Visible Light Induced Photocatalytic Degradation of Rhodamine B dye using Nitrogen Sulphur Co-doped TiO₂ Photocatalyst

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(Received on: November 4, Accepted: November 13, 2017)

ABSTRACT

In this study a visible light active N, S co-doped photocatalyst prepared using (NH₄)₂SO₄ as nitrogen and sulphur source, photocatalyst was calcined at 500°C and named as 1NS-TiO₂. The 1NS-TiO₂ photocatalyst is extensively characterized using several techniques including UV-vis spectroscopy, X-ray diffraction (XRD), SEM and EDAX. Rhodamine B dye as a model contaminant in order to investigate its photocatalytic activity under solar light irradiation. The effects of pH, catalyst concentration and dye concentration on degradation reaction were also investigated. The efficiency of photocatalytic degradation of rhodamine B tended to decrease with increasing the concentration of dye, increase as pH is increased up to 10.6. The degradation efficiency of rhodamine B is found to increase as the amount of the catalyst dosage increases up to an optimum value of 0.2 g / 100 ml. It was proven that the degradation process of rhodamine B reaction rate obeyed a pseudo-first-order reaction of the catalyst concentration of 1NS-TiO₂.

Keywords: Photocatalysis, 1NS-TiO₂ degradation, rhodamine B.

1. INTRODUCTION

An efficient method for the elimination of environmental pollutants is the use of titanium dioxide, because of its various qualities such as optical-electronic properties, low-cost, chemical stability and non-toxicity. But it cannot be applied widely, because of its wide band gap. For solving this problem, titanium dioxide was doped with different metals like Cu, Zn, Cr, Fe, Co, Ni and non-metals including N, S, C and F. Doping with metal and doping non-metal were the most feasible methods for improving the photocatalytic performance of
TiO$_2$. Non-metal doping of TiO$_2$ has shown great promise in achieving visible light active photocatalysis. First non-metal doped TiO$_2$ was described in 1986 by Sato et al.$^8$. Another one important method to extend the light-absorbing property of TiO$_2$ and to enhance its photocatalytic efficiency is the co-doping of TiO$_2$ with metal–nonmetal$^9$, metal-metal, nonmetal-nonmetal. This method has several advantages, including narrowing the energy band gap, the improvement of charge separation, the increase in the lifetime of the charge carrier$^{10}$.

Fig 1.1 and Fig 1.2 represents the structure and Zwitterion structure of rhodamine B. Rhodamine B is an organic dye which dissolves easily in water and widely used in the manufacturing of textile, printing, paper, pharmaceutical and food products$^{11-12}$. It is allergic to the respiratory system, skin and eyes. It is also a very well-recognized water tracer fluorescent. Rhodamine B is also an important representative of xanthene dyes, and it is usually used as a dye laser material because of its good stability. In recent years, there are many research works focusing on the degradation mechanism of rhodamine B$^{13-15}$. Most of them are concerned the mechanism under visible illumination. Therefore, the control against dye wastewater pollution is an important issue to tackle throughout the world.

2. EXPERIMENTAL

2.1 Preparation of nitrogen sulphur co-doped TiO$_2$ (1NS-TiO$_2$)

3.7 g $(\text{NH}_4)_2\text{SO}_4$ was dissolved in 6.3 ml deionised water and was slowly added to 1 ml titanium tetraisopropoxide in a 250 ml beaker. The obtained solution was stirred for further 20 minutes and was exposed under ultrasonic waves for 3 hours. Finally the sample was calcined at 500˚C for 2 hours in a muffle furnace and named as 1NS-TiO$_2$.

2.2 Photodegradation of rhodamine B

The photodegradation of rhodamine B was examined by sunlight of intensity 800 X100 Lux. The experiment was performed with 100 ml of water containing $10^{-4}$ M rhodamine B and 0.1g of 1NS-TiO$_2$ respectively. The described intensity allowed to pass through the reaction mixture and the progress of the degradation of rhodamine B was monitored every 30
minutes by UV–visible spectroscopy. The extent of decomposition can be measured using UV visible spectrometer at a wavelength of 554 nm, which corresponds to the absorption maximum of rhodamine B. At the same time 100 ml of water with 10^{-4} M rhodamine B was tested and monitored by UV–Visible spectroscopy to investigate if degradation also occurs in the absence of the photocatalyst.

3. RESULTS AND DISCUSSION

3.1 Effect of Catalyst Load

Fig 3.1 depicts that as the concentration of 1NS-TiO_2 increases from 0.1 g / 100 ml to 0.2 g / 100 ml, the percentage degradation increases from 84 % to 92 %. Further increase in the catalyst concentration of 1NS-TiO_2 from 0.3 g / 100 ml to 0.5 g / 100 ml decreases the percentage degradation to from 88 % to 72 %. So the maximum degradation rate has been observed with catalyst dose of 0.2 g / 100 ml and it was considered as the optimum dose for the degradation of rhodamine B using 1NS-TiO_2.

![Fig 3.1 Effect of catalyst concentration on % degradation using 1NS-TiO_2](image)

Catalyst amount is a major parameter affecting the photocatalytic degradation efficiency. Photocatalytic degradation is increases with an increase in catalyst mass, because of increase in the amount of active site on the surface of photocatalyst particles. As a result, an increasing the number of dye molecules adsorbed on the surface of photocatalyst lead to an increase in the density of particles in the area of illumination.

3.2 Effect of pH

Fig 3.2 shows the effect of pH on photocatalytic degradation rhodamine B at 10^{-4} M solution and 0.1 g / 100 ml 1NS-TiO_2.
It is evident from the graph, that as the pH of dye solution changes from acidic to alkaline the percentage of degradation is increasing. In the alkaline solution at pH 9.4 the % of degradation is 86 % likewise, at pH 10.6 the % degradation is 92 %. But when the pH is decreased from 10.6 to 4 the degradation was decreased upto 72 %. So the maximum degradation has been found at pH 10.6 after 90 min of exposure.

3.3 Effect of dye concentration

Fig 3.3 shows the influence of dye concentration on photocatalytic degradation of rhodamine B of 0.1g / 100 ml 1NS-TiO$_2$.

The effect of rhodamine B dye concentration on the degradation was studied by varying concentration. It reveals that the increase in dye concentration leads the decreased
activity. The initial dye concentration was varied from $0.15 \times 10^{-4}$ M to $1.5 \times 10^{-4}$ M with a constant catalyst dose of 0.1 g / 100 ml. It has been found that from Fig 5 that increasing the concentration of dye solution from $0.15 \times 10^{-4}$ M to $1.5 \times 10^{-4}$ M decrease the rate of degradation and it was found that at $0.15 \times 10^{-4}$ M dye concentration, degradation was 91 % within 90 minutes and at $1.5 \times 10^{-4}$ M concentration, degradation was 60 % within 60 minutes but it reaches to 80 % the time taken for such degradation is 2h 30 minutes.

3.4 Recycling of catalyst

To evaluate activity of the catalyst for photocatalytic degradation, recycling studies are conducted over 1NS-TiO$_2$ using 0.1 g / 100 ml catalyst and the results are provided in Fig 3.4.

![Fig 3.4 Efficiency on the recycling of 1NS-TiO$_2$ catalyst](image)

The first cycle the degradation is 70 %. After the completion of the first cycle, the catalyst is removed, dried and is reused as such for the second cycle, a slight decrease in the degradation is observed compared to the first cycle ie, 64 %. When the same catalyst is reused without calcinations for the third and fourth cycles the degradation % of rhodamine B is 52 % and 51 % respectively.

4. CHARACTERISATION OF 1NS-TiO$_2$, 2NS-TiO$_2$ PHOTOCATALYSTS

4.1 XRD analysis

The XRD pattern of 1NS-TiO$_2$ is shown in Fig 4.1. The diffraction peaks at 20 = 25.29°, 37.79°, 38.57°, 53.86°, 55.02°, 62.63°, 68.77°, 70.23°, 75.00° corresponding to the anatase phase of titania (JCPDS, file No. 89-4921) are observed in the sample calcined at 500°C that displayed pure anatase phase. The average crystallite sizes of particles were estimated by the Scherer's formula as shown below:
Where D is the crystallite size, λ is the X-ray wavelength, β is the broadening of the diffraction peak and θ is the diffraction angle for maximum peak. The calculated mean crystallite size of the 1NS-TiO₂ was 68 nm.

**Fig 4.1 XRD pattern of 1NS-TiO₂**

**4.2 SEM with EDAX analysis**

The morphology of the 1NS-TiO₂ particles measured by SEM was given in Fig 4.2. 1NS-TiO₂ sample appeared as agglomerations of smaller particles with a high tendency for crystallization.
The elemental description of 1NS-TiO$_2$ was obtained from energy dispersive X-ray analysis. In Fig 4.3 the peaks located between 4-5 keV represents titanium, 0-1 keV represents oxygen, 0-1 keV represents nitrogen and 2-3 keV represents sulphur.

5. DEGRADATION OF DYE

Several authors have studied the degradation of different dyes by the photocatalytic treatment and reported that the decolourisation due to complete mineralization of dye was observed in UV-visible spectrophotometer.

Fig 5.1 shows the absorption spectra of rhodamine B dye during the reaction time. The primary absorption peaks of the original dye solution are at 554 nm.
CONCLUSIONS

The synthesised 1NS-TiO₂ was employed as a photocatalyst for the degradation of rhodamine B dye. It was found that the dye is completely decomposed on irradiation in the presence of the 1NS-TiO₂ catalyst at alkaline pH under solar light irradiation. The complete decolourization of the dye was followed by UV-visible spectrophotometry. As formed 1NS-TiO₂ exhibit better photocatalytic activity. From the SEM, EDAX, UV-vis results, it was confirmed that the assimilation of nitrogen and sulphur in TiO₂ decreases the grain size and hence increases the photocatalytic degradation of rhodamine B under visible light irradiation, minimum catalyst amount (0.2 g/100 ml), lower dye concentration (0.15 x 10⁻⁴ M), alkaline media (pH = 10.6) are the factors which enhance the photocatalytic activity. On the whole 1NS-TiO₂ photocatalyst possesses the highest visible light absorption and fast degradation of rhodamine B in aqueous media using visible light.

REFERENCES