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Synthesis And Characterization Of Chitosan/Silver Nano composites Using Kumquat Aqueous Extract: A Green Approach

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Abstract: A simple and effective green approach has been developed to synthesize chitosan/Ag nanocomposites that were successfully employed using kumquat aqueous extract as a reducing agent. It indicates to be an eco-friendly, rapid green method for the synthesis providing a cost effective and an efficient route for the chitosan/Ag nanopcomposites' synthesis. The prepared chitosan/Ag nanocomposites have been characterized by UV-vis, FTIR, XRD, TEM and EDS. Result showed those chitosan/Ag nanocomposites have been obtained with an average particle size of ~15-25 nm. Thus, this eco-friendly method could be a competitive alternative to the conventional physical/chemical methods used for the synthesis of chitosan/Ag nanocompoites.

Keywords: Kumquat extract, chitosan/silver nanocomposites (CS/Ag NCPs), green synthesis

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I. INTRODUCTION

In the recent time, antimicrobial and antioxidative activities of chitosan were significant enhanced because of loading chitosan with various metals found in the previous reports [1, 2]. Chitosan is a natural biopolymer extremely abundant and relatively cheap. It has attracted significant interest by a lot of scientists due to its biological properties such as antitumor activity, antimicrobial activity and immune enhancing effect [3, 4].

Among all antibacterial metals, silver nanoparticles (Ag NPs) are well known for strong antimicrobial properties, nontoxic and no harm to human cells [5]. Thus, silver nanoparticles have widely attracted attention for medical applications due to their excellent properties such as antibacterial activity [6, 7]. A number of methods for producing silver nanoparticles (Ag NPs) have been developed using both physical and chemical approaches such as sonochemical and electrochemical methods, thermal decomposition, laser ablation, microwave irradiation, etc… [8, 9, 10, 11, 12]. However, they are also related to the limitations as using of toxic chemicals, high operational cost and energy needs. Therefore, considerable interest has been paid to the preparation of metallic nanoparticles by green synthesis in recent years [13, 14, 15, 16, 17].

Therefore, green synthesis is the green environment friendly processes in chemistry, in chemical technology and engineering; which are becoming more popular and much needed since the global's concern is about environmental problems in recent years [18]. Green synthetic methods have been used new alternative for metal nanoparticles as well as Ag NPs synthesis using natural polymers (chitosan, etc.), sugars, enzymes, microorganisms, plant extracts as reductants (e.g, lemon aqueous extract, Azadirachita indica aqueous leaf extract,…) and capping agents [19, 20, 21]. They are simple, one step, cost-effective, energy efficient, more stable materials and environment friendly [22, 23, 24].

According to our understanding, using kumquat aqueous extract to synthesize chitosan/silver nanocomposites have not been previously reported. Thus, the main objective of this study was to research the synthesis and characterization of chitosan/Ag nanocomposites. The chitosan/Ag nanocomposites were synthesized by green route using kumquat aqueous extract without using any additional harmful chemical/physical methods. Herein, the synthetic method used here is simple, rapid reaction time, cost effective, easy to perform, uniform particle size, stable and sustainable. Chitosan/Ag nanocomposites (CS/Ag NCPs) can be produced at low concentration of kumquat aqueous extract. Moreover, the synthesized chitosan/Ag nanocomposites have a significant promise as bactericidal agent for applications (i.e, biomedical, food, agriculture and cosmetics, etc…) in the current time and in future.

II. EXPERIMENTAL SECTION

2.1. Materials

Silver nitrate ($AgNO_3$), sodium tripolyphosphat (STPP, >98%) were purchased from Acros. Kumquat fruit (~3 months old, green shell) was purchased from a garden at Phong Dien, Can Tho City in Vietnam. All solutions were prepared using deionized water from a MilliQ system.

2.2. Methods

2.2.1. Preparation of kumquat extract

Fresh kumquat was squeezed and obtained the kumquat juice mixture. After that, the kumquat juice was filtered, centrifuged and washed with DI water for three times to obtain a juice extract from kumquat. This kumquat aqueous extract was used for synthesis of chitosan/Ag nanocomposites (CS/Ag NCPs) in following steps.

2.2.2 Preparation of chitosan/Ag nanocomposites by kumquat extract

Chitosan/Ag nanocomposites (CS/Ag NCPs) were synthesized by a green method using kumquat aqueous extract as a reducing agent for the bioconversion of chitosan polymer and silver ions into chitosan and Ag nanoparticles. In a typical synthesis, 2 mL of sodium tripolyphosphat (STPP) solution (1% in H_2O) was added to 40 mL of chitosan solution (2 mg/mL in acetic acid solution 2%) and stirred for 30 min at 50^{o}C to obtain chitosan nanoparticles. And then, 1 mL of $AgNO_3$ (0.01 M) was added to the above solution mixture and after 1 min, 2 mL of kumquat aqueous extract was also quickly added and stirred for 90 min at 70^{o}C. The solution was then centrifuged (12000 rpm; 15 min) and washed with deionized water (DI water) to remove excess. And then redispersed in DI water. The average particle size of the as-prepared chitosan/Ag nanocomposite is ~15-25 nm.

2.2.3. Characterization

The absorbance spectra of particle solutions were examined by UV–vis spectrophotometry (UV-675; Shimadzu). Fourier transform infrared spectroscopy (FTIR) spectra of chitosan/Ag nanocomposites were obtained by using a Renishaw 2000 confocal Raman microscope system.The particle size and morphology of chitosan/Ag nanocomposite was examined by transmission electron microscope (TEM) with a Philips Tecnai F20 G2 FEI-TEM microscope (accelerating voltage 200 kV). The EDX measurement was performed with a JSM 6500 EDX analyzer.

III. RESULTS AND DISCUSSION

As shown in Figure 1, the UV-vis spectra of chitosan/Ag nanocomposites (CS/Ag NCPs) exhibited with the maximum absorption peak in the range from 401-411 nm, respectively. Herein, the plasmon resonance peaks are quite match with the surface absorption of Ag nanoparticles [25, 26]. Since, it is demonstrated that Ag nanopaticles are created in the chitosan nanoparticles' solution. The maximum absorption peaks of chitosan/Ag nanocomposites measured in the range ~401-411 nm, which can be predicted the average particle size of chitosan/Ag nanocomposites being ~15-25 nm, as compared to Ag nanoparticles [25, 26]. Result that the maxium absorption peak intensity of chitosan/Ag nanocomposites (CS/Ag NCPs) at 401 nm and 407 nm are approximate – see Figure 1 (c, e), respectively. As known, the absorption peak in the range at 401 nm has nanoparticle size smaller than that of the absorption peak at 407 nm. Thus, the optimal sample will be chosen for following investigations respective for 90 min at 70^{o}C – see in Figure 1(c).

The presence of free ions in the kumquat extract solution has greatly accelerated for the polyol synthesis of chitosan/Ag nanocomposites. During the synthesis, we could easily monitor the progress of the nanoparticles production through its color changes from colorless to yellow, red-brown or blue, etc… due to a dramatic increase in the reduction rate of silver ions (Ag^+) and chitosan (high molecule mass) become Ag and chitosan nanoparticles (chitosan with low molecule mass). The absorption intensity of synthesized samples tend to proportional increase to the chitosan/Ag nanocomposites' solution color, corresponding to increase the concentration of $AgNO_3$ solution. It demonstrated that reaction rate of reducing agent using kumquat extract significantly affects to particle size control of synthetic chitosan/Ag nanocomposites in the mixture solution.

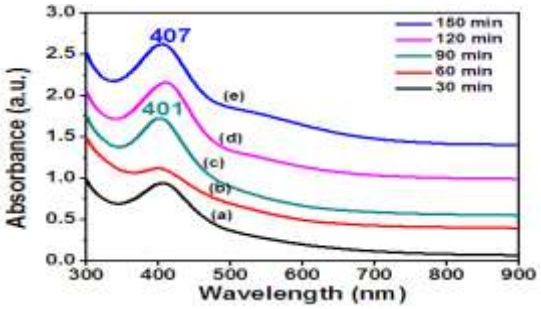

Figure 1. UV-vis spectra of chitosan/Ag nanocomposites using kumquat extract at 70^{o}C with various reaction times: (a) 30 min; (b) 60 min; (c) 90 min; (d) 120 min; and (e) 150 min, respectively.

Transmission electron microscopy (TEM) was used to observe the surface morphology of chitosan/Ag nanocomposites. Figure 2 shows representative TEM images of chitosan/Ag nanocomposites sample. The image of the chitosan and Ag nanoparticles reveal that the nanocomposite and that they are well disfersed and spherical in shape. Chitosan/Ag nanocomposites are uniform and spherical with average particle size ~15-25 nm. There is no agglomeration of nanoparticles may be due to the presence of chitosan as a capping agent. Especially, these particles are uniformly mixed in a chitosan matrix – see in Figure 2.

And the energy dispersive X-ray analysis (EDX) clearly shows the presence of Ag and chitosan in pure form with weights of 14.9% Ag, 58.1% C, and 4.3% N in the sample. It confirmed the formation of chitosan/Ag nanocomposites with initial content of 1 mL $AgNO_3$ solution (0.01 M) in 40 mL chitosan solution as shown in Figure 3. No additional impurities are detected in the EDS result – see in Figure 3.

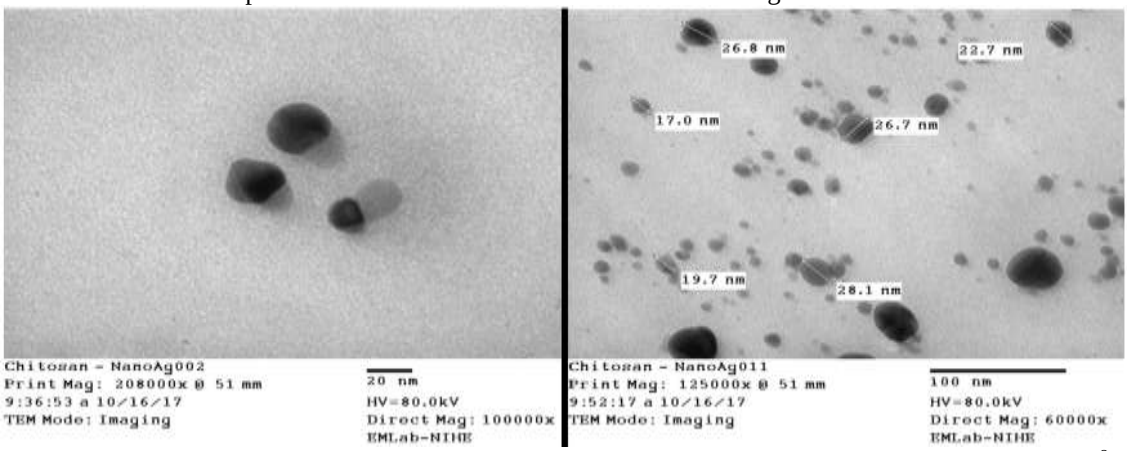

Figure 2. TEM images of chitosan/Ag nanocomposites (CS/Ag NPs) using kumquat aqueous extract at 70^{o}C for 90 min with concentration of $AgNO_3$ solution (0.01 M) in the chitosan solution.

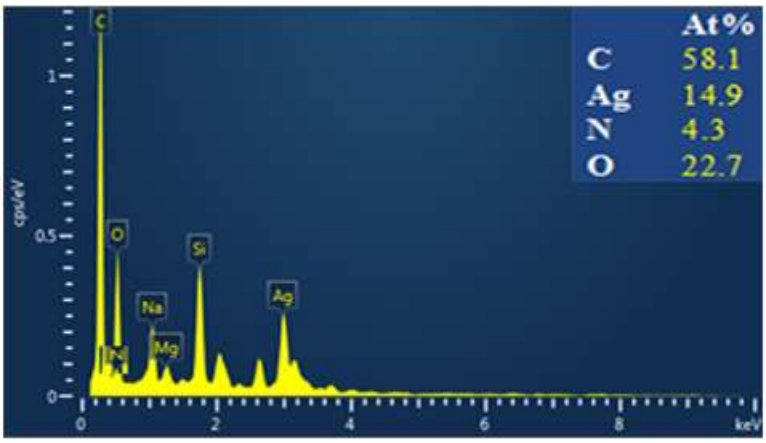

Figure 3. EDS profile of chitosan/Ag nanocomposites and quantitative analysis.

As shown in Figure 4, the FTIR spectrum of chitosan shows the presence of bands at ~3414-3423 cm^{-1} (O-H stretching), C-H and C-N stretching at ~2926-2850 cm^{-1}, N-H bending at 1641-1612 cm^{-1}, N-H angular deformation in CO-NH plane at 1410-1600 cm^{-1} and C-O-C band stretching at 1087 cm^{-1} [27, 28]. In the FTIR spectrum of chitosan/Ag nanocomposites, the shifting of the chitosan peaks is observed which may be due to the interaction of Ag with chitosan in the nanocomposite (e.g, from 1410 cm^{-1} shifted to ~1391 cm^{-1} (Figure 4(b) – see in Figure 4). Besides, the other changes that are significantly noticeable the reduction in the intensity of the hydroxyl (-OH) peak and the increase in the intensity of the C-O stretching, which is occurred when the presence of Ag nanoparticles in the chitosan matrix and formed the mixture solution of chitosan/Ag nanocomposites.

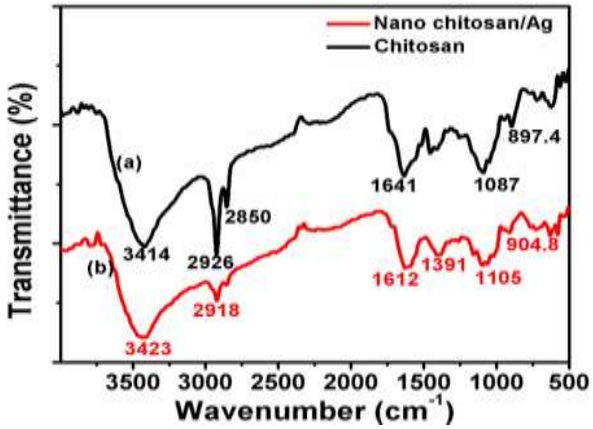

Figure 4. FTIR spectrums of (a) chitosan and (b) chitosan/Ag nanocomposites.

The X-ray diffraction (XRD) pattern of pure chitosan powder there is mainly peak at $2\theta = 29.3^{o}$, which according to literature could demonstrate crystalline structure form [29]. As shown in Figure. 5, the characteristic peaks for Ag nanoparticles appear at 38.14^{o}, 44.28^{o}, 65^{o}, and 78^{o}, which correspond to crystal facets of {111}, {200}, {220}, and {311} of silver (Ag) as compared and interpreted to standard data of JCPDS (No. 04-0783). Each crystallographic facet contains energetically distinct sites based on atom density. The adsorption of Ag^{+} ions changes crystalline structure and the degree of ordering of the tested sample be reduced – see in Figure. 5, which agrees to the previously reported result [30].

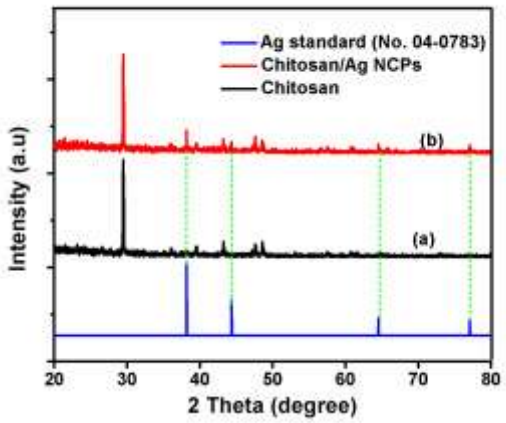

Figure 5. XRD patterns of (a) chitosan and (b) chitosan/Ag nanocomposites.

IV. CONCLUSIONS

A simple and rapid green synthesis of chitosan/Ag nanocomposites using kumquat extract have been successfully developed in this study. It proves to be an eco-friendly, rapid green approach for the synthesis providing a cost effective and an efficient route for the chitosan/Ag nanocomposites' synthesis. It indicated that synthesized chitosan/Ag nanocomposites have uniform, very well capped particle structures ~15-25 nm in size. It is demonstrated that using kumquat extract for the synthesis of chitosan/Ag nanocomposites have brought many benefits such as energy efficient, cost effective, rapid reaction time, protecting human health (non-toxic to humans in minute concentrations) and environment leading to safer products and lesser waste. Therefore, it has greatly potential and promising to use in biomedical applications and plays an important role in opto-electronics and medical devices in future.

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