Silver nanoparticles-chitosan composites: preparation, characterization and solubility in acidic medium

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ABSTRACT

Chitosan is a biocompatible, biodegradable and non-toxic biopolymer obtained by N-deacetylation of chitin, which is one of the abundant natural biopolymer. Chitosan finds its applications in different fields due its unique physiochemical properties. However, chitosan applications in acidic conditions are limited due to solubility in acidic medium. In the present study, chitosan beads impregnated with silver nanoparticles (AgNP-CB) were prepared by simple environmental friendly method. Chitosan beads (CB) and CB after impregnating with silver nanoparticles were characterized using Fourier transform infrared spectroscopy. Further, solubility of AgNP-CB was examined in different acidic media. The apparent change in color of chitosan beads after treating with silver nanoparticles showed that silver nanoparticles are distributed over the exterior and interior of the chitosan beads. The FTIR spectra of chitosan beads and AgNP-CB provide evidence that the silver nanoparticles are bind with the chitosan beads. AgNP-CB was found to be insoluble in all the studied acidic media. The results show that solubility of chitosan beads are significantly changed after treating with silver nanoparticles.

KEY WORDS: Chitosan, Silver nanoparticles, FTIR, solubility.

1. INTRODUCTION

Chitosan is a linear biopolymer of $\alpha(1\rightarrow4)$-linked 2-amino-2-deoxy-β-D-glucopyranose obtained by N-deacetylation of chitin. Chitin is one of the abundant natural biopolymer and it is extensively found in exoskeleton of crustaceans. Chitosan is commonly used in water treatment, pharmaceutics, cosmetics and agriculture and many another due to its unique properties such as non-toxic, high biocompatible, biodegradable and ease of chemical modifications. In spite of its prolific uses, applications of chitosan in acidic conditions are limited due to solubility in acidic media. Chitosan is soluble in acid medium due to protonation of free amine groups on chitosan polymer chain. In order to improve the insolubility of chitosan in acidic media, a number of chemically cross linked chitosan derivatives such as glutaraldehyde cross linked chitosan and epichlorohydrin cross linked chitosan were prepared.

In search of acid resistant chitosan, silver nanoparticles impregnated chitosan beads (AgNP-CB) were prepared and its solubility in different acidic media was investigated in the present study. To predict the interaction between chitosan beads (CB) and silver nanoparticles (AgNP), chitosan beads (CB) before and after impregnating with silver nanoparticles (AgNP-CB) was characterized using Fourier transform infrared spectroscopy (FTIR).

2. MATERIALS AND METHODS

Preparation of chitosan beads (CB): Chitosan beads were prepared as per the procedure reported in the literature. Shrimp shells are collected from the local market. First of all, the shells are washed thoroughly with distilled water and then dried at 50ºC in a hot air oven. Exactly, 5g of shells are soaked in 1N HCl for 24h. Acid treated shells are washed thoroughly with distilled water and then refluxed with 1N NaOH solution for 4h. Afterwards, the shells are washed thoroughly with distilled water and air dried. 1 g of chitosan is dissolved in 10% acetic acid and poured into saturated NaOH solution drop by drop to form chitosan beads. Finally, chitosan beads are washed thoroughly with distilled water and air dried.

Preparation of silver nanoparticles (AgNP): Silver nanoparticles were prepared from leaf extracts as reported in the literature. Leaf extracts of various plants have been used to prepare silver nanoparticles as Ag+ reducing agents. In the present work, silver nanoparticles were prepared from aqueous extract of Guava leaves. Exactly, 1 ml of 0.001M silver nitrate solution is added to 24 ml of aqueous Guava leaf extract. The solution is kept in dark for 24 h to form silver nanoparticles. Formation of silver nanoparticles is ensured by the change in color of extract to yellow. The centrifuged solution is used to prepare silver nanoparticles impregnated chitosan beads.

Preparation of silver nanoparticles impregnated chitosan beads (AgNP-CB): To prepare silver nanoparticles impregnated chitosan beads, 1 g of chitosan beads are added to 25 ml of solution containing silver nanoparticles. After 24 h white colored chitosan beads are turned to yellow due to distribution of silver nanoparticles over the exterior and interior of chitosan beads. The prepared silver nanoparticles impregnated chitosan beads are washed thoroughly with distilled water, dried and further used.

Characterization of silver nanoparticles impregnated chitosan beads (AgNP-CB): In order to identify the interaction between chitosan beads and silver nanoparticles, chitosan beads and silver nanoparticles impregnated chitosan beads were characterized by FTIR spectroscopy. The FTIR spectra of chitosan beads (CB) before and after

impregnating with silver nanoparticles were recorded in the range of 400 to 4000 cm^{-1} using Bruker FTIR spectrometer with a resolution of 4 cm^{-1}.

Study of solubility: Solubility of AgNP-CB was investigated in different acidic media. Solubility of silver nanoparticles impregnated chitosan beads was tested in different HCl and acetic acid solutions. Exactly, 0.1 g of silver nanoparticles impregnated chitosan beads were added to 10 ml of 1%, 5%, 10% HCl and 1%, 5%, 10% acetic acid solutions separately and solubility was observed.

3. RESULTS AND DISCUSSION

Characterization of silver nanoparticles impregnated chitosan beads: Chitosan polymer chain contains free hydroxyl and amine groups as shown in figure.1. The structure of prepared chitosan is confirmed from the FTIR spectral analysis. The FTIR spectrum of chitosan beads is presented in figure.2. The spectrum shows a broad absorption band at 3369 cm^{-1} due to OH and NH stretching vibrations. Sharp peaks at 1643 cm^{-1}, 1029 cm^{-1} and a shoulder peak at 1509 cm^{-1} are appeared due to OH bending, CO stretching and NH bending vibrations, respectively. FTIR spectrum of silver nanoparticles impregnated chitosan beads presented in figure 3 shows a significant change of NH stretching and bending vibrations indicating that silver nanoparticles are interacted with the amine functional groups of chitosan beads.
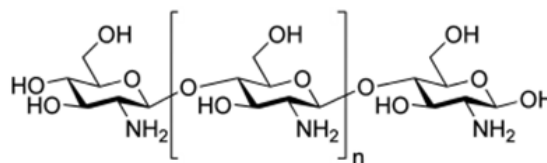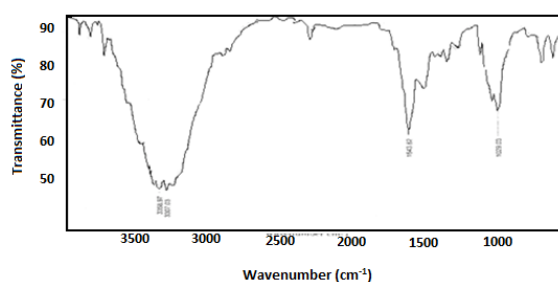

Figure.1.Structure of chitosan polymer chain
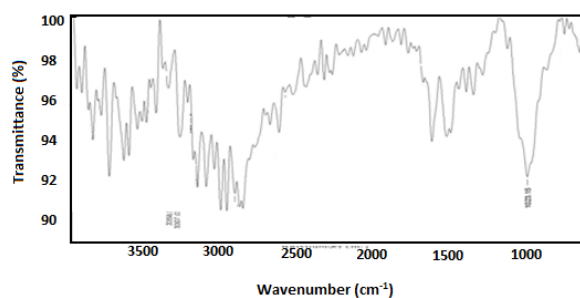

| **Figure.2. FTIR spectrum of chitosan beads** | **Figure.3. FTIR spectrum of silver nanoparticles impregnated chitosan beads** |

Solubility of AgNP-CB: Solubility of silver nanoparticles impregnated chitosan beads in different acidic media are presented in Table 1. From the Table it is clear that AgNP-CB is insoluble in all the studied acidic media. Chitosan is sparingly soluble in water and completely soluble in 1% acetic acid due to protonation of nitrogen of free amine groups of chitosan polymer chain. After treatment of chitosan beads with silver nanoparticles, the nitrogen of free amine group on chitosan beads is bind with the silver nanoparticles. As a consequence the chitosan beads are insoluble in all the studied acidic media.

Table.1. Solubility of AgNP-CB in different acidic media

Solubility of AgNP-CB in acetic acid			
Sample	**1% Acetic acid**	**2% Acetic acid**	**5% Acetic acid**	**10% Acetic acid**
Chitosan beads	Soluble	Soluble	Soluble	Soluble
AgNP-CB	Insoluble	Insoluble	Insoluble	Insoluble
Solubility of AgNP-CB in HCl			
Sample	**1% HCl**	**2% HCl**	**5% HCl**	**10% HCl**
Chitosan beads	Insoluble	Insoluble	Slightly Soluble	Slightly Soluble
AgNP-CB	Insoluble	Insoluble	Insoluble	Insoluble

4. CONCLUSIONS

Silver nanoparticles impregnated chitosan beads are prepared by adopting simple method. The FTIR spectral data analysis infers that silver nanoparticles bind with the free amine functional groups of chitosan beads. Chitosan beads are found to be insoluble in 1%, 5%, 10% HCl and also in acetic acid after impregnating with silver nanoparticles. This is due to absence of free amine functional groups on chitosan polymer chain. In the present work, acid resistant chitosan beads were successfully prepared.

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