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Photocatalytic activity of Chitosan/ZnO nanocomposites for degrading methylene blue

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Abstract: Chitosan encapsulated zinc oxide (ZnO) hybrid nanocomposite was prepared using chemical precipitation method. The prepared nanocomposite was characterised using XRD, FTIR and UV-Vis analysis. The XRD pattern showed the semicrystalline nature of chitosan and the hexagonal structure of ZnO. The shift and change in intensity of the various stretching and bending FTIR modes of chitosan shows the formation of the nanocomposite. The use of the composite as a photocatalytic agent was studied.
Key words- Chitosan; ZnO; composite; XRD; Spectroscopy; photocatalytic activity.

Introduction and experimental:

In the recent years, heterogeneous photocatalysts has paying attention because they not only converting photon energy into chemical energy but also display great potentials for the purifying environment of air and water. The semiconductor assisted photocatalysis has attracted considerable attention as a promising tool for implementing the purification of waste water and hydrogen energy production. Among inorganic nanoparticles, ZnO with a direct wide band gap (3.37 eV), is of special importance for the photocatalytic generation of hydrogen peroxide, which can be utilized for the degradation of organic pollutants, and the sterilization of microbial species[1]. Chitosan is actually a heteropolymer containing both glucosamine units and acetylglucosamine units. Hybrid materials based on chitosan along with oxide materials have been developed in recent years, due to excellent properties of individual compounds and outstanding synergistic effects simultaneously. Due to the biocompatibility, biodegradability, non-toxicity and absorption properties of chitosan, chitosan protected nanoparticles can be easily integrated into systems relevant for pharmaceutical, biomedical and biosensor applications[2].

Currently, Chitosan-ZnO complex attracted great importance for its potential use as UV protector and antimicrobial activity[3]. This work is focused on the preparation of Chitosan-ZnO complex using precipitation method. The prepared composite was characterized using Fourier transform infrared spectroscopy(FT-IR), X-ray diffraction (XRD) and UV-Vis spectroscopy. Application of Chitosan-ZnO composite as an agent for the photocatalytic degradation of organic dye was also investigated.

Materials:

Low molecular weight chitosan(CS) was purchased from Sigma Aldrich. Zinc Acetate dihydrate, Sodium Hydroxide(NaOH) and Acetic acidwere of analytical grade. Methylene blue (MB) was purchased from Aldrich chemicals.

Preparation of CS-ZnO nanocomposite:

ZnO nanoparticles were prepared by chemical precipitation method by using Zinc acetate as the precursor. 0.05M NaOH solution was added to 0.01M Zinc acetate dihydrate solution kept under stirring. The obtained precipitate was washed several times with the double distilled water, filtered and dried at room temperature for 2 days. The collected powder was calcined at 430°C for 30 minutes. The prepared ZnO nanoparticles, (equivalent to 40 weight% of chitosan) was dispersed in 100ml of 2% (v/v) acetic acid, where ZnO changed into cations. To this, 0.749g of CS was added. This solution was maintained under simultaneous sonication and stirring until a clear sol was obtained. NaOH solution(1M) was then added dropwise, until the solution attained PH 10. The white precipitate formed was washed and dried. For the photocatalytic experiment, 500mg of the catalyst mixed with 500ml of MB aqueous solution($3X10^{-5}$moles/litre).

Results and Discussion:

The XRD pattern of ZnO sample is shown in fig (1). The results revealed that the ZnO sample exhibits hexagonal structure and the peaks are in perfect agreement to that of the JCPDS Card No:79-0208[1]. The lattice parameters were determined to be a=3.257Å, b=3.257Å and c=5.204Å. The average crystallite size of the ZnO nanoparticles calculated using the Scherrer's formula was 23nm. The XRD pattern of CS/ZnO nanocomposite is shown in fig (1). The peaks of both chitosan and ZnO were observed, showing the formation of the composite.

The FT-IR spectrum of CS/ZnO composite is shown in fig (2). The peak observed at 3425cm^{-1}, corresponds to the stretching vibration of $–NH_2$ group and -OH group. The C-H stretching vibration is observed at 2924cm^{-1}. 1628 cm^{-1}indicated the amine I group(C-O stretching along the N-H deformation mode), 1589 $cm^{-1}$was assigned to the –NH deformation mode. 1381cm^{-1}showed C-H in plane bending vibrational group and 1350 $cm^{-1}$was attributed to the COO^- group of carboxylic acid, 1157 cm^{-1}showed a small shoulder peak of β(1-4) glycosidic band in polysaccharide unit and 1065 cm^{-1}indicated the stretching vibration of

C-O-C in glucose circle. The bond observed in the range of 555 cm^{-1}correspondsto the stretching vibration of N-Zn[4].

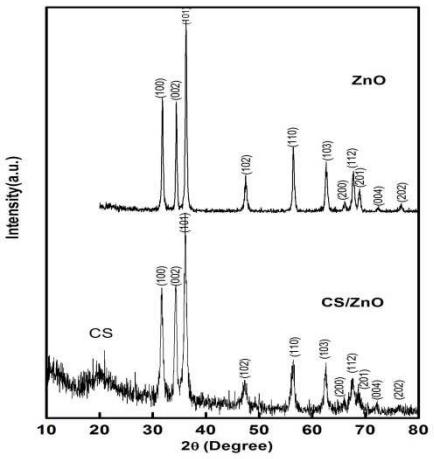

Fig. (1) XRD pattern of the ZnO and CS-ZnO

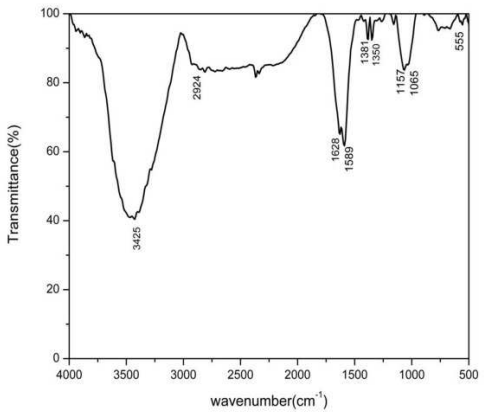

Fig.(2) FTIR spectrum of CS-ZnO

The degradation of contaminant water is usually due to the excitation of a semiconductor by irradiation of UV light thereby generating free radicals by using the electron hole pair which leads to the degrading organic pollutants. Fig (3) shows the photocatalytic activity of synthesized CS-ZnO nanocomposite for the degradation of methylene blue in aqueous solution under UV light irradiation. The required amount of the catalyst mixed

with 500 ml of MB aqueous solution under stirring was irradiated by UV light for various time intervals. The absorbance measurements were carried out by UV-Vis spectrophotometer.

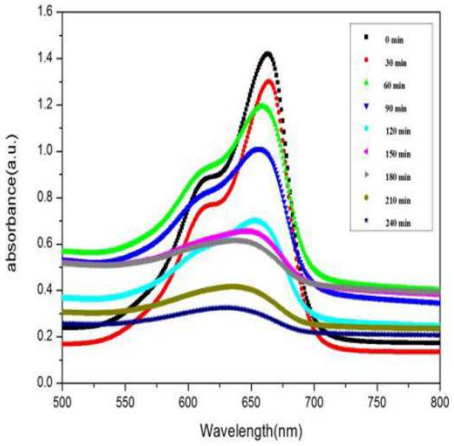

Fig.(3) The change in the absorption spectra of MB

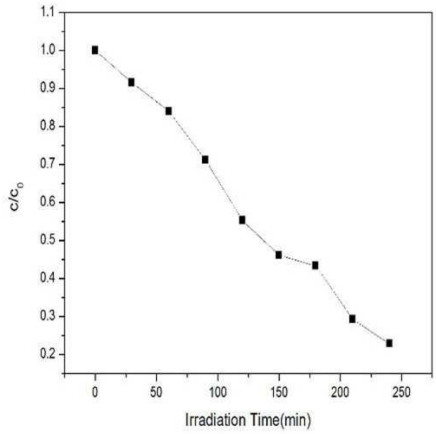

Fig (4). The time course degradation curve of MB

In the fig (3), disappearance of the band at 660nm indicates that most of the MB has been degraded by CS-ZnO nanocomposite under UV light irradiation within 4h time. The time course degradation curve of MB is shown in fig (4). Nearly 80% of the dye was degraded using this composite with in 4h. The enhanced photocatalytic activity is attributed to the good distribution of ZnO nanoparticle in the composite.

Conclusion:

Chitosan-ZnO nanocomposite was successfully prepared using a simple and cost effective chemical precipitation method. The XRD pattern clearly shows the formation of nanocomposite. FTIR shows the binding of ZnO to the $NH_2$and OH groups of chitosan.The composite shows high photocatalytic activity. Nearly 80% of the MB dye degraded under UV irradiation within 4h.

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