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Original Research Article

Enhanced photocatalytic activity of N, S-doped titania for degradation of amaranath

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Abstract

Heterogeneous photocatalytic degradation of amaranth has been investigated in aqueous medium using visible light using N, S-doped TiO_2. The doped titania has been prepared by sol-gel method. The rate of photocatalytic degradation of dye was monitored spectrophotometrically. The effect of variation of different parameters like pH, concentration of amaranth, amount of photocatalyst, dopant percentage and light intensity on the rate of photocatalytic degradation was observed. A tentative mechanism for the photocatalytic degradation of amaranth has also been proposed.

Keywords: Amaranth, N, S-doped titania, Photocatalytic degradation.

INTRODUCTION

The use of titanium dioxide as a semiconductor in photocatalysis is an efficient method for elimination of environmental pollutants especially for degradation of organic pollutants from water (Vargas and Nunez, 2009). However, TiO_2 can only be excited by UV light irradiation due to its large band gap (3.2 eV), which limits the application of TiO_2 photocatalyst, because the UV light only occupies a small portion of the sunlight spectrum (Litter, 1999). Hence, in order to solve the problem much effort has been devoted to developing the visible light activated photocatalysts (Sun et al., 2003). Now a days, many strategies, including transition metal (Pal et al., 1999; Willke and Breuer, 1999; Alem and Sarpoolaky, 2010; Devi et al., 2010; Saepurahman et al., 2010; Tian et al., 2009) and noble metal ions doping (Subramanian et al., 2001), dye sensitization, semiconductor coupling and the doping of TiO_2 with non-metal elements have attracted attention of researchers all over the world. Among these methods, the doping of TiO_2 with non metal elements has been proved to be the most feasible approach to enhance the photoactivity.

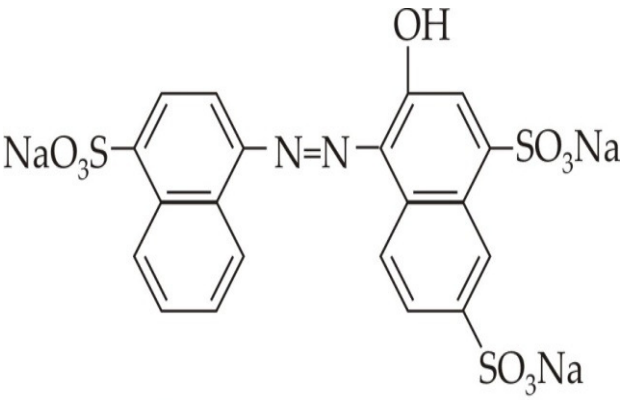
First non metal doped TiO_2 was described by Sato (1986). Gandhe and Fernandes (2005) have reported a simple method to synthesize N-doped rutile titania with enhanced photocatalytic activity in sun light. Asahi et al. (2001) reported that N-doping shifted the absorption edge of TiO_2 to visible light region, thereby exhibiting photocatalytic degradation of methylene blue solution and gaseous acetaldehyde under visible irradiation. Sathish et al. (2005) studied the synthesis, characterization, electronic structure, and photocatalytic activity of N-doped TiO_2 nanocrystals whereas Lee et al. (2008) studied the anion codoped titania for solar photocatalytic degradation of dyes. In order to investigate the effect of doping of C, N, B and F elements on TiO_2 for reducing the band gap, the heat treatment of TiO_2 was carried out with tetraethyl ammonium tetrafluoroborate. Li et al. (2011) reported the synthesis of highly efficient C-doped TiO_2 photocatalyst and its photo-generated charge-transfer properties. Liu and Chen (2008) prepared the S doped titania by acid catalyzed hydrolysis method using thiourea as sulfur source. The activity of the catalyst was examined by photodegradation of phenol in aqueous solution under both artificial visible light and solar light irradiation.

Guotian et al. (2011) prepared the doped TiO_2, the photocurrent of doped TiO_2 nanotube array films was greatly enhanced compared to that of undoped samples under visible light irradiation and the photocatalytic activities of the samples were evaluated on the removal of methylene blue under visible light irradiation. Qin et al. (2013) synthesized and studied the photocatalytic

properties of N, S-codoped TiO_2 prepared by micro plasma oxidation method in electrolyte with ammonium sulfate and thiourea. Rhodamine B was used to investigate the photocatalytic properties of modified TiO_2. The result showed that N, S-codoped TiO_2 films exhibits higher photocatalytic activity, which can be attributed to the increase of surface area and light utilization of N, S-codoped TiO_2 films.

MATERIALS AND METHODS

The commercial dye amaranth was obtained from sd fine Chem and was used as such without purification (λ_{max} = 520 nm). Other materials such as $Ti(OiPr)_4$, and Thiourea were purchased from spectrochem and and Himedia, respectively. The dye solutions were prepared using doubly distilled water. A 200 W tungsten lamp (Phillips) was used for irradiating the solution in the visible range. A Uv-visible spectrophotometer (Systronics Model 106) was used for measuring optical density at different time intervals. The pH of the solution was adjusted with previously standardized H_2SO_4 and NaOH solutions.



Structure of Amaranth

Synthesis of pure TiO_2

In a typical procedure, 50 mL of isopropyl alcohol and 100 mL of doubly distilled water was added into 10 mL of $Ti(OiPr)_4$ with vigorous stirring and the solution was kept overnight at room temperature. Then the solution was dried in an oven at 80ºC for 2 hrs and calcined at 400ºC for 3 hrs. Pure titania was obtained in the form of white powder.

Synthesis of N, S-doped TiO_2

In a typical procedure, 50 mL of isopropyl alcohol and 0.5, 1, 1.5, 2.0 and 2.5 g of thiourea in 100 mL of doubly distilled water was added into 10 mL of $Ti(OiPr)_4$ in five different beakers, respectively with vigorous stirring and calcined at 400ºC for 3 hrs to get N, S-doped titania as pale yellow powder. Here, the doped titania samples have been synthesized with different amount of thiourea as dopant source i.e. 0.5, 1.0, 1.5, 2.0 and 2.5%.

Experimental

A stock solution of amaranth of concentration 1.00×10^{-3} M was prepared in doubly distilled water. This stock solution was further diluted as and when required. The optical density of amaranth solution was determined with the help of a spectrophotometer at λ_{max}= 520 nm for amaranth. The solution of amaranth 3.90×10^{-5} M was prepared in doubly distilled water and 0.12 g of 2.0% N, S-doped TiO_2 was added to it. The pH of reaction mixture was kept 8.0 and this solution was exposed to a 200 W tungsten lamp. A decrease in absorbance of dye solution was observed with increasing time of exposure.

The rate constant for this reaction was determined with the help of the following rate equation:

Rate constant (k) = 2.303 × Slope .... (1)

The typical run for the photocatalytic degradation of amaranth in the presence of pure TiO_2 and N, S-dop TiO_2 has been presented in Table 1 and graphically represented in Figure 1.

The photocatalytic degradation of the dye is influenced by some factors and therefore, these were varied to find out the optimum conditions for the degradation of the dye.

Effect of pH

The pH of the solution is likely to affect the degradation rate of the amaranth. The effect of pH on the rate of degradation of the dye was investigated in the pH range 5.0–10.0. The results are reported in Table 2.

It has been observed that the rate of photocatalytic degradation of amaranth was increased with increase in pH upto 8.0. A further increase in pH above 8.0 results in a decrease in the rate of reaction. An increase in the rate of photocatalytic degradation of amaranth with increase in pH may be due to generation of more $^{\bullet}OH$ radicals, which are produced from the reaction between ^{-}OH ions and hole (h^+) of the semiconductor. Above pH 8.0, a decrease in the rate of photocatalytic degradation of the dye may be due to the fact that amaranth is present in its anionic from, which will experience a force of repulsion with negatively charged surface of the semiconductor due to adsorption of more ^{-}OH ions on the surface of photocatalyst.

Effect of amaranth concentration

The effect of dye concentration was also observed by

Table 1. A typical run
pH = 8.0; [Amaranth] = 3.90×10^{-5} M
N,S-doped TiO_2= 0.12 g (2.0%)
Light Intensity = 50.0 $mWcm^{-2}$

Time (min.)	Optical Density (O. D.)	1 + log O. D.
0	0.750	0.8750
10	0.712	0.8524
20	0.654	0.8155
30	0.612	0.7867
40	0.562	0.7497
50	0.501	0.6998
60	0.462	0.6646
70	0.411	0.6138
80	0.370	0.5682
90	0.305	0.4842

Rate constant for N, S-doped TiO_2; k = 1.47×10^{-4} sec^{-1}
Rate constant for Pure TiO_2; k = 0.81×10^{-4} sec^{-1}

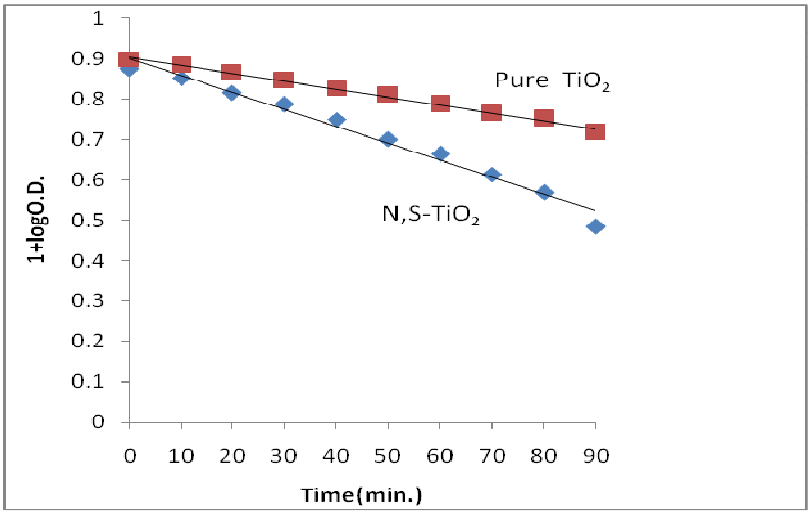


Figure 1. A Typical Run

Table 2. Effect of pH
[Amaranth] = 3.90×10^{-5} M; N, S-doped TiO_2 = 0.12 g
Light Intensity = 50.0 $mWcm^{-2}$; % of dopant = 2.0

pH	k × 10^4 (sec^{-1})
5.0	1.28
5.5	1.31
6.0	1.33
6.5	1.37
7.0	1.42
7.5	1.44
8.0	**1.47**
8.5	1.42
9.0	1.38
9.5	1.34
10.0	1.32

taking different concentrations of the dye. The results are tabulated in Table 3.

It is evident from the data that the rate of photocatalytic degradation of dye increases with an

Table 3. Effect of amaranth concentration
pH = 8.0; N, S-doped TiO_2 = 0.12 g
Light Intensity = 50.0 $mWcm^{-2}$; % of dopant = 2.0

[Amaranth] × 10^5 M	k × 10^4 (sec^{-1})
3.40	1.23
3.50	1.30
3.60	1.34
3.70	1.39
3.80	1.42
3.90	**1.47**
4.00	1.43
4.10	1.40
4.20	1.37
4.30	1.32
4.40	1.28

increase in concentration of the dye. It may be explained on the basis that as the concentration of the dye was increased, more dye molecules were available for excitation and consecutive energy transfer and hence, an increase in the rate of photocatalytic degradation of the dye was observed. The rate of photocatalytic degradation was found to decrease with an increase in the concentration of dye above 3.90 × 10^{-5} M. It may be due to the fact that the dye itself may start acting as an internal filter for the incident light and it will not permit the desired light intensity to reach the semiconductor particles and as a result, the degradation rate decreases.

Effect of amount of semiconductor

The effect of amount of semiconductor was observed by taking different amount of semiconductor. The results are reported in Table 4.

It was observed that the rate of reaction was increased with increase in the amount of semiconductor N, S-doped TiO_2. The rate of degradation was optimum at 0.12 g of the photocatalyst. Beyond 0.12 g, the rates of reaction become virtually constant. This may be due to fact that as the amount of semiconductor was increased, the exposed surface area of the semiconductor also increases. However, after this limiting value (0.12 g), an increase in the amount of semiconductor only increases the thickness of the semiconductor layer and not the exposed surface area. This was also confirmed by using reaction vessels of different dimensions. It was observed that the point of saturation is shifted to a higher value for vessels of larger capacities while it is shifted to lower value for vessels of smaller capacities.

Effect of % variation of dopant

The effect of % variation of dopant was observed by taking different % of dopant i.e. thiourea. The results are reported in Table 5.

It was observed that as the % of dopant was increased, the rate constant was also increased. At 2.0% of dopant, the rate of reaction was optimum but after that rate of reaction decreases. It is may be due to the reason that freely active site of titania decreases beyond 2.0% of dopant and accordingly, the rate of reaction starts decreasing.

Effect of light intensity

To investigate the effect of light intensity on the photocatalytic degradation of amaranth, the distance between the light source and the exposed surface area was varied. The results are summarized in Table 6.

The results indicate that photocatalytic degradation of amaranth was accelerated as the intensity of light was increased, because an increase in the light intensity will increase the number of photons striking per unit area of semiconductor surface per unit time. On further increasing the intensity of light above 50.0 $mWcm^{-2}$, there was a decrease in the rate of reaction. This may be due to some side reactions or thermal effect.

Mechanism

On the basis of these observations, a tentative mechanism for photocatalytic degradation of amaranth *is* proposed as –

$$^1AM_0 \xrightarrow{h\nu} {}^1AM_1 \text{ .... (2)}$$

$$^1AM_1 \xrightarrow{ISC} {}^3AM_1 \text{ .... (3)}$$

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

$$h^+ + {}^-OH \longrightarrow {}^\bullet OH \text{ .... (5)}$$

$$^3AM_1 + {}^\bullet OH \longrightarrow Leuco\,AM \text{ .... (6)}$$

$$Leuco\,AM \longrightarrow Products \text{ .... (7)}$$

Table 4. Effect of amount of semiconductor
pH = 8.0; [Amaranth] = 3.90×10^{-5} M
Light Intensity = 50.0 $mWcm^{-2}$; % of dopant = 2.0

Amount of semiconductor (g)	$k \times 10^4$ (sec^{-1})
0.02	1.22
0.04	1.29
0.06	1.33
0.08	1.38
0.10	1.42
0.12	**1.47**
0.14	1.46
0.16	1.46

Table 5. Effect of % variation of dopant
pH = 8.0*;* N, S-doped TiO_2 = 0.12 g
Light Intensity = 50.0 $mWcm^{-2}$; [Amaranth] = 3.90×10^{-5} M

Dopant (%)	$k \times 10^4$ (sec^{-1})
0.5	1.36
1.0	1.39
1.5	1.43
2.0	**1.47**
2.5	1.41

Table 6. Effect of light intensity
pH = 8.0; [Amaranth] = 3.90×10^{-5} M
N, S-doped TiO_2 = 0.12 g; % of dopant = 2.0

Intensity of light ($mWcm^{-2}$)	$k \times 10^4$ (sec^{-1})
20.0	1.31
30.0	1.36
40.0	1.41
50.0	**1.47**
60.0	1.43
70.0	1.38

Amaranth (AM) 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 semiconductor (SC) (pure TiO_2 and N, S-doped TiO_2) also utilizes the radiant energy to excite its electron from valence band to the 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 to products. The participation of $^{\bullet}OH$ radical as an active oxidizing species was confirmed by using hydroxyl radical scavenger (isopropanol), where the rate of degradation was drastically reduced.

CONCLUSION

Pure TiO_2 and N, S-doped TiO_2 semiconductors have been prepared by sol-gel method. The observations of photocatalytc degradation of amaranth dye revealed that N, S-doped TiO_2 extended the absorption of TiO_2 into the visible light range, which was confirmed by higher photocatalytic activity of doped TiO_2 than the pure TiO_2 under visible light irradiation. These improved properties can be attributed to the increased visible light absorption, the improved photogenerated electrons–hole separation and the surface defects produced by N and S doping.

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