

SWITCH TO GREEN METHODS FOR WASTE WATER MANAGEMENT

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Abstract

The proposed research work is indebted to the green solution for mitigation of water pollutant that was discharge from industries. In this modern era, water pollution caused by heavy metals is a serious concern to improve the quantity of drinking water. To solve this problem, an environmental friendly Zinc oxide (ZnO) photo catalyst has developed that is suitable for removal of arsenic impurities from wastewater originating from industries. ZnO is less hazardous metal oxide in compared to other mixed or metal oxide as increase in Zinc concentration has minimum impact on living organism, hence it is referred as green synthesis in this work. The physical characterization of zinc oxide performed using Scanning electron microscopy, Fourier Transform Infra-Red spectroscopy, Thermo gravimetric analysis, and X-ray diffraction analysis. To study the catalytic performance of ZnO, we have observed different O.D. values (at 380nm) for a series of ZnO solution ranging from control to 10%, 20% and 30% of ZnO. The photo catalytic activity was studied for 24 h with 10% and 20% ZnO (p H 7.8) at room temperature and it was found to be effective towards remediation of water pollution. It was found to be 78.46% in case of 10% ZnO and 78.04 % for 20% ZnO solution. Therefore, ZnO photocatalyst is proven to be an ecofriendly, and cost effective technique for water pollution mitigation.

Keywords: Green Methodology; Green Methods; Photo catalysts; Wastewater Management; Water Pollution; Zinc Oxide.



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1. Introduction

Metal and Mixed metal oxides were found to have variety of application as photocatalyst. To overcome the problem of polluted water it is essential to figure out energy efficient technologies, which should also be economic. Recent studies revealed the emergence of heterogeneous photocatalysis as an effectual method of contaminant removal from water as well as air. Photocatalysis can be defined as a process where rate of photoreaction is accelerated in the presence of catalyst [1]. Catalysts can be of two types-Homogenous and heterogenous catalyst [2]. If the phase is same as that of reagent then they are called Homogeneous catalysts, whereas if the phase is different they are called heterogeneous catalysts[3].

Various methods are needed for deposition of metal oxide on a reliable catalyst surface. A number of techniques are used such as sol gel, chemical vapour deposition, anodisation, etc. To select the best effective method for synthesis of photocatalyst, is essential to have the knowledge of that the type of pollutant which is needed to be degraded and the type of catalyst [4]. When the catalyst is loaded the active sites and the catalytic activity is affected to quite a level. Making variations in the chemical structure of metal oxide results in variation in the energy band gap [5]. We used Chemical vapor deposition technique for metal oxide synthesis. As the name suggested this technique works on the principle of deposition [6]. A thin film is formed onto a substrate. Here the substrate is exposed to a volatile precursor [7]. This is carried out under an inert atmosphere where high temperature and pressure are maintained respectively. The party products, which are formed, are discarded why passing gas through the reactor.

Their Physical and chemical characterization were done using UV–Vis absorption spectroscopy and X-ray diffraction (XRD) scanning electron microscopy (SEM), Fourier Transform Infra-Red (FTIR) spectroscopy.

Several Researcher has proposed the application of photocatalysts Arora et al have shown versatile use of metal and mixed metal oxides as photocatalyst. They used $\text{Cu}_x\text{S}/\text{TiO}_2$ composites in combustion of gases, Cu^{2+} removal from water, photo reductive removal of metal ions, for enhanced hydrogen generation and photocatalytic H_2 production. Different types of p-type Cu_2O powders were also prepared by using electrodeposition technique and analysed their photocatalytic activity in water reduction [8]. Alternative man-made sources of energy have made enormous growth in environmental pollution. So, the need of green energy begins.

Due to high chemical and electrical properties metal oxide and noble metal compounds are frequently used in green energy generation.

Sasikanth et al were synthesized and designed nanostructures constructs of the metal oxide for various applications [9]. The conventional methods that were used for the construction of high-performance nanomaterials are – coprecipitation, deposition, precipitation etc. There are several methods used for the synthesis of metal oxide nanocomposites such as TiO₂, CeO₂, ZrO₂ and ZnO. Photocatalytic activities of metal oxides such as ZnO, WO₃, TiO₂, CuO, and Cu₂O have also been emphasized by Danish et al [10]. They also focused on recent developments, modifications and challenges related to these metal oxides. This will enable them to solve limitations and maximize performance of metal oxide in photodegradation of pollutants.

Medhi et al have performed a study involving both anion- and cation-doped ZnO and TiO₂ nanoparticles along with doped perovskite nanoparticles (BaTiO₃ and SrTiO₃). This review provides basic information for the development of semiconducting nanoparticle architectures for next-generation applications [11].

Different metal oxide based photocatalytic materials have been reviewed by Yang for reduction of nitrogen into ammonia under controlled experimental conditions. It enlightens recent modernization in the field of photocatalytic materials including the challenges and prospects in this research field [12].

Another study related to different nano-materials such as multi-metal, single as well as doped metal oxides have also been of great importance since these materials possess high catalytic properties, high surface to volume ratio and increased magnetic property [13]. Different methods such as solvo thermal, chemical precipitation, sol-gel, etc. were accepted for the synthesis of specified oxides by various researchers [14]. Recent experimental as well as computational data have been reviewed by Nagpal et al based on the promising metal oxides for efficient removal of organic pollutants. It includes dyes, pesticides and chemical warfare agents [15]. Villa et al have been presented use of Fe₂O₃-decorated SiO₂/MnO₂ microjets for the concurrent removal of industrial organic pollutants and heavy metals present in wastewater. These microjets were easy to prepare due to low-cost and scalable methods. They also exhibit the highest reported speed of $485 \pm 32 \mu\text{m s}^{-1}$ (~ 28 body length per s) at 7% H₂O₂, for MnO₂-based tubular micromotors. Again, the photocatalytic and adsorbent properties of the microjets make them suitable for removal of heavy metals ions such as Cd²⁺ and Pb²⁺ as well as

degradation of organic pollutants, such as tetracycline and rhodamine B under visible light irradiation [16].

1. Experimental

1.1. Materials

The polluted water sample is collected from pond water (human, animal, slaughterhouse wastewater). Zinc oxide and other chemicals were purchased from Hi Media laboratories Pvt Ltd Mumbai, Maharashtra. Analytical grade reagents were purchased from Hi Media Mumbai. Adwa (AD12; 04505) water proof pH and temperature probe was used for pH observation of experiments. UV-VIS spectroscopy was performed using model Labtronics LT 291 microprocessor. FT-IR spectrometer (Shimadzu) – IRT- 100, Fourier transform infrared (FT-IR) spectra have done for functional groups analysis, using 4000cm^{-1} to 400cm^{-1} was used for the analysis. X-Ray Diffraction (XRD) was performed using model PANalytical Xpert PRO. Scanning Electron Microscopy (SEM) model ZEISS Gemini SEM 360 provides high resolution image used to study topography of the materials.

1.2. Methods

1.2.1. Synthesis of Zinc Oxide nanoparticles

Zinc Oxide nanoparticle was synthesized by using precipitation method which was reported by Omnia et al, with slight modifications [17]. In this research work, 50 ml of the extract was allowed to stir in a magnetic stirrer for 1h with the addition of 0.1M Zinc sulfate ml, followed by drop-by-drop addition of 0.1M NaOH solution to get precipitation, the stirring was continuous for 2 hr. Then, the mixture was centrifuged at 5000 rpm, for 8 minutes. The precipitate that was obtained was dried at 80°C to get fine powder. This was used for further characterization.

2. Result and Discussion

The crystalline phase of zinc oxide material was characterized by using UV-Vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy images (SEM) and X-Ray Diffraction (XRD) techniques.

2.1. UV-Vis Spectroscopy

UV-Vis spectroscopy has been determined using UV Labtronics LT 291 Microprocessor UV-Vis Spectrophotometer. UV-Visible absorption spectroscopy is widely used technique to study optical properties of nano sized particles. The synthesized zinc oxide particles are white in colour and insoluble in water as well as in most of the organic solvents.

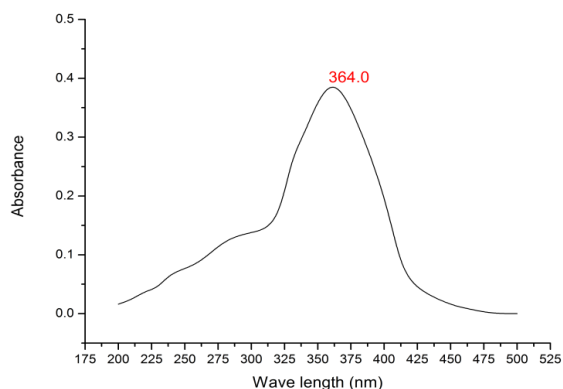


Figure 2: UV-Visible spectra of Zinc Oxide

ZnO particles UV-Vis spectra were recorded by dispersed in methanol and sonicated for 5 to 10 minutes for degassing of samples. Then, UV-Visible spectroscopy was performed in the range of 200 nm – 500 nm. Figure 2 shows the absorption spectroscopy of ZnO nanoparticle in the UV-spectral region. ZnO exhibits a sharp absorption peak at 364 nm that corresponds to formation of ZnO nanoparticles [18] and it also depicts the distribution of particle size is narrow.

2.2. Fourier Transform Infra-Red (FTIR) Analysis

Fourier Transform Infra-Red (FTIR) spectroscopy (Shimadzu model) has been performed in KBr pellet. FTIR spectra give information regarding chemical bonding between Zn and O. The spectrum showed broad peak 447cm^{-1} and a shoulder around which correspond to ZnO nanoparticles [19-21]. The remaining spectrum was relatively smooth with a few peaks of CO_2 . FTIR spectra of ZnO particles showed significant absorption peak at 573, and 1577, and 3372cm^{-1} . The absorption band at 573cm^{-1} was observed due to stretching vibration of Zn-O. The weak band due to H-O-H bending was found due to absorption of moisture, When FTIR sample disks are exposed to open air atmosphere. This result confirm the presence of hydration and a broad band near 3372cm^{-1} confirms hydrogen bonded O-H stretching vibration peak.

2.1.2. Scanning Electron Microscopy (SEM) Image

Surface study of ZnO nanoparticle was performed using scanning electron microscopy model ZEISS Gemini SEM 360, at 5000x magnification. SEM micrograph was recorded at 5000 x magnification. Powdered sample was used to study the exact morphology of the synthesized zinc oxide

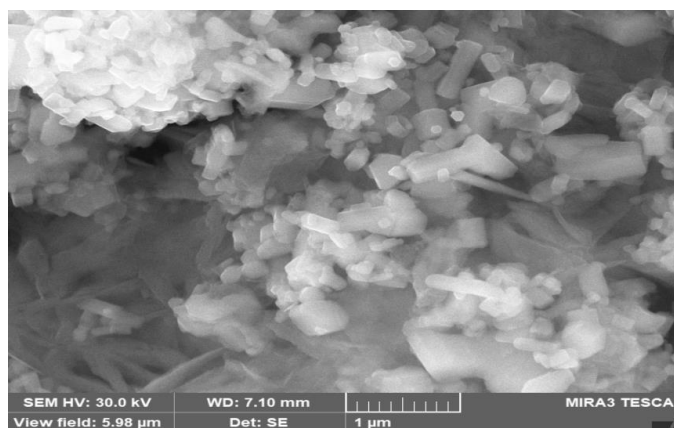


Fig 3: Scanning electron microscopy (5000x) image of Zinc oxide nanoparticles nanoparticle. A floral structural pattern was observed in the Figure 3 which is in great comprehension with the data available in literature for ZnO nanoparticles [22]. This morphological structure had seen throughout the sample so it is good evidence of homogenous nature of ZnO nanoparticles.

2.1.3. X-Ray Diffraction (XRD) Analysis

The crystal structure of synthesized ZnO was examined by X-ray diffraction (XRD) and the respective diffraction pattern shown in Figure ... The method used a copper K α radiation source at 40 KV and 200 m A in steps of 0.02. Data were recorded ranging from 0° to 80°. As observed, the major diffraction peaks are fall under 20° to 80°.

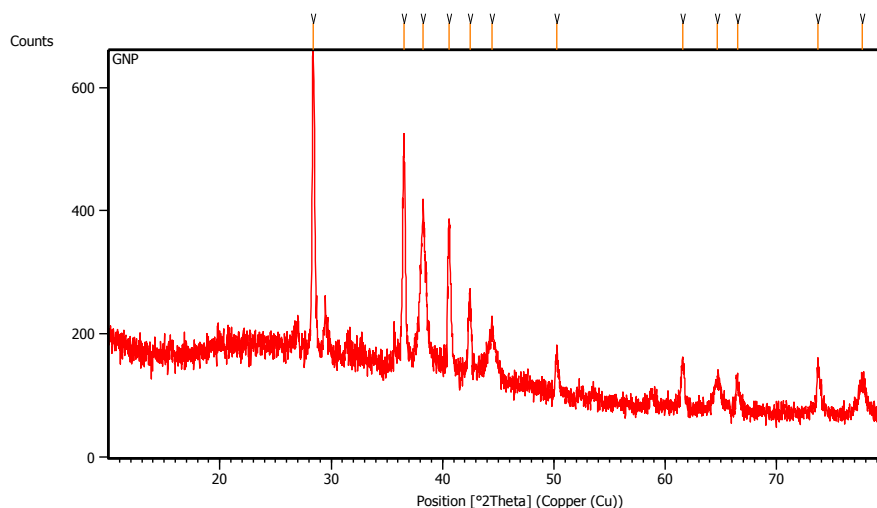


Figure 3: XRD data for Zinc Oxide

(2theta) corresponding to the hexagonal ZnO crystal structure. The diffraction peaks at 2 theta values of 31.65, 34.3, 36.14, 47.45, 56.43, 62.65, 67.96, and 69.09 correspond to the ((110, (002), (101), (102), (110), (103),(112) and (201)) planes of hexagonal ZnO respectively. The

crystalline particle size was determined by using the Debye-Scherrer's formula. The average size of ZnO nanoparticle diameter is within 32 nm.

$$D = 0.9 \lambda / \beta (\cos \theta)$$

Reference

2.1.4. Photo catalytic Activity

ZnO is a heterogenous catalysts for numerous organic reaction because of its ecofriendly nature. It has been analyzed as a powerful and recycling catalyst for most of the organic transformation. Oxygen anions on the surface of ZnO nanoparticle can act as Lewis, as well as Bronstead bases. As such, ZnO may absorb on aldehydes, which carried out nucleophilic oxidation of carbonyl functional group to corresponding carboxylates on ZnO nanoparticles surface [31]. ZnO nanoparticle catalyzed faster than bulk ZnO in oxidation reaction with greater rate of breakdown.

The catalytic performance of ZnO nanoparticles has been determined at room temperature with pH 7.8. Photocatalytic degradation of the polluted water sample was measured in the presence of sunlight. About 10 to 30 mg of ZnO nanoparticles was dispersed in 50 mL of polluted water. After string (50 rpm for 15 min) the samples were placed under sunlight and also placed under UV chamber for 6 hrs. Visual monitoring and UV-Vis spectroscopic analysis at 380 nm of the mixture were performed at different time intervals.

To study the catalytic performance of ZnO, we have observed different O.D. values for a series of ZnO solution ranging from control to 10% and 20% of ZnO . The photo catalytic activity was studied for 24 h with 10%, 20% and 30% ZnO (p H 7.8) at room temperature and it was found to be effective towards remediation of water pollution. Polluted water without any zinc oxide was used as control.

The calculated percentage activity for Water Sample solutions with or without ZnO was shown in Table 1. It was found to be 78.46% in case of 10% ZnO and 78.04 % for 20% ZnO solution. percentage (%) activity was calculated as follows-

$$\frac{\text{Control} - \text{Treated}}{\text{Control}} \times 100$$

Table1. UV-Vis study of ZnO photocatalyst

time intervals for UV-Vis analysis (hrs)	0.5	1.0	1.5	2.0	24.0
Control (o.d.) Water Sample without ZnO	0.469	0.469	0.469	0.469	0.469
Photocatalytic Activity (%) for Control					
10% ZnO+Sample	0.373	0.246	0.207	0.166	0.101
Photocatalytic Activity (%) for sample with 10% ZnO					
20% ZnO+Sample	0.349	0.216	0.174	0.129	0.103
Photocatalytic Activity (%) for sample with 20% ZnO					
30% ZnO+Sample	0.268	0.224	0.106	0.073	0.064
Photocatalytic Activity (%) for sample with 30% ZnO.					

Conclusion

In developing countries like India, the problems associated with wastewater reuse arise from its lack of treatment. The challenge thus is to find such low-cost, low-tech, user-friendly methods. In this regard, ZnO photocatalyst is observed as a strong and ecofriendly remedy that can easily degrade organic pollutant by heterogeneous photocatalysis. The applicability of ZnO as a photocatalyst for water pollution mitigation is due to its high availability, low toxicity, cost efficiency, and well known material properties, Therefore, the proposed research work results in eco-friendly, green and cost effective method for removal of water pollution through ZnO. The photocatalytic activity was found to be high for water sample treated with 20% ZnO.

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