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EFFECT OF DOPING MANGANESE ON PHOTOCATALYTIC PERFORMANCE OF TITANIA IN DEGRADATION OF ROSE BENGAL

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ABSTRACT

In the present work, nanoparticles of pure TiO_2 and manganese doped TiO_2 were prepared by sol-gel method. As-prepared photocatalyst performance was evaluated by degradation of rose Bengal in synthetic waste water system under visible light. The degradation of dye was studied spectrophotometrically. Optimum conditions were achieved for degradation of dye by varying different rate affecting parameters like pH, concentration of dye, amount of photocatalyst, and light intensity and these were found to be 7.0, 0.90×10^{-5} M, 0.12 g, and 60.0 $mWcm^{-2}$, respectively. The physicochemical properties of samples were characterized by XRD and SEM. The observations revealed that Mn doped TiO_2 showed better photocatalytic performance than pure TiO_2.

Key words: Mn doped TiO_2, Photocatalytic degradation, Rose Bengal, Zeolite.

INTRODUCTION

Many of the industries discharge their effluents in nearby water resources without treatment, which creates water pollution. Although dyeing and textile industries are important in our society but these are also a major source of water pollution. Although there are some methods available for removal of pollutants from water such as chemical oxidation, adsorption, coagulation and biological process but these are not sufficient to remove pollutants from waste water and also have their own demerits. Photocatalysis has emerged as a promising technology for waste water treatment in last few decades, which provides an eco-friendly solution for this problem. Tayade et al.[1] used nanocrystalline anatase and rutile TiO_2 for photocatalytic degradation of dyes and organic contaminants in waste water whereas Ameta et al.[2] used antimony trisulphide photocatalyst for degradation of naphthol green B. Sima and Hasal[3] reported degradation of different textile dyes by using TiO_2

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under ultraviolet light. Ameen et al.[4] prepared novel graphene/polyaniline nanocomposites and studied its photocatalytic activity toward the degradation of rose Bengal. Rauf et al.[5] reported photolytic decolorization of rose Bengal by UV/H_2O_2 and data optimization using response surface method while Li et al.[6] carried out photoelectrocatalytic oxidation of rose Bengal in aqueous solution using a Ti/TiO_2 mesh electrode. Kaur and Singhal[7] studied effect of operational parameters for degradation of rose Bengal using ZnO while Liu et al.[8] investigated degradation of rose Bengal by photocatalytic and photoelectrocatalytic reaction. Sharma et al.[9] studied photocatalytic degradation of rose Bengal using semiconducting zinc sulphide as the photocatalyst.

Jain et al.[10] prepared N, S-codoped titania and used it for degradation of amaranth while Tachikawa et al.[11] used nitrogen-doped TiO_2 powders for visible light-induced degradation of ethylene glycol. Sahoo et al.[12] carried out photocatalytic degradation of methyl red dye in aqueous solutions under UV irradiation using Ag^+ doped TiO_2 while Wang et al.[13] reported wavelength-sensitive photocatalytic degradation of methyl orange in aqueous suspension over iron(III)-doped TiO_2 nanopowders under UV and visible light irradiation. Zhao et al.[14] studied efficient degradation of toxic organic pollutants with $Ni_2O_3/TiO_{2-x}B_x$ under visible irradiation. Ameta et al.[15,16] investigated visible light induced photocatalytic degradation of toluidine blue-O and erythrosine using molybdenum doped titania and manganese doped titania supported on zeolite, respectively. In the present work, effect of manganese doping on titania has been investigated where rose Bengal dye has been selected as a model system.

EXPERIMENTAL

Materials and method

Rose Bengal is a bright bluish pink compound, which is soluble in water. Its maximum absorbance (λ_{max}) is at 540 nm in an aqueous solution. Its chemical structure in shown in Fig. 1.

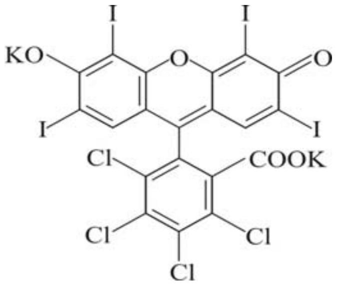

Fig. 1: Chemical structure of rose Bengal

Doubly distilled water was used for preparation of all solutions. A 200 W tungsten lamp was used for irradiation of the dye solution in the visible range. The progress of the reaction was monitored using a UV-visible spectrophotometer (Systronics 106). A digital pH meter (Systronic 335) was used to measure pH of the solutions and pH was adjusted by using previously standardized H_2SO_4 and NaOH solutions. Rose Bengal, $MnSO_4$, NaOH, H_2SO_4 were purchased from Himedia and titanium tetraisopropoxide from Spectrochem and used as received.

Preparation of Mn doped TiO_2/zeolite

Mn doped TiO_2 was prepared by sol-gel method. Ethanol and nitric oxide were mixed first and then it was added dropwise in titanium tetraisopropoxide solution with continuous stirring. Thereafter, manganese sulphate was added to the solution as a dopant. The obtained solution was stirred continuous for 10-12 hours at 4°C. After stirring, it was kept in ice bath for three days. This solution was then evaporated at 35°C, where its gel was formed. This gel was dried in oven for 5-6 hours and further calcined in furnace at 450°C for 20-30 min. At last, Mn doped TiO_2 was mixed with zeolite slurry in 1:2 ratio to prepare the final product.

Photocatalytic degradation

The photocatalytic activity of catalyst was measured by degradation of rose Bengal. A standard solution of the dye 1.0×10^{-3} M was prepared. This stock solution was diluted as required. pH of the solution was measured by digital pH meter. The prepared photocatalyst was used as a semiconductor in the present work. The reaction mixture was exposed 200 W tungsten lamp. The intensity of light was varied by changing the distance between the light source and reaction mixture. The absorbance of solution was measured at different time intervals at 540 mm.

Effect of various parameters like pH, concentration of dye, amount of semiconductor and light intensity was observed. As time of irradiation was increased, absorbance of solution decreases, which indicates that dye is degrading. A plot between time interval and 1 + log A was found linear, which means that the reaction followed pseudo-first order. The rate constant was measured by the expression;

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

RESULTS AND DISCUSSION

Characterization of pure TiO_2 and Mn-doped TiO_2

The average particle size and morphology of as-prepared pure and Mn-doped TiO_2 semiconductors were characterized by X-ray diffraction (XRD) and Scanning electron microscopy (SEM) techniques.

X-ray diffraction (XRD)

XRD studies of the sample were conducted using PANalytical, Singapore make, XPERT-PRO model with Cu K_α radiation ($\lambda = 1.54060$ A°, $2\theta = 10$ to 80° with generator setting 40 mA, 45 kV). Diffraction pattern was taken over the 2θ range 10º-100º. Figure 2 and 3 shows the XRD pattern of pure TiO_2 and Mn-doped TiO_2.

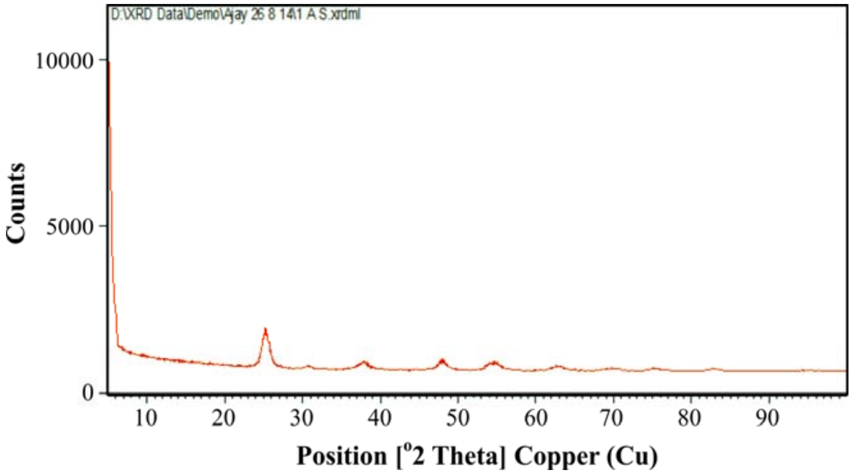

Fig. 2: XRD of pure TiO_2

X-ray diffraction was used to calculate the average particle size of the sample. The particle size of the synthesized pure TiO_2 and Mn-doped TiO_2 was calculated using Sherrer formula:

$$D = K\lambda / \beta \cos\theta \qquad \ldots(2)$$

Where K is a constant, which depends on the shape of the crystal and its value is 0.9 assuming spherical shape; λ is the wavelength (nm); D is the crystallite size (nm); β is full width of half maxima (FWHM-in radian), and θ is Bragg's diffraction angle (degree).

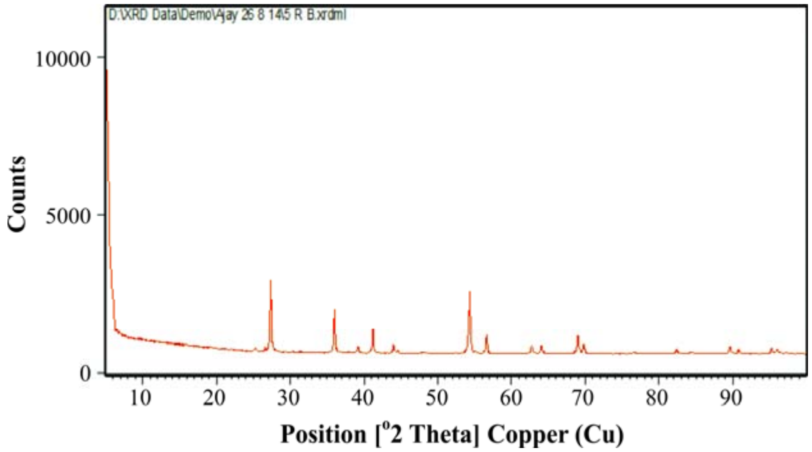

Fig. 3: XRD of Mn-doped TiO_2

Crystallite size was found to be 27.8 nm and 181.02 nm, respectively.

The intensity of XRD peaks of the semiconductors reflected that the as-prepared synthesized nanoparticles of TiO_2 were crystalline in nature. As the peaks in the XRD of pure TiO_2 and Mn-doped TiO_2 were observed at 25.30° and 25.20°, respectively, which confirms the formation of anatase form of titania. It was also observed that the peak remain almost unshifted in the doped sample indicating that doping of manganese did not perturbed TiO_2 lattices.

Scanning Electron Microscopy (SEM)

The morphology of pure and Mn doped titania was studied by scanning electron microscopy. SEM images of pure TiO_2 and Mn-doped TiO_2 are given in Figs. 4 and 5.

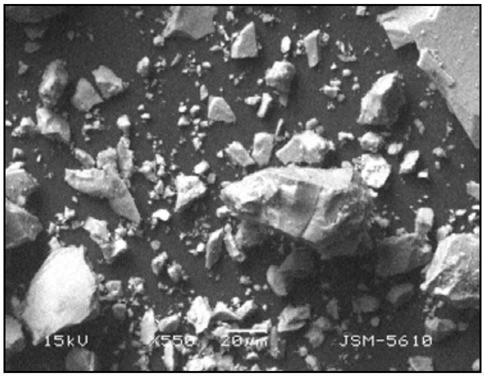

Fig. 4: SEM of pure TiO_2

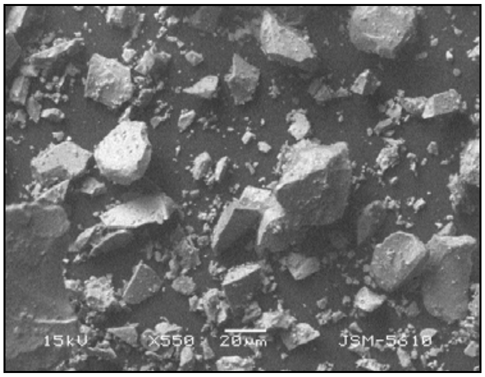

Fig. 5: SEM of Mn-doped TiO_2

SEM images indicate that particles are unevenly distributed in size. Zhang et al.[17] observed that the particle size of TiO_2 was reduced due to copper doping but no such results was observed in the Mn-doped TiO_2. This may be explained on the basis that manganese does not like to dwell in grain boundary regions or on the surface of TiO_2 particle to inhibit its growth. Doping of manganese is clearly visible in SEM image (Fig. 5) in form of blisters on the surface of TiO_2 particles.

Typical run

The results for typical run are given in Table 1 and represented in Fig. 6.

Typical run of pure TiO_2 and Mn doped TiO_2 showed that reaction rate of doped TiO_2 was more than of pure TiO_2.

Table 1: A typical run

pH = 7.0 [Rose Bengal] = 9.00×10^{-6} M

Pure TiO_2/Mn doped–TiO_2 = 0.12 g Light intensity = 60.0 $mWcm^{-2}$

Time (min.)	Pure TiO_2		Mn doped–TiO_2	
	Absorbance (A)	1 + log A	Absorbance (A)	1 + log A
0	0.718	0.8561	0.718	0.8561
20	0.700	0.8450	0.683	0.8344
40	0.684	0.8351	0.624	0.7952
60	0.661	0.8202	0.582	0.7649
80	0.638	0.8048	0.545	0.7364
100	0.624	0.7952	0.507	0.7050
120	0.602	0.7796	0.473	0.6749
140	0.582	0.7649	0.442	0.6454
160	0.569	0.7551	0.412	0.6149
180	0.549	0.7396	0.376	0.5752

Rate constant for Pure TiO_2; k = 2.44×10^{-5} sec^{-1}

Rate constant for Mn–TiO_2; k = 5.75×10^{-5} sec^{-1}

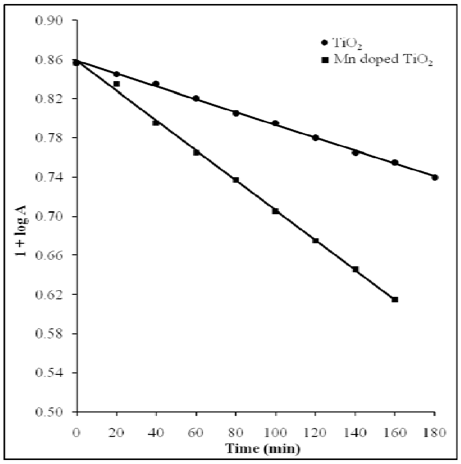

Fig. 6: Typical runs

Effect of pH

The pH of the solution is likely to affect the degradation of rose Bengal. 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.

Table 2: Effect of pH

[Rose Bengal] = 9.00×10^{-6} M Mn doped–TiO_2 = 0.12 g
Light intensity = 60.0 $mWcm^{-2}$

pH	k × 10^5 (sec^{-1})
5.0	4.84
5.5	5.19
6.0	5.49
6.5	5.51
7.0	**5.75**
7.5	5.02
8.0	4.69
8.5	4.25
9.0	3.95
9.5	3.75
10.0	3.42

It has been observed that the rate of photocatalytic degradation was increased with increase in pH from 5.0 to 7.0; further increase in pH leads to a decrease in the rate of reaction. The increase in the rate of photocatalytic degradation with increase in pH may be due to formation of more $^{\bullet}OH$ radicals, which are generated from the interaction of OH^{-} and hole (h^{+}) of the photocatalyst. These $^{\bullet}OH$ radicals are responsible for the oxidative degradation of dye. On further increasing pH, OH^{-} ions increase and these will be adsorbed on the surface of the semiconductor making it negatively charged so that the approach of anionic rose Bengal to the semiconductor surface will be retarded due to repulsion between two negatively charged species. This will result into decrease in the rate of degradation.

Effect of rose Bengal concentration

The effect of dye concentration was studied by taking different concentrations of rose Bengal. The results are tabulated in Table 3.

Table 3: Effect of rose Bengal concentration

pH = 7.0 Mn doped–TiO_2 = 0.12 g

Light intensity = 60.0 $mWcm^{-2}$

[Rose Bengal] × 10^5 M	**k × 10^5 (sec^{-1})**
0.60	2.70
0.70	3.84
0.80	5.12
0.90	**5.75**
1.00	3.23
1.10	2.58
1.20	1.70
1.30	1.68

It has been observed that the rate of photocatalytic degradation increases with increase in concentration of dye up to 9.00×10^{-6} M. This may be attributed to the fact that as the concentration of dye was increased, more dye molecules were available for excitation followed by inter system crossing and hence, there was an increase in the rate. The rate of photocatalytic degradation was observed to decrease with further increase in the concentration of dye. Here, the dye starts acting as a filter for the incident light and it does not allow the desired light intensity to penetrate into solution and reach the semiconducting particles and thus, decreasing the rate of the photocatalytic bleaching of dye.

Effect of semiconductor

The effect of amount of Mn-doped TiO_2 was observed by taking different amounts of semiconductor. The results are reported in Table 4.

Table 4: Effect of amount of Mn-doped TiO_2 semiconductor

pH = 7.0 [Rose Bengal] = 9.00×10^{-6} M

Light intensity = 60.0 $mWcm^{-2}$

Mn-doped TiO_2 (g)	**$k \times 10^5$ (sec^{-1})**
0.02	3.62
0.04	3.71
0.06	3.82
0.08	4.22
0.10	4.94
0.12	**5.75**
0.14	4.54
0.16	4.23

Amount of semiconductor was varied in range from 0.02-0.16 g. It was observed that rate of reaction increases on increasing semiconductor amount upto 0.12 g because its exposed surface area also increases. Thereafter, rate showed a declining behaviour because now only thickness of semiconductor layer will increase and not the exposed surface area.

Effect of light intensity

To investigate the effect of light intensity on the photocatalytic degradation of rose Bengal, the distance between the light source and the exposed surface area was varied. The results are summarized in Table 5.

It was observed that degradation of dye was enhanced on increasing the intensity of light because number of photon striking per unit area in per unit time increases. After achieving optimum conditions, rate of degradation decreases because of some side thermal reactions.

Table 5: Effect of light intensity

pH = 7.0 [Rose Bengal] = 9.00×10^{-6} M

Mn doped TiO_2 = 0.12 g

Intensity of light ($mWcm^{-2}$)	$k \times 10^5$ (sec^{-1})
20.0	2.49
30.0	3.14
40.0	3.48
50.0	5.66
60.0	**5.75**
70.0	5.48

Mechanism

On the basis of the observations, a tentative mechanism for photocatalytic degradation of rose Bengal dye is proposed as –

$$^1Dye_0 \xrightarrow{h\nu} {}^1Dye_1 \qquad ...(3)$$

$$^1Dye_1 \xrightarrow{ISC} {}^3Dye_1 \qquad ...(4)$$

$$SC \xrightarrow{h\nu} e^-(CB) + h^+(VB) \qquad ...(5)$$

$$h^+ + {}^-OH \longrightarrow {}^\bullet OH \qquad .... (6)$$

$$^3Dye_1 + {}^\bullet OH \longrightarrow \text{Leuco Dye} \qquad ...(7)$$

$$\text{Leuco Dye} \longrightarrow \text{Products} \qquad ...(8)$$

Rose Bengal dye absorbs radiations of suitable wavelength and gives rise to its first excited singlet state. Then it undergoes intersystem crossing (ISC) to give its triplet state. On the other hand, the semiconducting Mn doped TiO_2 (SC) also 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 will oxidize the 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 scavengers (2-propanol), where the rate of degradation was drastically reduced.

CONCLUSION

The results of the present investigation revealed that the doping of titania with manganese enhances its photocatalytic activity, which was confirmed from the higher values of rate constants observed for photocatalytic degradation of rose Bengal in presence of Mn-doped TiO_2 in compare to pure titania.

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