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PREPARATION AND APPLICATION OF CARBON DOPED ZINC OXIDE AS PHOTOCATALYST

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ABSTRACT

In the present work, carbon doped ZnO has been prepared and used as a photocatalyst to degrade new fuchsin. The rate of photocatalytic degradation of the dye was monitored spectrophotometrically. The effect of variation of different parameters, such as pH, dye concentration, amount of photocatalyst and light intensity on the rate of photocatalytic degradation of the dye was observed. A tentative mechanism for the photocatalytic degradation of new fuchsin has also been proposed.

Key words: Photocatalytic degradation, C-Doped zinc oxide, New fuchsin.

INTRODUCTION

Water pollution is a major problem all over the globe, which is mainly caused by the effluents discharged by various industries in their near by natural water resources. These effluents from different dyeing, textile and printing industries pollute the water. This polluted water can not be used for drinking, cleaning, irrigation and other useful purposes.

The significance of the wastewater treatment, management and its disposal gradually increases in the modern times and it becomes a major concern for public health scientific interest. All existing protocols for treatment of wastewater are categorized as physical, chemical and biological processes.[1] The sequential and concurrent use of those processes combinedly tends to create a greater efficient method in removing the pollutant aspects in liquid residues. Restrictions in terms of execution, efficiency, and price are a factor, however, biological processes, as an example, have been extensively used and show potential towards dairy and agricultural wastewater treatment.[2] The chemical process deals with the photocatalysts like TiO_2, ZnO etc. mediated degradation of the industrials waste waters.[3] These processes have limitations, which can potentially affect degradation efficiency through control pH range, rapid organic-load variations, and also the effluent's physicochemical behavior.[4]

The use of a heterogeneous photocatalyst is a conventional method for water purification, which includes reduction and oxidation reactions from adsorbed wastewater, oxygen molecules and hydroxyl

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anions, or other organic molecules.[5,6] Uses of semiconductors like TiO_2, ZnO ZnS,WO_3 etc. in photocatalysis employ semiconductors in suspension. Integral to this study, it was an assessment of the efficiency of heterogeneous photocatalyst processes for dairy and agricultural wastewater treatment with immobilized TiO_2 and ZnO to reduce organic pollutant load.[7] Semiconductor catalysts TiO_2 and ZnO have been widely used to mineralize harmful organic pollutants in wastewater into less damaging inorganic non-toxic compounds like CO_2, HCl and water.[8]

Nanosized TiO_2 and ZnO photocatalysts in the form of nanorods, nanospheres, thin porous films, nanofibers and nanowires have been utilized in various applications, including photocatalysis because of their high activity, low cost and environmental safety.[9-11] Interestingly, very high surface to volume ratio of nanostructures make them efficient for photocatalysis and other application. In recent studies, authors have reported that zinc oxide and titanium dioxide have excellent photocatalytic properties and both catalysts are designated to be capable substrates for photodegradation of dyes.[12]

Kothari et al.[13] reported the photocatalytic degradation of evans blue, an azo dye and its mixture with amaranth in presence of ZnO. Egzar et al.[14] carried out the photocatalytic degradation of aniline blue dye using different semiconductors such as ZnO, ZnS and SnO_2. Increase in photocatalytic activity of ZnO was reported by Benjamin et al.[15] by coating it with some natural pigment. Yang et al.[16] synthesized SnO_2/ZnO/TiO_2 composite photocatalyst and tested its photocatalytic activity for photodecomposition of methyl orange under both; visible and UV light irradiations. Gandhi et al.[17] studied the ZnS-CdS catalyzed photocatalytic bleaching of malachite green and brilliant green dyes. Pare et al.[18] 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.[19] Peng et al.[20] 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.

EXPERIMENTAL

Material and method

Preparation of ZnO nanoparticles

Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) (13.16 g) was dissolved in 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 160^0C 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 60^0C for 3 hr and labelled as uncalcined zinc oxide (Znc). A portion of this product (10 g Znc) was calcined at 400^0C 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 carbon-doped ZnO

The C-doped ZnO was synthesized in a solvent free reaction. 20 g of uncalcined zinc oxide was added to 40 g of glucose and grinded in an agate mortar. The mixture was calcined in a ceramic crucible at 400^0C for 4 hr and cooled. The product was ground to fine powder and labeled as carbon-doped zinc oxide (CZ).

New fuchsine

New fuchsine, is an organic compound with the formula $[(CH_3N(H)CH_3C_6H_3)_3C]Cl$. It is a magenta-colored solid that is used as a dye. It is prepared by condensation of N-methyl toluidine with xylidene in the presence of hydrochloric acid.

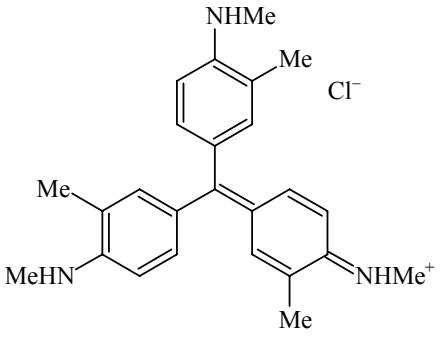

Fig. 1: Structure of new fuchsin

It is used to dye polyacrylonitrile, paper, and leather. New fuchsine can be used for staining acid fast organism, e.g. by Ziehl-Neelsen stain, and for making Schiff's reagent. As a primary amine, the dye can be diazotized in the laboratory, and the resulting diazonium salt used as a trapping agent in enzyme histochemistry.

New fuchsine dye has been used as a model system in the present investigation to compare the photocatalytic activity of pure ZnO and C-doped zinc oxide. 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 = 30.0 $mWcm^{-2}$). 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 new fuchsine 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 new fuchsine 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 solution was observed with increasing time of exposure. A plot of 1 + log A against time were found linear for pure ZnO and carbon doped ZnO, which indicates that the degradation of new fuchsine follows pseudo-first order kinetics. The rate constant was measured with the help of equation (1).

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

RESULTS AND DISCUSSION

Various factors, which affect degradation of new fuchsine 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 C-doped ZnO was investigated in the pH range 6.5 to 10. The results are reported in Table 1.

Table 1: Effect of pH

[New Fuchsine] = 3.80×10^{-5} M, C-doped ZnO = 0.06 g**,** Light intensity = 30.0 $mWcm^{-2}$

pH	Rate constant (k) × 10^4 (sec^{-1})
6.5	0.79
7.0	0.81
7.5	0.91
8.0	1.12
8.5	**1.49**
9.0	1.33
9.5	1.24
10	1.12

It has been observed that the rate of photocatalytic degradation of new fuchsin was increased as pH was increased and it attained optimum value at pH 8.5. 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 new fuchsin concentration

Effect of variation of dye concentration on the rate of reaction was also studied by taking different concentration of new fuchsine solution. The results are tabulated in Table 2.

Table 2: Effect of new fuchsine concentration

pH = 8.5, C-doped ZnO = 0.06 g**,** Light intensity = 30.0 $mWcm^{-2}$

[New fuchsine] × 10^5 M	Rate constant (k) × 10^4 (sec^{-1})
3.40	0.93
3.60	1.16
3.80	**1.49**
4.00	0.96
4.20	0.89
4.40	0.79
4.60	0.76

It was observed that the rate of photocatalytic degradation of dye was increased on increasing the concentration of new fuchsin upto 3.80×10^{-5} M. It may be attributed to the fact that as the concentration of the new fuchsin 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 3.80×10^{-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 C-doped ZnO

The effect of amount of C-doped zinc oxide on the rate of photodegradation of new fuchsine was observed by keeping all other factors identical. The results are tabulated in Table 3.

Table 3: Effect of amount of C-doped ZnO

pH = 8.5, [New fuchsine] = 3.80×10^{-5} M, Light intensity = 30.0 $mWcm^{-2}$

C-doped ZnO (g)	Rate Constant (k) × 10^4 (sec^{-1})
0.04	1.23
0.06	**1.49**
0.08	1.09
0.10	0.91
0.12	0.77
0.14	0.72
0.16	0.71

The rate of reaction was found to increase on increasing the amount of semiconductor, C-doped zinc oxide. The rate of degradation reached to its optimum value at 0.06 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 0.06 g, the rate of reaction becomes almost constant. After a particular value (0.06 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.

Effect of light intensity

The effect of light intensity on the photodegradation of new fuchsine was also observed. The results obtained are reported in Table 4.

Table 4: Effect of light intensity

pH = 8.5, [New fuchsine] = 3.80×10^{-5} M, C-doped ZnO = 0.06 g

Light intensity ($mWcm^{-2}$)	Rate constant (k) × 10^4 (sec^{-1})
20.0	0.98
30.0	**1.49**
40.0	1.17
50.0	1.06
60.0	0.91
70.0	0.72

These data indicate that photocatalytic degradation of new fuchsin 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 30.0 $mWcm^{-2}$.

A typical run

After keeping the values of the above parameters constant for maximum degradation rate of the dye, a typical run was observed for the photocatalytic degradation of the dye. The results are shown in Table 5 and graphically presented in Fig. 2. Here, a comparative observation has been made for pure ZnO and C-doped ZnO, which confirms that the rate was almost three times increased in the case of C-doped ZnO in compare to pure ZnO.

Table 5: A typical run

pH = 8.5, [New fuchsin] = 3.80 x 10^{-5} M, C-Doped ZnO = 0.06 g, Light intensity = 30.0 $mWcm^{-2}$

Time (min.)	Abs. Pure ZnO	1 + log Abs.	Abs. C-doped ZnO	1 + log Abs.
0	0.193	0.28	0.193	0.28
10	0.186	0.27	0.182	0.26
20	0.182	0.26	0.160	0.20
30	0.182	0.26	0.143	0.15
40	0.173	0.24	0.133	0.12
50	0.169	0.23	0.120	0.07
60	0.162	0.21	0.117	0.06

Rate constant (k): For pure ZnO = 0 .52 x 10^{-4} sec^{-1}; C-doped ZnO = 1.49 x 10^{-4} sec^{-1}

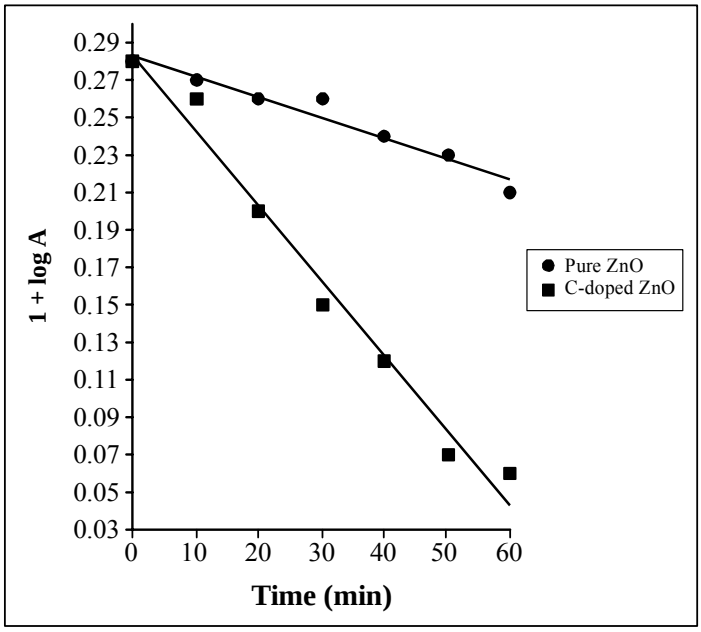

Fig. 2: A typical run

Mechanism

On the basis of the experimental observations, a tentative mechanism of photocatalytic degradation of new fuchsine can be proposed as-

New fuchsine absorbs radiation of suitable wavelengths and it is excited to its first singlet excited state followed by intersystem crossing (ISC) to triplet state. On the other hand, the semiconducting carbon doped zinc dioxide also utilize the incident light energy to excite its electron from valence band to conduction band; thus, leaving behind a hole. This hole may abstract an electron from hydroxyl ions to generate hydroxyl radicals. These hydroxyl radicals will then oxidize the dye molecules to harmless products. The participation of $^{\bullet}OH$ radical as an active oxidizing species was confirmed by using hydroxyl radical scavenger (2-propanol), where the rate of degradation was drastically reduced.

$$1\,NF0 \xrightarrow{hv} 1NF1 \quad \ldots(2)$$

$$1\,NF1 \xrightarrow{ISC} 3NF1 \quad \ldots(3)$$

$$SC \xrightarrow{hv} e^{-}\,(CB) + h^{+}\,(VB) \quad \ldots(4)$$

$$h^{+} + {}^{-}OH \longrightarrow {}^{\bullet}OH \quad \ldots(5)$$

$$^{\bullet}OH + 3NF1 \longrightarrow \text{Products} \quad \ldots(6)$$

CONCLUSION

C-doped zinc oxide was prepared by precipitation method by doping pure ZnO with glucose. Different rate affecting parameters like pH, dye concentrations, catalyst amount and light intensity were studied for the dye degradation. The observations revealed that new fuchsine dye could be degraded successfully by using C-doped ZnO under visible light. In comparative study, we found that the C-doped ZnO has shown three times enhanced photocatalytic activity than pure ZnO.

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