when AN and AA were used, respectively. The percent graft yield slightly increases until the concentration of H_2O_2 reached to 0.3%, then decreases thereafter. The higher H_2O_2 concentrations more than 0.3% will lead to decrease in the OH free radical concentration of the reaction medium. The decrease in percent graft yield above 0.3% H_2O_2 was explained in view of the radical termination. Namely, a lot of free radicals formed above 0.3% H_2O_2 mainly contributed to the termination between growing chains and the oligomeric vinyl radicals. The maximum graft yield was obtained at a pH 3 (Table I). This could be interpreted in term of an accelerated oxidation/reduction reaction at lower pH. It is apparent from table II that, increase in the monomer concentration led to a significant increase in graft yield up to 300% (V/W) and leveled off thereafter, where the grafted polymer inhibited the diffusion of OH free radicals and monomer into chitin for further grafting. At low monomer concentrations the percentage of grafting was low. The effect of temperature on the graft yield are shown in Table II. The optimum temperature for 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 decrease in percent grafting. Table II also shows the effect of polymerization time on the percent graft yield for AN and AA monomers. The increase of polymerization time up to 180 minutes increased the percent of graft yield, thereafter it leveled off. Leveling off could be attributed to a drop in monomer and initiator concentration as well as to a decrease in the available active grafting sites on the chitin backbone.

Adsorption of heavy metals

Three types of chitin derivatives were prepared and their ability of removing metal ions were evaluated. Chitin polyacrylic acid graft copolymers containing numerous carboxyl 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 chitin AN

copolymer with methanolic sodium hydroxide and hydroxylamine, respectively. Table III shows the adsorption amounts of metal 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 in 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.

Exhaustion of acid and basic dye

0.4g of four types of chitin derivatives were evaluated to determine their acidic and basic dye desorption characteristics from aqueous solutions. Figure 1 shows the rate of the acid dye exhaustion using the chitin derivatives. It is clear that regardless of the derivative used percent exhaustion increases substantially by increasing duration of the treatment. Figure 1 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 by using 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 removal, as determined by the results of dye exhaustion, brings up the following order : Type I > Type II > Type III > Type IV

Figure 2 shows the exhaustion percent of basic dye for different types of chitin derivatives. From Figure 2 we notes that the exhaustion percent increases with the increase of the treatment time up to 60 minutes, further prolongation of the treatment duration resulted in slower rates of exhaustion. In addition, the product type II and III have the higher ability of dye absorption rather than type I and IV. This is due to the carboxylic acid groups present in the chitin derivatives of type II and III.

Table I : Effect of reaction conditions on the graft yield of ChAN and ChAA

Reaction Conditions		Graft Yield		Remarks
		ChAN	ChAA	
[Fe ²⁺] gm	0	20.5	13.6	[H ₂ O ₂] = 0.3% pH = 3
	0.05	62	22	
	0.1	81	40	
	0.15	85	41.7	
	0.2	79	38	
[H ₂ O ₂] %	0.07	79	24	[Fe ²⁺] = 0.15 gm 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 gm
	2	63		
	3	85		
	5	34		

Monomer Concentration : 200% . Time : 90 min . Temp : 60°C

Table II
Effect of monomer concentration, Time, and temperature upon graft yield

Time (min)	Temp (°C)	[Monomer]%	G-Y%	
			AN	AA
120	60	100	43	32
120	60	200	80	44
120	60	300	92	56
120	60	400	101	58.5
30	60	200	43	27
60	60	200	79	39
130	60	200	89	44
120	40	200	28	16
120	70	200	89	46
120	80	200	86	41

Reaction conditions :
Chitin = 1gm : Material to liquor ratio, 1 : 40 ; [Fe²⁺], 0.15% ; [H₂O₂], 0.3% .
pH, 3.

Table III
Adsorption amounts of the metal cations on chitin derivatives

Type of substrate	Adsorption amount PPM			
	Cu ⁺⁺	Cd ⁺⁺	Cr ⁺⁺	Fe ⁺⁺
Type II	617	398	1980	181
Type III	1430	418	2210	420
Type IV	600	359	1270	57

1gm sample : pH, 3.5 : Volume of metal solution 50ml : Temp, 25°C : Time, 24 hrs

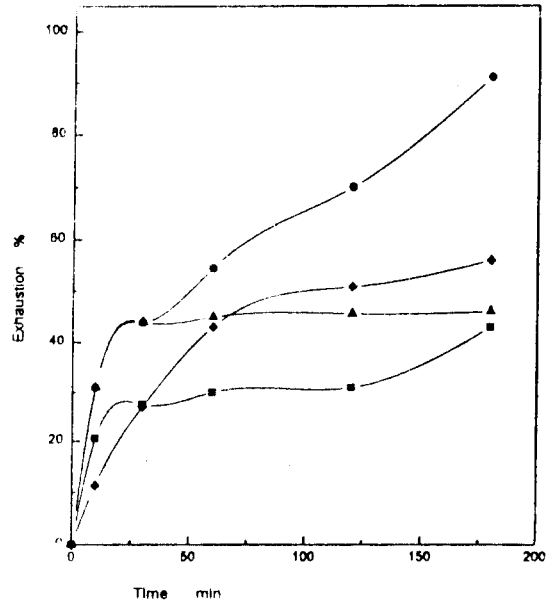


Figure 1. Type I (●); Type II (■);
Type III (Δ); Type IV (◆)

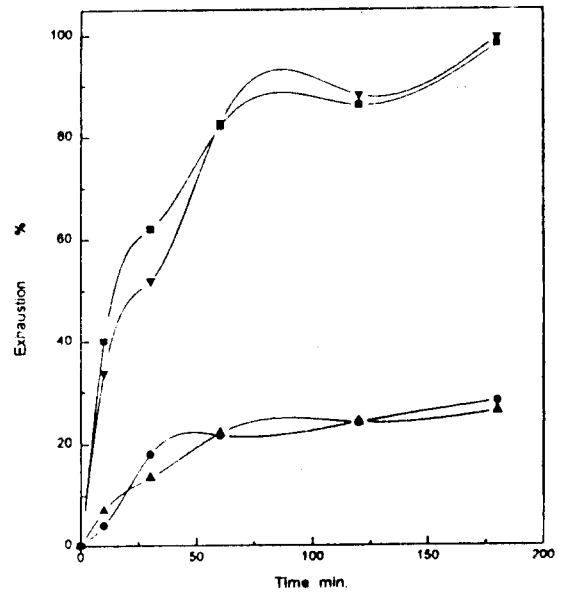


Figure 2. Type I (●); Type II (▼);
Type III (■); Type IV (▲)