PHOTOCATALYTIC DEGRADATION OF AZURE A ON CARBON DOPED ZINC OXIDE

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ABSTRACT

The photocatalytic activity of pure ZnO and Carbon doped ZnO was compared by investigating the photodegradation of azure A under visible light. The reaction was monitored spectrophotmetrically. The effect of various parameters on the rate of reduction was observed. It was observed that carbon doped catalyst showed higher activity than the pure ZnO under visible light irradiation.

Key words; ZnO, C-Doped zinc oxide, Azure A, Visible light activity

INTRODUCTION

The science of chemical phenomena in the environment is called 'Environmental chemistry' Environmental chemistry is the study of the sources, reactions, transport, effect and fate of chemical species in the air, water and soil and effect of human activites upon these. The entire world is facing a burning problem in the form of water pollution. Organic synthetic dyes represent relatively large group of organic chemicals, which are present in practically all spheres of daily life. Dyes are all around us, they make out our world beautiful but they also bring pollution and therefore, attention has to be focused on possible solutions of environmental problems caused by dye industries. The manufacturing and the processing of dye involve the handling and the production of many organic compounds that are toxic and hazardous to human health.

Various studies have focused on treatment of industrial wastewater using different treatment methods; however, most of these treatments have intricacy in realistic uses[1]. In recent years, investigation on different systems have been carried out, such as, advanced oxidation processes (AOP), ozonation, sonolysis, gamma–radiolysis, electro-coagulation, H_2O_2/UV, photocatalysis, photo-Fenton, biological and combined anaerobic–photocatalytic treatment[2-7]. Photocatalytic oxidation processes, which involves the generation of highly reactive hydroxyl radical have emerged as a promising water and wastewater treatment technology for the degradation or mineralization of a wide range of organic contaminants[8]. The photoactivated reactions are characterized by the free radical mechanism initiated by the interaction with photons of a proper energy level with the catalyst.[9]

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Till date, many types of semiconducting systems have been studied for photocatalysis including TiO_2, ZnO, ZrO_2, CdS, WO_3, and so on. Most of them have band gap in the UV (ultraviolet) region. Thus, these catalysts promote photocatalytic reactions under the illumination of UV radiation. Zinc oxide is an excellent wide band gap, natural n-type semiconducting material with binding energy (60 MeV), abundant in nature, nontoxic and environment friendly. It can absorb wider range of spectrum of radiation, which also makes it more applicable for dye sensitized solar cells and solar photovoltaic applications.

The photocatalytic efficiency of ZnO nanomaterials is believed to be much better than normal photocatalysts.[10] It is extensively used to treat wastewater, such as printing, dyeing, dairy, food, drugs, pesticides, textile papermaking, etc. Zinc oxide is a photoactive semiconducting material oxide and able to activate itself by taking energy for the photocatalytic reaction from photons.

The use of ZnO nanostructures as a potential photocatalyst material to decompose the environmental pollutants have also been rigorously studied.[11,12] Interestingly, to achieve better photocatalytic efficiency in many realistic applications, it is expected that ZnO photocatalyst should absorb not only ultraviolet radiation but also visible light.[13] To absorb visible spectrum of solar radiation, band gap energy of ZnO photocatalysts must be decreased or divided into different sub-band gaps, which can only be obtained either by incorporating transition metal ions (Cu, Co, Ni, Mn, Ag, Mo, Pt) or by doping nitrogen, sulphur, carbon atoms, etc.

ZnO has been doped by nitrogen, Ni and Co under visible irradiation[14]. Degradation of sulphonyl urea herbicide and methylene blue has been carried out by tin doped TiO_2 and Ag-ZnO catalyst, Punjabi et al.[15] observed the reduction of Congo red by ascorbic acid and EDTA over CdS as a photocatalyst. Mansoori et al.[16] used ZnO as photocatalysts for the photocatalytic bleaching of rhodamin 6G. Pare et al.[17] carried out the photocatalytic degradation of lissamine fast yellow in the aqueous suspension of ZnO under artificial light.

EXPERIMENTAL

Zinc acetate dihydrate (13.16 g) was added to 3 L of deionized water under vigorous stirring till homogeneous solution was obtained. 17.28 g of sodium dodecyl sulphate and 0.2 M of sodium hydroxide were added into the above solution under continuous stirring till pH value reached 12 and then it was heated at 160^0C for 14 h 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 h. A portion of this product (10 g ZnO) was calcined at 400^0C for 4 h, cooled to room temperature and grind in agate mortar. At the end of the reaction, sodium dodecyl sulphate and CH_3COONa were eliminated during washing of $Zn(OH)_2$. The final yield of ZnO was 90%.

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 grind in an agate mortar. The mixture was calcined in a ceramic crucible at 400^0C for 4 h and cooled. The product was grind to fine powder to obtain carbon-doped zinc oxide.
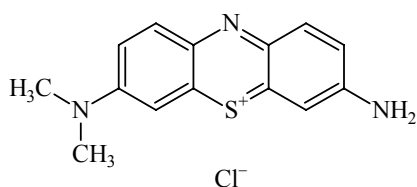

Fig. 1: Chemical structure of azure-A

The photocatalytic degradation of the dye azure A was investigated by taking dye solution and zinc oxide together. Irradiation was carried out by keeping the whole assembly exposed to a 200 W tungsten lamp at 40.0 mWcm^{-2}. The intensity of light at different distances from the lamp was measured using a solarimeter. The pH of the solutions was measured with of digital pH-meter. 0.0292 g of azure A was dissolved in 100 mL of doubly distilled water to prepare their 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 the azure A dye solution were determined using a spectrophotometer at λ max = 620 nm. The progress of reaction was investigated by measuring absorbance of the reaction mixture at regular time interval during exposure. A decreasing trend of absorbance indicated that dye azure A was degraded in 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 as well as C-doped ZnO, which indicates that the degradation of azure A followed pseudo-first order kinetics. The rate constant was measured using this equation.

$$k = 2.303 \times slope \qquad \qquad …(1)$$

RESULTS AND DISCUSSION

Various factors affecting degradation of azure A dye were studied to get optimum conditions for degradation.

Effect of pH

The effect of pH on the rate of degradation of C-doped ZnO was investigated in the pH range 6.0 to 10.5 The results are graphically represented in Fig. 2.
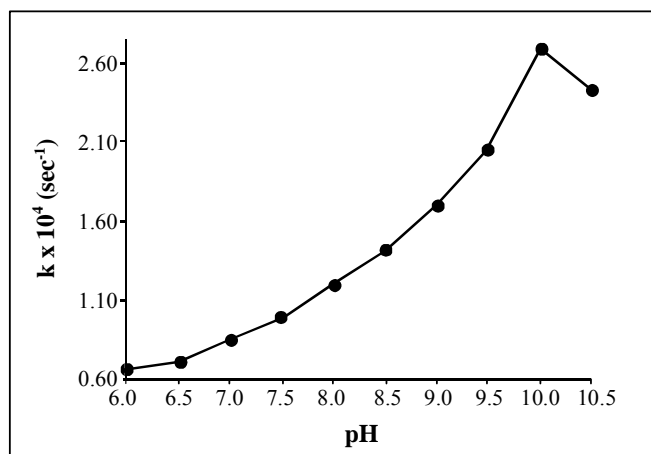

Fig. 2: Effect of pH

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 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 are converted into neutral form and hence, there is no attraction between neutral dye molecule and negatively charged surface of semiconductor. As a result, the rate was retarded.

Effect of azure A concentration

Effect of variation of dye concentration on the rate of reaction was also studied by taking different concentrations of azure A solution. The results are graphically represented in Fig. 3.
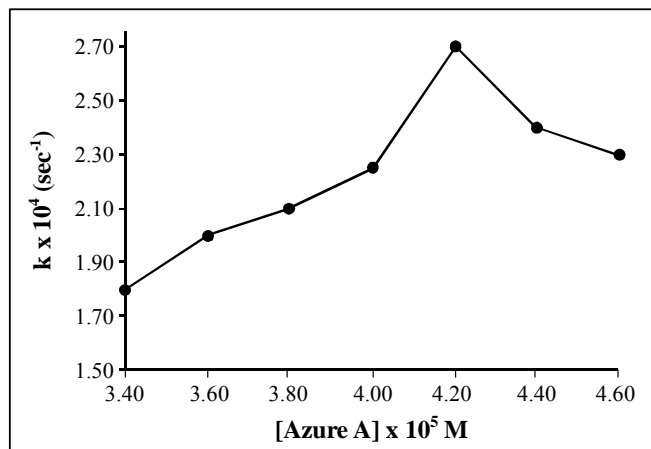
Fig. 3: Effect of azure A concentration

It was observed that the rate of photocatalytic degradation of dye increases on increasing the concentration of azure A up to 4.20×10^{-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 4.20×10^{-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 azure A was observed by keeping all other factors identical. The results are graphically represented in Fig. 4.
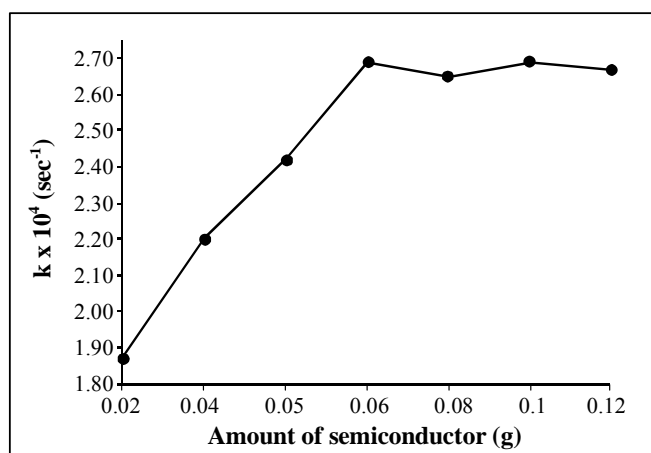

Fig. 4: Effect of amount of C-doped ZnO

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 azure A was also observed. The results obtained are reported in graphically presented in Fig. 5.
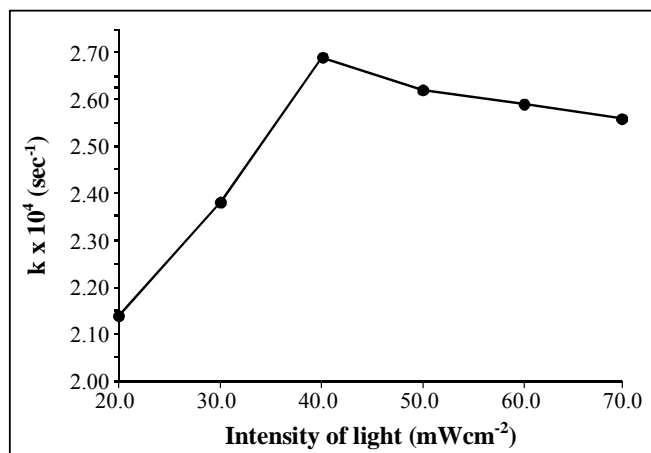

Fig. 5: Effect of light intensity

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 decrease in the rate of reaction as the intensity of light was increased beyond 40.0 mWcm^{-2}.

A typical run

After keeping the values of all parameters constant, a typical run was observed for the photocatalytical removal of the Azure A. The results are reported in Table 1 and graphically presented in Fig. 6. Here, a comparative observation was made for pure ZnO and C-doped ZnO, which confirms that the rate was greater in the case of C-doped ZnO as compared to pure ZnO.

Table 1: A typical run

[Azure-A] = 4.20 x 10^{-5} M			C-Doped ZnO = 0.06 g	
Light intensity = 40.0 mWcm^{-2}			pH = 10.0	
Time (min.)	**Pure ZnO Absorbance (A)**	**1 + log A**	**C-doped ZnO Absorbance (A)**	**1 + log A**
0	0.320	0.5051	0.320	0.5051
10	0.303	0.4814	0.280	0.4471
20	0.282	0.4502	0.240	0.3802
30	0.270	0.4313	0.219	0.3404
40	0.246	0.3909	0.201	0.3031

Cont…

Time (min.)	Pure ZnO Absorbance (A)	1 + log A	C-doped ZnO Absorbance (A)	1 + log A
50	0.240	0.3802	0.170	0.2304
60	0.224	0.3502	0.148	0.1703

Rate constant (k): For pure ZnO = 1.10×10^{-4} sec^{-1}

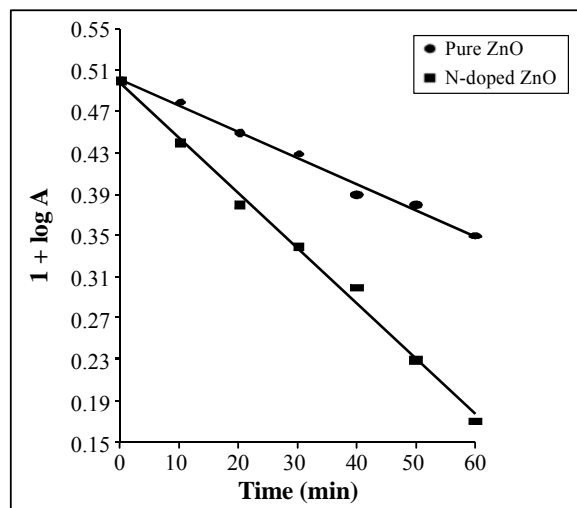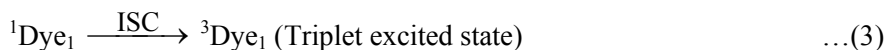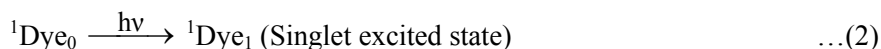C-doped ZnO = 2.69×10^{-4} sec^{-1}

Fig. 6: A typical run

Mechanism

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

$$^1\text{Dye}_0 \xrightarrow{\ h\nu\ } {}^1\text{Dye}_1 \text{ (Singlet excited state)} \qquad \qquad …(2)$$

$$^1\text{Dye}_1 \xrightarrow{\ \text{ISC}\ } {}^3\text{Dye}_1 \text{ (Triplet excited state)} \qquad \qquad …(3)$$

$$\text{SC} \xrightarrow{\ h\nu\ } e^- \text{ (CB)} + h^+ \text{ (VB)} \qquad \qquad …(4)$$

$$\text{SC*} (h^+) + {}^-\text{OH} \longrightarrow {}^{\bullet}\text{OH} \qquad \qquad …(5)$$

$$^{\bullet}\text{OH} + {}^3\text{Dye}_1 \longrightarrow \text{Product} \qquad \qquad …(6)$$

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 dye. On the other hand, the semi-conducting C-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 A dye 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 much reduced.

The observations revealed that azure A dye could be degraded successfully by using C-doped ZnO under visible light. It was found that the C-doped ZnO has shown more than two times enhanced photocatalytic activity than pure ZnO.

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