



Photocatalytic Degradation of Pollutants in Industrial Effluents Using Undoped and N-Doped ZnO Under Sunlight Irradiation

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ABSTRACT

A well defined photoactive N-doped ZnO catalyst was synthesized by a low temperature co-precipitation of zinc acetate dihydrate precursor in presence of ammonium sulfate as dopant' source. The catalyst was characterized by X-ray diffraction (XRD), scanning electronmicroscopy (SEM), UV-visible analysis and FT-IR spectroscopy. The diffraction peaks of undoped and N-doped lines materials are in accordance with the wurtzite hexagonal phase of ZnO. The insertion of the dopant (N) and the vigorous agitation during the catalyst preparation caused a decrease in the crystallites size from 129 to 101nm, and reduction in band gap from 3.28 to 2.84eV. Photocatalytic activity of the N-doped ZnO sample was investigated by irradiation of the effluent in a period of 100 minute to aid the purification of industrial wastewater and compared with photocatalytic activity of the undoped ZnO. The results indicated that photocatalytic activity of N-doped ZnO sample on the pollutant under sun light irradiation was 97.3% in 100min, and that of undoped ZnO was found to be 70.5% on the same pollutant, the same condition and under sunlight irradiation. The difference in the performance of the two photocatalysts is attributed to the shift in the band gap energy due to insertion of the dopant.

Keywords: Photocatalyst, Irradiation, Semiconductor, sunlight, effluent and N-doped ZnO.

INTRODUCTION

Industrial effluents are discharges from various industries, and various organic pollutants have been found in different water resources[1]. They belong to various classes such as pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, oils, greases, pharmaceuticals, etc Industrial effluents are liquid wastes which are produced in the course of industrial activities[2]. Over the years, the improper disposal of industrial wastewater effluents has been a major problem and a source of concern to both government and industrialists. In most cases, the disposal or discharge of effluents, even when these are technologically and economically achievable for particular standards, do not always comply with pretreatment requirements and with applicable toxic-pollutant-effluent limitations or prohibitions[3]. The consequence of these anomalies is a high degree of environmental pollution, leading to serious health hazards. The effluents generated from domestic and industrial activities constitute the major sources of the natural water pollution. This is a great burden in terms of wastewater management and can consequently lead to a point-source pollution problem,



which not only increases treatment cost considerably, but also introduces a wide range of chemical pollutants and microbial contaminants to water sources[3] [4]. Industrial activities and urbanization in developing countries including Nigeria has gradually led to the deterioration of the environment in recent years. This situation has invariably increased the problem of waste disposal. Untreated wastes from processing factories located in cities are discharged into inland water bodies resulting to stench, discoloration and a greasy oily nature of such water bodies [5].

The industries use considerable quantities of water and consequently their wastewater containing dyes and other phenollic compounds in significant quantities are discharged into natural waters. Some of these dyes are toxic, mutagenic and carcinogenic [5]. Moreover, these dyes, by preventing the penetration of solar light into water, reduce photosynthetic activity and thus cause a disturbance of the aquatic equilibrium. Shakoore, S.; Nasar, A. et al. (2016) mentioned that without appropriate treatments, these dyes can remain in the natural water for a long time [6]. This is why various physical methods such as adsorption [6], coagulation and various chemical methods such as chlorination, ozonation, etc. [7] have been used to reduce the environmental effects of dyes. However, physical and biological methods do not remove pollutants; they only transform them into another phase. As for chemical methods, they have the drawback of using strong oxidants such as chlorine and ozone which are themselves pollutants. The most suitable way to eliminate this waste is their degradation by photocatalysis. In fact, dyes can be degraded in the presence of photocatalyst when irradiated with sunlight due to their absorption in the visible region.

In the last decades, particular interest has been focused on heterogeneous photodegradation by metal oxides because of their wide use in organic synthesis and their environmental applications [7]. Among the different metal oxides used, it has been reported that titanium dioxide (TiO_2) and zinc oxide (ZnO) are the most chemically stable and are not toxic [8]. Incorporation of N in ZnO is expected to reduce the energy band gap for more photocatalytic performance.

Photocatalytic reactions mainly occur at or very close to the surface of an illuminated photocatalyst [9],[10]. As particles of the photocatalyst become smaller, the amount of atoms found at the surface increases relative to the proportion inside its volume. The higher surface energy can also make particles interact strongly and stick together. For particles nearly 70–80% of all the atoms reside on the surface. This has important implications for photocatalysis and especially for the issues of charge separation. With such a large number of atoms on the surface it is quite easy to understand how the surface chemistry could dominate the properties of the particles of photocatalyst [11]. However, recent studies have shown that photocatalytic reactions can also occur at certain distances from the illuminated surface, through the diffusion of reactive species in air or solution phase, or through the diffusion of reactive species on the surface. This discovery is important for the design of photocatalytic systems [12].

MATERIALS AND METHODS

Chemicals Used

All the chemicals used in this experiment are of high analytical grade and include, Zinc acetate dihydrate (99%) Kermel product, Ammonium (99.5%) Aldrich product NaOH (98%, Sigma), effluent with pH of 9.5, HCl (97% Sigma) ethanol (98.5%), as well as other chemicals, were used in the synthesis of catalyst as received. Deionized distilled water was used in the preparation of the reagents and other reagents as used in this research.

Synthesis of Undoped ZnO

Zinc acetate dihydrate was used as the precursor for ZnO , ethanol was used as reducing agent and sodium hydroxide as precipitating agent.

100 cm^3 of ethanol was added into 250 cm^3 zinc acetate solution and stirred for 5 min, then was transferred into an empty 1000 cm^3 beaker. The mixture of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ /ethanol in the 1000 cm^3 beaker was then subjected to vigorous stirring with the aid of magnetic stirrer for 30 min in order to get proper mixing. The



mixture was then heated to 50°C and precipitated using 0.1M NaOH solution until the pH of the solution was 7[13], [14]. The temperature was maintained at 50°C and with further vigorous stirring for two hours with the aid of magnetic stirrer. The mixture was then removed from the heat source, and allowed to cool for four hours. A white precipitate was obtained, leaving the clear liquid at the upper layer. The clear liquid was ran off, leaving the white substance at the bottom of the beaker. The white substance (precipitate) was subjected to centrifugation at 3000rev/min for 15min, and the liquid free white precipitate was obtained[15]. The precipitate was washed three times with distilled water, and then with ethanol to removed any traces of unwanted substances that may be present in the mixture. It was then transferred to crucibles and taken in to oven and dried at 60°C for 12h. It was followed by calcinations at 450°C for two hours at the rate of 5°C/min, and the resulting substance is a whitish powdered substance, which was labeled as undoped ZnO [16].

Synthesis of N-doped ZnO

Zinc acetate dihydrate was used as the precursor for ZnO and ammonium as modifying agent (source of N), ethanol was used as reducing agent and sodium hydroxide as precipitating agent. In a typical procedure, 100ml of ethanol was added into 250ml zinc acetate solution and stirred for 5min, was then transferred in to an empty 1000ml beaker. Another 100ml of ethanol was added to 250ml of ammonium in a separate beaker and stirred for 5min, and then transferred into the 1000ml beaker containing the zinc acetate/alcohol mixture. The heterogeneous mixture of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ /ethanol and ammonium /ethanol in the 1000ml beaker was then subjected to vigorous stirring with the aid of magnetic stirrer for 30min in order to get proper mixing[17]. The mixture was then heated to 50°C and precipitated using 0.1M NaOH solution until the pH of the solution was 7. The temperature was maintained at 50°C and further stirring vigorously for two hours with the aid of magnetic stirrer[18],[19]. The mixture was then removed from the heat source, and allowed to cooled down for four hours. A white precipitate settled down, leaving the clear liquid at the upper layer. The clear liquid was ran off, leaving the white substance at the bottom of the beaker. The white substance (precipitate) was subjected to centrifugation at 3000rev/min for 15min, and the liquid free white precipitate was obtained. The precipitate was washed three times with distilled water, and then with ethanol to removed any traces of unwanted elements or ions that may be present in the mixture[20]. It was then transferred to crucibles and taken in to oven and dried at 60°C for 12h. It was followed by calcinations at 450°C for two hours at the rate of 5°C/min, and the resulting substance is a dark whitish powdered substance, was labeled as N-doped ZnO.

Scanning Electron Microscopy (SEM) Analysis of the S-doped ZnO

To study the surface morphology (form and structure) of the synthesized particles, Scanning electron microscopy (SEM) was carried out using Phenom SEM machine model “pro X”, at magnification of 2500times, accelerating voltage of 15kv and distance of 30µm[21].

Fourier Transform Infrared (FT-IR) Analysis

Fourier transform infrared spectrometer (Cary 630) Agilent Technologies was used for FTIR spectral analyses in the wave number range of 4000 - 400cm⁻¹ and background scan rate of 32 based on Attenuated Total Reflectance (ATR) system[22],[23]. The analysis was necessary in order to confirm the structural features of the N-doped ZnO and undoped ZnO. It was also to determine local orientation of the group and its local environment and/or location in the structure, which is responsible for absorption and optical properties of the synthesized samples[23].

PHOTOCATALYTIC EXPERIMENTS

In a typical experiment 0.2g of calcined sample of N-doped ZnO particles was dispersed in 100cm³ of industrial waste water at pH of 9.5 obtained from three different locations (Chalawa, Sharada and Bompai industrial estates in Kano state, Nigeria) at certain pH. The above suspension was stirred for 30min in the dark to obtain adsorption-desorption equilibrium to eliminate the error due to any initial adsorption effect[24]. This was then irradiated in a glass photo reactor using 500W high-pressure Hg lamp of intensity 0.0129w/m². Degradation was monitored by taking 5cm³ aliquots at the time intervals of 20min. These aliquots were centrifuged for 15 min at 2000rev/min prior to absorbance measurements in order to eliminate the error due to

scattering[25],[26]. Changes in the concentration base on colour and odour were observed from its characteristic absorption at 316 nm. The concentration was determined spectrophotometrically using Perki Elmer Lamda 35 UV-Visible spectrometer. The temperature reached during the irradiation was $30 \pm 2^\circ\text{C}$ [27]. The experiment was repeated by varying the experimental variables (pH, effluent volume and temperature) each in triplicates and recorded.

Percentage Degradation

The photocatalytic activity was evaluated by the decomposition of the effluent. The percentage degradation was determined for every run by the equation (3.1):

$$\text{Percentage Degradation} = \frac{C_0 - C_t}{C_0} \times 100 \quad 3.1$$

Where C_0 and C_t are the initial and final concentrations of the dye at a time t_0 and t [28].

RESULTS AND DISCUSSIONS

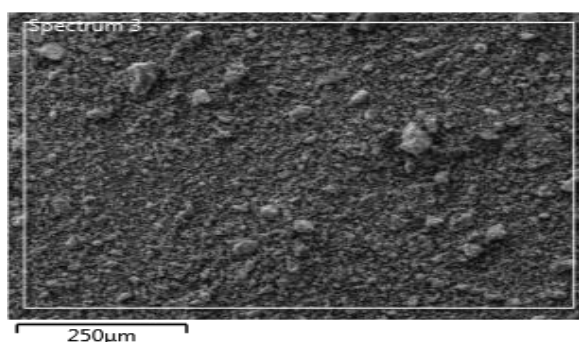


Figure 1: SEM image of Undoped ZnO

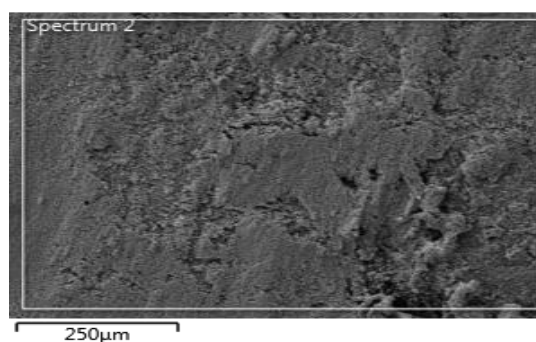


Figure 2: SEM image of N-doped ZnO

SEM image of undoped ZnO and N-doped ZnO prepared by co-precipitation method is presented in Figure 1 and 2 respectively. It is obvious, that the N-doped ZnO crystal was closely packed together significantly as shown in the images. The N-doped ZnO catalyst in figure 2 has a whitish shades of which may be attributable to the dopant deposited on the ZnO particles. The morphology of the N-doped ZnO catalyst seems more compact than the undoped ZnO catalyst and that the doped catalyst is seen with additional whitish deposition covering the spaces between the ZnO crystals[29].

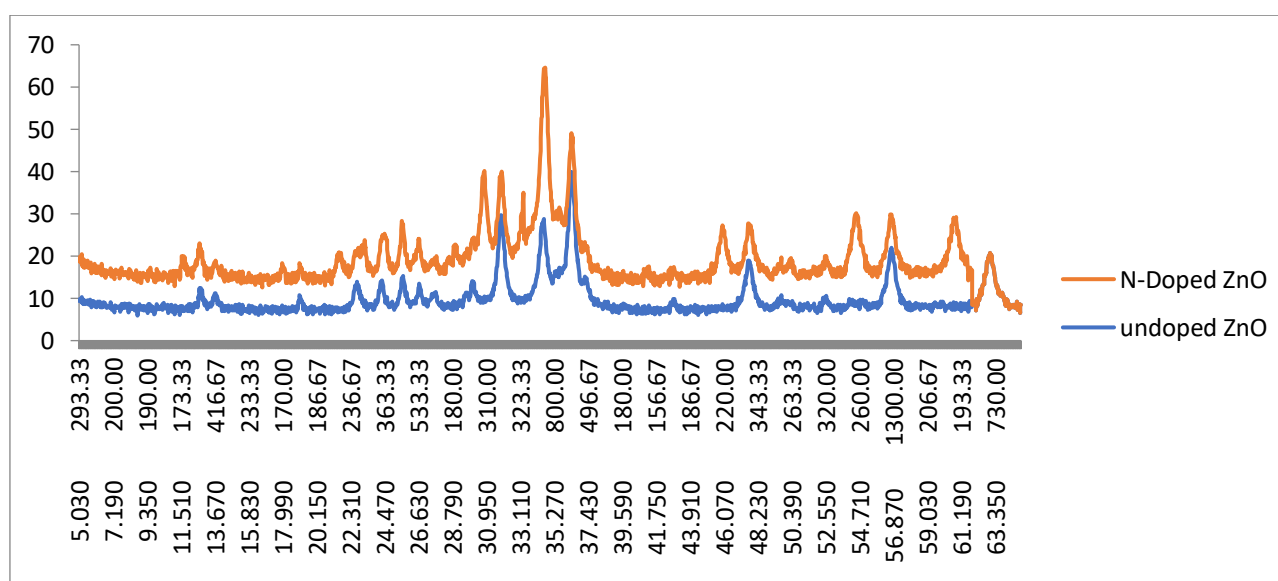


Figure 3: Overlaid XRD patterns of undoped and N-doped ZnO

Powder X-rays diffraction (XRD) patterns were recorded with a *Thermo scientific* XRD machine of model *ARL X'' TRA with X-ray diffractometer*. The intensities were obtained in the 2θ ranges between 20° and 70° . The FULPROF software was used for estimating the average size of the crystallites. Rietveld refinement was performed on the diffraction patterns to determine the crystallite size and relative abundance of phases. XRD patterns for the synthesized samples as shown in the Figure 3, The diffraction peaks of undoped and doped lines materials are attributable to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), and (2 0 1) planes which are in accordance with the wurtzite hexagonal phase of ZnO. These patterns are similar in both undoped and doped samples, assessing that neither the introduction of the dopant (N) nor the agitation during synthesis changes the crystal structure of ZnO[30], [31]. The average crystallite sizes of particles were estimated by the Scherer's formula as shown below:

$$D = 0.89\lambda / \beta \cos\theta$$

Where D is the crystallite size, λ is the X-ray wavelength, β is the broadening of the diffraction peak and θ is the diffraction angle for maximum peak[32]. These values are 118 and 100 nm for undoped ZnO and N-doped ZnO samples respectively. The synthetic method employed shows that the insertion of dopant and the vigorous agitation caused a decrease in the crystallites size.

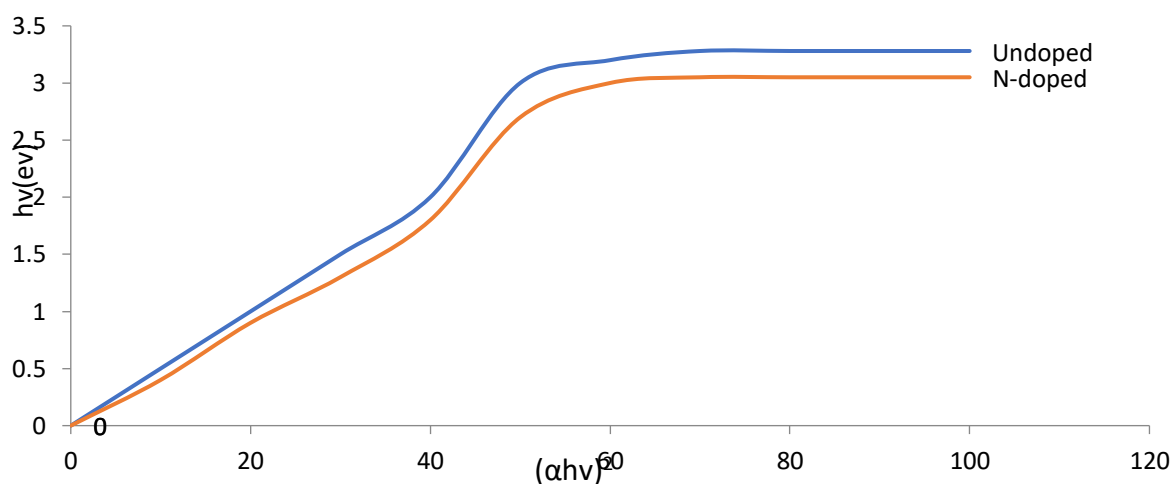


Figure 4: Extrapolation curves of undoped and N-doped ZnO for band gap determination

The UV visible spectrum of the samples for the undoped ZnO absorbs the radiations in the UV range up to 365.14nm, while the N-doped ZnO absorbs up to the range of 358nm, and almost all the visible spectrum radiations are transmitted by the ZnO particles.

The band gap of the ZnO particles was calculated by extrapolating the curve drawn between $(h\nu)$ and $(\alpha h\nu)^{1/2}$ shown in figure 4[32]. Where ν is the frequency and α is the optical absorption coefficient. The band gap energy obtained by extrapolating the curves was found to be 3.28 and 2.84eV for undoped and N-doped ZnO eV respectively. This imply that the doping process has induced some small modification in the material band gap. This effect is one of the espected phenomenon for any semiconductor which undergo doping[33]. The ordinates of the plot are basically the Schuster-Kubelka-Munk remission function $(F(R)/h\nu)$ 0.5 while the abscissae are the photon energies $(h\nu)$. The power 0.5 is the optical transition constant for ZnO, being an indirect band gap semiconductor. From both the spectral plot and the table, red shift can be readily noticed. This may be due to an increase in the percentage of the dopant (N). This may be attributed to the introduction of new energy levels into the ZnO band gap as a result of the introduction of N.

Table 1: Particles Size and Band Gap Energy of Undoped and N-doped ZnO

Catalyst	Average Particle size(nm)	Band Gap Energy (ev)
Undoped ZnO	129	3.28

N-doped ZnO	101	2.84
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These values are 126 and 102 nm for undoped ZnO and N-doped ZnO samples respectively. The synthetic method employed shows that the insertion of dopants and the vigorous agitation caused a decrease in the crystallites size, i.e more dopants lead to decrease in crystallite size[34].

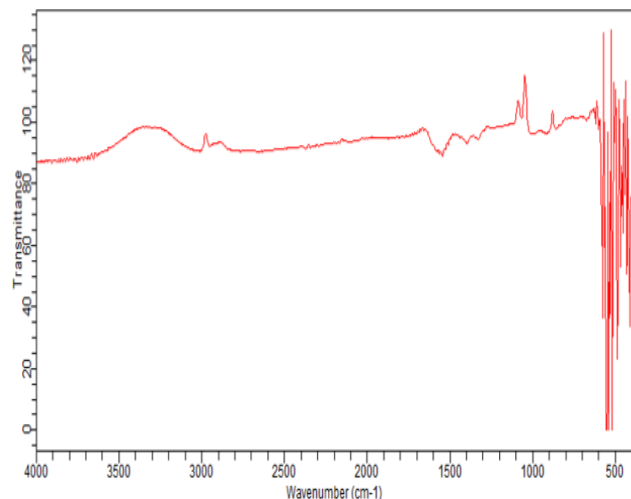


Figure 5 FTIR spectra of Undoped ZnO

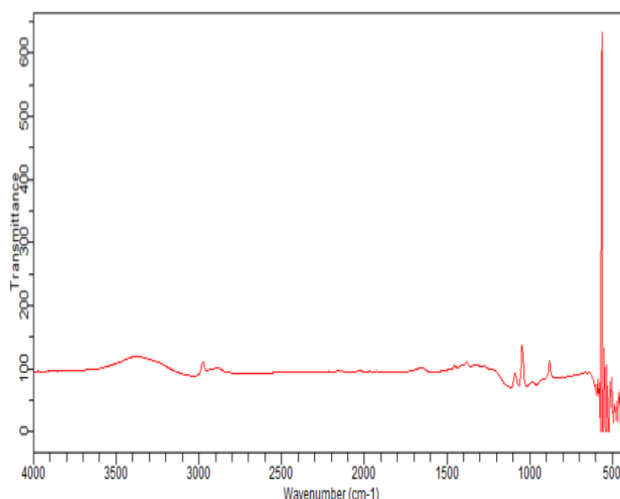


Figure 6 FTIR spectra of the N-Doped ZnO

Figure 5 and 6 and the FTIR peaks of the undoped and the N doped ZnO respectively. The peaks at $3712\text{--}3610\text{cm}^{-1}$ and $2102\text{--}1569\text{cm}^{-1}$ were assigned to the stretching vibration and bending vibration of surface --OH group. The band at $1018\text{--}675\text{cm}^{-1}$ was assigned to the Zn-O stretching vibration, and Zn-O-N bonds of the doped sample emerged at 1167cm^{-1} [33]. The shape appearance long peak at the extreme end and the subsequent dispersion of the initial peaks in the doped ZnO is a visible evidence of the successful insertion of nitrogen in the crystal lattice of the ZnO.

Effects of Operational Parameters

Irrespective of the concentration of pollutant, the percentage degradation increases with time which is shown in figure 7 below (Andre *et al.*, 2014). similarly Figure 6 shows the increase in initial concentration of the pollutant from 2Mg/L to 10Mg/L. There is a decrease in the percentage degradation with increase in concentration of the dye at fixed pH, catalyst dosage and at room temperature in the same interval of time. This is due to the fact that the higher the concentration of the pollutant, the stronger the bond between its molecules and the more difficult it is for the photocatalyst to brake them [34].

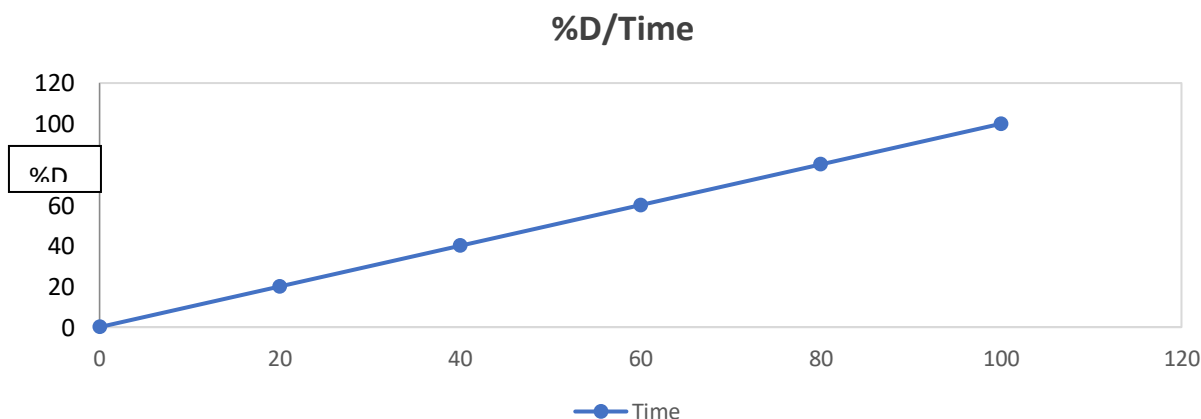


Figure 7 Effect of Time in Degradation of effluent with N-doped ZnO particles and sun light Irradiation.

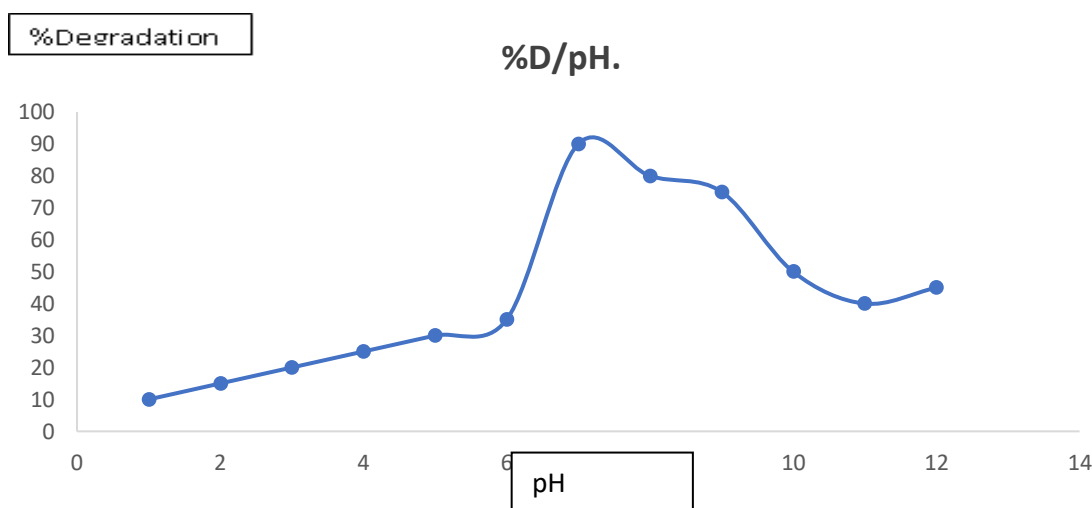


Figure 8: Effect of pH on Degradation of effluents

The most important parameter that influences the photocatalytic degradation is the solution pH [35]. The efficiency of the catalyst is affected by the pH of the solution. The effect of varying the pH from 1 to 12 on the degradation of the pollutant is shown in Figure 8. It was found that the degradation efficiency increases with an increase in pH from 2 to 5. Increase of pH of the solution from 1 to 5 increases the degradation from 29% to 65% at the time of 100 min. A sharp increase in the degradation rate was observed for further rise in pH from 5 to 7. Many workers observed similar behavior in their studies [36]. At low pH, the N doped ZnO particles agglomeration reduces the pollutant adsorption as well as photon absorption. The increased efficiency in the alkaline pH range may be explained on the basis of increase in the formation of hydroxyl radicals with an increase in pH. In acid and neutral solutions the formation of $\text{OH}^\bullet$ can be given by the equation (2).



In alkaline solution the OH radical is also formed from hydroxide ion as shown in equation (3) below:

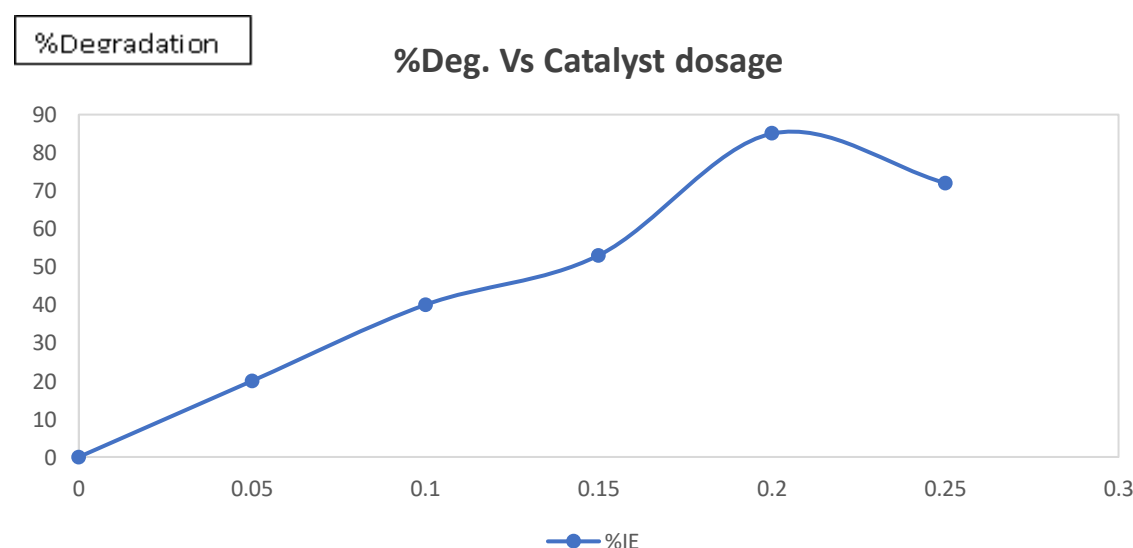


Figure 9: Effect of Increase in Amount of Catalyst on Degradation of pollutant

The effect of the amount of catalyst on the photocatalytic degradation of effluent has been carried out in the range of 0.025-0.2g of the catalyst per 100 ml of the effluent as shown in figure 9. As the concentration of the catalyst is increased from 0.025 to 0.1g/50 ml, degradation increases from 25% to 94.9 % at 100min of irradiation time. This is due to an increase in the number of N-doped ZnO particles, which increases the absorption of photons and adsorption of pollutant molecules[37]. Further increase in catalyst loading decreases the removal rate. Increase of the catalyst loadings beyond 0.1g/50 ml may cause screening effect which reduce the specific activity of the catalyst [38].

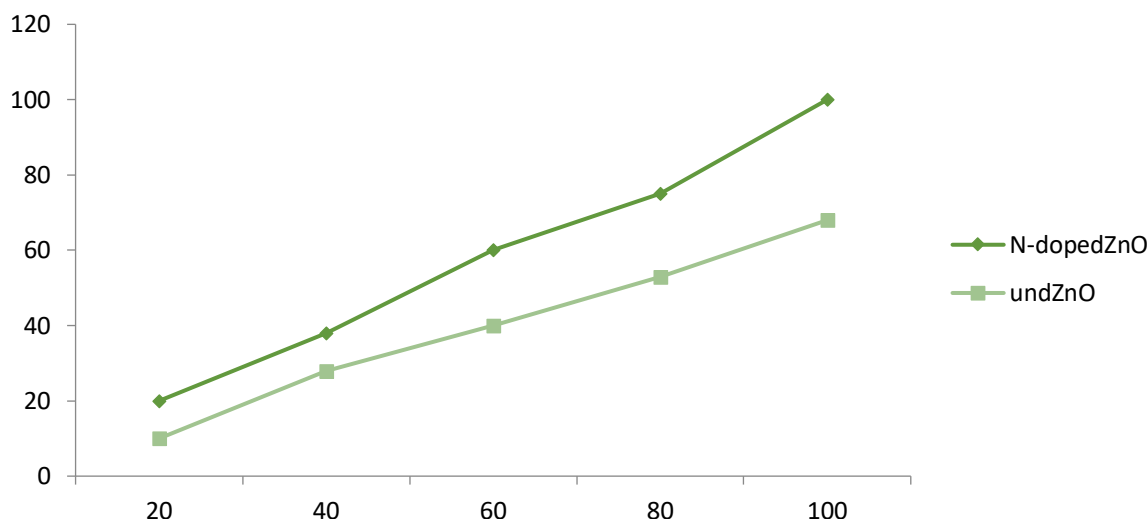


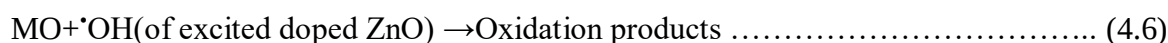
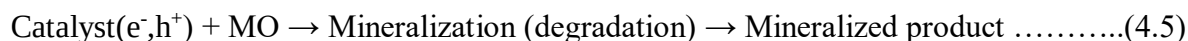
Figure 10: Percentage Degradations of Undoped and N-doped ZnO.

The photocatalytic efficiency of both the N-doped and undoped ZnO on the pollutant was studied under the same conditions, and the performances were compared.

Figure 10 shows that the N-doped ZnO has better photocatalytic activity on industrial effluents than the undoped ZnO under sun light at the same conditions, with 97.5 and 73.3 percentage degradations for doped and undoped ZnO respectively. For each of the experiment, irrespective of the concentration of pollutant, the same effect was observed using undoped ZnO with the sun light irradiation on the pollutant (industrial effluent) in which concentration of 2mg/L has the highest percentage degradation at optimum pH, catalyst and temperature of 7, 0.2g/100ml and 35°C respectively[39]. The percentage degradation over the doped ZnO was found to be higher than undoped ZnO under the same conditions. These were 98.3% and 73% respectively over 100min irradiation time.

Effect of SunLight And Photocatalyst On Methyl Orange Solution

In the absence of the photocatalyst, the effluent on irradiation with the sun light has been found to be stable even after 100 min. In the presence of N-doped zinc oxide and in the absence of light there is a small decrease in concentration initially and then found to be stable. The initial decrease is due to the adsorption of the pollutant (mostly dyes) by N-doped zinc oxide particles, and the pollutant undergoes 98.7% degradation in 100 min on irradiation with sun light. On the basis of the experimental observations and corroborating with the existing literature, a tentative mechanism has been proposed for the purification the industrial effluent by heterogeneous photocatalyst. The overall mechanism of photocatalytic degradation of pollutant in the presence of N-doped ZnO and sun light can be proposed as follows [40].





Oxidation products → Mineralization → Mineralized products [40]

The electrons are scavenged by the oxygen adsorbed on the surface of N-doped ZnO as in (Eq.4). The pollutants (mostly dyes) behaves like an electron donor in the excited state and injects electrons directly to the conduction band of catalyst on irradiation. The hydroxyl radical is a non-selective and strong oxidizing agent with high oxidation potential, which is relatively high as compared to common oxidizing agents like H_2O_2 , O_3 , O_2 [41].

CONCLUSION

In this research nitrogen doped ZnO was successfully achieved by using ammonium as the modifying agent of zinc acetate dihydrate. XRD patterns show some decrease in crystallite size due to insertion of the dopant, this has been justified by the SEM image and the FTIR peaks. Photocatalytic activity of the N-doped ZnO sample was investigated by purification of industrial wastewater and compared with photocatalytic activity of the undoped ZnO. The results indicated that photocatalytic activity of N-doped ZnO sample on the pollutant under sun light irradiation was 97.3% in 100min, and that of undoped ZnO was found to be 70.5% on the same pollutant, the same condition and under sunlight irradiation. N-doped ZnO photocatalyst with high activity for industrial effluents purification under sun light was synthesized through co-precipitation method. The doped photocatalyst performed better in the degradation of the pollutant than undoped one under the same conditions due to successful reduction of band gap and particle size which also means more surface exposure.

RECOMMENDATIONS

The following are the recommendation for future studies

1. A detailed study of the mechanism for N-doping on zinc oxide should be carried out and also parametric studies on the factors the influence deposition of the element using other different precursors.
2. Diffuse reflectance spectroscopic analysis (DRS) should be carried out on the N-doped ZnO catalyst to see the effect of the non-metal doping in the bandgap of the catalyst.
3. Complete solar spectrum degradation studies should be carried out using solar simulators to explore the effect of the rest of the solar spectrum.

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