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Ag/Nd2o3-Zno Nanocomposite: Visible Active Efficient Photocatalytic Degradation of Methylene Blue and Its Antibacterial Activity

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Abstract: In this scenario, the photocatalyst Ag/Nd2O3-ZnO (ANZ) are prepared under hydrothermal method and the complete build was confirmed by X-ray diffractometer, Scanning electron microscope with EDX spectroscopy. From the results, the crystalline structure was confirmed by PXRD spectroscopy. And in the SEM, spherical with sponge-like clustered morphology structure was shown and the presenting elements are confirmed by EDX spectroscopy. The suitable light needed for the degradation was selected by DRS-UV spectroscopy. The dye Methylene blue (MB) is degraded under visible light within 30 minutes with the efficiency of 98.12%. The catalyst is further analysed optimized concentration, different catalyst loading, and the catalyst efficiency was analyzed by reusability study. From the recyclability, the catalyst is stable up to the fifth run. Besides, the photocatalytic study the catalyst is analysed antibacterial activity. For the results, the Bacillus bacteria having more antibacterial activity compared to E.coli bacteria.

Keywords: Photocatalyst, Methylene blue, Rare earth metal, visible light, antibacterial activity

I. INTRODUCTION

In this modern world, day by day the uses of cosmetics, pharmaceutical drugs, colouring agents (dyes), chemicals are increased by human beings. Over two thirds in the world, water have circulated the earth. The overall water resources are polluted by waste drugs, industrial dyes, and other chemical compositions. Besides, it affected by a human beings and animals [1]. The polluted water is not completely removed by treating of a conventional, physical and chemical method [2]. Advanced Oxidation Processes (AOPs) comprise a series of methods such as ozonation, photocatalysis, electrochemical oxidation, Fenton and Fenton-like processes, etc., but in the above advanced oxidation process, including photocatalytic degradation process, can be done to remove waste from the pollutant water. Photocatalytic degradation has been great environmental remediation for the pollutant removal from the wastewater. In this work Methylene blue (MB) dye was degraded under AZG nanocomposite. The dye MB is a major ingredient to polluted water from the dyeing and printing textile industries and it has an intensely coloured compound [3].

From this nanocomposite, Nd2O3 having a hexagonal crystal lattice structure and has a good electric and catalytic behaviour. It is mostly used to study the luminescent, photonic and protective coating applications [4-7]. By the quantum confinement effects ZnO particles having some optical properties [8]. Besides, the applications of ZnO are catalysts, transistors in Besides, the applications of ZnO are catalysts, transistors in a transparent thin film, surface wave acoustic devices, cancer-detecting biosensors, degradation of dyes, pharmaceuticals and other organic compounds, etc., [9-10]. The Ag-doped Nd2O3-ZnO nanoparticles are synthesis by hydrothermal method and it is having a good surface area, non-toxicity, good ability and high efficient in photocatalytic degradation process and it is confirmed by the following characterization techniques, like Scanning electron microscope (SEM) with EDX spectroscopy, X-Ray diffractometer spectroscopy and DRS- UV spectroscopy. The degradation of pollutant is detected by UV-Visible spectroscopy technique. By the Ag/ Nd2O3-ZnO catalyst, the pollutant (MB) is converted into CO2, water and some mineral acids.

II. ANTIBACTERIAL ACTIVITY TEST BY DISC DIFFUSION METHOD

The biological study (antibacterial activity) of the synthesized material was performed by disc diffusion method. The test was used to measure the sensitivity of the test material in terms of diameter of clear zone of inhibition in the disc. Lucia agar plates were prepared and overnight culture of Bacillus and E.coli (100μl) were swabbed on the surface of Luria-Bertani medium (Becton Dickinson). The disc is commercially prepared which can impregnate with a standard concentration of nanoparticles and slightly pressed the agar surface. The plates were incubated at 37^0C for 24 hours for the diffusion of the sample into the agar medium. The pharmaceutical material (streptomycin) and the distilled water were used as a positive and the negative control for the bacterial system. The zone of Inhibition formed around the well was measured the biological activity [11].

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III. MATERIALS AND METHODS

A. Materials and characterization

Silver nitrate, Neodymium acetate, Zinc acetate raw materials are purchased from Sigma Aldrich. And Oxalic acid, Sodium hydroxide, C4H6O4Zn•2H2O, Methylene blue (Merck Chemicals, India) are the other raw materials. All the solutions are prepared to use distilled water. The Scanning electron microscope with a model (EVO-80, CARL ZEISS) and the (EDX) spectroscopy (AMETEK-EDAX (Z2e Analyzer)) is used to predict surface morphology and the presence of elements to the nanocomposite. The crystalline structure of the sample was analyzed by powder X-ray diffraction (PXRD) (Shimadzu XRD-6000 X-ray diffractometer (Cu Kα source)). The bandgap was analyzed by UV-Vis diffuse reflection spectroscopy (DRS) was performed on a Shimadzu UV-2450 spectrophotometer. The UV-visible spectroscopy with the model Shimadzu UV-1800 spectrophotometer is used to analyze the degradation efficiency of the collecting photocatalytic degradation samples.

B. Preparation of Catalysts
Synthesize of Nd2O3–ZnO (NOZ)

In 100mL of deionized water Nd (CH3CO2)3.6H2O (6mmol) solution was dissolved at room temperature. The pH of the solution was adjusted to 10 with NaOH for the complete precipitation. From the suspension mixture 100 mL 0.4 M Zn(CH3CO2)2•2H2O solution was added and stirred for 30 min. 100 mL of dissolved oxalic acid (0.6 M) was added to the above suspension until dropwise and stirred for 4 h to the complete precipitation. After completion, the reaction the suspension mixer was transferred in Teflon lined stainless steel autoclave at 115°C for 12 h. The hydrothermally treated samples were dried in an oven at 80°C for 12 h and annealed at 650 °C for 12 h in a furnace.

Synthesize of Ag/Nd2O3-ZnO (AOZ)

The catalyst NOZ (1mmol) and silver nitrate (0.5 mmol) are dissolved in 100 ml of distilled water with a Stoichiometry ratio, then these solutions the reducing agent solution form of sodium borohydride are added with drop wisely. And subsequently, the solution was allowed to cool at room temperature. After some time the precipitate was formed. The formed precipitate was collected by filtration and washed with water and ethanol. And the precipitate was dried in a vacuum oven at 60°C at overnight. Finally, the dry samples are annealed at 650°C for 8h in a furnace.

Photocatalytic experiments

In the visible light degradation, Heber multi-lamp as a (tungsten lamp as a light source and the intensity is 150mW/cm^{-2}) photoreactor for the degradation of MB under visible light (λ> 400nm) irradiation by ANZ. In 250 ml beaker, 50mg of the catalyst was mixed in 100ml solution of MB with 30μm concentration Above dispersed mixture was agitated for 1/2h in dark condition, to ensure the adsorption-desorption equilibrium of the reaction solution. After stirring, the dispersed solution was transferred into a 200ml reaction vessel. After 5 min time intervals, 5ml of the reaction solution was collected from the reaction vessel and monitored the absorption peak of CIP at 668nm using UV visible spectrometer. The catalyst was separated by an ultracentrifuge, and the catalyst is washed with de-ionized water for three times and dried at 60^{o}C. Finally, it is used for the reusability test. The above procedure is similar to the MB dye solution degradation.

IV. RESULTS AND DISCUSSIONS

A. X-Ray Diffractometer Spectroscopy

In ANZ composite, the purity and the crystal structure of the sample are analyzed by powder X-ray diffraction (PXRD) in the range between 10-80^{o}. The X-ray diffraction peaks of ZnO, Nd_2O_3, Ag/Nd_2O_3-ZnO nanocomposites are seen in Fig. 1 The observed peaks in Nd_2O_3 (JCPDS no. 74–2139) are 26.58, 29.48 and 30.52° corresponds to the reflection planes (100), (002) and (011) with the structure Primitive hexagonal of Nd_2O_3 [12].

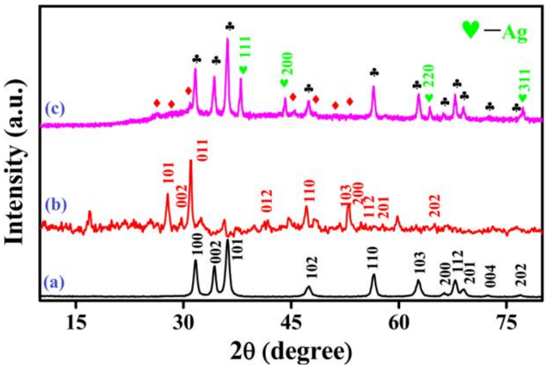

Fig. 1 X-ray diffraction for a) ZnO, b) Nd2O3 and c) Ag/ Nd2O3-ZnO nanocomposite.

XRD patterns of Nd2O3 shows that the material is of highly purity, because there are no impurity peaks were observed. For Ag (JCPDS – 89-3722), the intense peak present at 38.1, 44.5, 64.5 and 77.6o attributes to the plane (111), (200), (220) and (311) plane with Cubic structure system. The ZnO (JCPDS - 36-1451) diffraction peaks are observed at 31.6, 34.23, 36.18, 47.38, 56.54, 62.81, 66.22, 67.89, 69.08o respectively. In ANZ composite, the complete formation was confirmed by the presence of the diffraction peaks of Ag, ZnO, and the very low intense peak of Nd2O3 are represents. The Nd2O3 peaks are having visible very hard because the weight of loading of Nd2O3 is very low.

B. Scanning Electron Microscope and EDX Spectroscopy

From Fig. 2 explains the morphological structure of the different nanomaterials Nd2O3, ZnO, Nd2O3-ZnO and Ag/ Nd2O3-ZnO by SEM micrographs. The NO (Fig. 2b) nanoparticles having the spherical with microsponge shape structure and the ZnO exhibits hexagonal like clustered structural (Fig. 2a) morphology. Besides, the Nd2O3-ZnO materials having a cluster like a microsponge (Fig. 2c) structure and the NO are anchored in the ZnO surface with a good number of particles are observed. In Ag/ Nd2O3-ZnO, the Small spherical structure of silver particles (mentioned by Round mark)

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with cluster like microsponge structures are seen in Fig. 2 and it is evidenced for the confirmation of nanocomposite. From Fig. the presenting elements like Ag, Nd, Zn, O and C in the NOZG were analyzed by EDX spectrum and it confirms the complete formation of nanocomposites.

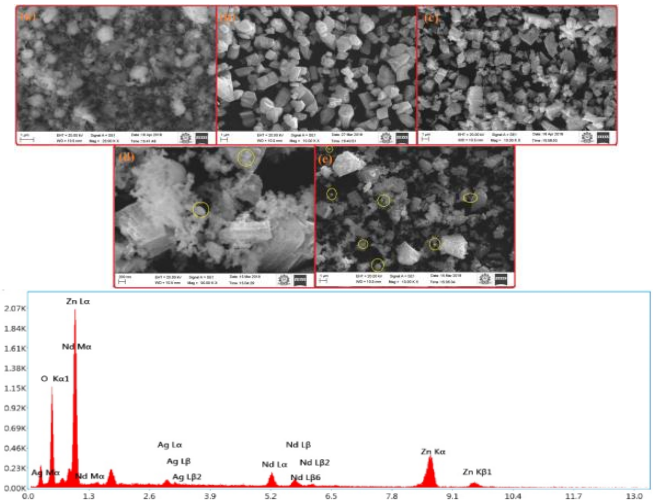

Fig. 2 SEM images of a) Nd2O3, b) ZnO, c) Nd2O3-ZnO, (d, e) Ag/ Nd2O3-ZnO at different magnification range and EDX Spectroscopy of the prepared nanocomposite

C. DRS- UV spectroscopy

In the photocatalytic process, the bandgap energy is to select the suitable light needed for the degradation of MB dye.

DRS-UV spectrum is predicting the band energy value. In Fig - 3 the diffuse reflectance absorption spectra of NO, ZnO, NOZ, and ANZ are shown. The bandgap value is calculated by Tauc's plot with a linear extrapolation line, where $((\alpha h\upsilon)^2$ is plotted against the photon energy (hυ). The bandgap value for free NO is 4.9eV, for ZnO 3,23eV, for NOZ is 3.21eV and the ANZ values are 2.8eV. The bandgap energy decreased from 4.9eV to 2.8eV. This bandgap degreasing is indicated that the ANZ photocatalyst is degraded under visible light irradiation.

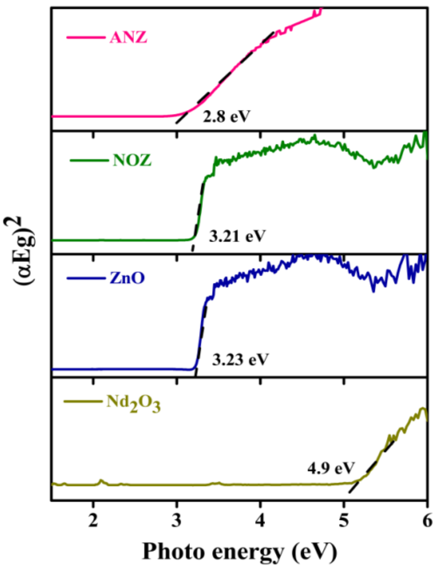

Fig. 3 DRS-UV spectrum for NO, ZnO, NOZ, and ANZ nanocomposites

D. Antibacterial activity test

By disc diffusion method, the antibacterial activity study was carried out under the catalyst ANZ. In ANZ composite the activity was studied against the E.Coli (Gram-negative bacteria) and Bacillus (Gram-positive bacteria) bacteria. From Fig. 4 the Zone image is obtained by the ANZ composite, the positive control having a standard pharmaceutical and the negative control having distilled water. From these figures, the Zone image of two bacteria by ANZ composite, the Zone surface area of Bacillus is higher compared to the E.Coli bacteria. Therefore higher antibacterial activity of Bacillus is noticed to the study than E.Coli bacteria.

Fig. 4 Antibacterial study: The Zone image photographs of Bacillus and E.coli bacterias

V. PHOTOCATALYTIC DEGRADATION OF MB DYE

A. The optimization of different catalyst

The reaction conditions i.e) catalyst dosage, a suitable concentration of MB and degradation of different catalyst are to be optimized. From Fig. 5(a) the different catalyst ZnO, Nd_2O_3, Nd_2O_3-ZnO and Ag/ Nd_2O_3-ZnO nanocomposite are degraded under visible light with the time taken 30 minutes. Compare to the different catalyst the efficiency is much more in Ag/ Nd_2O_3-ZnO nanocomposite compare to the others. After the (30 minutes) complete degradation the C/C_0 value reach almost zero. The absorption spectrum is shown in Fig. 5(b) and the absorption value is 668nm respectively.

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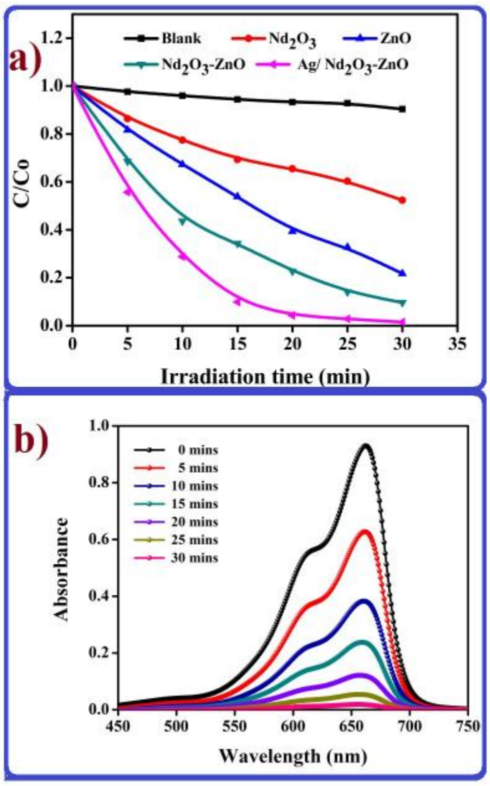

Fig. 5 a) Photocatalytic degradation of different catalyst and b) Absorption spectrum MB degradation

B. The optimization of catalyst dosage

From the degradation process, the amount of catalyst loading is very important. Fig. 6 shows the different catalyst loading (ANZ: 30-60mg) of the prepared nanocomposite. The photocatalytic degradation process 50mg of ANZ catalyst is suitable for the degradation of MB dye under visible light.

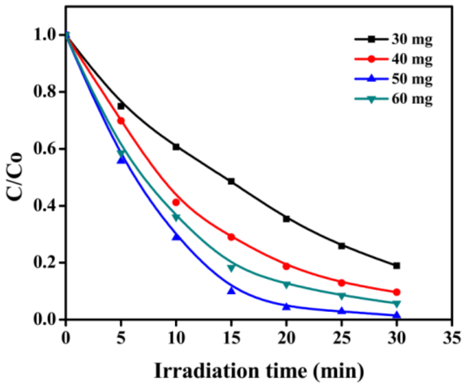

Fig. 6 Photodegradation of MB under the optimization of different catalyst dosage

At the time the degradation efficiency is increased. If used a high amount of catalyst the efficiency is decreased. Because add the high amount of catalyst to the degradation process the surface area of the degradation material is increased which leads to an increase in the reactive sites [13].

C. Optimization of concentration

The MB concentration was optimized between 5 µM to 15 µM. Because of 10 µM is the best of (MB) pollutant degradation. If the concentration of pollutant was increased, then decrease the rate of photodegradation. Therefore, the MB was degraded with the concentration of 10 µM and it is shown in Fig. 7.

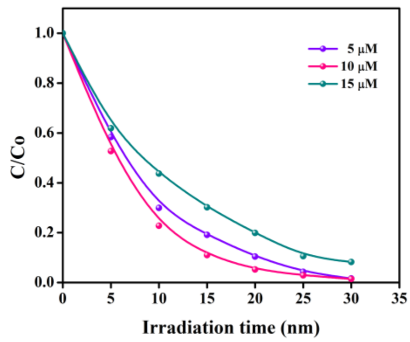

Fig. 7 Photodegradation of MB with the optimized concentration

D. Recyclability test

After degradation of completion, the remaining catalyst was filtered and washed with water and then dried. Further, it re-used to degrade the pollutant.

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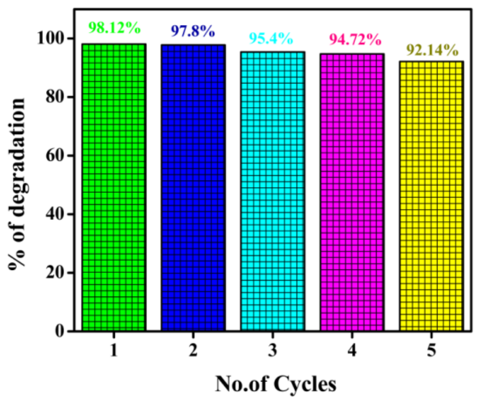

Fig. 8 Recycle efficiency of MB degradation

The catalyst was, again and again, reacted to involve the degradation under five successive runs. Fig. 8 contains the recyclability of the MB dye. In spite of this, after the fifth run, the degradation efficiency of MB by ANZ catalyst remains 92.14%. The result shows the catalyst having good mechanical stability and corrosive resistance of the catalyst [14].

VI. CONCLUSION

In summary, the ANZ nanocomposite was successfully synthesized by hydrothermal method, and detailed its spectral information's. For the results, the degradation for the MB dye under visible light irradiation is carried out by ANZ catalyst. The catalytic efficiency of ANZ is much more compared to the undoped ZnO, Nd_2O_3, and NOZ nanocomposite. The spherical with sponge-like hexagonal structure morphologies were found for ANZ nanocomposite observed from SEM. The presence of elements such as Ag, Nd, O, Zn and C is confirmed by EDX analysis.

The MB was completely degraded within 30 minutes under Visible light irradiation. The ANZ nanocomposite contains superior chemical stability and good reusability for after the fifth degradation runs. And the antibacterial study, the higher activity is noticed in Bacillus bacteria by ANZ catalyst than the E.Coli bacteria.

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