



Preparation of chitosan nanoparticles from shrimp shells and investigation of its catalytic effect in diastereoselective synthesis of dihydropyrroles



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ABSTRACT

Preparation of chitosan nanoparticles (CS-NPs) was examined from shrimp shells for their catalytic activity. The yield of crude chitosan was 87.8%. The structure of chitosan nanoparticles was determined by FT-IR, SEM and XRD analysis. Then, diastereoselective synthesis of dihydropyrroles was done using chitosan nanoparticles in water under ultrasonic irradiation. This polymeric nanocatalyst could be used instead of the old toxic commercial organic basic catalysts and could be readily isolated from the reaction mixture and recycled several times without significant loss of catalytic activity.

1. Introduction

Chitin is a natural polysaccharide synthesized by a great number of living organisms and functions as a structural polysaccharide [1]. Chitosan is the only pseudo natural cationic polymer which has many potential biomedical and other applications. Chitosan is natural, non-toxic, copolymer of glucosamine and N-acetylglucosamine prepared from chitin by deacetylation, which in turn, is a major component of the shells of crustaceans. Recently, biocatalysis and sustainable chemistry researchers are directed to develop new green methodologies that aim to reduce and prevent pollution at its source [2–4]. Biocatalysis is a promising technique based on the use of natural renewable biological materials, such as enzymes and polymers, that provide cleaner methodologies with high selectivity and energy-efficient operation under mild conditions in contrast to the traditional chemical catalysts [5,6]. Chitosan (2-acetamido-2-deoxy- α -D-glucose-(N-acetylglucosamine)) is a partially deacetylated polymer of chitin and is usually prepared from chitin by reflux with a strong alkaline solution [7–9]. Some time ago, the utility of chitosan as an efficient eco-friendly basic biocatalyst for Michael additions was reported and it could already be shown that chitosan can catalyze the addition of bi-functional active methylenes to arylidenemalononitriles and enamines [10–13]. Pyrroles are known to be widely important heterocycles, key structural units of chlorophyll and hemoglobin ensuring the photosynthesis in plants and oxygen exchange in animals. A great variety of natural compounds includes the pyrrole scaffold fulfilling a number of diverse major biological functions. No wonder that many potent drugs actually represent various pyrrole derivatives. A lot of pyrroles have been recently shown to be

COX-2 isoenzyme inhibitors, DNA minor groove recognition reagent DB884, bioantioxidants [14–16]. Different pyrroles are known to possess anti-inflammatory, antiviral, antiproliferative, antibacterial, antidepressant, antipsychotic, antihyperglycemic activities [17]. In recent years, ultrasonic chemistry has received an increasing attention [18]; ultrasound irradiation, by virtue of cavitation collapse, is able to activate numerous organic reactions. A large number of organic reactions could be carried out in higher yields, shorter reaction time and milder reaction conditions under ultrasound irradiation than that of conventional methods [19–26]. Compared to conventional heating which provides thermal energy in the macro system, ultrasound irradiation is able to activate many organic reactions by providing the activation energy in micro environment [27–28]. Therefore, we developed an environmentally benign methodology for the synthesis of diastereoselective dihydropyrrole derivatives via three component reaction of 2-arylidemalononitrile, hydantoin, and aromatic amines in the presence of Cs-NPs under ultrasonic irradiation (scheme 1).

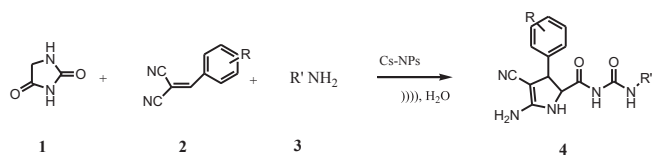
2. Experimental

2.1. Materials and apparatus

All reagents were used as purchased from commercial suppliers without further purification. Shrimp shells were obtained from Persian Gulf in Hormozgan province, Bandarabbas (Fig. 1). The IR spectra of all compounds were recorded on FT-IR Magna 550 apparatus using with KBr plates. NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer (400 MHz for ¹H and 100 MHz for ¹³C). Chemical shifts

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Scheme 1. Diastereoselective synthesis of dihydropyrroles by Cs-NPs.

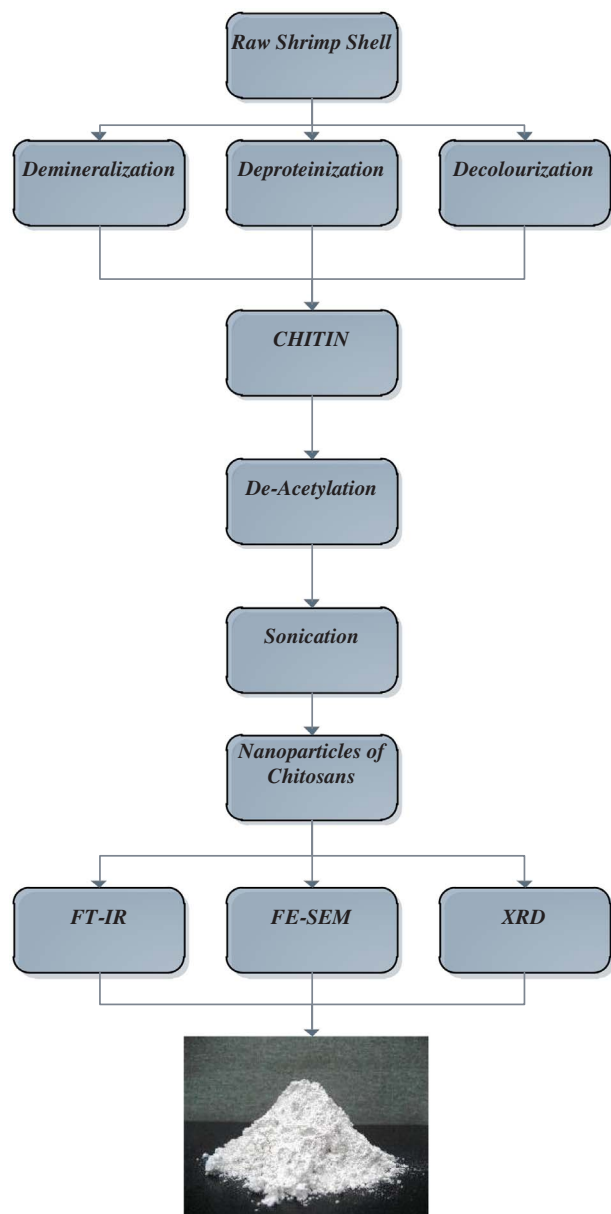


Fig. 1. Manufacturing process.

are reported in δ ppm referenced to an internal TMS standard. Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert company with mono chromatized Cu K α radiation ($k = 1.5406 \text{ \AA}$). Microscopic morphology of products was visualized by SEM (LEO 1455VP).

2.2. General procedure for the preparation of chitin

The collected shrimp shells were washed with distilled water, and then the samples were sun light dried for 24 h and further dried on the furnace at a temperature of $80 \text{ }^\circ\text{C}$ for 24 h. The dried samples were blended and sieved to 80 meshes.

Stage of deproteination. A total of 20 g samples of shrimp shell powders were added to 3.5% sodium hydroxide as much as 1:5 (w/v). Excerpts stirred over heat and left for 1 h at $90 \text{ }^\circ\text{C}$, then the solution was filtered and the residue was washed with tap water until neutral pH, then after the residue was re-dried in a furnace at a temperature of $60 \text{ }^\circ\text{C}$ for 4 h and resulted in chitin powder.

Stage of demineralization. Chitin powder result of deproteination is then added with 2-N-hydrochloric acid in the ratio 1:5 (w/v), allowed to stand for 1 h at $90 \text{ }^\circ\text{C}$ to separate the residue from the filtrate, and then the residue was washed with distilled water until neutral pH, then dried in a furnace at $60 \text{ }^\circ\text{C}$ for 4 h.

Stage of depigmentation. The demineralization of chitin extracted with acetone 1:5 (w/v) for 4 h in soxhlet, then the residue is bleached with 0.32% sodium hypochlorite for 5 min at room temperature, then the residue was washed with distilled water until neutral pH and dried in an oven at $60 \text{ }^\circ\text{C}$ for 4 h.

2.3. General procedure for deacetylation of chitin into chitosan nanoparticles

A total of 5 g of chitin were added 20 ml deionized water and sonicated for 20 min then dried. The sonicated sample was reacted with 50 ml of 50% sodium hydroxide, then heated using a hot plate at $90 \text{ }^\circ\text{C}$ for 80 min, then filtered and the residue was washed until neutral pH and then dried in a furnace with a temperature of $60 \text{ }^\circ\text{C}$ for 4 h.

2.4. General procedure for synthesis of dihydropyrroles catalyzed by catalyzed by Cs-NPs

2.4.1. Typical heating method

A mixture of 2-arylidene malononitrile (2.0 mmol), hydantoin (2.0 mmol), and amine (aromatic or aliphatic) (2.0 mmol), Cs NPs (20 mol%) and water (2.0 mL) were refluxed for required time. After completion of reaction as evidenced by TLC, the resulting precipitate was collected by filtration and washed with ethanol. The crude precipitate was recrystallized by ethanol to give pure products.

2.4.2. Ultrasound irradiation

To a mixture of 2-arylidene malononitrile (2.0 mmol), hydantoin (2.0 mmol), and amine (aromatic or aliphatic) (2.0 mmol), Cs NPs (20 mol%) and water (2.0 mL) were added and mixture was sonicated at 70 W for 1.5–2 h until completion of reaction as evidenced by TLC. The resulting precipitate was collected by filtration and washed with ethanol. The crude precipitate was recrystallized by ethanol to give pure products. The structures of the products were fully established on the basis of their ^1H NMR, ^{13}C NMR and FT-IR spectra (See Supporting information).

3. Results and discussion

To start with this study, we extracted chitosan from shrimp shells in the optimized conditions [29]. Then, in order to investigation of structure of prepared chitosan, a series of techniques including SEM, FTIR, XRD was performed. The FTIR spectra of chitin exhibited a characteristic band at 3442 cm^{-1} is attributed to -NH and -OH groups stretching vibration and the band 2925 cm^{-1} were an aliphatic C–H stretching bands that converges to OH stretching. The characteristic carbonyl C=O stretching of chitin at 1627 cm^{-1} are attributed to the vibrations of the amide band. The vibrations bands at 1074 cm^{-1} showed C–O–C vibration inside chitin ring and produced many peaks caused by the presence of hydroxide from chitin which contains a single bond C=O [30]. Characteristic of chitosan was shown by a broad absorption band in the range 3000 to 3500 cm^{-1} which is attributed to O–H stretching vibrations and the 3436 cm^{-1} to vibration of NH. The stretching vibrations of methylene C–H at 2923 cm^{-1} , absorption peak at 1560 cm^{-1} correspond to the NH_2 . The spectra of chitosan showed

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