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Hydrothermal synthesis of zinc oxide nanospheres with sodium alginate as template and its photocatalytic application for degradation of diclofenac and chloramphenicol

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ZnO nanospheres of average diameter of 5.0±0.2 nm have been prepared by simple hydrothermal method using sodium alginate as a template. The prepared ZnO nanospheres are characterized by XRD, TEM, EDX and fluorescence spectra. The photodegradation of the drugs diclofenac (DCF) and chloramphenicol (CHL) are studied in presence of UV light of wavelength 365 nm. Formation of wurtzite structure of ZnO nanospheres is confirmed by XRD analysis. The decrease in intensity of fluorescence emission spectra of the nanospheres indicated the interaction between the drug molecules and the excited species. The peroxide radicals and the hydroxyl radicals formed due to electron and the hole further affect the degradation of the drug molecules. The TOC content of DCF and CHL is reduced to 12.8% and 6.8% after 180 min under the conditions of the reaction.

Keywords: Photodegradation, Hydrothermal synthesis, Zinc oxide nanospheres, Diclofenac, Chloramphenicol

The pharmaceutical industry manufactures various chemical compounds used as prescriptions in treatment of wide range of diseases. Some amounts of these pure drugs are found to be present in the waste generated during their large scale industrial production[1-6]. These drug containing effluents are also found to affect the plants[7] apart from their toxicological effect[8-10]. Efforts have been made to develop means by which the contaminated water resources are to be purified[11-15]. Therefore, development of new energy efficient, cost effective and environmentally benign methods has received considerable attention during recent past. Diclofenac (DFC), derived from benzene acetic acid is a non-steroidal antiinflammatory drug of cyclooxygenase inhibitor[16] used in the treatment of osteoarthritis, rheumatoid arthritis, and ankylosing spondylitis, while chloramphenicol[17] is an antibiotic. Both these drugs are found to be present in waste water and require treatment[11-15] due to their high insistence and low biodegradability. Methods like advanced oxidation processes (AOPs) are being utilized for treatment of polluted aqueous environments.

The degradation or mineralization of these drugs have been investigated both by uncatalyzed[18,19] and catalyzed[20-29] photochemical methods as well as by electrochemical method[30]. The probable mechanism of photodegradation of dyes or pharmaceuticals is through the generation of electron hole pair. The main disadvantage of these methods is the rapidness of the combination of these electron hole pairs, thus decreasing the efficiency of the photocatalyst. Therefore, to overcome the recombination, these photocatalysts like TiO_2 or ZnO are supported on various substrates[31]. These supports reduce the recombination rate by offering an alternative mechanism for the electron transport.

Nanomaterials are promising candidates due to their unique physicochemical properties due to large surface/volume ratios[32,33]. These nanomaterials have been utilized as solutions for environmental problems as either photocatalysts or as catalysts for advanced oxidation processes in presence of sacrificing oxidants[32,33]. One such material is zinc oxide (ZnO) with a wide band gap energy of 3.37 eV at room temperature which in its nano form enhances catalytic properties in presence of reduced graphene oxide[31]. In literature, a variety of methods have been employed for the ZnO nanostructures with different morphologies[34-36]. These methods suffer drawbacks like low dispersion of starting materials and wide particle size distribution and to overcome this difficulty, polymer templates have been used[37]. In the present study, an attempt has been made to utilize sodium alginate as a polymer template to prepare ZnO nanomaterial and its application for treatment of pharmaceutical effluents contaminated with the drugs like diclofenac and chloramphenicol has been studied.

Experimental

Zinc sulfate heptahydrate, sodium hydroxide and sodium alginate were of analytical reagent grade obtained from SD Fine Chemicals (Mumbai, India)

and deionized water was used for the preparation of solutions. Chloramphenicol and diclofenac sodium salt (99.5% purity) were purchased from Sigma-Aldrich and were used as obtained. Doubly distilled water was used to prepare the buffer solution by adding appropriate amounts of NaOH (0.1 mol/L) or HCl (0.1 ml/L) from Merck.

ZnO nanospheres were synthesis as follows: To an aqueous solution of zinc sulfate(0.01 mol dm^{-3},100 mL), sodium alginate (1 g) as a polymer template was added with constant stirring followed by the dropwise addition of sodium hydroxide solution(0.02 mol dm^{-3}, 100 mL) in a molar ratio of 1:2 under vigorous stirring for 12 h. The template containing the highly viscous mixture was poured on cleaned glass plate to make thin films. The thickness of the prepared films was measured with the help of micrometer screw gauge and was found to be 40±3 μm. These films were allowed to dry and were heated at 550 °C in a muffle furnace (Bio-Technics, India) and maintained at that temperature for 5 h, after which it was cooled to room temperature at a rate of 10 °C/min. The resulting solid product was used for characterization and as a catalyst for drug degradation.

X-ray diffraction (XRD) measurements were made using Goniometer Rigaku Ultima IV diffractometer with Cu-K beta source. The energy dispersive X-ray analysis was made using a Hitachi S-4700 instrument The TEM images were recorded on Phillips CM 200 instrument. The fluorescence spectra of ZnO nanospheres were recorded on JASCO FP 750 spectrofluorimeter at an excitation wavelength of 334 nm from 430–700 nm. The fluorescence spectra of pure ZnO nanospheres and in presence of diclofenac and chloramphenicol were recorded.

For the photocatalytic degradation experiments, stock solutions of diclofenac (DCF) and chloramphenicol (CHL) (100 ppm each) were prepared in doubly distilled water and diluted to the desired concentrations. The experimental setup consisted of a 300 mL cylindrical reactor with a quartz tube at the center of the reactor, UV light source (λ_{max} = 365 nm), a water jacket provided for cooling, fitted with a magnetic stirrer. During the degradation experiments, to a solution (230 mL) of either chloramphenicol or diclofenac, an appropriate quantity of the zinc oxide was added and stirred magnetically for half an hour to establish absorption equilibrium. After the establishment of the adsorption equilibrium, the UV light source was switched on and aliquots of the mixture were withdrawn at regular intervals. The catalyst in the aliquots was removed by centrifugation. The concentration of the remaining DCF and CHL were determined by measuring their absorbance at 276 and 278 nm respectively[18, 20] on a Specord 210 plus UV-vis spectrophotometer. The degradation reaction was monitored up to 180 min. The kinetics of degradation was followed by plotting (C/C_0) against time where C_0 and C represent the initial concentration and the concentration at time t of either DCF or CHL respectively. The total organic carbon (TOC) of the reaction mixtures for both DCF and CHL were also determined as a function of time on Multi N/C 2100 TOC Instrument (Analytik Jena Instrumentation).

Results and discussion

The XRD of the ZnO nanospheres shows peaks at 2θ (°) = 31.79, 34.66, 36.2, 47.56, 56.45, 62.69, 68.12, 72.78, 76.77, 81.2, corresponding to (100), (002), (101), (102), (110), (103), (201), (004), (202) and (104) planes respectively. The spectrum matches the reported[31] hexagonal wurtzite structure (JCPDS 80-0074) of ZnO. The energy dispersive X-ray analysis (EDX) spectrum (Fig. 1) shows the presence of Zn and O and the molar ratio of Zn:O was found to be 1:1.74. The TEM images are shown in Fig. 2 along with SAED pattern. It can be noticed that the ZnO particles have nanosphere morphology of an average size of 5.0±0.2 nm as determined from TEM image (Fig. 2). The size of ZnO nanospheres was determined from TEM image and the minimum size of sphere was found to be 4.29 nm, while the maximum size was 6.16 nm. The average size of the nanosphere was 5.18 nm.

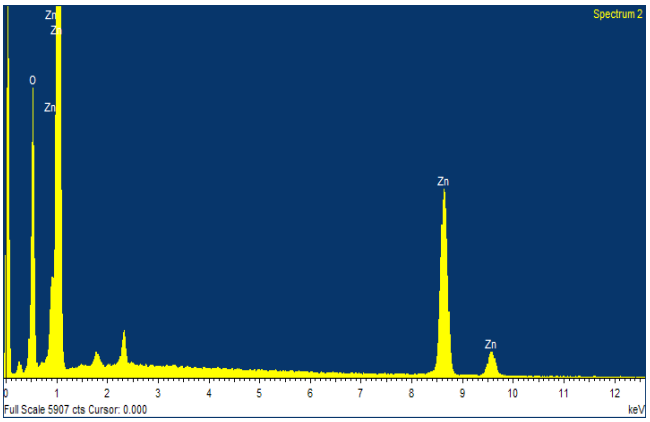


Fig. 1 – EDAX spectrum of ZnO nanospheres.

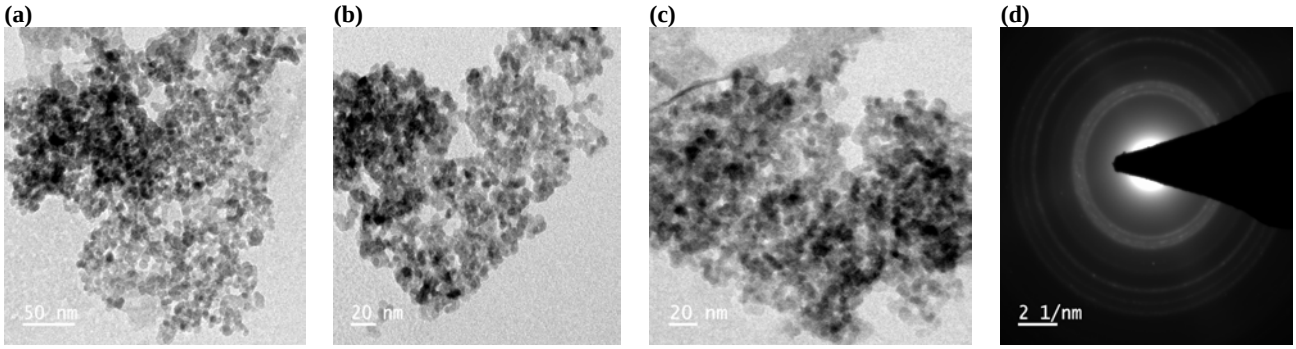


Fig. 2 – (a-c) TEM images, and, (d) SAED pattern of the Zno nanospheres.

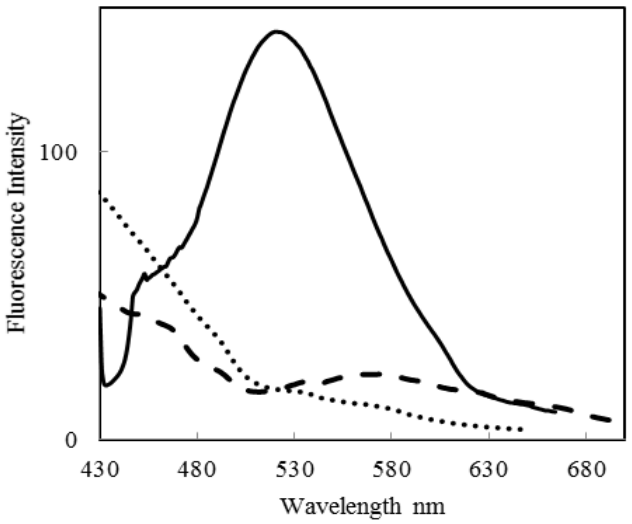


Fig. 3 – Fluorescence spectra of ZnO nanospheres in presence of diclofenac (solid line) (dotted line), and in presence of chloramphenicol (dashed line).

The fluorescence spectrum of ZnO nanospheres at an excitation wavelength of 334 nm shows an emission peak at 530 nm due to electron-hole recombination[38] (Fig. 3). The intensity of the emission peak at 530 nm of ZnO nanospheres decreases in presence of diclofenac and chloramphenicol, indicating an interaction between the drug molecules and the excited ZnO nanospheres. The excitation of ZnO occurs due to absorption of light, and the emission is due to electron hole combination. However, since the emission in presence of either drugs is not observed, it indicates that the excited hole and electron interact with the drug molecules, thus offering an alternative path for the decay. Such an interaction also further leads to the degradation of the drugs.

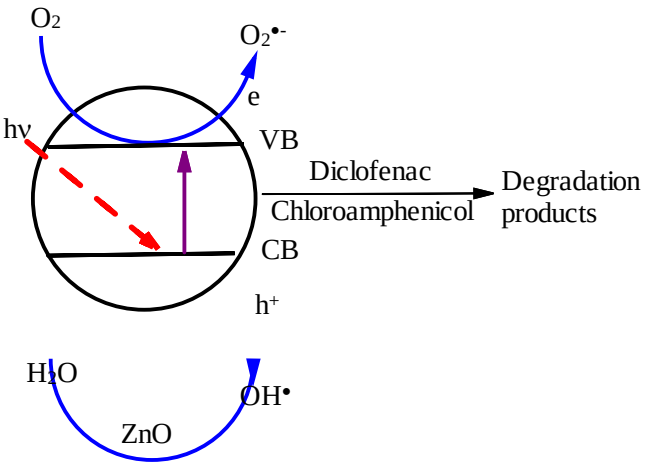
Table 1 – Rate constants for the photodegradation of DCF and CHL at different concentration of catalysts in water at 25 °C. {[DCF] = [CHL] = 10 ppm}

Amt of catalyst (mg)	10^3 Rate constant (min^{-1})	
	Diclofenac	Chloramphenicol
0.0	0.91	1.60
30.0	9.21	6.93
50.0	13.8	9.24
70.0	6.91	4.61
100.0	4.60	4.62

The effect of amount of catalyst on photodegrdation of DCF and CHL was studied between 0 and 100 mg at a concentration of 10 ppm of each drug. The rate constants for degradation of DCF and CHL are given in Table 1. The photodegradation without catalyst is negligible for both the drugs, while it was observed that the photodegradation increased with increase in the amount of catalyst till 50 mg (Table 1) and thereafter there is no significant increase. The increase in photodegradation with an increase in the amount catalyst depends on the total illumination of the ZnO particles and at an amount of catalyst more than 50 mg, turbidity hinders further penetration of light into the reactor thus limiting the photodegradation activity to a maximum value

The effect of initial concentration of either DCF or CHL was carried out from 8–14 ppm in presence of 50 mg of catalyst. It was observed that complete degradation of 10 ppm of DCF and CHL is achieved at 180 min, while it decreases with increase in initial concentration of drugs. This may be due to the fact that at higher concentrations, the drug molecules present in the solution may interrupt the path of photons reaching the catalyst surface.

The general mechanism[31] of photocatalysis by ZnO is due to the generation of electron-hole pair as a



Mechanism of photodegrdation of diclofenac and chloramphenicol in presence of ZnO nanospheres

Scheme 1

result of excitation of its valance band electron to the conduction band. The electron will further react with dissolved oxygen to form peroxide radical whereas the hole will react with the water to produce hydroxyl radical. Therefore, the mechanism of degradation of both the drugs DCF and CHL under the present conditions is initiated by the generation of electron hole pair due to the absorption of light by ZnO nanospheres. The intermediate peroxide free radicals and the hydroxyl radicals from generated electron and hole respectively will further effect the degradation of the drugs as shown in Scheme 1. In order to understand the total mineralization of the drugs, the total organic content (TOC) was analyzed as a function of time for both the drugs and the results are shown in Figs 4 and 5. The changes in the absorbance for DCF and CHL at 276 and 278 nm respectively are also shown in Figs 4 and 5 for comparison. From Figs 4 and 5 it can be noticed that the decrease in the absorbance is parallel to the decrease in TOC for both the drugs. The total TOC for DCF is 12.33%, while for CHL it is 6.83%, indicating that both the drugs are degraded almost completely within 180 min in presence of ZnO nanospheres. The mechanism of degradation of diclofenac[39,40] and chloramphenicol[41] have been studied using various photocatalysts. The degradation of diclofenac generally proceeds through two hydroxylation steps due to its reaction with photogenerated hydroxyl radicals. The hydroxylated product further reacts with either the hydroxyl radicals or holes undergoing complete mineralisation. In the case of chloramphenicol, initially two intermediates

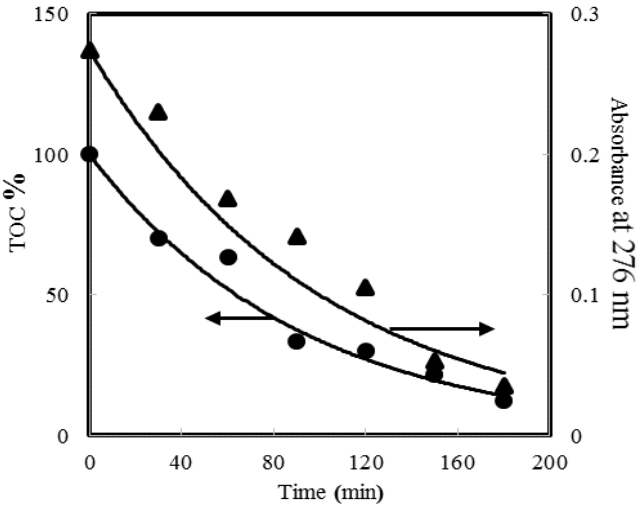


Fig. 4 – Variation of TOC (%) and absorbance at 276 nm as a function of time for DCF.

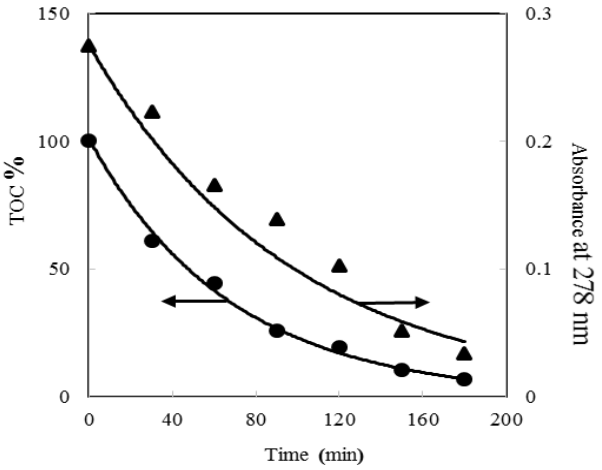


Fig. 5 – Variation of TOC (%) and absorbance at 278 nm as a function of time for CHL.

were predicted due to loss of either dicloroacetic acid moiety or denitration. Removal of dicloroacetic acid moiety leads to 4-(2-Amino-1,3-dihydroxy-propanyl)-nitrobenzene, while denitration generates 2,2-dicloro-N-[1,3-dihydroxy-1-(4-hydroxyphenyl)-propan-2-yl]-acetamide. Both these two products react with photogenerated hydroxyl radicals and holes leading to the complete mineralisation.

The photodegradation of both the drugs was found to increase up to 50 mg of catalyst and thereafter there was no significant increase. The increase in photodegradation with an increase in the catalyst amount depends on the total illumination of the ZnO particles and with more than 50 mg catalyst, turbidity hinders further penetration of light into the reactor thus

reaching a limiting value for the photodegradation. Similarly, complete degradation of 10 ppm of DCF and CHL is achieved at 180 min, which decreases with increase in initial concentration of drugs. This may be due to the fact that at higher concentrations, the drug molecules present in the solution may interrupt the path of photons reaching the catalyst surface.

In conclusion, ZnO nanospheres have been prepared by hydrothermal method in presence of sodium alginate as a template. The XRD of ZnO nanospheres indicates formation of wurtzite structure with the average size of nanospheres found to be 5.0±0.2 nm as obtained from TEM analysis. The EDX analysis shows the presence of Zn and O elements with the ratio 1:1.74. The fluorescence spectrum of the nanospheres shows a band gap excitation emission, the intensity of which decreases in presence of drug molecules. Such a decrease indicates the interaction between the drug molecules and the species obtained as a result of excitation of an electron from the conduction band to the valance band of ZnO. The degradation of the drug molecules was also confirmed by measuring the total organic content (TOC). The drugs were found to be degraded within 180 min. The mechanism proposed involves formation of electron hole pair leading to the formation of reactive species. The reaction between reactive species, hydroxyl and peroxide radicals, obtained in solution leads to the degradation of the drug molecules. The method of synthesis is simple and the ZnO nanospheres are found to be a efficient heterogeneous photocatalyst in presence of UV light of wavelength 365 nm.

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