

Photocatalytic Degradation of Azure A Using N-Doped Zinc Oxide

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Received 16 October 2015; accepted 22 November 2015; published 25 November 2015

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Abstract

Photocatalysis has been predicted as a promising technology for waste water treatment. N-doped zinc oxide has been used as an effective catalyst for carrying out number of chemical reactions, but limited work has been reported on use of N-doped ZnO as photocatalyst. In the present work, the photocatalytic degradation of Azure A was carried out in the presence of N-doped zinc oxide and the progress of the reaction was observed spectrophotometrically. The morphologies and structures of the as-synthesized nanomaterials were investigated by using FT-IR and DRS techniques. On the basis of observations, a tentative mechanism has been proposed for the photocatalytic degradation of dye.

Keywords

Azure A, Nanoparticles, N-Doped Zinc Oxide, Photocatalysis

1. Introduction

Water pollution is a serious threat for the environment. The sources of pollutants are generally textile and chemical industries using organic dyes. Therefore, methods for treatments of such polluted water are required. The waste water flows in the drains corrodes and incrusts the sewerage pipes. If allowed to flow in drains and rivers, it also effects the quality of drinking water in hand pumps making it unfit for human consumption. It leads to leakage in drains increasing their maintenance cost. Such polluted water provides breeding ground for bacteria and virus. All the organic materials present in the wastewater from a textile industry have a great concern in water treatment.

Dye degradation is a process, in which the large dye molecules are broken into smaller molecules like water, CO₂ and mineral byproducts. The waste water that the industry releases contains some amount of these dye mo-

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lecules, which cause water pollution because many of them are non-reactive towards light, acids, bases and O_2 . So the colour of the material becomes permanent.

Photocatalysis is the addition of light to semiconductor generally metal oxides and sulphides, which results in moving electrons from valence band to conduction band. The electron hole pairs formed will react with O_2 and H_2O molecules to form superoxides anions and $\cdot OH$ radical, which have more oxidizing and reducing properties for the dye compounds used in many industries. Due to the importance of photocatalysis, researches are applying photocatalytic decomposition process to degrade the organic pollutants of industrial waste water before discharging it in mainstream.

Various metal oxide semiconductors, such as TiO_2 , ZnO , WO_3 and SnO_2 , have been studied and applied as photocatalysts. Among them, TiO_2 is considered the most efficient photocatalyst due to its abundant availability, cost-effectiveness and chemical stability. However, recent researches have shown that ZnO can be used as a more efficient photocatalyst compared with TiO_2 [1] [2]. An important characteristic is that ZnO contains various intrinsic defects. Introducing defects into ZnO structure can not only narrow the band gap to increase the solar light harvesting capability, but also bring many split energy gaps to set up a possible catalytic systems, which sense and shoot environmental contaminants [3] [4].

Kothari *et al.* [5] reported the photocatalytic degradation of evans blue, an azo dye and its mixture with amaranth in presence of ZnO . Photocatalytic mineralization of methylene blue using buoyant TiO_2 -coated polystyrene beads was observed by Fabiyi and Skelton [6]. Ameta *et al.* [7] have used Iron(III) oxide for photobleaching of methylene blue, crystal violet and malachite green. Punjabi *et al.* [8] observed the reduction of Congo red by ascorbic acid and EDTA over CdS as a photocatalyst. Increase in photocatalytic activity of ZnO was reported by Benjamin *et al.* [9] by coating it with some natural pigments.

Egzar *et al.* [10] carried out the photocatalytic degradation of aniline blue dye using different semiconductors such as ZnO , ZnS and SnO_2 . Photocatalytic degradation of various dyes *i.e.* orange-II, orange-G, Congo red, indigo carmine, crystal violet and malachite green has been reported by Hachem *et al.* [11]. Pare *et al.* [12] carried out the photocatalytic degradation of lissamine fast yellow in the aqueous suspension of ZnO under artificial light. The photocatalytic bleaching of eosin using ZnO and effect of surface charge was investigated by Vyas *et al.* [13]. Ameta *et al.* [14] carried out the photodegradation of naphthol green B dye using antimony trisulphide as a heterogeneous catalyst.

Attia [15] has reported the photocatalytic oxidation of iodide ion in the aqueous suspension of zinc oxide and its sensitization with riboflavin where as Habibi and Askari [16] used Mn-doped ZnO nanocomposite thin film coated on glass by a simple spin-coating method to degrade an azo textile dye. Ahmad *et al.* [17] synthesized Al-doped ZnO photocatalysts with different Al concentrations (0.5 - 6.0 mol%). Their results showed that this photocatalyst doped with 4.0 mol% Al exhibited five times enhanced photocatalytic activity compared to pure ZnO . Peng *et al.* [18] have prepared Ag-sensitized ZnO and compared the activity of ZnO and Ag/ZnO . They found that Ag/ZnO showed better photocatalytic performance under simulated solar light for the degradation of phenol and methyl orange.

2. Material and Method

2.1. Preparation of ZnO Nanoparticles

Zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] (131.6 g) was added to 3 L of deionized water under vigorous stirring till homogeneous solution was obtained. Then 172.8 g of sodium dodecyl sulphate (SDS) and 0.2 M of sodium hydroxide were added into the above solution under continuous stirring till pH value reached 12 and heated at $160^\circ C$ for 14 h in an oven. The precipitates were recovered by centrifugation and washed with deionized water and ethanol several times [19]. The product was dried at $60^\circ C$ for 3 h and labelled as uncalcined zinc oxide (Znc). A portion of this product (10 g Znc) was calcined at $400^\circ C$ for 4 h, cooled to room temperature, ground in agate mortar and labelled as calcined zinc oxide (Zc). At the end of the reaction, sodium dodecyl sulfate (SDS) and CH_3COONa were eliminated during washing of $Zn(OH)_2$. The final yield of ZnO was 90%.

2.2. Preparation of Nitrogen-Doped ZnO

The N-doped ZnO was synthesized in a solvent free reaction. 20 g of uncalcined zinc oxide was added to 40 g of urea and grinded in an agate mortar. The mixture was calcined in a ceramic crucible at $400^\circ C$ for 4 h and cooled [20]. The product was ground to fine powder and labeled as nitrogen-doped zinc oxide (NZ).

3. Characterization of Compound

3.1. Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR analysis of both the prepared samples were done using Bruker FT-IR. FT-IR results showed an absorption peak at $450 - 540 \text{ cm}^{-1}$ and 1562 cm^{-1} , which confirmed the presence of ZnO nanoparticles [21]-[24]; another intense, broad peak near 3360 cm^{-1} represented the hydrogen bonded O-H stretching vibration [25]. Strong peaks obtained at 1562 cm^{-1} and at 1404 cm^{-1} confirmed the presence of hydrolyzed particles.

3.2. Diffuse Reflectance Spectroscopy (DRS)

As-prepared pure ZnO and N-doped ZnO were analyzed by DRS to know the band gap. DRS analysis was done using UV Vis spectrophotometer with DRS, Model UV vis-3000+, Lab-India. The samples were run with the mixture of dry BaSO_4 at room temperature. It was found in DRS results that the band gap of pure ZnO was 3.4 eV and it was 3.2 eV for N-doped ZnO. It confirms the reduction of band gap by doping ZnO with nitrogen, as a consequence N-doped ZnO was found better in compare to pure ZnO for degradation of Azure A.

3.3. Scanning Electron Microscope (SEM)

SEM were recorded on SEM Jeol Japan make, 5610LV model of undoped as well as nitrogen doped Zinc Oxide (Figure 1 and Figure 2). It is clearly from micrograph that undoped Zinc Oxide was larger in size as compared to nitrogen doped Zinc Oxide. These, it may be concluded that nitrogen doping of Zinc Oxide reduces its particle size. It was substantiated by XRD data where particle size of undoped ZnO is 45.31 nm and it was reduced to 29.16 nm after doping.

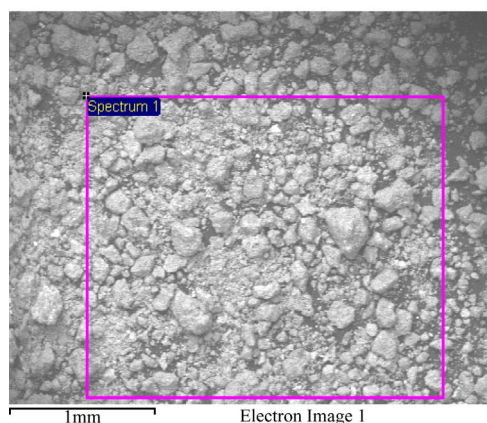


Figure 1. SEM undoped ZnO.

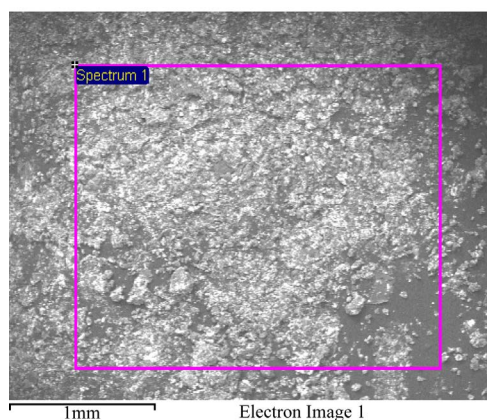


Figure 2. SEM nitrogen doped ZnO.

4. Experiment

Azure A dye and semiconducting N-doped zinc oxide powder were used in the present investigation of AR grade. All the solutions were prepared in doubly distilled water. The photocatalytic degradation of the dye was observed by taking dye solution and zinc oxide together. Irradiation was carried out by keeping the whole assembly exposed to a 200 W Tungsten lamp (Philips; light intensity = $50.0 \text{ mW}\cdot\text{cm}^{-2}$). The intensity of light at various distances from the lamp was measured with the help of a solarimeter. The pH of the solutions was measured with the help of digital pH-meter.

0.02918 g of Azure A was dissolved in 100 mL of doubly distilled water to prepare their $1.0 \times 10^{-3} \text{ M}$ solution, which was used as stock solution. The stock solution was further diluted as and when required. The absorbance of the dye solution were determined with the help of a spectrophotometer at $\lambda_{\text{max}} = 620 \text{ nm}$ for Azure A. The progress of reaction was observed by measuring absorbance of the reaction mixture at regular time interval during exposure. Decreasing trend of absorbance showed that dye was degraded during this process.

A decrease in absorbance of Azure A solution was observed with increasing time of exposure. A plot of $1 + \log A$ against time was found linear for pure ZnO and nitrogen doped ZnO, which indicates that the degradation of Azure A follows pseudo-first order kinetics. The rate constant was measured with the help of Equation (1).

$$k = 2.303 \times \text{slope} \quad (1)$$

4.1. Azure A

Azure A is an organic compound with the chemical formula $\text{C}_{14}\text{H}_{14}\text{ClN}_3\text{S}$ (Figure 3). It is a light blue to dark blue dye. It is used for screening test for mucopolysaccharides. It is also known as Giemsa stain, Azure A chloride and dimethylthionine.

IUPAC name	(7-Amino-8-methyl-phenothiazin-3-ylidene)-dimethyl-ammoniumchloride
Molecular formula	$\text{C}_{14}\text{H}_{14}\text{ClN}_3\text{S}$
Molecular weight	$291.80 \text{ g}\cdot\text{mol}^{-1}$
Appearance	Green to dark brown powder
Solubility	Water

5. Results and Discussion

Various factors, which affect degradation of Azure A dye have been studied to get the condition for optimum degradation rate.

5.1. Effect of pH

The effect of pH on the rate of degradation of N-doped ZnO was investigated in the pH range 6.0 to 10.0. The results are reported graphically in Figure 4.

[Azure A] = $1.6 \times 10^{-5} \text{ M}$, N-doped ZnO = 0.10, Light intensity = $60.0 \text{ mW}\cdot\text{cm}^{-2}$.

It has been observed that the rate of photocatalytic degradation of Azure A increases as pH was increased and it attained optimum value at pH 8.0. The rate was decreased when pH of the dye solution was further increased. It may be due to the fact that on increasing the pH of the solution, there is an attraction between cationic dye molecule and negatively charged OH^- ions. But, at higher pH, the cationic dye molecules convert into neutral form and hence, there is less attraction between neutral dye molecule and negatively charged surface of semiconductor. As a result, the rate was retarded.

5.2. Effect of Azure A Concentration

The effect of dye concentration was observed by taking different concentrations of Azure A. The results are shown in Figure 5.

pH = 8.0, N-doped ZnO = 0.10 g, Light intensity = $60.0 \text{ mW}\cdot\text{cm}^{-2}$.

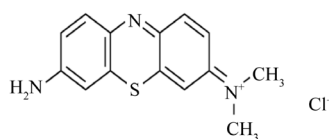


Figure 3. Structure of Azure A.

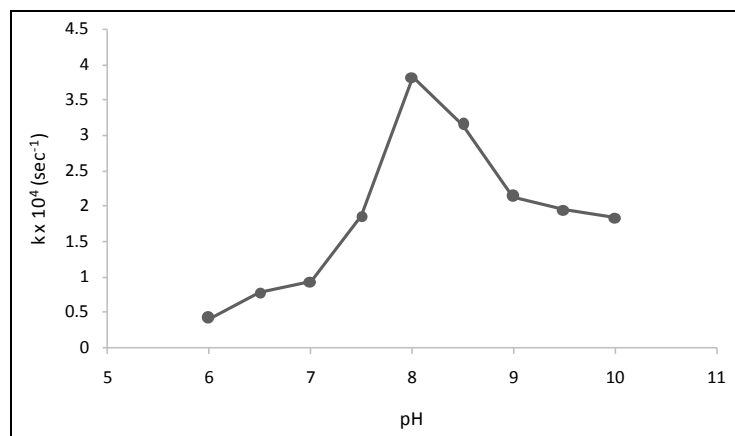


Figure 4. Effect of pH.

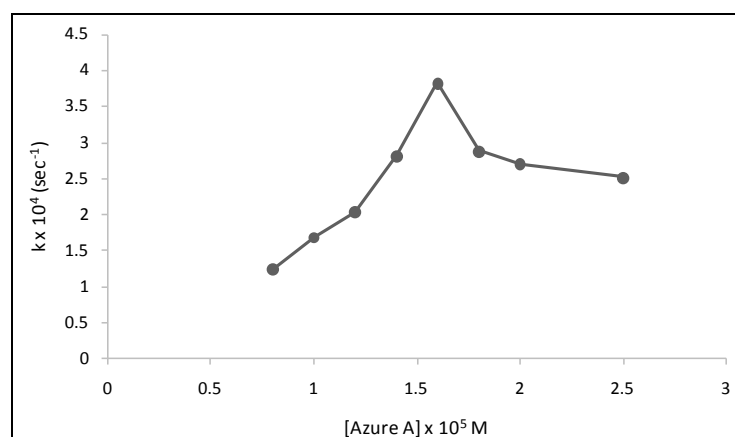


Figure 5. Effect of Azure A concentration.

It was observed that the rate of photocatalytic degradation of dye increases on increasing the concentration of Azure A upto 1.60×10^{-5} M. It may be attributed to the fact that as the concentration of the Azure A was increased, more dye molecules were available for excitation and consecutive energy/electron transfer and hence, an increase in the rate of degradation of the dye was observed. There was a decrease in degradation rate on increasing the concentration of dye above 1.6×10^{-5} M. This may be due to the fact that after a particular concentration, the dye may start acting as an internal filter and it will not permit the sufficient light intensity to reach the surface of the photocatalyst at the bottom of reaction vessel.

5.3. Effect of Amount of Semiconductor

The amount of semiconductor may also affect the degradation of dye and hence, different amounts of N-doped ZnO were used. The results are reported in **Figure 6**.

pH = 8.0, [Azure A] = 1.6×10^{-5} M, Light intensity = $60.0 \text{ mW} \cdot \text{cm}^{-2}$.

The rate of reaction was found to increase on increasing the amount of semiconductor, N-doped zinc oxide. The rate of degradation reached to its optimum value at 0.10 g of the photocatalyst, because as the amount of the

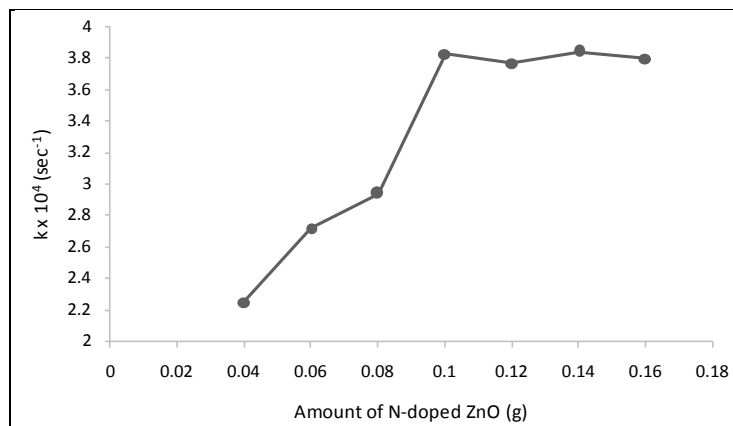


Figure 6. Effect of amount of N-doped ZnO.

semiconductor was increased, it provides more exposed surface area for degradation of dye molecules. Beyond 0.10 g, the rate of reaction becomes almost constant. After a particular value (0.10 g), an increase in the amount of semiconductor will only increase the thickness of layer of the semiconductor and not its exposed surface area. This was confirmed by taking reaction vessels of different sizes. It was observed that this point of saturation was shifted to a higher value for vessels of larger volumes while a reverse trend was observed for vessels of smaller capacities.

5.4. Effect of Light Intensity

The effect of light intensity on the photocatalytic degradation of Azure A was also investigated. The light intensity was varied by changing the distance between the light source and the exposed surface area of semiconductor. The results are given in Figure 7.

pH = 8.0, [Azure A] = 1.6×10^{-5} M, N-doped ZnO = 0.10 g.

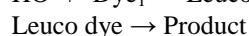
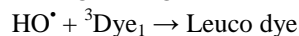
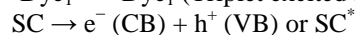
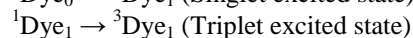
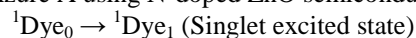
These data indicate that photocatalytic degradation of Azure A was enhanced with the increase in intensity of light, because an increase in the light intensity will increase the number of photons striking per unit area per unit time of photocatalyst surface. There was a slight decrease in the rate of reaction as the intensity of light was increased beyond $60.0 \text{ mW} \cdot \text{cm}^{-2}$.

5.5. A Typical Run

After keeping the values of the above parameters constant for maximum rate constant, a typical run was observed for the photocatalytic degradation of the dye. The results are shown in Table 1 and graphically presented in Figure 8. Here, a comparative observation was made for pure ZnO and N-doped ZnO, which confirms that the rate was almost six times increased in the case of N-doped ZnO in compare to pure ZnO.

6. Mechanism

On the basis of above observations, a tentative mechanism is proposed for the photocatalytic degradation of Azure A using N-doped ZnO semiconductor.



Azure A absorbs radiations of suitable wavelength and gives rise to its excited singlet state. Then it undergoes intersystem crossing (ISC) to give the triplet state of the dyes. On the other hand, the semi-conducting N-doped ZnO utilizes the radiant energy to excite its electron from valence band to the conduction band; thus, leaving behind a hole. This hole abstracts an electron from OH^- ions to generate ${}^-\text{OH}$ radicals. These radicals further

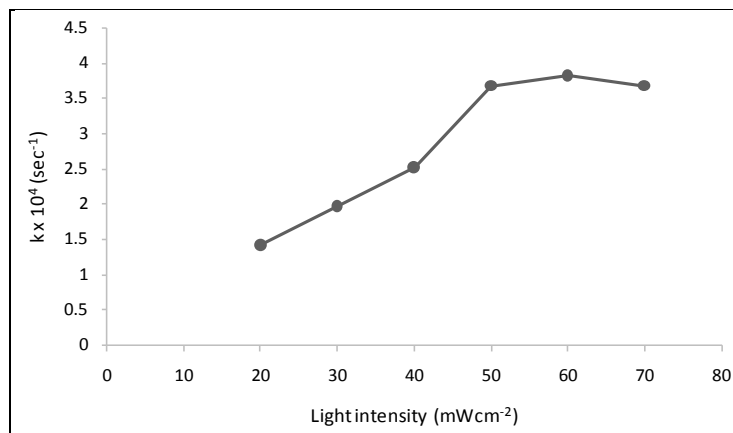


Figure 7. Effect of light intensity.

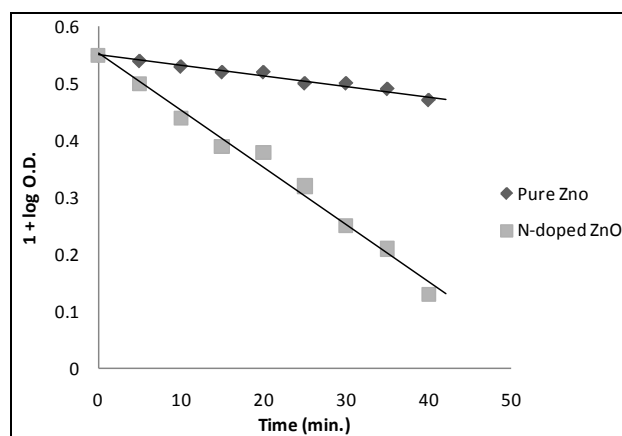


Figure 8. A typical run.

Table 1. A typical run.

Time (min.)	Pure ZnO (O.D.)	1 + log O.D.	N-doped ZnO (O.D.)	1 + log O.D.
0	0.356	0.55	0.356	0.55
5	0.347	0.54	0.318	0.50
10	0.339	0.53	0.278	0.44
15	0.337	0.52	0.249	0.39
20	0.333	0.52	0.241	0.38
25	0.322	0.50	0.213	0.32
30	0.317	0.50	0.178	0.25
35	0.300	0.49	0.163	0.21
40	0.301	0.47	0.138	0.13

pH = 8.0, [Azure A] = 1.6×10^{-5} M, N-Doped ZnO = 0.10 g, Light intensity = $60 \text{ mW}\cdot\text{cm}^{-2}$; Rate constant (k) for Pure ZnO = $0.60 \times 10^{-4} \text{ sec}^{-1}$ and for N-doped ZnO = $3.83 \times 10^{-4} \text{ sec}^{-1}$.

oxidize the Azure A dye to its leuco form, which may ultimately degrade to products. The participation of $\cdot\text{OH}$ radicals as an active oxidizing species was confirmed by using hydroxyl radical scavenger 2-propanol, where the rate of degradation was drastically reduced.

7. Conclusion

Nitrogen doped zinc oxide was prepared by precipitation method by doping pure ZnO with urea and further the as-prepared samples were characterized by FT-IR, DRS and SEM techniques. Different rate affecting parameters like pH, dye concentrations, catalyst amount and light intensity were studied for the dye degradation. The observations revealed that Azure A dye could be degraded successfully by using N-doped ZnO under visible light. In comparative study, we found that the N-doped ZnO has shown six times enhanced photocatalytic activity than pure ZnO.

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