J. Indian Chem. Soc.,
Vol. 96, January 2019, pp. 5-6

Synthesis and characterization of SiO_2-chitosan/AgNPs composite and its application for catalysis

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Manuscript received online 29 August 2018, accepted 09 October 2018

In the present work, a new composite silver supported chitosan-silica (SiO_2/chitosan/AgNPs) has been synthesized and characterized through XRD and SEM analyses. The catalytic activity of the newly synthesized composite was investigated in degradation of malachite green as a model reaction and the reaction followed pseudo first order.

Keywords: SiO_2, chitosan, Ag, malachite green.

Introduction

Malachite green (MG) has been used as an organic dye and antimicrobial agent for many years. Traditionally, it is used as a dyestuff for materials such as silk, paper, and leather. Several processes are there for degradation of dyes[1] which includes membrane filtration, electrochemical technology, advance oxidation process and catalytic degradation. However, all these process have disadvantages such as high operating, ultraviolet (UV) irradiation at an exact wavelength, long reaction times, and cost effective. Among these methods catalytic degradation is considered as the efficient method to remove dye pollutants from industrial effluents due to its comparably easy operation, low cost and insensitivity to toxic substances[2].

Recently, the natural polymer, such as chitosan and its derivatives has significantly attracted interest[3] due its low-cost and unique structure. To improve the properties of chitosan materials for use in catalysis, chitosan has been modified with ceramic alumina, and silica. Among these silica plays vital role due to its thermal stability, tunable porosity, physical rigidity, chemical inertness and negligible swelling in aqueous solutions. Recently, nanoparticle Ag has taken considerable attention to provide maximum catalytic property with minimum amount of Ag. In this study, synthesis and characterization of silver supported chitosan-silica (SiO_2/chitosan/AgNPs) composite and its catalytic property were investigated.

Experimental

Reagent grade chemicals of silver nitrate (Kojima, Japan), sodium hydroxide (Merck), nitric acid (SRL, Mumbai), chitosan, acetone (SRL, Mumbai), tetraethyl orthosilicate (TEOS) (98%, Acros, USA), ammonia (28 wt%, SRL, Mumbai) and anhydrous ethanol (99.5%, SRL, Mumbai) were used as received without further purification.

Ultraviolet-Visible (UV-Vis) spectra were recorded in Lambda 35 spectrophotometer. The surface morphology study was performed using HITACHI SU 6600 scanning electron microscope (SEM). X-Ray powder diffraction (XRD) data were collected on PAN analytical instruments. To 100 mL of 7 ppm malachite green solution in distilled water, 10 mg of SiO_2/chitosan/AgNPs composite and 0.01 mL of $NaBH_4$ (0.1 *M*) were added and the mixture was stirred constantly using magnetic stirrer. The progress of degradation was studied at different time intervals and measured the absorbance of the supernatant through UV-Vis spectrophotometer.

Synthesis of chitosan-SiO_2 conjugate:

Initially, 1 g of chitosan was dissolved in 2% acetic acid (50 mL) which results in pale yellow viscous solution and to this 30 mL of TEOS was added. Then the solution was poured into a flask containing 100 mL of 3% NH_3 solution to catalyze the condensation reactions. The resulting white suspension was strongly stirred for 24 h at room temperature. The obtained white precipitate was centrifuged and dried at 80°C for 5 h.

Synthesis of SiO_2/chitosan/AgNPs composite:

Briefly, 1g of chitosan-SiO_2 conjugate, 0.1 mmol of $AgNO_3$ and 10 mL ethanol were taken in the RB and stirred for 2 h. It is observed that the solution changes from colourless to dark brown. The resulting solution was centrifuged and dried at 80°C for 5 h.

Results and discussion

The FE-SEM micrograph of SiO_2 nanospheres were shown in Fig. 1a. It can be observed that the SiO_2 nanospheres are fine porous structure, which confirms the presence of a porous structure of silica. Whereas, AgNPs showed nanosphere like morphology (Fig. 1b), SiO_2-chitosan conjugate showed aggregated porous polymer morphology (Fig. 1c) and SiO_2/chitosan/AgNPs composite showed porous and aggregated nanospheres morphology (Fig. 1d). Fig. 2. shows the XRD patterns of SiO_2/chitosan/AgNPs composite. The 2θ peaks appeared at 10.7 and 21.2 corresponds to chitosan. The 2θ peak value obtained at 37.9, 44.0 and 63.9 corresponds to AgNPs which are in perfect agreement to the JCPDS card no. 89-3722. But there is no peak for SiO_2 which may be due to chitosan overlapped with SiO_2.

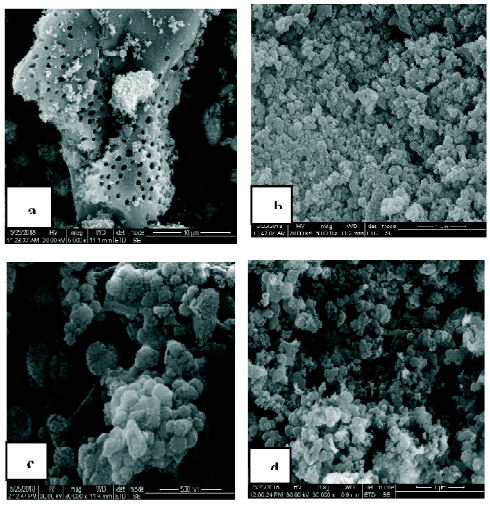
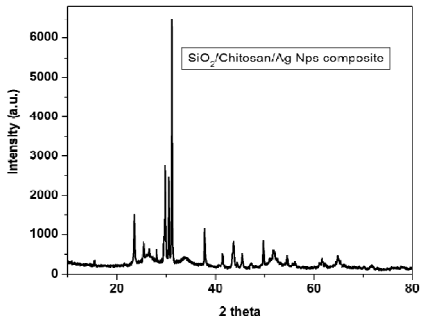


Fig. 1. SEM images of (a) SiO_2, (b) AgNPs, (c) SiO_2-chitosan and (d) SiO_2/chitosan/AgNPs composite.

Here, the degradation of MG with $NaBH_4$ in aqueous phase was chosen as a model reaction to quantitatively evaluate the catalytic activities of SiO_2/chitosan/AgNPs composite. The degradation of MG in the presence of SiO_2/chitosan/AgNPs composite was shown in Fig. 3. From the results, it can be concluded that, both SiO_2-chitosan conjugate and AgNPs plays vital role on the degradation of MG.



Fg. 2. XRD pattern of SiO_2/chitosan/AgNPs composite catalytic degradation of malachite green (MG).

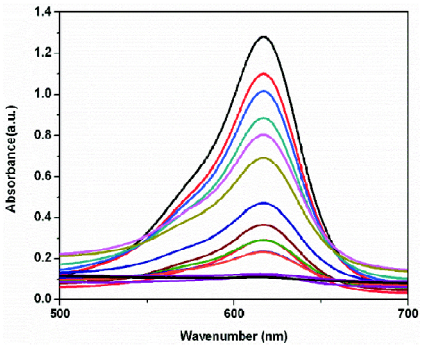


Fig. 3. Catalytic degradation of MG using SiO_2/chitosan/AgNPs.

Conclusions

In summary, a facile method was used to develop SiO_2/chitosan/AgNPs composite and employed for the catalytic degradation of malachite green. Similarly, synergetic effect of the composite also evaluated using their controls. The results reveal that, both SiO_2-chitosan conjugate and AgNPs plays vital role on the degradation of MG and the reaction followed pseudo first order.

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