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Degradation of chitosan by hydrodynamic cavitation

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ABSTRACT

A novel method of degradation of chitosan, by hydrodynamic cavitation using an orifice plate, was investigated. The effects of initial concentration, solution pH, upstream pressure and geometry of the orifice plate on the degradation of chitosan were evaluated. It was found that lower initial concentration of chitosan solution, lower solution pH, higher upstream pressure of the orifice plate, and longer treatment time are favourable for the degradation of chitosan solution. It was also found that the degradation of chitosan solution was dependant on the geometry of the orifice plate. The plates with a larger number holes and smaller hole diameter favoured chitosan degradation. Structures of the degraded products were characterized with Fourier-transform infrared spectra (FT-IR) and X-ray diffraction (XRD). The present study conclusively establishes that hydrodynamic cavitation can be effectively used for the degradation of chitosan.

1. Introduction

Chitosan is a linear copolymer of β(1–4) linked 2-acetamido-2deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glycopyranose. It is easily obtained by deacetylation of chitin, the second most abundant polymer next to cellulose widely existing in crustaceans, insect and certain fungi [1–3]. Due to many unique properties such as biodegradability, biocompatibility and non-toxicity, chitosan has been reported for use in numerous applications, such as agriculture, water-treatment, food processing, biomedical field, etc [1,4–6]. Generally, chitosan obtained by deacetylation of chitin has a high molecular weight and low solubility in aqueous solvents, which limits its applications in various fields, because many applications depend upon not only chemical structure of chitosan, but also the molecular weight [1]. However low molecular weight chitosan has potentially some important properties, such as fat-binding, antithrombotic activity, antitumour activity and antimicrobial activity [7–10]. Thus the development of an efficient process for reducing the molecular size of chitosan, without altering its chemical structure, is of great interest.

Usually there are three different methods to degrade chitosan, chemical methods, enzyme methods and physical methods. Chemical method involves the using of chemicals and generates waste, which increases the difficult of controlling the subsidiary reactions in the degradation and to separate and purify [11,12]. Enzyme approach is an effective method for degradation of chitosan, but due to its prohibitive cost and limited availability, the industrial application of the enzyme approach is limited [13–15]. Compared with chemical and enzyme methods, physical method has the advantages of low cost, no pollution, energy saving and high efficiency, etc [16–19].

Ultrasonic cavitation is an important physical method to degrade chitosan, and it has been used to degrade polymers, dextran, pullulan, agarose, carrageenan, chitosan, etc [20–23]. However, it has been observed that use of ultrasonic devices poses significant problems for design and efficient operation at large scale operation due to substantially lower energy efficiencies and higher costs of operation [24–27]. An alternative method is hydrodynamic cavitation, which can provide better scale-up possibilities, higher bubble densities and lower investment costs [28,29].

Hydrodynamic cavitation occurs when a liquid undergoes a dynamic pressure reduction due to constriction devices like venturi, orifice plates, etc.; when the pressure at the throat or vena-contracta of the constriction falls below the vapour pressure of the liquid, the liquid flashes, generating numerous vapour cavities. When cavities are carried to a higher-pressure region they implode violently and very high pressures and temperatures can occur. In addition, the collapsing cavitation bubble also initiates some physicochemical effects such as production of shear forces, shock waves and the formation of reactive radicals. The radicals produced by hydrodynamic cavitation can react with molecules in solution to promote a variety of reactions, similar to ultrasonic cavitation [30]. Hydrodynamic cavitation has some applications including the degradation of organics, the destruction of microbial cells,

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hydrolysis of fatty acids and the preparation of biodiesel [29,31–34]. However, up to now there are no reports on the applications of hydrodynamic cavitation in the degradation of chitosan.

In this study, the degradation of chitosan was investigated by hydrodynamic cavitation using an orifice plate. The effects of initial concentration, solution pH, treatment time of solution, upstream pressure and geometry of the orifice plate are discussed. Some degradation products of chitosan were also analysed.

2. Experimental

2.1. Materials

Chitosan was purchased from Kabo Industrial Co., Ltd. (Shanghai, China). The degree of deacetylation and viscosity-average molecular weight of the commercial chitosan used in this study were determined experimentally. The results are as follows: degree of deacetylation was 89.6%, viscosity-average molecular weight was 1200 kDa. All other chemicals were of analytical reagent grade quality and were employed without further purification.

2.2. Experimental set-up

The schematic of the experimental setup for hydrodynamic cavitation is shown in Fig. 1. It is a closed loop system designed to draw chitosan solution from a holding tank of 30 L volume, then taking it into the cavitation zone and then discharging the treated solution back to the tank by a centrifugal pump. The other components of the system include control values (V_1, V_2, V_3), flanges to accommodate the orifice plate, pressure gauges (G_1, G_2) and a glass rotameter. The suction side of the pump is connected to the bottom of the tank and the discharge from the pump branches into two lines, mainline and bypass line. The orifice plate cavitation reactor is fixed in the mainline. The bypass line is used to control liquid flow through the mainline.

The cavitation was generated in the setup by an orifice plate. In this study, eleven orifice plates were considered and the detailed information of the plates is given in Table 1.

For a typical degradation experiment, 10 L of aqueous solution of chitosan with desired concentration was placed in holding tank. The pump was started and inlet pressure was adjusted by controlling the flow through by-pass line using valve (V_2). The operating temperature was kept constant by circulating water through the jacket. Initially, the effect of solution concentration of chitosan on degradation was investigated with the solution concentrations of 0.3, 0.5, 1.0, 1.5, 2.0 g L^{-1}. To study the effect of inlet pressure, the pressure was varied from 0.1 to 0.5 MPa. Experiments were carried out at varying pH of 3.6, 4.0, 4.4, 4.8, 5.2. In addition, to study the effect of treatment time, the solution was treated in the experimental set-up for 13 h and degradation samples were collected after every hour. Finally, the effect of the geometry of the orifice plate on degradation of chitosan was discussed by changing to plates 1-10.

Table 1
Flow geometry of the orifice plates.

No.	n	δ (mm)	d (mm)	A (mm^2)	α (mm^{-1})	β_0	C (mm)
1	1	3	10	7.065	1.33	0.0144	9.42
2	1	3	5	7.065	1.33	0.0144	9.42
3	1	4	12	12.56	1	0.0256	12.56
4	1	4	15	12.56	1	0.0256	12.56
5	1	5	15	19.625	0.8	0.04	15.7
6	3	2	10	9.42	2	0.0192	18.84
7	4	2.5	5	19.625	1.6	0.04	31.4
8	4	2	6	12.56	2	0.0256	25.12
9	3	2.5	6	14.719	1.6	0.03	23.55
10	4	2.5	10	19.625	1.6	0.04	31.4
11	1	2	10	3.14	2	0.016	6.28

Note: No. — Plate number, n — Number of holes, δ — Diameter of each hole, d — Thickness of each plate, A — Flow area, α —The ratio of total perimeter of holes to the total area of the opening, β_0 — The ratio of total flow area to the cross sectional area of the pipe, C — Total perimeter of holes.

2.3. Measurement of intrinsic viscosity reduction rate

Intrinsic viscosity reduction rate was determined by a one-point literature method [35]. Chitosan samples were prepared in 0.2 mol L^{-1} CH_3COOH/0.1 mol L^{-1} CH_3COONa aqueous solutions. The efflux times (t_s) and solvent efflux times (t_0) were measured using an Ubbelohde capillary viscometer at 25 ± 0.5 °C. The intrinsic viscosity [η], was calculated according to formulae:

$$[\eta] = \frac{\left[\eta_{sp} + 3\ln \eta_r\right]}{4c} \quad (1)$$

$$\eta_r = t_s/t_0 \quad (2)$$

$$\eta_{sp} = \eta_r - 1 \quad (3)$$

which η_r is relative viscosity, η_{sp} is specific viscosity and c is concentration of chitosan.

The effect on the degradation of chitosan was characterised by the intrinsic viscosity reduction rate $[\eta]_r$.

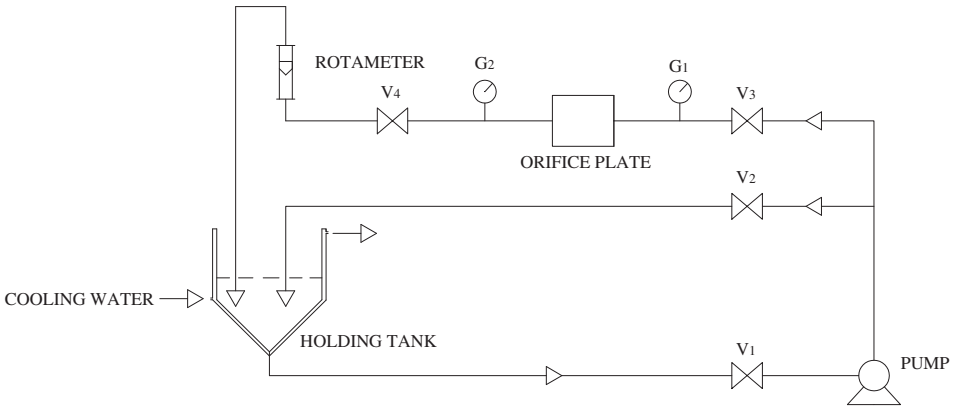

Fig. 1. Schematic of hydrodynamic cavitation reactor set-up.