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ENHANCEMENT OF PHOTOCATALYTIC ACTIVITY OF ZINC OXIDE BY DOPING WITH NITROGEN

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ABSTRACT

The photocatalytic activity of pure ZnO and nitrogen doped ZnO was compared by investigating the photodegradation of azure B dye under visible light. The nanophotocatalysts pure ZnO and N-doped ZnO was prepared by precipitation method. The morphologies and structural properties of as-synthesized nanomaterials were investigated by using FT-IR, DRS, XRD and SEM techniques. The results revealed that the N-doped zinc oxide photocatalyst showed higher photocatalytic activity compared to pure zinc oxide. Different rate affecting parameters were also studied.

Key words: ZnO, N-doped ZnO, Photocatalysis, Azure B.

INTRODUCTION

Water pollution is a serious threat for the environment. The sources of pollutants are generally textile and chemical industries. Therefore, methods of treatment of polluted water are urgently required. The waste water flows in the drains corrodes and incrusted the sewerage pipes. If allowed to flow in drains and rivers, it effects the quality of drinking water making it unfit for human consumption. It also leads to leakage in drains increasing their maintance cost. Such polluted water also 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, CO_2 and mineral by products. The waste water that the industry releases contains some amount of these dye molecules, 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 a 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 $^{\bullet}OH$ radical, which have more reducing and oxidizing properties for the dye compounds used in many industries. Photocatalytic

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decomposition process may be applied to degrade the organic pollutants of industrial waste water before discharging it in mainstream.

Nanostructured semiconductors are useful for the decomposition of organic dyes[1] because they have a strong oxidizing ability i.e. hydroxyl radical ($^{\bullet}OH$). Many metal oxides like ZnO, TiO_2, WO_3, $SrTiO_3$, Fe_2O_3 etc. have been used as photocatalyst to decompose various organic dyes.

ZnO nano-particles are very useful for the water detoxification due to the following reasons:

- It produces H_2O_2 more efficiently and shows high rate of mineralization.
- It provides high surface for reaction due to higher number of active sites[2].
- It is better photocatalyst as compared to TiO_2 because it absorbs high efficiency with solar light and have higher rates of activities.
- It is inexpensive.
- It is non-toxic in nature.
- It exhibits tunable properties, which can be modified by size reduction, doping, sensitizers, etc.

Band-gap energies for several common semiconductor materials are given as below[3,4].

Semiconductor	**Band-gap energy (eV)**
Diamond	5.4
TiO_2	3.0~3.2
WO_3	2.7
ZnO	3.2
SnO_2	3.5
$SrTiO_3$	3.4
Fe_2O_3	2.2
CdS	2.4
ZnS	3.7
CdSe	1.7
GaP	2.3
GaAs	1.4
SiC	3.0

Baruah et al.[5] have reported that heterogeneous photocatalytic systems *via* metal oxide semiconductors like TiO_2 and ZnO, are capable of operating effectively and efficiently for waste water treatment, which has been discussed along with other nanotechnology routes that can be useful for water treatments. Multifunctional photocatalytic membranes using ZnO nanostructures are considered beneficial over freely suspended nanoparticles due to their easy removal from the purified water.

Tiwari et al.[6] reported nanotechnology as a better option for water purification and for removal of pollutants and germs. Nanoparticles, nanomembrane and nanopowder used for detection and removal of chemical and biological substances like metals (e.g. cadmium, copper, lead, mercury, nickel, zinc), nutrients (e.g. phosphate, ammonia, nitrate and nitrite), cyanide, organics, algae (e.g. cyanobacterial toxins) viruses, bacteria, parasites and antibiotics. Basically four classes of nanoscale materials can be used as functional materials for water purification e.g. metal-containing nanoparticles, carbonaceous nanomaterials, zeolites and dendrimers. Carbon nanotubes and nanofibers also show some good results. Nanomaterials reveals good result than other techniques used because of their high surface area (surface/volume ratio). It was suggested that these may be used in future at large scale for water purification.

Colour is the main attraction of any fabric[7]. No matter how excellent its constitution, if unsuitably coloured, it is bound to be a failure as a commercial fabric. Manufacture and use of synthetic dyes for fabric dyeing has become a massive industry today. Synthetic dyes have provided a wide range of colourfast, bright hues. However, their toxic nature has become a cause of grave concern to environmentalists. Use of synthetic dyes has an adverse effect on all forms of life. Presence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, cobalt and certain auxiliary chemicals all collectively make the textile effluent highly toxic. Other harmful chemicals present in the water may be formaldehyde based dye fixing agents, chlorinated stain removers, hydrocarbon based softeners, non-biodegradable dyeing chemicals. These organic materials react with many disinfectants especially chlorine and form by products (DBP'S) that are often carcinogenic and therefore, undesirable. Many of these show allergic reactions. The colloidal matter present along with colours and oily scum increases the turbidity, gives the water a bad appearance, foul smell and prevents the penetration of sunlight necessary for the process of photosynthesis. This interferes with the oxygen transfer mechanism at air water interface, which in turn interferes with marine life and self purification process of water. This effluent, if allowed to flow in the fields', clogs the pores of the soil resulting in loss of soil productivity. If allowed to flow in drains and rivers, it affects the quality of drinking water in hand pumps making it unfit for human consumption. It is important to remove these pollutants from the waste waters before their final disposal.

Zee et al.[8] carried out the decolourisation of 20 selected azo dyes by granular sludge from an upward-flow anaerobic sludge bed (UASB) reactor. Complete reduction was found for all azo dyes tested, generally yielding colourless products. The reactions followed first-order kinetics and reaction rates varied greatly between dyes: half-life times ranged from 1 to about 100 hr. The slowest reaction rates were found for reactive dyes with a triazine reactive group. Since granular sludge contains sulphide, eight dyes were also monitored for direct chemical decolourisation by sulphide. All these dyes were reduced chemically albeit at slower rates than in the presence of sludge at comparable sulphide levels. Increasing sulphide concentrations, even when present in huge excess, stimulated the azo reduction rate. The results indicate that granular sludge can decolourise a broad spectrum of azo dye structures due to non-specific extracellular reactions.

Meng and Juan[9] reported that zinc oxide is an excellent photocatalytic oxidation material. It has been widely used to deal with wastewater, such as pharmacy wastewater, printing and dyeing wastes, papermaking wastewater, and so on. The catalytic activity of nano-ZnO is much better than normal materials. It can also absorbs the light in wider spectrum.

Material and method

Preparation of ZnO nanoparticles

Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) (13.16 g) was added to 3 L of deionized water under vigorous stirring till homogeneous solution was obtained. Then 17.28 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°C for 14 hr in an oven. The precipitates were recovered by centrifugation and washed with deionized water and ethanol several times[10]. The product was dried at 60°C for 3 hr and labelled as uncalcined zinc oxide (Znc). A portion of this product (10 g Znc) was calcined at 400°C for 4 hr, cooled to room temperature, ground in agate mortar and labelled as calcined zinc oxide (Zc). At the end of the reaction, sodium dodecyl sulphate (SDS) and CH_3COONa were eliminated during washing of $Zn(OH)_2$. The final yield of ZnO was 90%.

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°C for 4 hr and cooled[11]. The product was ground to fine powder and labeled as nitrogen-doped zinc oxide (NZ).

Characterization of as-prepared pure ZnO and N-doped ZnO

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 cm^{-1} and 1562 cm^{-1}, which confirmed the presence of ZnO nanoparticles[12-15]. Another intense, broad peak near 3360 cm^{-1} represented the hydrogen bonded O-H stretching vibration[16]. Strong peaks obtained at 1562 cm^{-1} and at 1404 cm^{-1}confirmed the presence of hydrolyzed particles.

Scanning electron microscope (SEM)

SEM were recorded on SEM Jeol Japan make, 5610LV model of undoped as well as nitrogen doped zinc oxide. It is clearly from micrograph that undoped zinc oxide was larger in size as compared to nitrogen doped zinc oxide. Thus, it may be concluded that nitrogen doping of zinc oxide reduces its particle size. It was substainated by XRD data where particle size of undoped ZnO is 45.31 nm and it was reduced to 29.16 nm after doping.

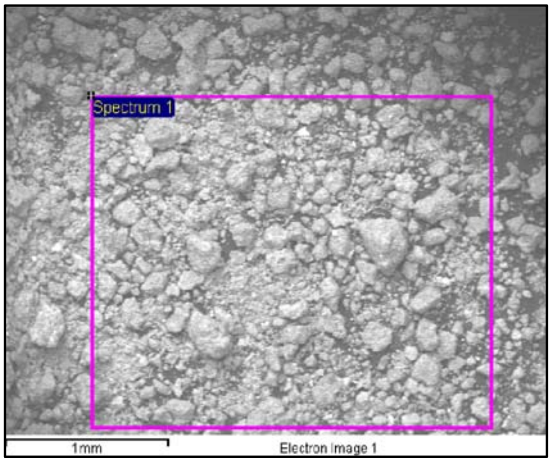

Fig. 1: SEM Undoped ZnO

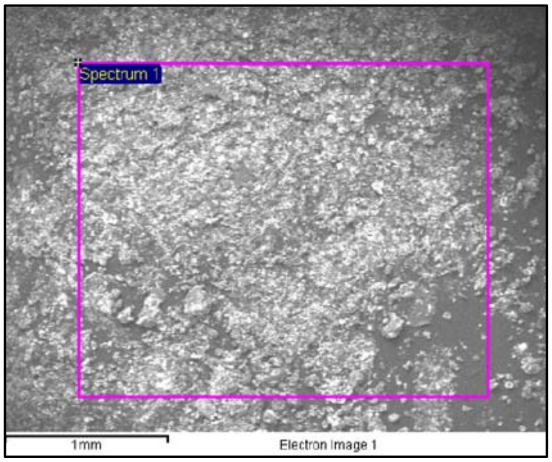

Fig. 2: SEM Nitrogen doped ZnO

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 confirmed 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 B.

X-Ray diffraction (XRD)

X-ray diffraction pattern of pure and nitrogen doped zinc oxide were recorded on a Philips X'pert pro MPD model X-ray diffractometer using Cu Kα radiation as the X-ray source. These are presented in Figs. 3 and 4, respectively. The particle size was calculated using Scherer equation:

$$D = K \lambda / \beta \cos \theta \qquad \ldots(1)$$

Where, D = Average particle size,

K = Scherer constant (0.9 for spherical particles),

Λ = Wavelength of X-ray used,

B = The peak width of half maximum and

θ = Bragg diffraction angle

The particle size of undoped ZnO was 45.31 nm while that for doped ZnO was 29.16 nm.

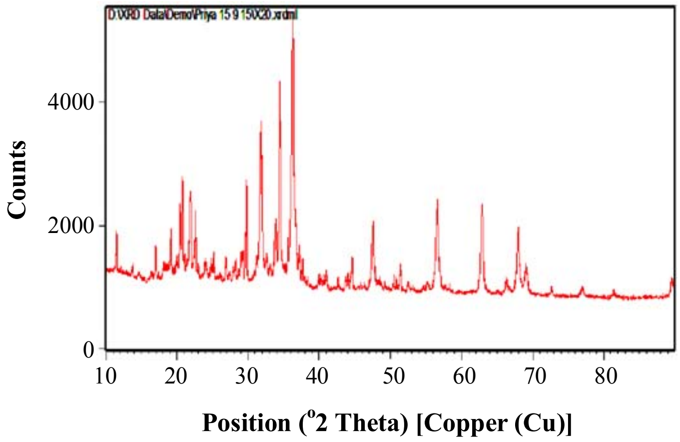

Fig. 3: XRD Spectra of undoped ZnO

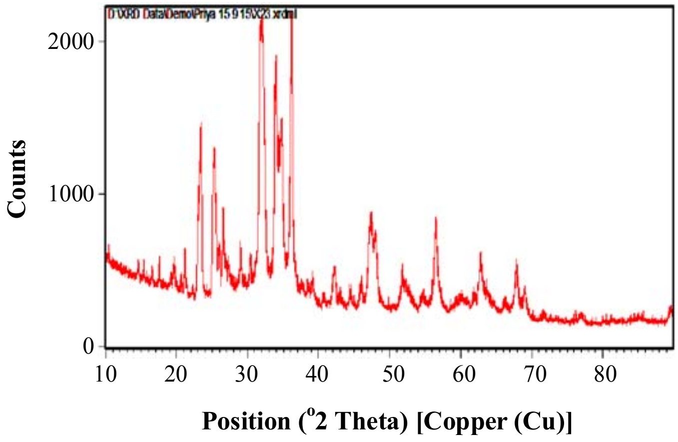

Fig. 4: XRD Spectra of nitrogen doped ZnO

Azure B

It is also called methylene azure B trimethylthionine chloride; a dye used in biological stain a component of polychrome Giemsa's stain for blood protozoa. Used for staining semi-thin sections of plant tissue. Azure, a methylated thiazine dye, is a metachromatic basic dye ranging from green (to chromosomes) and blue (to nucleoli and cytoplasmic ribosomes), to red color (to deposits containing mucopolysaccharides). There are many methylated homologues used as components of many polychrome stains in combination with eosin and methylene blue in pH adjusted solutions.

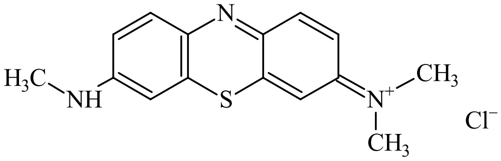

Fig. 5: Structure of Azure B

IUPAC Name	3-(Dimethylamino)-7-(methylamino)phenothiazin-5-ium chloride
Molecular formula	$C_{15}H_{16}ClN_3S$
Molecular weight	305.83 g mol^{-1}
Appearance	Dark green crystalline powder
Solubility	Soluble (sparingly soluble in alcohol)
λ_{max}	650 nm

EXPERIMENTAL

Azure B dye has been used as a model system in the present investigation to compare the photocatalytic activity of pure ZnO and N-doped ZnO. All the solutions were prepared in doubly distilled water. Irradiation was carried out by keeping the whole assembly exposed to a 200 W tungsten lamp (Philips; light intensity = 70.0 $mWcm^{-2}$). The intensity of light at various distances from the lamp was measured with the help of a solarimeter. The pH of the solution was measured with the help of digital pH-meter. 0.0306 g of azure B was dissolved in 100.0 mL of doubly distilled water to prepare its 1.0×10^{-3} M solution, which was used as stock solution. The stock solution was further diluted as and when required. The absorbance of azure B dye solution was determined with the help of a spectrophotometer at λ_{max} = 650 nm. The progress of reaction was observed by measuring absorbance of the reaction mixture containing dye and semiconductor at regular time intervals during exposure. Decreasing trend of absorbance showed that dye was degraded during this process.

A decrease in absorbance of azure B solution was observed with increasing time of exposure. A plot of 1 + log A against time were found linear for pure ZnO and nitrogen doped ZnO, which indicates that the degradation of azure B follows pseudo-first order kinetics. The rate constant was measured with the help of equation 2.

$$K = 2.303 \text{ x Slope} \qquad \ldots(2)$$

RESULTS AND DISCUSSION

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

Effect of pH

The effect of pH on the rate of degradation of N-doped ZnO was investigated in the pH range 7.0 to 10.5. The results are reported in Table 1 and graphically represented in Fig. 6.

Table 1: Effect of pH

[Azure B] = 3.60×10^{-5} M, N-doped ZnO = 0.10 g, Light intensity = 70.0mWcm^{-2}

pH	Rate constant (k) × 10^4 (sec^{-1})
7.0	0.76
7.5	0.82
8.0	1.28
8.5	2.26
9.0	2.73
9.5	3.50
10.0	**4.19**
10.5	2.83

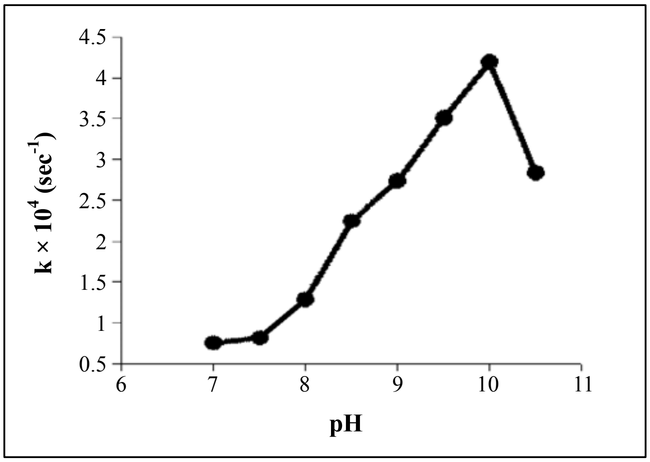

Fig. 6: Effect of pH

It has been observed that the rate of photocatalytic degradation of azure B increases as pH was increased and it attained optimum value at pH 10.0. 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.

Effect of Azure B concentration

Effect of variation of dye concentration on the rate of reaction was also studied by taking different concentration of azure B solution. The results are tabulated in Table 2 and graphically represented in Fig. 7.

Table 2: Effect of Azure B concentration

pH = 10.0, N-doped ZnO = 0.10 g, Light intensity = 70.0 mWcm^{-2}

[Azure B] × 10^5 M	Rate constant (k) × 10^4 (sec^{-1})
2.80	2.09
3.00	2.35
3.20	3.09
3.40	3.34
3.60	**4.19**
4.00	3.19
4.20	2.50

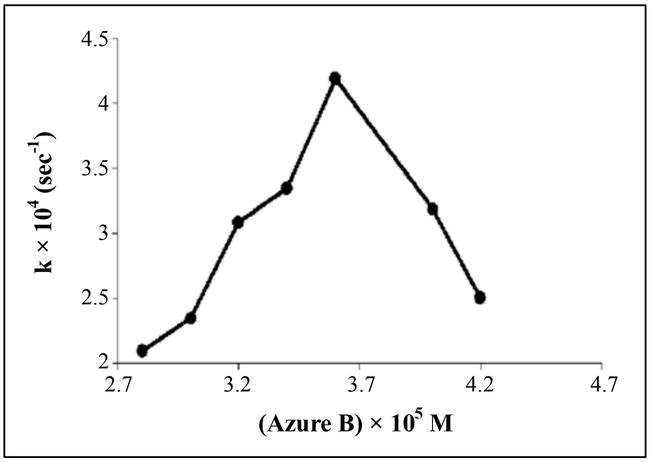

Fig. 7: Effect of Azure B concentration

It was observed that the rate of photocatalytic degradation of dye increases on increasing the concentration of azure B upto 3.60 × 10^{-5} M. It may be attributed to the fact that as the concentration of the azure B 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 increasingthe concentration of dye above 3.60 × 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.

Effect of amount of N-doped ZnO

The effect of amount of N-doped zinc oxide on the rate of photodegradation of azure B was observed by keeping all other factors identical. The results are tabulated in Table 3 and graphically represented in Fig. 8. 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 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.

Table 3: Effect of amount of N-Doped ZnO

pH = 10.0, [Azure B] = 3.60×10^{-5} M, Light intensity = 70.0 $mWcm^{-2}$

N-doped ZnO (g)	Rate constant (k) × 10^4 (sec^{-1})
0.04	2.10
0.06	2.85
0.08	3.24
0.10	**4.19**
0.12	4.17
0.14	4.20
0.16	4.18

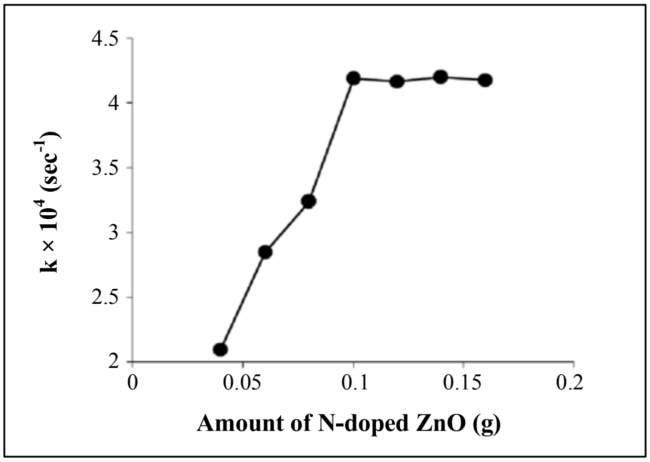

Fig. 8: Effect of amount of N-Doped ZnO

Effect of light intensity

The effect of light intensity on the photodegradation of azure B was also observed. The results obtained are reported in Table 4 and graphically presented in Fig. 9.

Table 4: Effect of light intensity

pH = 10.0, [Azure B] = 3.60×10^{-5} M, N-doped ZnO = 0.10 g

Light intensity ($mWcm^{-2}$)	Rate Constant (k) × 10^4(sec^{-1})
20.0	0.21
30.0	1.69
40.0	1.98
50.0	2.62
60.0	3.52
70.0	**4.19**

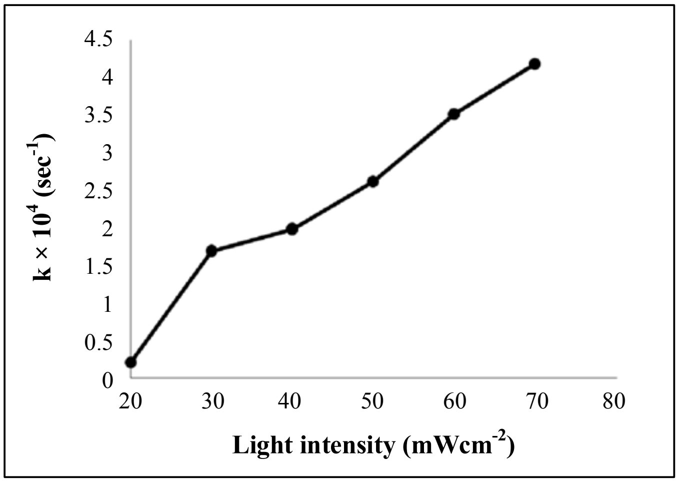

Fig. 9: Effect of light intensity

These data indicate that photocatalytic degradation of azure B 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 70.0 $mWcm^{-2}$ and therefore, it was avoided.

A typical run

After keeping the values of the above parameters constant for maximum rate constant, a typical run was observed for the photocatalytical degradation of the dye. The results are shown in Table 5 and graphically presented in Fig. 10. Here, a comparative observation was made for pure ZnO and N-doped ZnO, which confirmed that the rate was almost three times increased in the case of N-doped ZnO in compare to pure ZnO.

Table 5: A typical run

pH = 10.0, [Azure B] = 3.60 x 10^{-5} M, N-Doped ZnO = 0.10 g, Light intensity = 70.0 $mWcm^{-2}$

Time (min)	Pure ZnO (Abs.)	1 + log A	N-doped ZnO (Abs.)	1 + log A
0	0.75	0.87	0.75	0.87
10	0.58	0.82	0.66	0.76
20	0.45	0.80	0.64	0.65
30	0.36	0.76	0.58	0.56
40	0.27	0.73	0.54	0.43
50	0.20	0.70	0.51	0.31
60	0.16	0.68	0.48	0.22
70	0.11	0.65	0.45	0.05

Rate constant (k): For Pure ZnO = 1.50 x 10^{-4} sec^{-1} and N-doped ZnO = 4.19 x 10^{-4} sec^{-1}

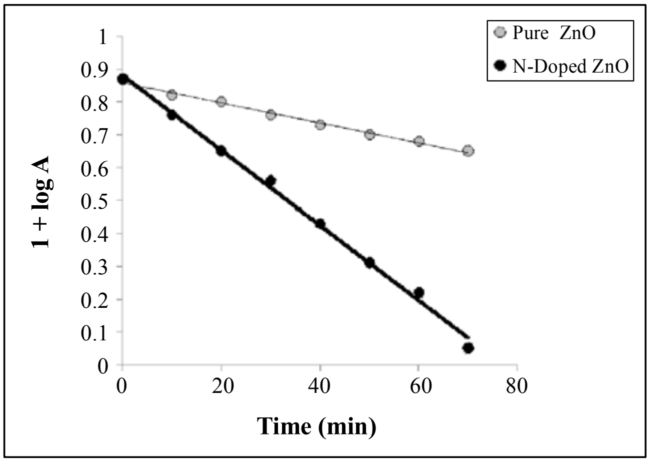

Fig. 10: A typical run

Mechanism

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

$$^1AB_0 \xrightarrow{h\nu} {}^1AB_1 \text{ (Singlet excited state)}$$

$$^1AB_1 \xrightarrow{ISC} {}^3AB_1 \text{ (Triplet excited state)}$$

$$SC \xrightarrow{h\nu} e^-(CB) + h^+(VB) \text{ or } SC^*$$

$$h^+ + {}^-OH \longrightarrow {}^\bullet OH$$

$$HO^\bullet + {}^3AB_1 \longrightarrow \text{Leuco dye}$$

$$\text{Leuco dye} \longrightarrow \text{Product}$$

Azure B 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 $^\bullet OH$ radicals. These radicals further oxidize the azure B dye to its leuco form, which may ultimately degrade to products. The participation of $^\bullet OH$ radicals as an active oxidizing species was confirmed by using hydroxyl radical scavenger 2-propanol, where the rate of degradation was drastically reduced.

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, SEM-EDX 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 B dye could be degraded successfully by using N-doped ZnO under visible light. In comparative study, it was found that the N-doped ZnO has shown three times enhanced photocatalytic activity than pure ZnO.

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