

## USE OF NANOSIZED CHROMIUM DOPED TiO<sub>2</sub> SUPPORTED ON ZEOLITE FOR METHYLENE BLUE DEGRADATION

Aarti Ameta<sup>1,\*</sup>, Indu Bhati<sup>1</sup>, Rakshit Ameta<sup>2</sup>, and Suresh C. Ameta<sup>1</sup>

<sup>1</sup>Photochemistry Laboratory, Department of Chemistry, M. L. Sukhadia University, Udaipur - 313001 (Raj.) INDIA

<sup>2</sup>Department of Pure and Applied Chemistry, University of Kota, Kota - 342005 (Raj.) INDIA

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### ABSTRACT

The photocatalytic degradation of methylene blue dye under visible light has been investigated using chromium modified titanium dioxide supported on zeolite (Cr-TiO<sub>2</sub>/zeolite). The photocatalyst was prepared by sol-gel method and characterized by X-ray diffraction and SEM. The rate of photodegradation 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 showed that the use of Cr-doped TiO<sub>2</sub> increased the rate of photocatalytic degradation of methylene blue as compared to untreated TiO<sub>2</sub>. The photocatalytic mechanism of Cr-TiO<sub>2</sub> catalyst has been tentatively discussed.

**Keywords:** Methylene blue, zeolite, chromium, photocatalytic degradation

### INTRODUCTION

Dyes are normally discharged to aquatic ecosystem by three major sources from (a) dye manufacturing unit (b) dyeing industries and (c) household discharges. Therefore, dyes are becoming a major source of organic pollutants, which is creating environmental contamination.

Semiconductor based photocatalysis has been increasingly addressed by many research groups for the removal of numerous organic pollutants from water. On exposing to light of suitable wavelength, electron jumps to conduction band leaving behind a hole in valence band. Thus, a hole-electron pair is generated, which can be utilized for the oxidation or reduction of any contaminants.

TiO<sub>2</sub> is the most commonly used photocatalyst, because it is non-toxic, chemically stable, low cost and very efficient [1-3]. 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 sun light, (ii) high dispersion in the water, which causes difficulties in sedimentation, and (iii) quick recombination between photoinduced charge carriers (electrons and holes), which decreases its photocatalytic activity.

Hence, search for newer methods, which can increase the photocatalytic activity of TiO<sub>2</sub> 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<sub>2</sub> is effective as this doping will extend the absorption of light towards higher wavelength region [4-5]. As titania particles remain mobilized (suspended) in solution, efforts have been made to use fine TiO<sub>2</sub> 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<sub>2</sub>, zeolite seems to be an attractive candidate [6-8].

Photooxidation of phenol and benzene using TiO<sub>2</sub> supported on zeolite was examined by Chen et al. [9]. Several parameters are to be controlled in order to obtain highly effective degradation of organic molecules utilizing TiO<sub>2</sub> photocatalyst. Habibi et al. [10] have developed an efficient way to achieve the optimized photocatalysis operational parameters such as temperature, catalyst loading, light irradiation, pH and

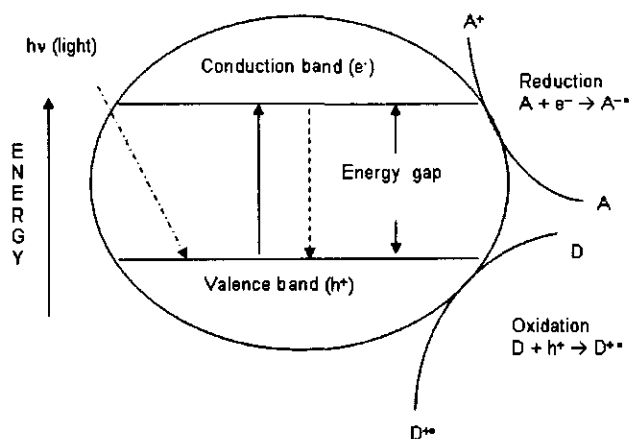


Fig 1. Mechanism of photocatalysis

\* Corresponding author.  
Email address : aarti\_ameta@yahoo.com

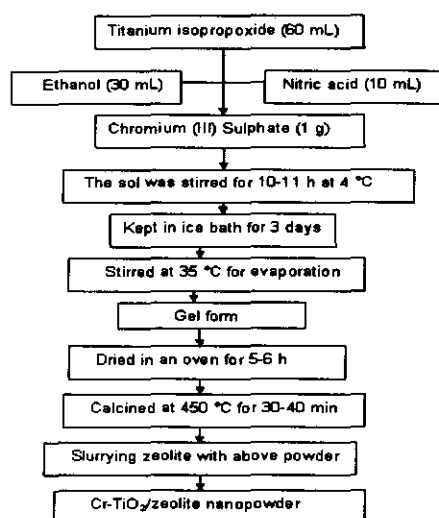


Fig 2. Flow chart for the preparation of semiconductor (nanoparticles)

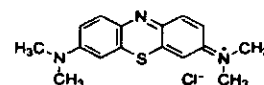
inorganic ions were investigated for the complete degradation of dyes.

The photooxidation process of organic sulfides using  $\text{TiO}_2$  photocatalyst was better in the presence of pure oxygen rather than in atmospheric oxygen or in the absence of oxygen [11]. It has been further proved that specific and controlled oxidative chemistry is needed to achieve higher photodegradation rate of the pollutants. Nahar et al. [12] made a comparative assessment of the efficiency of iron (III) doped  $\text{TiO}_2$  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  $\text{TiO}_2$  films prepared by sol-gel process was reported by Subramanian et al. [13]. Photocatalytic reactivity of transparent titania sols prepared by peptization of titanium tetraisopropoxide was examined by Yamazaki and Nakamura [14]. Klosek and Raftery [15] prepared V doped  $\text{TiO}_2$  photocatalyst and used it for photooxidation of ethanol in visible light. Negligible efforts have been made to use metal-doped  $\text{TiO}_2$  on zeolite support [16] and therefore, the present work has been undertaken.

## EXPERIMENTAL SECTION

### Materials

Titanium isopropoxide, molecular sieves (zeolite) and methylene blue (MB) dye were purchased from Aldrich. All other chemicals like ethanol, nitric acid, sulfuric acid and sodium hydroxide were from BDH/Merck. Doubly distilled water was used throughout the study. The structure of methylene blue dye is as shown:



### Procedure

#### Preparation of photocatalyst

The supported photocatalyst was prepared by sol-gel method [17].  $\text{TiO}_2$  (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 h. In this solution, chromium (III) sulphate was added as a 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  $\text{TiO}_2$  photocatalyst was obtained by slurrying the above prepared solid powder with the zeolite (in the form of molecular sieves).

#### Physical characterization of the photocatalyst

**XRD Analysis.** XRD diffraction data of the powder were obtained on an 18 Kw X-ray diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.540\text{\AA}$ ) having rotating anode X-ray source. Diffraction pattern was taken over the  $2\theta$  range 10-70°. The crystallite size of the synthesized powder was determined from the X-ray line broadening using Scherrer'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;  $\lambda$  is the wavelength used in XRD; D is the crystallite size;  $\beta$  is full width of half maxima (FWHM) value (calculated for the entire XRD pattern) and  $\theta$  is Bragg's angle.

Titanium dioxide can be prepared in three crystalline forms: anatase, rutile and brookite. Several reports suggest that  $\text{TiO}_2$  is most photoactive in the anatase form [18]. The XRD pattern for pure zeolite has been shown in Fig 3. The X-ray powder pattern of modified  $\text{TiO}_2$  ( $\text{Cr-TiO}_2/\text{zeolite}$ ) in Fig 4, is having prominent peaks around  $2\theta = 25.4^\circ$  which indicates that anatase form of titanium dioxide is the main constituent [19] and rutile and brookite are present in very small amounts. The peaks in this XRD pattern are either broad or absent. The sharp peaks in Fig 4 correspond to the peaks observed in XRD of zeolite. On the basis of Scherrer formula, the particle size of modified  $\text{TiO}_2$  ( $\text{Cr-TiO}_2/\text{zeolite}$ ) was calculated to be 3.60 nm.

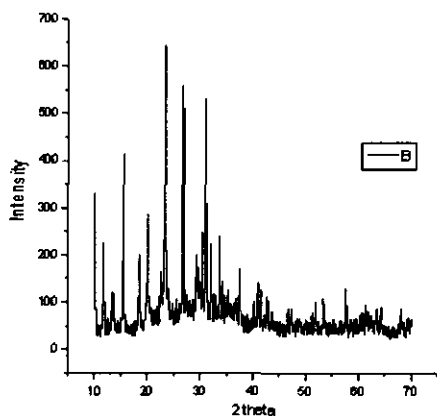


Fig 3. XRD of pure zeolite

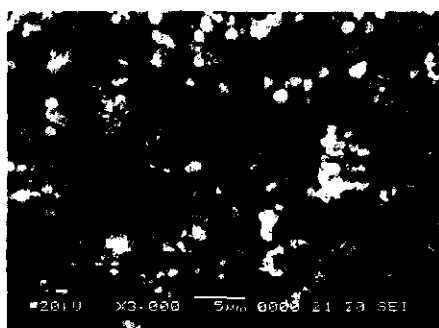
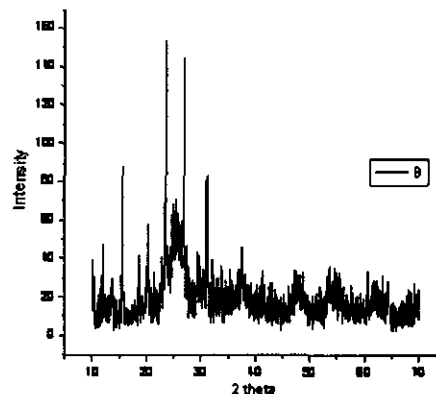
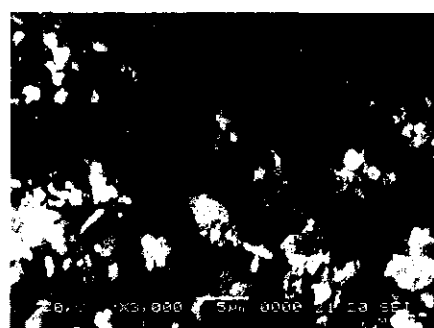


Fig 5. SEM of Zeolite

Fig 4. XRD of Cr-TiO<sub>2</sub>/zeoliteFig 6. SEM of Cr-TiO<sub>2</sub>/zeolite

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

The SEM of zeolite and Cr-TiO<sub>2</sub>/zeolite have been shown in Figs 5 and 6.

It is clear from a comparison of two SEM that the modified TiO<sub>2</sub> has been loaded successfully on zeolite as evident from lumps seen in the Fig 6. It indicates that the TiO<sub>2</sub> particles were not aggregated in nucleus like but rather present in sparsely agglutinated shape [20].

#### Photocatalytic Degradation

The photocatalytic activity of catalyst was evaluated by measuring the rate of degradation of methylene blue. A standard solution of dye ( $1.0 \times 10^{-3}$  M) was prepared by dissolving 1.0080 g of methylene blue in 100 mL of doubly distilled water. pH of the dye solution was measured by a digital pH meter (Cyberscan 1000). The prepared semiconductor was used as photocatalyst in the present work. The reaction mixture (40 mL dye solution + Cr/TiO<sub>2</sub>-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  $\lambda_{\text{max}}$  660 nm with the help of a spectrophotometer (Systronics Model 106).

#### RESULT AND DISCUSSION

The results of a typical run for degradation of methylene blue in presence of normal TiO<sub>2</sub> and modified TiO<sub>2</sub> (Cr-TiO<sub>2</sub>/zeolite) have been graphically represented in Figs 7 and 8. It was observed that absorbance decreases with the time of exposure. A plot of log Absorbance 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:

$$k = 2.303 \times \text{slope}$$

#### Effect of pH

The effect of pH on the rate of degradation of methylene blue was investigated in the pH range (6.5-10.0). The results are graphically represented in Fig 9. The rate of photochemical degradation increases with the increase in pH; but beyond pH 9.0, the rate of photocatalytic degradation decreases. The rate of degradation decreases in acidic medium as the surface

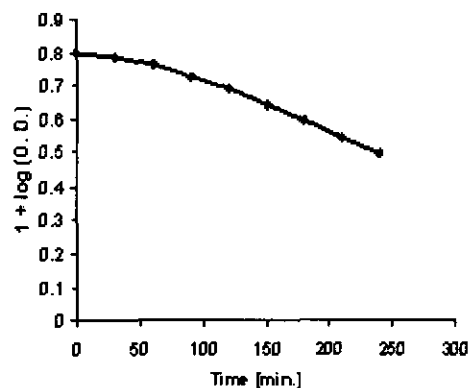
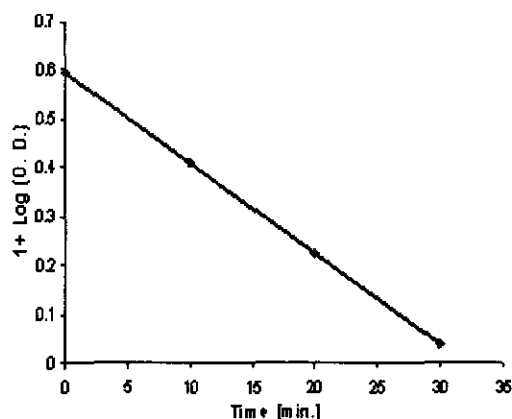
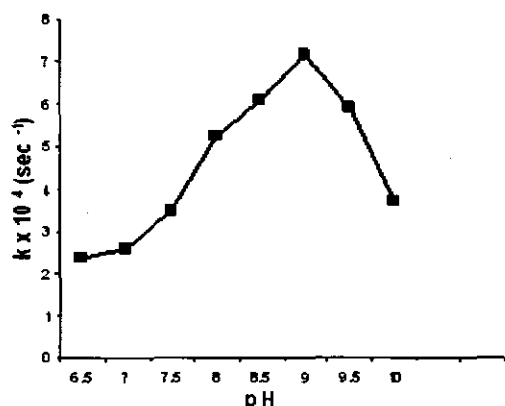
Fig 7. Typical run for  $\text{TiO}_2$ ;  $k = 5.11 \times 10^{-5} \text{ sec}^{-1}$ Fig 8. Typical run for modified  $\text{TiO}_2$ ;  $k = 7.16 \times 10^{-4} \text{ sec}^{-1}$ 

Fig 9. Effect of pH

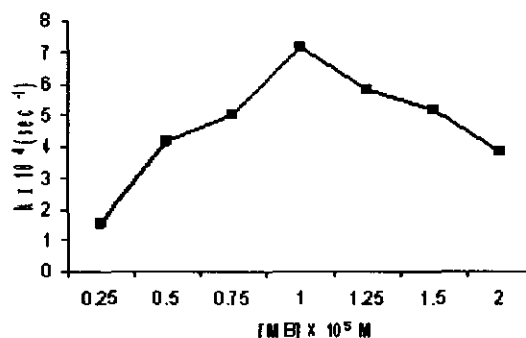


Fig 10. Effect of dye concentration

of the semiconductor becomes positively charged due to adsorption of  $\text{H}^+$  ion and there will be repulsion between this positively charged surface and the cationic dye methylene blue. On increasing the pH of the medium above 9.0, the surface of the semiconductor becomes negatively charged due to adsorption of  $\text{OH}^-$  ions and the dye remain in its neutral form (ofcourse, electron rich due to lone pairs on nitrogen atoms). Thus, there will be repulsion between electron rich dye and the negatively charged surface of the semiconductor resulting into a decrease in the rate of reaction.

In this case, the presence of a specific  $\cdot\text{OH}$  radical scavenger i.e. 2-propanol does not affect the rate of reaction adversely and thus, it may be concluded that  $\cdot\text{OH}$  radical does not participate in the degradation as an active oxidizing species. Hence, the degradation of methylene blue proceeds by reduction via its leuco form.

#### Effect of Dye Concentration

Effect of dye concentration on rate of reaction was also observed by taking different concentrations of methylene blue solutions and the results are represented graphically in Fig 10. It has been observed that rate of

photocatalytic degradation increases with increase in concentration up to  $1.00 \times 10^{-5} \text{ M}$  of the dye, but a 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 excitation, electron transfer and degradation and hence, the rate increases. At higher concentration i.e. above  $1.00 \times 10^{-5} \text{ M}$ , the dye molecule itself starts acting like a filter for the incident light. It will not permit the desired light intensity to reach the dye molecule in the bulk of the solution [21] and thus, a decrease in the rate of photochemical bleaching of methylene blue has been observed.

#### Effect of Amount of Semiconductor

The effect of amount of semiconductor was also investigated and the results are presented graphically in Fig 11. It was observed that rate of reaction increases with increase in amount of semiconductor till 0.16 g. When the amount of semiconductor was increased further, then there was virtually no effect on the rate of photodegradation; rather, it becomes almost

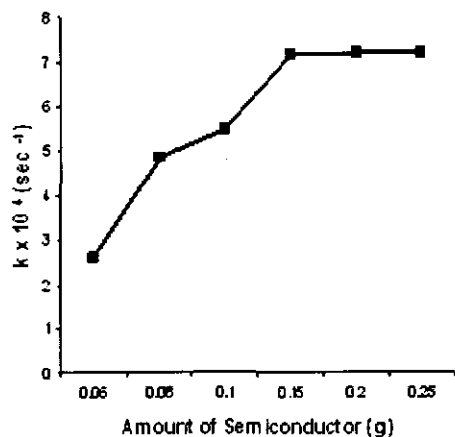


Fig 11. Effect of amount of semiconductor

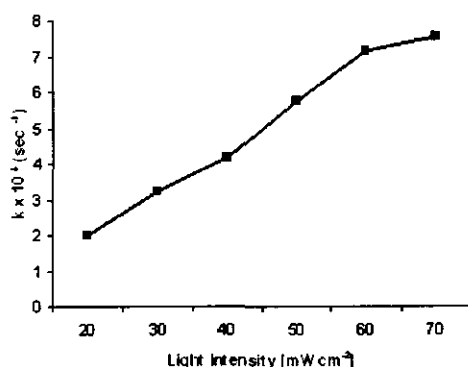


Fig 12. Effect of light intensity

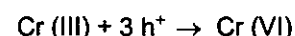
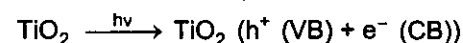
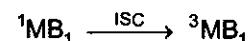
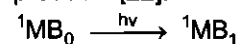
constant. This may be attributed due to fact that on increasing the amount of semiconductor, the exposed surface area of semiconductor also increases. As a result, the rate of reaction also increases but on further increasing the amount of semiconductor above 0.16 g, only the thickness of the layer will increase, i.e. there is no increase in the exposed surface area of semiconductor. Thus, saturation like behavior (constant rate of reaction) was achieved.

#### Effect of Light Intensity

The effect of light intensity on the photocatalytic degradation of methylene blue was studied and the results are represented graphically in Fig 12. The rate of dye degradation was found to increase on increasing light intensity because an increase in the intensity of light will increase the number of photons 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.

#### 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 inter system crossing (ISC). 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 [22].



#### CONCLUSION

The rate of photocatalytic degradation of methylene blue was enhanced by doping  $\text{TiO}_2$  with transition metal ( $\text{Cr}^{3+}$ ) as compared to pure  $\text{TiO}_2$ . An appreciable increase in the rate (14 times) was observed.

Further the modified  $\text{TiO}_2$  ( $\text{Cr-TiO}_2/\text{zeolite}$ ) settles down and it doesn't remain suspended in the solution and hence, the problem of spectrophotometric measurements is solved and secondly, it absorbs in the visible range utilizing a major portion of sunlight. Hence, the modified semiconductor can be reused again and it is more effective for degradation of dye due to its nanosize 3.60 nm (having more surface area).

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