Ultrasonics Sonochemistry 18 (2011) 149–157

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultsonch

Sonolytic, sonocatalytic and sonophotocatalytic degradation of chitosan in the presence of TiO_2 nanoparticles

Mohammad Taghi Taghizadeh *, Reza Abdollahi

University of Tabriz, Faculty of Chemistry, Department of Physical Chemistry, Tabriz, Iran

ARTICLE INFO

Article history:
Received 11 November 2009
Received in revised form 24 March 2010
Accepted 12 April 2010
Available online 20 April 2010

Keywords:
Chitosan
Degradation
Sonolysis
Sonocatalysis
Sonophotocatalysis

ABSTRACT

The degradation of chitosan by means of ultrasound irradiation and its combination with heterogeneous (TiO_2) was investigated. Emphasis was given on the effect of additives on degradation rate constants. Ultrasound irradiation (24 kHz) was provided by a sonicator, while an ultraviolet source of 16 W was used for UV irradiation. The extent of sonolytic degradation increased with increasing ultrasound power (in the range 30–90 W), while the presence of TiO_2 in the dark generally had little effect on degradation. On the other hand, TiO_2 sono-photocatalysis led to complete chitosan degradation in 60 min with increasing catalyst loading. TiO_2 sonophotocatalysis was always faster than the respective individual processes due to the enhanced formation of reactive radicals as well as the possible ultrasound-induced increase of the active surface area of the catalyst. The degraded chitosans were characterized by X-ray diffraction (XRD), gel permeation chromatography (GPC) and Fourier transform infrared (FT-IR) spectroscopy and average molecular weight of ultrasonicated chitosan was determined by measurements of relative viscosity of samples. The results show that the total degree of deacetylation (DD) of chitosan did not change after degradation and the decrease of molecular weight led to transformation of crystal structure. A negative order for the dependence of the reaction rate on total molar concentration of chitosan solution within the degradation process was suggested.

1. Introduction

Chitosan, (1,4)-2-amino-2-deoxy-β-D-glucan, is a natural polymer generally obtained by extensive deacetylation of chitin isolated from crab shells. Due to its special biological, chemical and physical properties, chitosan and its derivatives have applications in many industrial and agriculture activities [1–3]. Every year approximately 100 billion tons of chitin is produced on the earth. Chitosan, the deacetylated derivative of chitin, is one of the non-toxic and biodegradable carbohydrate polymers, and has received much attention as a functional biopolymer for diverse applications from pharmaceuticals to commodity chemicals [4,5]. These functions undoubtedly depend upon not only their chemical structure but also the molecular weight [6,7]. Therefore, it is necessary to produce different molecular weights of chitosan. Chitosans of different molecular weights are usually prepared by different hydrolysis methods such as acid hydrolysis, an oxidative degradation method, enzyme hydrolysis, a microbial method, mechanical energy methods including shearing, ultrasonic, and microfluidization, and radiation degradation. The ultrasonic method has the merits of high efficiency, the ability to handle large quantities of sample, equipment which is easy to obtain, almost no effects on the DD of treated chitosan, no by-products etc. [8]. In addition, chitosan can be used in many areas, including wastewater treatment, food processing, pharmaceuticals, biomaterials and agriculture [9].

High-intensity ultrasonic treatment can be applied to degrade polymers and to facilitate emulsifying and cleaning processes. The ultrasonic energy is dissipated in solution, resulting in cavitations. Cavitation produces vibrational wave energy, shear stresses at the cavitation interphase, and local high pressure and temperature. These are the major factors causing the degradation of polymers [10–12]. Application of high-intensity ultrasound to dispersions of carbohydrates can lead to depolymerization because of the intense mechanical and chemical effects associated with cavitation [13–16]. Cavitational thermolysis may produce hydroxyl radicals and hydrogen atoms that can be followed by formation of hydrogen peroxide [17–19]. Some cavities exist only for one cycle of the sound field and collapse violently (transient cavities), while other are long-lived and oscillate around some equilibrium size (stable cavities) [20].

These transient reactive species can subsequently react with carbohydrates. In addition, hydrolysis and cleavage due to the strong mechanical forces has been reported for a variety of polysaccharides [21]. In recent years, the simultaneous use of ultrasound and photocatalysis, i.e. the so-called sonophotocatalysis

---

* Corresponding author. Tel.: +98 4113393137; fax: +98 4113340191.
E-mail address: mttaghizadeh@tabrizu.ac.ir (M.T. Taghizadeh).

1350-4177/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ultsonch.2010.04.004

has been studied regarding process efficiency to degrade various organics and dyes [22–27].

However, some researchers were investigated this combined method on degradation of some water soluble polymers [28,29] and recently Saien et al. studied the kinetic of sono-assisted photocatalytic degradation of styrene-acrylic acid copolymer and applied this technique as an enhanced degradation process [30]. Nano TiO_2 as a photocatalyst has a great many advantages such as low cost, non-toxicity, high catalyst efficiency, long-term stability etc. [31,32] on the other hand, by using ultrasound some complicated reactions can be performed with inexpensive equipment and often in fewer steps than with the conventional methods [33] in this regard, researchers have used sono-photocatalysis in a variety of investigations. This process provides an excellent opportunity to reduce reaction time without the need for extreme physical conditions [34].

Although photocatalysis and sonolysis have been extensively employed individually for the degradation applications, their combined use (i.e. sonophotocatalysis) has received appreciably less attention. The aim of this work was to study the degradation of high-molecular weight chitosan by means of sonolysis, photocatalysis and their combined application, sonophotocatalysis, concerning the effect of catalyst presence on the kinetics of degradation process. Moreover, the synergistic effect of different degradation processes was investigated and compared with individual effect of them.

2. Experimental

2.1. Materials

High-molecular weight chitosan from crab shells with ~81% degree of deacetylation and an average molecular weight of approximately 880 kDa according to manufacturers specification was obtained from Aldrich Chemical Co. Degussa TiO_2 P-25 (anatase:rutile = 65:35, BET 50 m^2g^{-1}) was employed as photocatalyst in heterogeneous catalytic experiments and it was supplied by Degussa Huels. All other chemicals were of laboratory reagent grade and were purchased from Merck. All solutions were prepared using distilled and deionized water.

2.2. Methods

2.2.1. Chitosan solution preparation

Chitosan solutions containing 5 g/L chitosan in 1% acetic acid were prepared using the following procedure. The chitosan was hydrated by heating 0.5 g of chitosan in a sufficient amount of water to 60 °C. The dispersion was cooled to room temperature while stirring and 10% acetic acid was added to obtain 1% acetic acid in the final solution. The solution was stirred overnight to ensure complete solubilisation of the chitosan molecules. The solution was then filtered to remove any impurities and 100 ml samples were immediately sonicated.

2.2.2. Experimental setup and procedure

Reactions were carried out in a cylindrical 100 ml Pyrex glass vessel which is schematically shown in Fig. 1. An ultrasound generator (Dr. Hielscher Ultrasonic Processor UP200 H) operating at a fix frequency of 24 kHz and a variable power output up to 100 W nominal value, in aqueous media was used for sonication experiments. A titanium-made H3 sonotrode ($\varphi = 3$ mm) immersed in liquid from the open to the atmosphere top of the vessel was used to deliver the ultrasound energy in the reaction mixture. The bottom of the vessel was fitted with a glass cylindrical tube housing the light source; there were a pair of 8 W UV lamp, which emits in the 200–300 nm wavelength range with a maximum at 254 nm. The incident photon flow of UV light, estimated under the same conditions as in the photocatalytic experiments, was 1.8×10^{-4} Einistein L^{-1} min^{-1}. The vessel was fed with a 100 ml chitosan solution and the reaction temperature in the case of sonolysis, sonocatalysis and sonophotocatalysis was kept constant at 25 ± 1 °C through the use of cooling water circulating through the double-walled compartment, thus acting as cooling jacket. The reaction vessel was covered with a dark cloth to avoid unwanted photochemical reactions induced by natural light.

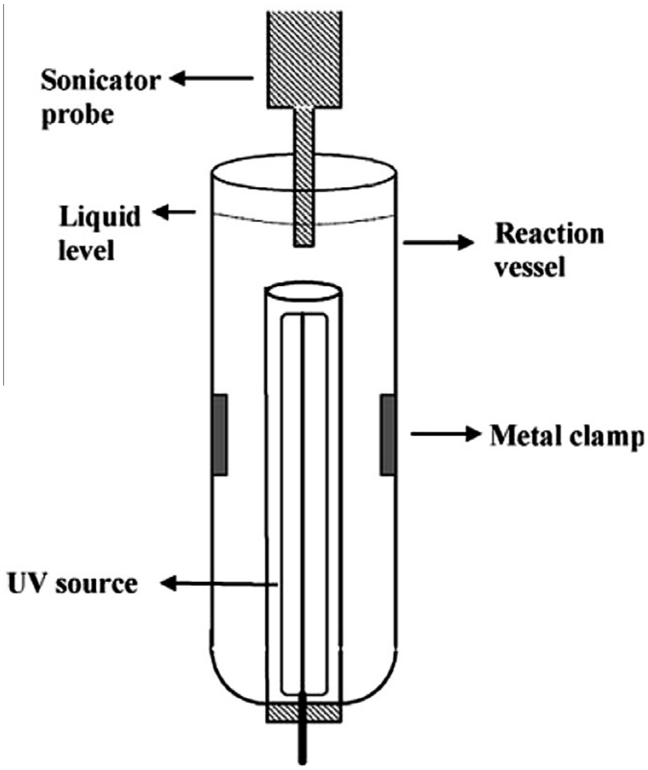

Fig. 1. Schematic of the experimental setup.

Different treatments were tested, namely: TiO_2 sonolysis (US), photocatalysis (UV), combined sonolysis and photocatalysis (US + UV). For the experiments in the presence of TiO_2, a concentration range of 0.1–0.6 g/L of TiO_2 nanoparticles was used.

2.3. Characterization

Infrared spectrometry was used to determine the DD of the chitosans [35]. Chitosan powder was sieved through a 200 mesh, then mixed with KBr (1:100) and pressed into a pellet. The absorbances of amide 1 (1650 cm^{-1}) and of the hydroxyl band (3450 cm^{-1}) were measured using a Simadzu RF50 infrared spectrophotometer. The band of the hydroxyl group at 3450 cm^{-1} was used as an internal standard to correct for the disc thickness and for differences in the chitosan concentration in making the KBr disc. The percentage of the amine group's acetylation in a sample is given by $(A_{1650}/A_{3450}) \times 115$. Here, A_{1650} and A_{3450} are the absorbances at 1650 and 3450 cm^{-1}, respectively. Thus, the DD of degraded samples was calculated with the following equation:

$$DD = 100 - (A_{1650}/A_{3450}) \times 115 \quad (1)$$

Gel permeation chromatography (GPC) (HLC6A, Shimadzu) was used to compare molecular weight and molecular weight distribution (polydispersity) of the original chitosan and degraded samples