

Preparation of Methacrylic Acid-Grafted Chitin Using Cerium (IV) Ion and its Application in Adsorbing Paraquat

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ABSTRACT: Chitin-grafted-poly(methacrylic acid) (chi-g-PMAA) was synthesized and characterized as an adsorbent of paraquat. Chi-g-PMAA copolymers were prepared using various concentrations of ammonium cerium(IV) nitrate (Ce^{+4}) to determine the optimal concentration of Ce^{+4} . Grafting was verified by differential scanning calorimeter thermograms, FTIR, and solid-state ^{13}C -NMR spectra. A representative chi-g-PMAA copolymer was neutralized to a sodium salt (chi-g-PMANa) and used to adsorb paraquat. The adsorption equilibrium data are strongly related to both the Langmuir and the Freundlich isotherms. The maximal adsorption capacity is 147.0 mg/g-adsorbent. This value exceeds those of Fuller's earth and activated carbon, which are the most common binding agents that are currently used for paraquat. The results suggest that chi-g-PMANa has potential as a paraquat adsorbent. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Chitin, poly- β -(1 \rightarrow 4)-*N*-acetyl-D-glucosamine, is a cellulose-like biopolymer that is widely distributed in nature and especially found in marine invertebrates, insects, fungi, and yeasts.¹ Chitosan, the most important derivative of chitin, is a partially deacetylated polymer that is obtained by the alkaline deacetylation of chitin. It exhibits such properties as biocompatibility, antimicrobial, and nontoxicity.² Chitosan and modified chitosan have potential applications in fields such as biomedicine,^{3,4} waste water treatment,^{5,6} and biotechnology^{7,8} as well as in functional membranes.⁹

Although chitin, the precursor of chitosan, is structurally similar to chitosan and is one of the most abundant organic resource materials on earth, it has attracted much less attention than the chitosan mainly because it is insoluble. Only a few solvent systems have been found to induce hydrolysis of the amide or glycosidic linkages.¹⁰ Its insolubility in ordinary organic solvents makes chitin difficult to be characterized and processed.¹¹ However, some vinyl monomers can be grafted onto chitin using ammonium cerium (IV) nitrate as initiator by graft copolymerization.¹² Acrylic acid monomer was recently grafted onto chitin

and successfully used to dress wounds.¹³ Publications on the grafting of carboxylic acid monomers onto chitin and its application to the adsorption of toxic organic matter are very few.

Paraquat, 1,1'-dimethyl-4,4'-bipyridinium dichloride, has been extensively used as a broad-spectrum herbicide. Recently, studies of paraquat have focused on the mechanism of paraquat-induced Parkinson's disease^{14,15} and its damage to animal organs¹⁶ or plants.¹⁷ Few studies of the emergency treatment of a paraquat-poisoned human body have been published. Extracorporeal removal may be the only hope for patient survival.¹⁸ Extracorporeal removal combines hemoperfusion using an activated carbon cartridge and an enema, which involves putting Fuller's earth into the patient's stomach to capture the unabsorbed paraquat. The adsorption capacities of activated carbon and Fuller's earth are around 100 and 60 mg/g-adsorbent,¹⁹ respectively, and are not sufficient for the urgent clinical treatment of paraquat-poisoned patients. Poly(methacrylic acid) (PMAA)-modified rice husk has been prepared and applied in adsorbing paraquat²⁰ with the monolayer adsorption capacity of 317.7 mg/g-adsorbent, which exceeds that of currently used adsorbents of paraquat. However, the lower blood compatibility of rice husk is a disadvantage in clinic application. A paraquat

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adsorbent with a higher adsorption capacity, made from biocompatible and nontoxic natural materials, is required.

The present investigation elucidates the preparation and characterization of chitin-grafted-poly(methacrylic acid) (chi-g-PMAA). Because it is easy to precipitate in most common solvent, chitin has the great advantage of making chi-g-PMAA using a more environmentally friendly process than that of chitosan. Because methacrylic acid (MAA) is anchored directly to chitin, chi-g-PMAA occupies many carboxylic groups. In this study, chi-g-PMAA was neutralized to a salt and used to adsorb paraquat in aqueous solution.

MATERIALS AND METHODS

Material

Chitin, commercial grade and comprising particles that can pass through 180–200 meshes, was supplied by Kio Tech. Co. (Hsin-chu, Taiwan). Solid-state ^{13}C -NMR spectra revealed 18% deacetylation of the chitin. Ammonium cerium (IV) nitrate, purchased from Panreac Co. (Spain), was used as the initiator without further purification. MAA, ammonium chloride, sodium dithionite, sodium hydroxide, and acetone were of analytical grade or better and used as received. Paraquat (24% w/w, which can be fatal when 10 mL is swallowed), supplied by COMLET Chemicals Co. (Taichung, Taiwan), was diluted to a suitable concentration for use.

Graft Copolymerization

The graft copolymerization was performed in a 250-mL flask, with a magnetic stirrer in a temperature-controlled water bath. A series of preliminary experiments was carried out and found that the optimal reaction time is 1 h. Chitin (5.00 g) was stirred in 200-mL deionized water, and the flask was purged gently with nitrogen for around 30 min at 60°C. MAA monomer (10.00 g) and ammonium cerium (IV) nitrate with different concentrations ($[\text{Ce}^{+4}]$) were separately added to the flask to initiate the 1-h reaction. The copolymerization products were filtered, washed thoroughly with deionized water, and extracted using acetone in Soxhlet for 48 h to yield the grafted copolymer, free of the PMAA homopolymer. The grafting percentage and efficiency were evaluated gravimetrically.^{21,22}

Differential Scanning Calorimetry

Differential scanning calorimeter (DSC) measurements were made using a DSC (Perkin Elmer Pyris diamond DSC). DSC thermograms were obtained using a standard aluminum pan. The flow gas was nitrogen at a flow rate of 30 mL/min. The samples were heated from 30°C at a rate of 10°C/min to 260°C to prevent decomposition of amine at around 295°C.²³ Glass transition temperature (T_g) was taken as the intersection of the extrapolated baseline with the extrapolation of the curve from the point of inflection.²⁴

Solid-State ^{13}C -NMR Characterization

Solid-state ^{13}C -NMR spectra were obtained using a 400 MHz BRUKER ADVANCE NMR spectrometer. Each spectrum was obtained by averaging 1200 scans. The experiment was conducted with the sample's spinning at a rate of 6.2 kHz. A 5.5- μs pulse, corresponding to the 90° P1 angle, was chosen. A contact time of 1 ms and a delay of 5 s were set. All spectra were recorded at a sample temperature of 25°C.

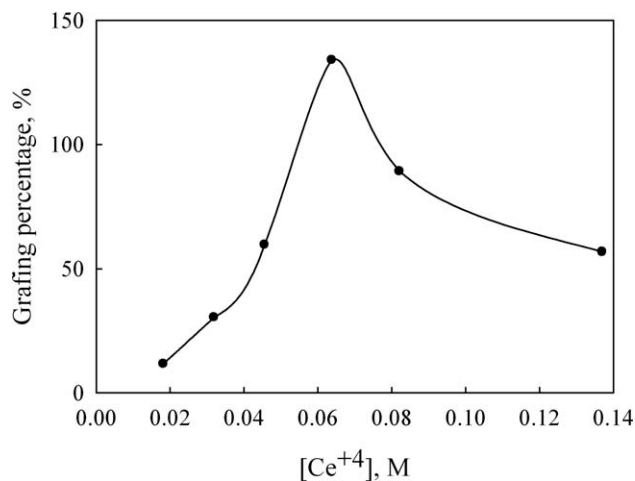


Figure 1. Grafting percentages of chi-g-PMAA at various Ce^{+4} concentrations.

Infrared Spectroscopy

FTIR analysis of copolymer samples was performed using a Perkin Elmer FTIR spectrometer in wave numbers from 2000 to 400 cm^{-1} .

Neutralization of Grafted Copolymer

The prepared chi-g-PMAA copolymer was placed in a conical flask that contained 0.1M aqueous NaOH. The solution was stirred for 1 h before it was filtered; it was then washed in distilled water until it became neutral filter liquor. It was then dried at 50°C under vacuum until constant weight. The neutralized product was the sodium salt of PMAA-grafted chitin (chi-g-PMANa), which was used to absorb paraquat from aqueous solution.

Adsorption of Paraquat

Adsorption experiments were carried out in a 1-L resin kettle at 37.5°C with agitation at a rate of 600 rpm for 2 h. The adsorption solution comprised 0.1 g of chi-g-PMANa, sieved using 140–100 meshes, as the adsorbent. Initial concentrations of paraquat were to 36, 48, 72, 84, 96, and 120 ppm from the 24% w/w aqueous solution. Samples (0.2 mL) were extracted using a micropipette at various times. The collected samples were then added to a sodium dithionite/saturated ammonium chloride solution and analyzed using a Spectrumlab model-22PC spectrophotometer at wavelength 394 nm.

RESULTS AND DISCUSSION

Preparation of Chi-g-PMAA Copolymers

Graft copolymerizations of a fixed MAA monomer at various concentrations of Ce^{+4} ($[\text{Ce}^{+4}]$), which was used as the initiator, at 60°C were performed on powdered chitin that was dispersed in water under heterogeneous conditions to yield chitin-grafted-poly(methacrylic acid) (chi-g-PMAA) copolymers. Figure 1 presents the relationship between the grafting percentage of copolymers and $[\text{Ce}^{+4}]$. The grafting percentage initially increased with $[\text{Ce}^{+4}]$ reaching a maximum at about 0.064 M and then decreased. This result is attributable to the competitive reaction between the copolymer main chain and the monomer, which increases the amount of homopolymer and reduces

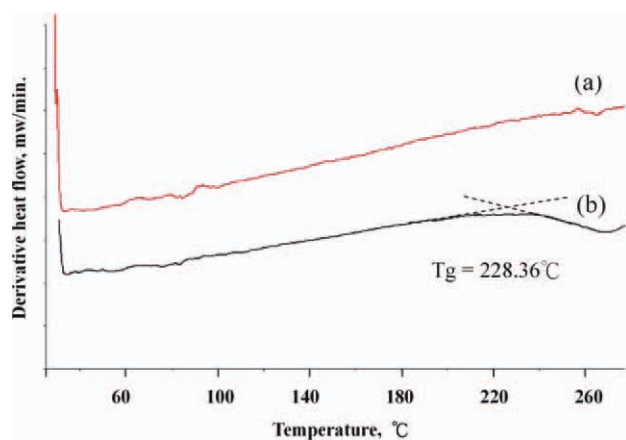


Figure 2. DSC thermograms of (a) chitin and (b) chi-g-PMAA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

grafting. Graft copolymerization proceeded reproducibly under these conditions. Grafting of produced copolymer was evaluated gravimetrically as high as 134%.

DSC Measurement

Figure 2 presents the DSC thermograms of chitin and chi-g-PMAA. The latter includes a more T_g at 228.4°C than the chitin. This temperature is the T_g of PMAA homopolymer.²⁵ The results reveal the grafting of MAA to chitin. Based on the T_g obtained, the chi-g-PMAA copolymer contains a PMAA-rich microdomain.

Solid-State ^{13}C -NMR Characterization

Figure 3(a,b) presents the solid-state ^{13}C -NMR spectra of chitin and chi-g-PMAA, respectively. The signals C1–C8 were assigned

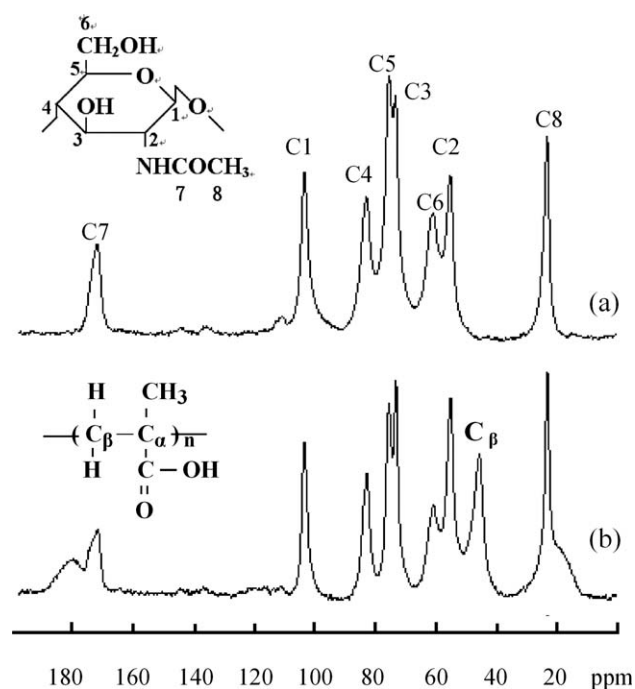


Figure 3. Solid-state ^{13}C -NMR spectra of (a) chitin and (b) chi-g-PMAA.

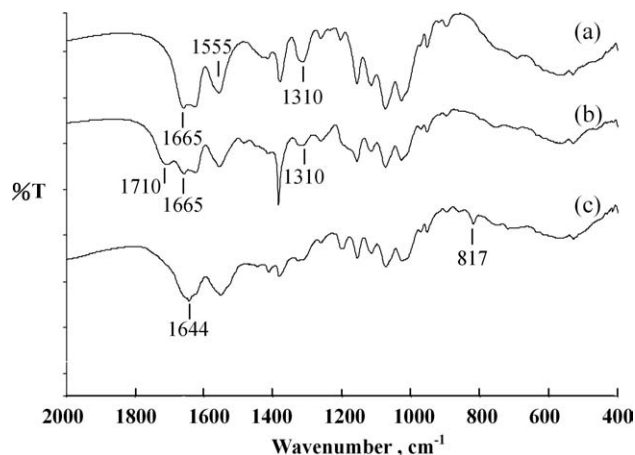


Figure 4. FTIR spectra of (a) chitin, (b) chi-g-PMAA, and (c) chi-g-PMAA after adsorption of paraquat.

as literature.¹³ The spectrum of chi-g-PMAA exhibits an extra peak at 45.9 ppm, which corresponds to the C_β of PMAA, and a peak at 181.8 ppm, which is associated with the carbonyl carbon of PMAA. A shoulder-type peak at around 18 ppm is attributed to the methyl carbon of grafted PMAA. This result proves that PMAA was grafted onto chitin.

FTIR Analysis

FTIR investigations were performed to elucidate the complex interaction between chitin and PMAA. Figure 4(a) presents the spectrum of chitin. The adsorption peak at 1665 cm^{-1} is associated with the carbonyl stretching of secondary amides (amide I band) and that at 1555 cm^{-1} is assigned to the N–H bending vibration of the amide II band.¹³ The peak at 1310 cm^{-1} is characteristic of the amide III band. Figure 4(b) displays the spectrum of chi-g-PMAA. The peak at 1710 cm^{-1} corresponds to the absorbance of carbonyl group on grafted PMAA²⁶ and reveals that PMAA was grafted onto chitin.

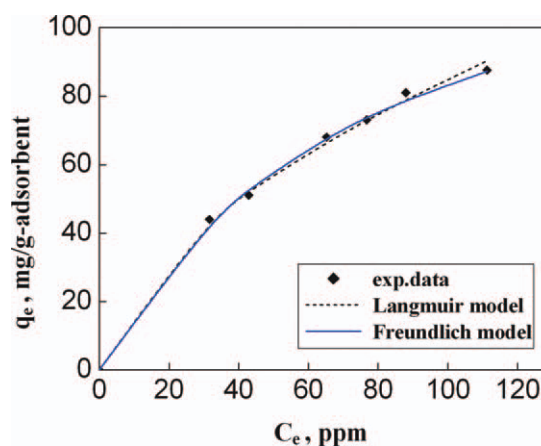


Figure 5. Langmuir and Freundlich isotherms for paraquat adsorption of chi-g-PMAA adsorbent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Neutralization of Grafted Copolymer

The chi-g-PMAA copolymer with 134% grafting percentage was neutralized in 0.1M NaOH_(aq) to prepare the chi-g-PMANa. A large number of —COO^- groups were formed when chi-g-PMANa was added to aqueous solution. However, the chi-g-PMANa powder did not dissolve in aqueous solution because of the insolubility of the chitin backbone.

Adsorption of Paraquat

The chi-g-PMANa was used to adsorb paraquat in aqueous solution. The adsorption was rapid in the first few minutes, reaching equilibrium in around 20 min. Data were collected on the equilibrium adsorptions (q_e) and equilibrium concentrations of paraquat in aqueous (C_e) at 2 h for various initial concentrations of paraquat. Figure 4(c) presents the FTIR spectrum of chi-g-PMANa after the adsorption of paraquat. The peak at 817 cm^{-1} corresponds to the out-of-plane deformation vibration of the trisubstituted alkenes²⁷ in the paraquat, and the peak at 1644 cm^{-1} is associated with the stretching vibration of C=N/C—N in the paraquat molecules. These results reveal that chi-g-PMANa absorbed the paraquat. Figure 5 shows the relationship between q_e and C_e and plots the Langmuir and Freundlich correlations. The Langmuir and Freundlich isotherms and their corresponding relationship coefficient, r , are given as follows:

$$\text{Langmuir } q_e = 1.941C_e / (1 + 1.320 \times 10^{-2}C_e) \quad r = 0.9952$$

$$\text{Freundlich } q_e = 6.399 \log C_e^{(1/1.789)} \quad r = 0.9930$$

Both relationship coefficients exceed 0.99 indicating that the two models both fit the experiment results closely. The monolayer adsorption capacity obtained from the Langmuir isotherm is 147.0 mg/g-adsorbent and 1.5 times higher than that of an activated carbon cartridge, which is used in the hemoperfusion process for paraquat poisoned humans, and 2.5 times higher than that of Fuller's earth, which is used as the adsorbent during the enema.¹⁹ It also exceeds that of activated bleaching earth, which is a new adsorbent of paraquat.²⁸ The capacity of MMA-modified rice husk to absorb paraquat was 292.5 mg/g-adsorbent with a grafting percentage of $\sim 65\%$ as in our earlier study,²⁹ in which better adsorbent properties were obtained at lower grafting percentages than herein. The results may be attributed to the difference between the main-chain structures of rice husk and chitin.

The free energy change (ΔG) was evaluated to verify the mechanism of adsorption. The Langmuir constant can be used to calculate the change in free energy, using the following equation.³⁰

$$\Delta G = -RT \ln k$$

where R is the gas constant, T is the absolute temperature, and k is the adsorption constant. The calculated ΔG , -6.653 kJ/mol, reveals that paraquat adsorption is favorable at low concentration.

As presented in Figure 5, the curve of q_e versus C_e is convex. It reveals that the adsorption efficiency of paraquat is higher at lower concentrations in aqueous solution. The results reveal that chi-g-PMANa is a potential adsorbent of paraquat to be administered to paraquat-poisoned patients in emergencies.

CONCLUSIONS

Chi-g-PMAA was prepared by grafting copolymerization using Ce^{+4} as the initiator. Grafted copolymers were characterized using DSC, FTIR, and solid-state ^{13}C -NMR. Carboxylic groups of PMAA, grafted on chitin, were neutralized to a salt using dilute NaOH_(aq) and readily used to adsorb paraquat from an aqueous solution. Both Langmuir and Freundlich isotherms closely fitted the adsorption data. The monolayer adsorption capacity was 147.0 mg/g-adsorbent, whose value exceeds those of currently used paraquat absorbents. The favorable adsorption of paraquat at low concentrations reveals that PMAA-grafted chitin is a potential adsorbent for the urgent clinical treatment of paraquat-poisoned patients.

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