“FABRICATION OF ZINC OXIDE-CHITOSAN BASED PHOTOCATALYTIC REACTOR FOR DEGRADATION OF TEXTILE DYE CONGO RED”

PROJECT REFERENCE NO. : 37S0067

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Keywords: Congo red, Zinc oxide/Chitosan conjugate, photo catalysis, photo degradation.

Introduction:

One of the major causes of water pollution is discharging of toxic textile dyes from industries. Salehi, R. et al., 2010 prepared composite of zinc oxide and chitosan to study adsorption of Direct Blue 78 (DB78) and Acid Black 26 (AB26) from aqueous solutions onto CS/n-ZnO. Results showed that zinc oxide nanoparticles were immobilized onto Chitosan. Zhu, H. et al., 2009 describes synthesis of crosslinked chitosan/nano-CdS (CS/n-CdS) composite catalyst by simulating bio mineralization process for the degradation of azo dye, Congo red under visible light irradiation. The present work concentrates on degradation of congo red using conjugate of zinc oxide and chitosan. Zinc oxide is known for its photo catalytic activity under visible spectra and chitosan is known for its good adsorption properties. Chitosan has been used to increase stability and reusability of zinc oxide. Effect of pH and concentration of dye has been studied. FTIR and SEM analysis has been done for conjugate formed. The formed conjugate has shown dual activity, one by adsorption of dye through chitosan and another by degradation of dye by ZnO. This shows that the conjugate can be used as solution for environmental problem created by dye pollution.
Objectives:

This project is an improvement over the conventional waste water treatment where coagulation and degradation are carried out by chemical species (one case for e.g., such as alum and semiconductor oxides). The alum that is used for coagulation is closely linked to Alzheimer’s disease which attracts special attention towards the use of biological materials (in this case chitosan) which are more environmental friendly. This study aims at the following objectives:

1. To synthesize zinc oxide – chitosan biocompatible hybrid photocatalytic materials by precipitation.
2. To characterize the prepared zinc oxide – chitosan biocompatible hybrid photocatalytic materials.
3. To research and check the feasibility of zinc oxide – chitosan biocompatible hybrid photocatalytic materials for the degradation of toxic textile dye Congo red.

Materials:

Congo red was purchased from SD Fine Chemicals, Chitosan was purchased from a local vendor, Zinc Oxide, Sodium hydroxide, Acetic acid, Hydrochloric acid and Sodium Chloride were purchased from SD Fine Chemicals.

Methodology

1. Preparation of ZnO/Chitosan Conjugate
1g Chitosan added to 70 ml of 0.1 M acetic acid and stirred overnight. Simultaneously 1 g ZnO is added to 20 ml of 0.1 M Acetic acid and stirred at 140 rpm for 20 hours. The 2 solutions were mixed together and their volume is made up to 120 ml. Gel was formed on keeping the solution undisturbed for a few minutes. It was then allowed to get solidified for 2 hrs. After obtaining a firm gel, it was carefully taken out from beaker. pH was adjusted to 7 by washing gel cake with distilled water and it was dried in hot air oven. The conjugate was crushed to get powder. Through this method the first sample containing 1:1 ZnO/Chitosan ratio was obtained.

For the second sample, the ratio of ZnO/Chitosan was changed to 1.5:1 by taking 1.5g ZnO and 1g Chitosan. Same procedure was followed as mentioned above to get dried powder of second sample. To check the effect of salt concentration on the photocatalytic
activity, 1:1 ZnO/Chitosan conjugate with 20 ml NaCl was synthesized as per the above procedure, dried and crushed to obtain our third sample.

2. Characterization of Zinc oxide/Chitosan (ZnO/Ch) conjugates
Infrared spectra were recorded using the KBr disc method on a Fourier Transform-infrared spectrometer (PerkinElmer Spectrum Version 10.03.09, India). Ultraviolet-visible (UV-vis) spectra were observed on ELICO-1901 spectrophotometer (ELICO India, Ltd). EDAX analysis was carried out on JEOL JXA-8530F (IISc, India). Scanning electron micrographs were recorded on a JSM-6701F instrument (JEOL, India). Powder X-ray Diffraction studies were carried out on (IISc, India).

3. Preparation of Congo red dye solution
Congo red dye stock solution of $10^{-2}$ M solution was prepared by adding Congo red dye powder in distilled water. Working solutions were prepared. $10^{-4}$ M solution of Congo red had been used for further study.

4. Effect of conjugate load and type
10ml of $10^{-4}$ M Congo red dye solution was taken as 10 aliquots. 3 types of conjugates were formed according to different ratios of ZnO and chitosan. Each sample was added in the concentration of 0.25g, 0.5g and 0.75 g to 3 beakers respectively. Similarly, native chitosan and zinc oxide were also weighed accordingly and added in the same way to evaluate the efficiency of conjugate.

5. Effect of pH
Based on the efficiency of the conjugate observed, the sample with best activity was selected for further analysis. This sample is used to check its activity at 7 different pH. Congo red dye solution of concentration $10^{-4}$ M was taken in 7 beakers and in each beaker’s pH was optimised up to pH 4, 5, 6, 7, 8, 9 and 10, respectively using 1N HCl and 1M NaOH. For this optimised pH solution conjugate of higher activity was added and efficiency was observed by carrying out same protocol as above.

6. Effect of dye concentration
Two dye concentrations were used for this: $10^{-3}$ and $10^{-5}$ M. 10 ml of each were taken in 2 different beakers and to them the sample which showed high efficiency was added. Again efficiency test was carried using same protocol as mentioned above.

7. Reusability of conjugate
All the conjugates, ZnO and chitosan used to check the effect of conjugate load and type over degradation were recovered by filtering through filter paper. Each sample was weighed to check the recovery. Each of the samples was again appointed for degradation
by following same method used till now. Degradation was recorded by measuring absorbance.

8. Fabrication of reactor

Figure 1: a) Proposed Photocatalytic reactor, b) Photocatalytic reactor that is designed accordingly, c) Photocatalytic reactor that is in working state.

Fabrication of the photoreactor system for the Congo red dye degradation was done according to the proposed figure 1.

9. Working of reactor

A 500 mL pilot glass reactor was fabricated to carry out degradation of large amount of dye solution. Reactor was charged with 250 mL, $1 \times 10^{-4}$ M congo red dye solution and the conjugate of higher catalytic activity, in required amount. The suspension in the reactor was subjected to continuous stirring using mechanical stirrer. The system as exposed to high intensity visible light.
**Results and Discussion**

On comparing the effect of conjugate load and type in different samples, it was inferred that sample 2 contained 1.5:1 ZnO/Chitosan ratio was the most effective with highest catalytic activity and it also showed high stability.

![Figure 2. Bar graph for the comparison of photodegradation by 1.5:1 ZnO/Ch conjugate](image1)

When the conjugates were checked for reusability but recovering the samples by passing them through filter paper and subjecting them to degradation procedures again, sample 2 ZnO/Ch conjugate showed the highest reusability capacity.

![Figure 3. Line graph showing degradation efficiency of recovered 1.5:1 ZnO/Ch conjugate.](image2)

**Scanning Electron Microscopy (SEM) analysis**

The surface morphology of the conjugate samples so prepared was analyzed by Scanning Electron Microscopy.
Figure 4: SEM image of 1:1 ZnO/Ch conjugate
Figure 5: SEM image of 1.5:1 ZnO/Ch conjugate
The surface morphology and grain size of ZnO/Ch nanostructures of different ratios (1:1, 1.5:1 and 1:1 +NaCl) analyzed by SEM are as shown in figures 4, 5 and 6. Figure 4 reveals the SEM of 1:1 ZnO/Ch nanogeometries presented with in the scale of 50nm and the grain sizes are estimated to be in the range of 20-30 nm, with the increase of ZnO and sodium chloride concentration more number of nanogeometries were observed than nanoparticles as shown in figures 5 and 6. The sizes of these ZnO/Ch conjugates of 1.5:1 and 1:1 +NaCl samples were in...
good agreement with the calculated crystallite sizes of nanoparticles using Debye-Scherer formula.

**FTIR analysis**

PerkinElmer Spectrum Version 10.03.09 has been used to carry out FTIR analysis for sample 1:1 ZnO/Ch conjugate, 1.5:1 ZnO/Ch conjugate and 1:1 ZnO/Ch- NaCl conjugate.

![Figure 7](image7.png)

Figure 7: FTIR image of chitosan.[18]

![Figure 8](image8.png)

Figure 8: FTIR image of 1:1 ZnO/Ch conjugate
Figure 7 depicts the FTIR of chitosan and figures 8, 9, 10 represents the FTIR of chitosan/ZnOnanaoparticles of different ratios 1:1, 1.5:1 and 1:1 + NaCl respectively. For chitosan (Figure 7) shows absorption peak at 3427 cm$^{-1}$. This attributed to the combined peaks of the NH$_2$ and OH group stretching vibration. Compared with chitosan, the broader and stronger peak moved noticeably to lower wave number at 3419 cm$^{-1}$ which indicated the strong interaction between these groups and ZnO. The absorption peaks at 2925, 2882 cm$^{-1}$ are attributed to asymmetric stretching of CH$_3$ and CH$_2$ of chitosan polymer. While the absorption peaks at 1647 and 1078 cm$^{-1}$ are ascribed to bending vibration of NH$_2$ group and C–O stretching group, compared with chitosan, there are new absorption peaks at 659 cm$^{-1}$ and 465 cm$^{-1}$ which are due to the attachment of amide group and stretching mode of ZnO. In addition to these results, the characteristic peaks are shifted to lower wavenumber, the wide peak at 3427 cm$^{-1}$, corresponding to the stretching vibration of hydroxyl, amino and amide groups, moved
noticeably to lower wavenumbers $3419 \text{ cm}^{-1}$, and became broader and stronger, which indicated the strong interaction between groups and ZnO, compared with Figure 7, a point which could be explained in terms of strong attachment of ZnO to the amide groups of chitosan molecules. [7]

**ENERGY-DISPERSIVE X-RAY (EDX)**

The EDX study of the ZnO/Ch conjugate are shown in Figures 11, 12&13 that the ZnO/Ch conjugate are composed of Zn and O atoms, however, some amount of carbon atoms also appears in the graph, which may be due to the presence of carbon in chitosan. Chitosan is composed of carbon, hydrogen, oxygen, and nitrogen atoms, but these elements do not appear in the EDX graph because of the low percentage of these atoms in the chitosan molecule. In figure 11, the presence of Cesium (Cs) is may be due to impurities that were previously present in Chitosan as it was purchased from a local vendor. The same explanation holds good for the presence of Aluminium (Al) and Calcium (Ca) in Figure 12 and Niobium (Nb) in Figure 13. In addition to all the above the Chloride content in Figure 6.3.3 is due to the addition of Sodium Chloride (NaCl) to study the salt effect of on the working efficiency of ZnO/Ch conjugate.
Figure 11. EDX image of 1:1 ZnO/Ch conjugate
Figure 12. EDX image of 1.5:1 ZnO/Ch conjugate
Figure 13. EDX image of 1:1 ZnO/Ch – NaCl conjugate
X ray diffraction (XRD)

XRD analysis was carried out with the help of JDX-8030, JEOL, IISc, Bangalore, using Cu Kα wavelength (λ = 1.54059) and scanning range from 10° to 90°.

Figure 14. XRD image of 1:1 ZnO/Ch conjugate

Figure 15. XRD image of 1.5:1 ZnO/Ch conjugate
Figure 14, 15 and 16 shows the X-ray diffraction patterns of chitosan/ZnO nanoparticles of three different ratios 1:1, 1.5:1 and 1:1 + NaCl respectively. The typical peaks of chitosan appear at 10.67° and 19.99° [9], while these peaks become weak in the XRD pattern of chitosan/ZnO nanoparticles as that can be observed in the figures 6.4.1, 6.4.2 and 6.4.3. Other diffraction peaks in these figure are sharper and stronger at 31.7°, 34.36°, 36.2°, 56.59°, 62.7°, and 67.90° and were assigned to the (1 0 0), (0 0 2), (1 0 1), (1 1 0), (1 0 3), and (1 1 2) planes of hexagonal zinc oxide can be indexed to the wurtzite ZnO with high crystallinity. All the diffraction peaks are in good agreement with those of hexagonal wurtzite structure of ZnO (JCPDS card 36-1451, a= 0.3249 nm, c= 0.5206 nm). This, indeed, revealed that it is successful formation of nanosized chitosan/ZnO complex. The calculated crystallite size using Scherer (D= 0.94λ/ cos) equation for 1:1 ZnO/Ch, 1.5:1 ZnO/Ch and 1:1 ZnO/Ch – NaCl conjugates are 16, 32 and 53 nm, respectively. The increase in crystallite size mainly depends on the sodium chloride as evidenced from SEM analysis. The calculated crystallite sizes were small and are in good agreement with characteristics of nanostructures as reported in literature.
EFFECT OF pH

On studying effect of pH on the 1.5:1 ZnO/Ch conjugate, it was found that the sample showed best activity at pH 9 due to stability of chitosan in basic pH.

![Bar graph showing comparison of activity of 1.5:1 ZnO/Ch conjugate at different pH](image)

**Figure 17.** Bar graph showing comparison of activity of 1.5:1 ZnO/Ch conjugate at different pH

EFFECT OF DYE CONCENTRATION

On studying the effect of dye concentration, it was seen that at lower concentration dye degrades faster. At higher concentration also degradation is seen but at very low rate, i.e., $1 \times 10^{-5}$ M dye solution was degraded faster than $1 \times 10^{-3}$ M solution.

EFFECT OF CATALYST LOAD AND TYPE

On studying the effect of catalyst load and type, it was observed that 1.5:1 ZnO/Ch conjugate worked the best at optimum pH and dye concentration. The optimum catalyst load was found to be 1.25 g/10 ml of dye solution.

PHOTO DEGRADATION EFFICIENCY

The reactor fabricated after the above procedures showed 99.4% efficiency. This was calculated using a degradation efficiency formula

$$C = \left(\frac{(A_\infty - A)}{A_\infty}\right) \times 100$$

Where, $A_\infty$ is absorbance of azo dye at its maximum absorbance wavelength $A$ is absorbance at same wavelength of extracted solution.

In our study, absorbance of initial Congo red dye solution was observed as 1.177 at 495 nm and for degraded dye solution it was 0.007.
Thus, ZnO/chitosan conjugate prepared in the ratio of 1.5:1 showed greater efficiency in degradation of congo red dye compared to other prepared conjugates, ZnO and chitosan. Its higher activity has been recorded at a pH of 9. Its activity increases with decrease in the dye concentration. FTIR and SEM analysis show that there is uniform binding of ZnO over chitosan surface with higher interaction. Reusability of the prepared sample was higher compared to naïve chemicals. The degradation efficiency of 99.4% has been recorded when a large amount of dye solution was subjected to degradation.

**Scope and Future aspects**

The above results show that ZnO-Chitosan conjugate can be used for azo dye degradation at large scale for water purification. Its higher efficiency and reusability makes it more suitable. Till now no toxic compounds have been recorded after degradation of dye using photocatalyst, so it will add new toxic compounds to the water system. It works under sunlight which adds on to its advantage. It is more affordable compared to other compounds present for degradation.

**Acknowledgement**

The authors would like to acknowledge KSCST SPP 37th series for their financial support and Sapthagiri College of Engineering.

**References**


