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Effect of solution plasma process with bubbling gas on physicochemical properties of chitosan

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ABSTRACT

In the present work, solution plasma process (SPP) with bubbling gas was used to prepare oligochitosan. The effect of SPP irradiation with bubbling gas on the degradation of chitosan was evaluated by the intrinsic viscosity reduction rate and the degradation kinetic. The formation of OH radical was studied. Changes of the physicochemical properties of chitosan were measured by scanning electron microscopy, X-ray diffraction, and thermogravimetric analysis, as well as ultraviolet-visible, Fourier-transform infrared, and ^{13}C nuclear magnetic resonance spectroscopy. The results indicated an obvious decrease in the intrinsic viscosity reduction rate after SPP irradiation with bubbling gas, and that the rate with bubbling was higher than that without. The main chemical structure of chitosan remained intact after irradiation, but changes in the morphology, crystallinity, and thermal stability of oligochitosan were observed. In particular, the crystallinity and thermal stability tended to decrease. The present study indicated that SPP can be effectively used for the degradation of chitosan.

1. Introduction

Chitosan is a natural nontoxic polymer that is mainly composed of β (1–4)-linked glucosamine and *N*-acetylglucosamine. The polysaccharide has attracted tremendous research interest owing to its biological properties such as antimicrobial, hypocholesterolemic, immunity, and antitumor effects [1,2]. However, its high molecular weight and low solubility in aqueous solvents has thus far limited its applications [3,4]. Oligochitosan shows good solubility and some specific biological, chemical, and physical properties. Therefore, there has been increasing interest in methods for preparing oligochitosan by using a variety of techniques [5–7]. Solution plasma process (SPP) technology has been recognized as an advanced oxidation process. SPP involves the application of voltage to generate discharge plasma in a liquid, which leads to the formation of active radicals ($H^\bullet$, $O^\bullet$, $OH^\bullet$) and molecules (e.g., H_2O_2, O_3) [8–10]. The oxidizing species can effectively degrade the recalcitrant organic substances such as pharmaceutical compounds, dioxins, or agricultural chemicals [11]. Especially, OH radicals play the critical role for the strong oxidation property of SPP technology [12]. The SPP method has been extensively applied in wastewater treatment owing to its excellent performance, including high degradation efficiency, complete degradation, no secondary pollution, and requirements of normal temperature, pressure and low power consumption [9,13,14].

In recent years, SPP has also been used to degrade chitosan. For example, the decomposition of chitosan was successfully achieved using a solution plasma system [7,15]. However, the solution plasma was produced by pulsed discharge without bubbling gas. Bubbling gas is often used to improve the liquid discharge performance in pulsed discharge systems [16]. The injection of gas bubbles can significantly increase the contact surface area of the

Abbreviations: SPP, solution plasma process; SEM, scanning electron microscopy XRD X-ray diffraction TGA thermogravimetric analysis; FT-IR, fourier-transform infrared; NMR, nuclear magnetic resonance.

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gas and liquid and enhance higher-energy electron production, thus resulting in the creation of more oxidizing species [17]. In addition, bubbling gas can enhance the mass transfer rate and increase the efficiency of the diffusion of reactive species into the liquid, thus promoting oxidation reactions [9]. We previously carried out studies on the degradation of chitosan by SPP in the presence of H_2O_2 with bubbling gas and concluded that this method could be used for effective degradation of chitosan [18]. At treatment time of 30 min, the intrinsic viscosity reduction rate reached 82.19% and 70.04% with and without bubbling gas, respectively. The results confirmed the decomposition effect of bubbling gas in pulsed discharge systems.

Therefore, in the present study, the effect of SPP with bubbling gas (air) on the degradation of chitosan was evaluated, and the characteristics of the chitosan obtained after SPP irradiation with bubbling gas were investigated, including the morphology, crystallinity, thermogravimetry, and chemical structure.

2. Materials and methods

2.1. Materials

Chitosan was obtained from Sinopharm Chemical Reagent Co. Ltd., China. The degree of deacetylation (*DD*) of chitosan is greater than 90%. The viscosity average molecular weight (Mv) of chitosan is 1138 kDa based on viscosity measurements [19]. Acetic acid, ethyl alcohol, and other chemicals were of analytical reagent grade and were obtained from Sinopharm Chemical Reagent Co. Ltd., China. All chemicals were used without any further purification.

2.2. Experimental setup

The experimental setup is shown in Fig. 1. The apparatus consisted of a power supply and a cylindrical plexiglass vessel as a reactor, with an inner diameter of 40 mm. The pulsed electrical discharge for the test solution was provided by needle-plate electrodes. The needle electrode was a copper needle of 2 mm in diameter. The plate electrode was a copper foursquare plate (40 mm × 40 mm). The peak pulse voltage was 60 kV, the power was 350 W, the pulse width was 40 ns, the frequency was 4.67 kHz and the distance between the electrodes was 2 mm. When the pulsed power system was activated, the plasma was generated. Air was bubbled into the bottom of the reactor through a bubble diffuser for studying the effect of degradation by SPP with bubbling gas. Magnetic stirrer was used for studying the effect of degradation by SPP without bubbling gas.

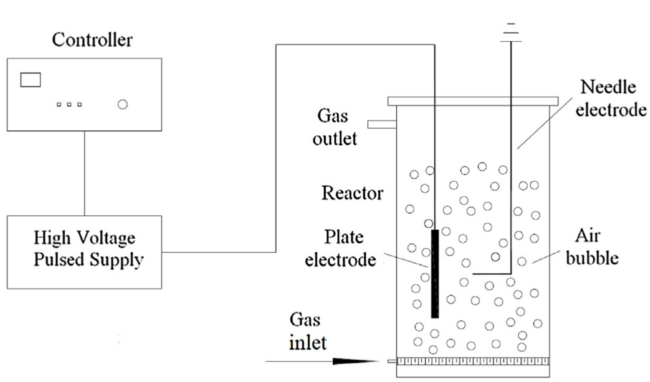

Fig. 1. Schematic of the solution plasma process experimental apparatus.

2.3. Preparation of oligochitosan

Chitosan (3 g) was dissolved in 1 L of a 1% (v/v) acetic acid solution. A 80 mL of the resulting solution was placed in the reactor. The degradation of chitosan by SPP irradiation with and without bubbling gas was performed at atmospheric pressure and ambient temperature for 0, 30, 60, 90, 120, 150, and 180 min, respectively. The reaction mixture was then adjusted to pH 7.0 with 2 M NaOH and precipitated by adding a volume (2 V) of absolute ethyl alcohol. After centrifugation, the precipitate was filtered, washed with alcohol several times, and dried at 60 °C to obtain powder chitosan samples. Experiment under each condition was performed at least thrice.

2.4. Determination of OH radical relative production

To determine the relative production of OH radical during the SPP irradiation, salicylic acid was added to the chitosan solution which can react with OH radical to produce 2,3-DHBA and 2,5-DHBA. Then the samples collected at different irradiation time were measured by a TU-1810 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China) at 510 nm. The production of OH radical was evaluated relatively. Increased absorbance in the samples indicated increased OH radical relative production [20,21].

2.5. Gravimetric analysis to calculate yield

According to the method in Section 3.2. The precipitate and supernatant were dried respectively to obtain solid samples. The weights of the solid samples were measured to calculate the percent yield of the water-soluble or water-insoluble chitosan. The percent yield was calculated according to the following experience equations:

$$Yield\,(\%) = \frac{\text{Total weight of water} - \text{soluble or water-insoluble chitosan}}{\text{Total weight of chitosan in acetic acid solution}} \times 100\% \tag{1}$$

2.6. Characterization

2.6.1. Measurement of intrinsic viscosity reduction rate

The intrinsic viscosity was determined by a viscometric method [19]. The relative viscosities of the original chitosan and its degraded solutions were determined at 25 ± 0.5 °C using an Ubbelohde capillary viscometer (Shanghai Longtuo Instrument Co., Ltd., China). The efflux times for the chitosan solutions (t_s) and the solvent (t_0) were measured in triplicate. The intrinsic viscosity $[\eta]$ was calculated according to the following experience equations:

$$\eta_r = \frac{t_s}{t_0},\ \eta_{sp} = \eta_r - 1 \tag{2}$$

$$[\eta] = \frac{\left(\eta_{sp} + 3\ln \eta_r\right)}{4c} \tag{3}$$

where η_r is the relative viscosity, η_{sp} is the incremental viscosity, and c is the concentration of chitosan (g/mL).

The effect of SPP on the degradation of chitosan was characterized by the intrinsic viscosity reduction rate $\eta_{\%}$, which was calculated according to the following experience equation:

$$\eta_{\%} = \frac{[\eta]_0 - [\eta]_t}{[\eta]_0} \times 100\% \tag{4}$$

where $[\eta]_0$ and $[\eta]_t$ are the intrinsic viscosities of the initial time and action time, respectively.