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PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE BY NANOSIZED VANADIUM DOPED TiO_2 LOADED ON ZEOLITE

AARTI AMETA, INDU BHATI, RAKSHIT AMETA[a] and SURESH C. AMETA[a,*]

Photochemistry Laboratory, Department of Chemistry, M. L. Sukhadia University,
UDAIPUR – 313001 (Raj.) INDIA
[a]Department of Chemistry, PAHER University, UDAIPUR – 313003 (Raj) INDIA

ABSTRACT

Photocatalytic decolourization of methylene blue dye under visible light has been investigated using vanadium modified titanium dioxide supported on zeolite (V-TiO_2/zeolite). The photocatalyst was prepared and characterized by X-ray diffraction and SEM. The rate of photobleaching of dye was monitored spectrophotometrically. The effect of pH, dye concentration, amount of photocatalyst and intensity of light on the rate of photocatalytic reaction was observed. The results show that the use of V-doped TiO_2 increases the rate of photocatalytic decolourization of methylene blue to 5.7 and 8.6 times for 1% and 2% loading, respectively. The photocatalytic mechanism of V-TiO_2 catalyst has been tentatively discussed.

Key words: Methylene blue, Zeolite, Vanadium, Photocatalytic decolourization.

INTRODUCTION

Dyes are normally discharged to aquatic ecosystem by three major sources (a) from dye manufacturing unit (b) from dyeing industries and (c) from household discharge. Therefore, dyes are becoming a major source of organic pollutants, which is creating environmental contamination. Semiconductor photocatalysis has been increasingly addressed by many research groups for the removal of numerous organic pollutants from water. TiO_2 is the most commonly used photocatalyst, because it is non-toxic, chemically stable, low cost and very efficient.[1-4] However, it has some disadvantages also. These are (i) relatively high value of the band gap, around 3.2 eV, which limits its use in presence of visible light, (ii) high dispersion in the water, which causes difficulties in sedimentation, and

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[*]Author for correspondence; E-mail: ameta_sc@yahoo.com, aarti_ameta@yahoo.com

(iii) quick recombination between photoinduced charge carriers (electrons and holes), which decreases its photocatalytic activity.

Hence, methods which can increase the photocatalytic activity of TiO_2 or its efficiency to degrade dyes in presence of visible light always remained an important issue. In this respect, it has been observed that addition of transition metal ions as dopant on TiO_2 is effective as doping will extend the absorption of light towards higher wavelength region.[5-6] As titania particles remain mobilized (suspended) in solution, efforts have been made to use fine TiO_2 particles on solid supports. In this regard, porous materials of larger particle sizes have been investigated like silica gel, sand, clay and zeolite; but among various supports for TiO_2, zeolite seems to be an attractive candidate.[7] Photooxidation of phenol and benzene using TiO_2 supported on a zeolite was examined by Chen et al.[8] Several parameters are to be controlled in order to obtain highly effective degradation of organic molecules utilizing TiO_2 photocatalyst. Habibi et al.[9] have developed an efficient way to achieve the optimized photocatalytic process. The most optimal photocatalysis operational parameters for complete decolourization of dye are temperature, catalyst loading, UV light irradiation, pH and inorganic ions.

The photooxidation process of organic sulfides using TiO_2 photocatalyst was better in the presence of pure oxygen rather than in atmospheric oxygen or in the absence of oxygen.[10] It has been further proved that specific and controlled oxidative chemistry is the need to achieve higher photodegradation rate of the pollutants. Nahar et al.[11] made a comparative assessment of the efficiency of iron (III) doped TiO_2 prepared by two doping methods using photocatalytic degradation of phenol in domestic water as a model system. The effect of cobalt doping on the structural and optical properties of TiO_2 films prepared by sol-gel process was reported by Subramanian et al.[12] Photocatalytic reactivity of transparent titania sols prepared by peptization of titanium tetraisopropoxide was examined by Yamazaki and Nakamura.[13] Klosek and Raftery[14] prepared V doped TiO_2 photocatalyst and used it for photooxidation of ethanol in visible light. Negligible efforts have been made to use metal-doped TiO_2 on zeolite support[15] and therefore, the present work has been undertaken.

EXPERIMENTAL

Materials

Titanium isopropoxide, molecular sieves and methylene blue dye were purchased from Aldrich. All other chemicals like ethanol, nitric acid, sulphuric acid and sodium hydroxide were from BDH/Merck. Doubly distilled water was used throughout the study.

Preparation of photocatalyst

The supported photocatalyst was prepared by sol- gel method.[16] TiO_2 (sol) was synthesized by the controlled hydrolysis of titanium isopropoxide in presence of ethanol and nitric acid at 4°C with vigorous stirring for 10-11 hrs. In this solution, vanadium (V) sulphate was added as dopant. After stirring, the solution was stored in an ice bath for 3 days with occasional shaking. The solvent was then finally removed by rotatory evaporation at 35°C. The dried solid was heated in an oven and calcined at 450°C for 20-30 min. Finally, the supported TiO_2 photocatalyst was obtained by slurrying the above prepared solid powder with the zeolite (in the form of molecular sieves).

Characterization

XRD diffraction data of the powder were obtained on an 18 Kw X-ray diffractometer using Cu Kα radiation (λ = 1.540Å) having rotating anode X-ray source. Diffraction pattern was taken over the 2θ range 10°-70°. The crystallite size of the synthesized powder was determined from the X-ray line broadening using Sherrer's equation as follows:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

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 used in XRD, D is the crystallite size, β is full width of half maxima (FWHM) value and θ is Bragg's angle.

Scanning electron microscopy (SEM) was performed on JEOL JSM 5600 operated at 0.5 to 30 kV, with resolution power upto 3.5 nm.

Physical characterization of the photocatalyst: XRD Analysis

Titanium dioxide can be prepared in crystal forms: anatase, rutile and brookite. Several reports suggest that TiO_2 is most photoactive in the anatase form.[17] The X-ray powder pattern of TiO_2 prepared in this study are shown in Fig. 1, which indicates that anatase is the main constituent and rutile and brookite are present in very small amounts. The peaks in this XRD pattern are either broad or absent. Hence, the crystallite size (as calculated using Sherrer's equation) comes to be in nanometers (3.98 nm). The crystal data are shown in Table 1.

Table: 1 XRD Data

2 Theta	d spacing (Å)	Crystal size as calculated from Sherrer's equation
25.4	1.795	3.30
37.7	1.259	-
47.9	1.037	-
54.6	0.940	-
62.4	0.854	-

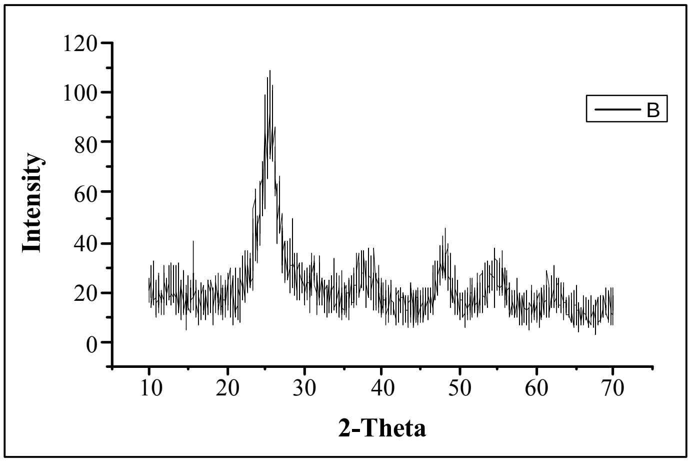

Fig. 1: XRD of V-TiO_2/zeolite

SEM Analysis

The SEM for zeolite and V/TiO_2-zeolite have been shown in Fig. 2 and Fig. 3, respectively. It is clear from the comparison of two SEM that the modified TiO_2 has been loaded successfully on zeolite as evident from lumps seen in the Fig. 3.

Photocatalytic degradation

The photocatalytic activity of catalyst was evaluated by measuring the rate of degradation of methylene blue. For this, first of all a standard solution of dye (1.0 x 10^{-3} M) was prepared by dissolving (1.008 g) of methylene blue in 100 mL of doubly distilled water. pH of the dye solution was measured by a digital pH meter (Systronics Model 335). The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions. The prepared semiconductor was used as photocatalyst in the present work. The reaction mixture (40 mL dye solution + V/TiO_2-zeolite) was exposed to a 200 W tungsten lamp. The intensity of light was varied by changing the distance between the light source and reaction mixture and it was measured by Suryamapi (CEL Model SM 201). The absorbance of solution at various time intervals was measured at λ_{max} 660 nm with the help of spectrophotometer (Systronics Model 106).

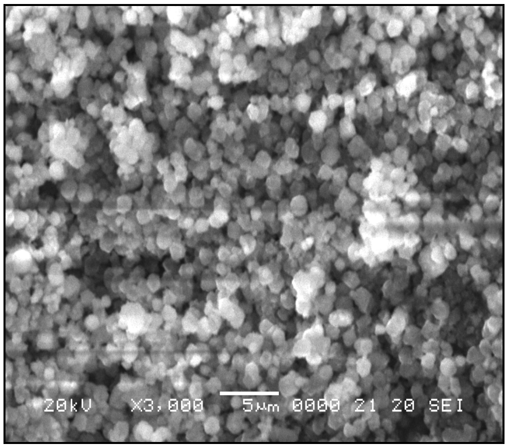

Fig. 2: SEM of Zeolite

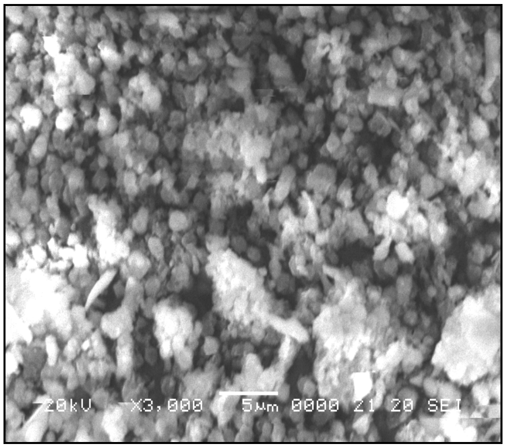

Fig. 3: SEM of V-TiO_2/zeolite

RESULTS AND DISCUSSION

The results of a typical run for normal and modified TiO_2 have been shown in Table 2. It was observed that absorbance (A) decreases with the time of exposure. A plot log O. D. versus time of exposure was found to be linear and hence, this reaction follows pseudo-first order kinetics. The rate constants were determined by the following expression:

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

Effect of pH

The effect of pH on the rate of degradation of methylene blue was investigated in the pH range (6.5-9.5). The results are reported in Table 3. The photochemical degradation depends strongly on the pH of the reaction medium. The rate of degradation increases with the increase in pH; but beyond pH 7.5, the rate of photocatalytic degradation decreases. In this case, the presence of scavenger i.e. 2-propanol does not affect the rate of reaction adversely and hence, it may be concluded that $^{\bullet}OH$ radical does not participate in the degradation as an active oxidizing species.

Table 2: A typical run

[Methylene blue] = 1.00 x 10^{-5} M pH = 7.5

Light Intensity = 60.0 mW cm^{-2} Semiconductor = 0.12 g

Time (min)	TiO_2	$V\text{-}TiO_2$/Zeolite	
	1 + log A	1 + log A	
		1 % Loading	2 % Loading
0.0	0.6149	0.6117	0.6124
10.0	0.6020	0.5729	0.5002
20.0	0.5843	0.4928	0.3880
30.0	0.5705	0.4014	0.2758
40.0	0.5622	0.3243	0.1636
50.0	0.5441	0.2528	0.0514
60.0	0.5250	0.2095	-
70.0	0.4265	0.1238	-
	k = 4.99 x 10^{-5} sec^{-1}	k = 2.84 x 10^{-4} sec^{-1}	k = 4.31 x 10^{-4} sec^{-1}

Table 3: Effect of pH

[Methylene blue] = 1.00 x 10^{-5} M V-TiO_2/zeolite = 0.12 g (1% loading)

Light intensity = 60.0 mW cm^{-2}

pH	k x 10^4 (sec^{-1})
6.5	2.16
7.0	2.50
7.5	**2.84**
8.0	2.33
8.5	2.00
9.0	1.66
9.5	1.10

Effect of concentration of dye

Effect of variation of dye concentration on rate of reaction was also observed by taking different concentrations of methylene blue solutions and the results are represented in Table 4. It has been observed that rate of photocatalytic degradation increases with increase in concentration up to 1.0 x 10^{-5} M but further increase in dye concentration results in decreasing the rate of reaction. This may be explained on the basis that on increasing the concentration of methylene blue, more molecules of dye are available for degradation and hence, the rate increases, but at concentration higher than 1.0 x 10^{-5} M, the dye molecule itself starts acting like a filter for the incident light and it will not permit the desire light intensity to reach the dye molecule in the bulk of the solution photocatalyst and thus, a decrease in the rate of photochemical bleaching of methylene blue has been observed.

Table 4: Effect of dye concentration

V-TiO_2/zeolite = 0.12 g (1% loading) Light intensity = 60.0 mW cm^{-2}

pH = 7.5

[Methylene blue] x 10^5 M	**k x 10^4 (sec^{-1})**
0.25	2.06
0.50	2.35
0.75	2.50
1.00	**2.84**
1.25	2.66
1.50	2.01
2.00	1.53

Effect of amount of semiconductor

The effect of amount of semiconductor was investigated from in the range of 0.04-0.16 g and results are tabulated in Table 5. It was observed that rate of reaction increases with increase in amount of semiconductor till 0.12 g; but if the amount of semiconductor is increased further, then there is virtually no effect on the rate of photodegradation and it becomes almost constant. This may be attributed due to fact that as the amount of semiconductor was increased, the exposed surface area of semiconductor also increases and as a result, the rate of reaction also increases but further increase in the amount of semiconductor will only increase the thickness of the layer at the bottom of reaction vessel, which was completely covered by the semiconductor. Thus, saturation like behaviour (constant rate of reaction) was achieved.

Table 5: Effect of amount of semiconductor

[Methylene blue] = 1.00 x 10^{-5} M Light intensity = 60.0 mW cm^{-2}
pH = 7.5

V-TiO_2/zeolite (g) (1% loading)	**k x 10^4 (sec^{-1})**
0.04	1.83
0.06	2.34
0.08	2.50
0.10	2.68
0.12	**2.84**
0.14	2.78
0.16	2.81

Effect of light intensity

The effect of light intensity on the photocatalytic degradation of methylene blue was studied in the range of 20.0-60.0 $mWcm^{-2}$ and the results are summarized in Table 6.

Table 6: Effect of light intensity

pH = 7.5 [Methylene blue] = 1.00 x 10^{-5} M
V-TiO_2/Zeolite = 0.12 g (1% loading)

Light intensity (mW cm^{-2})	**k x 10^4 (sec^{-1})**
20.0	1.45
30.0	1.66
40.0	1.83
50.0	2.50
60.0	**2.84**

The rate of bleaching of dye was found to increase on increasing light intensity up to 60.0 $mWcm^{-2}$ because an increase in the intensity of light will increase the number of photon striking semiconductor particles per unit time per square cm. As, a result more electron-hole pairs will be generated, which results in an increase in the rate of reaction. Higher intensities were avoided as these may cause some thermal side reactions.

Mechanism

Methylene blue absorbs radiations of suitable wavelength and it is excited to its first excited singlet state; which is then converted to its triplet state through (ISC) inter system crossing. The semiconductor also absorbs light to excite an electron from its valence band (VB) to its conduction band (CB), leaving behind a hole in the valence band. This electron will reduce the dye to its leuco form, which ultimately degrades into products. Thus, the use of nanosized particles of V-TiO_2/zeolite enhances the rate of photocatalytic bleaching of methylene blue to 5.7 and 8.6 times for 1% and 2% loading of vanadium (V) on TiO_2/zeolite, respectively.

$$^1MB_0 \xrightarrow{h\nu} {}^1MB_1 \quad \ldots(2)$$

$$^1MB_1 \xrightarrow{ISC} {}^3MB_1 \quad \ldots(3)$$

$$TiO_2 \xrightarrow{h\nu} TiO_2\ (h^+\ (VB) + e^-\ (CB)) \quad \ldots(4)$$

$$^3MB_1 + e^- \longrightarrow {}^3MB_1^-\ \text{(leuco form)} \quad \ldots(5)$$

$$^3MB_1^-\ \text{(Leuco form)} \longrightarrow \text{Products} \quad \ldots(6)$$

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