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## Removal of methylene blue dye aqueous solution using photocatalysis

### ABSTRACT

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The nano sized TiO<sub>2</sub> and ZnO are the most active photocatalysts. Methylene blue was used as a reference molecule for the photocatalytic degradation. The TiO<sub>2</sub> and ZnO can totally remove methylene blue dye. The effect of various process parameters like initial concentration, contact time, dose of catalyst and pH on the extent of removal of dye by photocatalysis in presence of TiO<sub>2</sub> and ZnO was studied. The results showed that the percentage of dye removal increases with increase in contact time. The optimum contact time was fixed at 180 minutes for both nanomaterials. The results of this study reveal that the dyes could be removed by semiconducting nanomaterials assisted photocatalytic degradation. The semiconducting materials were analyzed by XRD and SEM before and after degradation of methylene blue.

**Keywords:** *Photocatalysis; SEM; XRD; FTIR; TOC; COD.*

### INTRODUCTION

Contaminants from industrial effluents often pose a major environmental problem. Various dyes have been used in textile, dyeing, paper pulp, plastic, leather, cosmetics and food industries [1], Colour, dye stuff discharge from these industries possess certain hazards and environmental problems [2]. Photocatalysis is one of the new techniques for removal of dyes from wastewater [3,4]. Nowadays, more than 9000 different types of dyes have been incorporated in the colour index [5]. Dyes usually have complex aromatic molecular structure which makes them more stable and difficult to biodegrade. Many dyes are toxic, and may cause destruction or inhabiting of their catalytic capabilities [6]. To reduce the risk of environmental pollution from such waste it's necessary to treat them before discharging to the receiving environment [7]. Due to their low biodegradability, a conventional biological treatment process is not very effective in treating dye wastewater [8,9]. Photocatalytic degradation has a great potential to control aqueous contaminants or pollutants [10].

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The photocatalysis is new, fast, convenient and less expensive method for degradation of the dye Methylene blue (MB) was applied [11]. Among the various oxides semiconducting photocatalysts  $\text{TiO}_2$  and  $\text{ZnO}$  are important photocatalysts, because they are very effective due to high band gap, safe, inexpensive, stable to photocorrosion, and maximum removal of the dyes [12].

Advanced Oxidation Process (AOP) has been considered as an effective technology in treating organic chemical including dyes in wastewater. AOP include photocatalysis system as combination of semiconductor ( $\text{TiO}_2$ ,  $\text{ZnO}$ ) with UV light [13]. Nano sized semiconductor such as  $\text{ZnO}$  and  $\text{TiO}_2$  are one of the most basic functional materials. The effect of  $\text{TiO}_2$  on the rate of photodegradation of methylene blue is very high. Zinc Oxide has a band gap of 3.17 eV while  $\text{TiO}_2$  has 3.2 eV.  $\text{ZnO}$  also adsorb more UV light than any other photocatalysts. The high UV absorption efficiency leads to generation of more electron ( $e^-$ ) and hole ( $h^+$ ) are considered as main species involved in photodegradation process (Figure 1) [14,15].

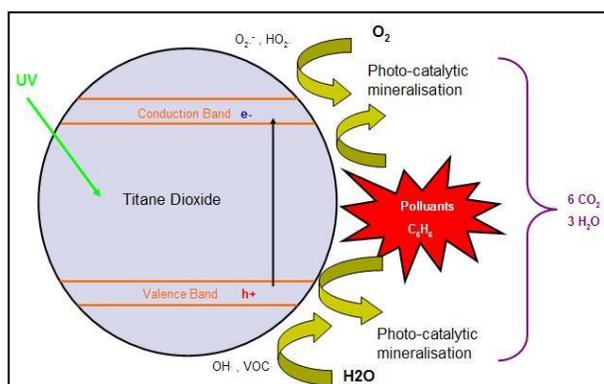


Fig.1. Photocatalysis on anatase  $\text{TiO}_2$

In this paper the photocatalytic degradation of MB by using  $\text{TiO}_2$  and  $\text{ZnO}$ , a total degradation of MB is possible. Advanced Oxidation Process (AOP) is an effective technology in treating organic chemical, including dyes in wastewater.

The photocatalytic degradation of Methylene blue was studied spectrophotometrically by using  $\text{TiO}_2$  and  $\text{ZnO}$  [16]. The parameters, effect of concentration on MB, pH, amount of photocatalysts and light intensity on the rate of the photocatalytic degradation were studied [17, 18].

## EXPERIMENTAL

### Materials

The basic dye used in this study is Methylene blue, A.R. grade supplied by S.D. Fine Chemicals Mumbai. MB in commercial purity was used without further purification. MB is a heterocyclic aromatic compound (CI=52015, M.wt.=319.86, M. formula =  $C_{18}H_{18}N_3SCl_3H_2O$ ,  $\lambda_{max}$ =665 nm Nature= cationic). The accurate weighted quantity of the dye was dissolved in double distilled water to prepare a stock solution (0.1g/L). Dye concentration was determined by using adsorbance measured before and after the treatment with UV-Visible Spectrophotometer. The solution was obtained by diluting a stock solution of MB dye in accurate proportion in between 0.01 to 0.05 g/L.

### Preparation of photocatalysts

For the preparation of anatase  $\text{TiO}_2$ , Titanium trichloride (20-30 % HCl) solution and ammonia were used. By hydrolysis of  $\text{TiCl}_3$  and pH was adjusted by  $\text{NH}_3$  in between 10-12. The  $\text{TiO}_2$  particles were heated at 393 K overnight. The dried sample was calcined at 753 K under air for 8 hrs. The calcined samples are termed as AT (anatase  $\text{TiO}_2$ ).

Nano sized  $\text{ZnO}$  particles are prepared by using Zinc sulphate and sodium hydroxide solution. During the reaction, zinc oxide precipitation was formed, and it was annealed in the air at  $250^\circ\text{C}$  for half an hour. After annealing,  $\text{ZnO}$  nanoparticles are formed. Surface morphology and characteristics of  $\text{TiO}_2$  and  $\text{ZnO}$  nano particles were analyzed by using XRD and SEM technology.

Many studies have confirmed that the anatase  $\text{TiO}_2$  is superior photocatalytic material. The bleaching of Methylene blue was carried out in presence of semiconductor  $\text{TiO}_2$  and  $\text{ZnO}$  [19, 20]. The photocatalytic degradation of MB for both initial concentration and irradiation sample was determined by using with UV- Visible Spectrophotometer. The supernatant dye solution was separated by centrifuging. All the experiment were carried out at pH 7 [21].

### Photocatalytic Study

The removal of the dye was observed by using UV Vis- spectrophotometer (Systronic

Model-2203). The calibration curve of Methylene blue dye was obtained at  $\lambda = 665\text{nm}$ . The dye solution was exposed to UV light (PHILIPS-400Watt) by addition of  $\text{TiO}_2$  and  $\text{ZnO}$  at a distance 30 cm from the reaction vessel (Figure 2). Double distilled water was used for the experiment. UV-spectrophotometer in glass cuvette with path length 1.00 cm and the progress of photocatalytic reaction can be observed. The sample separated from the photocatalysts by centrifuging. Samples were withdrawn at different time interval (15min.). To study the effect of important parameters like pH, contact time, initial concentration and photocatalyst dose on the MB, a batch experiment were conducted for each experiment. The kinetic study was determined by analyzing decolourization of dye from aqueous solution at specific time intervals [22]. In the adsorption process by using an agricultural waste or any bioadsorbents the dye can remove, But disposal of bioadsorbent waste materials after adsorption problem remain same and the soil pollution as well as water pollution was increases. In the photocatalysis the nano sized photocatalytic materials can degrade the organic dyes and the nanoparticle can be reused.

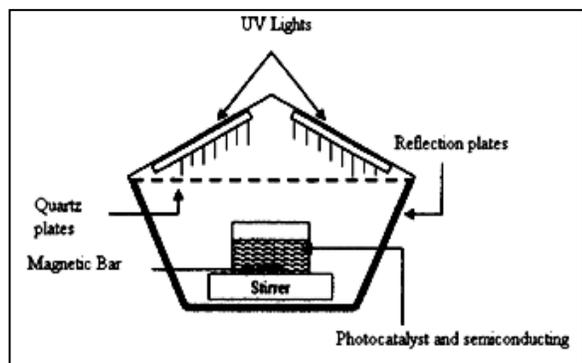


Fig. 2. Photocatalysis Reactor

## RESULTS AND DISCUSSION

### Effect of pH

The pH is one of the most important factors for controlling the removal of dye. PH of the dye solution was studied with the change in pH the percentage of removal was also changed. The pH of Methylene blue solution was adjusted in the range of 4 to 10 pH by adding HCl and NaOH (0.05 M). About 0.2 gm of photocatalyst was added

in the solution in different concentration from 10 mg/L to 50 mg/L MB [23]. Solution was irradiation by UV light for the given time interval and the percentage of removal was determined [24, 25].  $\text{ZnO}$  was dissolved in presence of highly acidic media and therefore photocatalytic bleaching could not be investigated at lower pH range. The highest percentage of dye removal pH was selected for the study of photocatalysis. The rate of photocatalytic bleaching of Methylene blue was increasing with increase in pH [26]. The pH increases from pH 4 to pH 7 as the percentage of removal increases from 34.2% to 91.4 % and from pH 7 to pH 14 the removal of the dye was decreased, from 91.4 % to 77 % (Figure 3). The removal of the dye by  $\text{TiO}_2$  and  $\text{ZnO}$  was less at lower pH. The highest percentage of removal was 91.4 %, at pH 7.0 was suitable for further study.

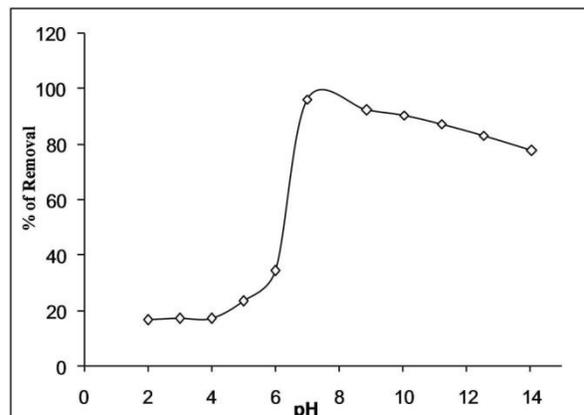


Fig. 3. Effect of pH on adsorption of Methylene blue on  $\text{TiO}_2$

### Effect of Contact Time

Effect of contact time and dye concentration on the removal of Methylene Blue from aqueous solution in presented in Figure 4 and 5 by  $\text{TiO}_2$  and  $\text{ZnO}$  respectively The experiments were carried out at 200 rpm 5.0 g/L mass adsorbent at room temperature, pH 7.0 and the dye concentrations of Methylene Blue (10 to 50 mg /L) for different time intervals up to 240 min. The percentage dye removal decreases with increasing in adsorbent  $\text{TiO}_2$  and  $\text{ZnO}$  dye concentration.

The percentage removal decreases with increase in dye concentration and remained nearly constant after equilibrium time. Photocatalytic degradation capacity at equilibrium for MB increased from 15.5 to 85 mg/g for 50 ppm, 20.7 to

95.4 mg/g for 30 ppm, and for 10 ppm it is very high 21.4 to 99.8 mg/g respectively for TiO<sub>2</sub>. For ZnO photocatalyst it is increases from 14.6 to 66.7 mg/g 18.7 to 86.9 mg/g and 19.9 to 99.5 mg/g for 50, 30 and 10 mg/L respectively. The equilibrium established within 180 min for both photocatalysts for all the concentration studies. It is established that removal of dye depends upon the concentration of dye. It is observed that the amount of photocatalyst increases from 0.2 g/L to 1.0 g/L the degradation increases. Irradiation time for complete degradation of MB decreases, as the concentration increases, because when all dye molecule are degraded by TiO<sub>2</sub> surface, any further addition of TiO<sub>2</sub> could have no effect on the degradation efficiency [27].

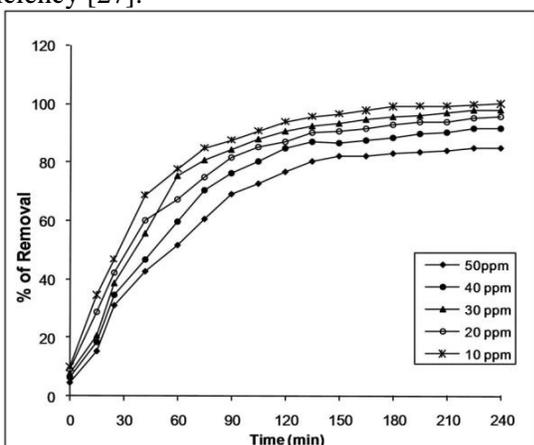


Fig. 4. Effect of contact time with % of removal of different initial concentration of methylene blue on TiO<sub>2</sub> (dose .5gm/100ml at pH 7)

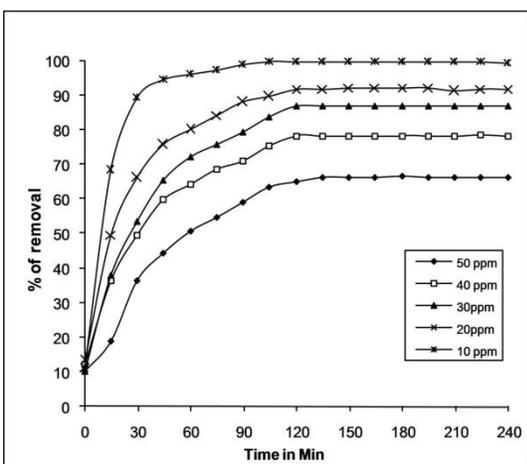


Fig. 5. Effect of contact time with % of removal of different initial concentration of MB on ZnO (dose =0.5gm/100ml at pH 7)

#### Effect of photocatalysts

In order to examine the effect of Photocatalyst dose on the removal efficiency of MB degradation experiments were set up with varying the dose (2.0 mg/L, 5.0 mg/L and 10.0 mg/L) for TiO<sub>2</sub> and ZnO while keeping initial dye conc. of 40 g/L and temp was 30 +0.1 °C and pH 7.0 was constant at different. Contact time up to 180 min. The percentage removal was increased and equilibrium time was decreased with dose of photocatalysts. The percentage removal increases from 58.6 to 92 % as the TiO<sub>2</sub> dose was increased from 2.0 g/L to 5.0 g/L at the equilibrium time. Similar for ZnO, degradation increases from 86 to 92.8 % as the dose of adsorbent was increased from 2.0 g/lit to 5.0 g/lit (Figure 6). Most of the dye was sequestered from the solution within 180 min. after the start of experiment. For each photocatalyst the amount of dye removal per unit weight of photocatalysts is different. The rate of reaction increases with increase in amount of TiO<sub>2</sub> and ZnO, as the amount of semiconductor increases the exposed surface area of the semiconductor also increases.

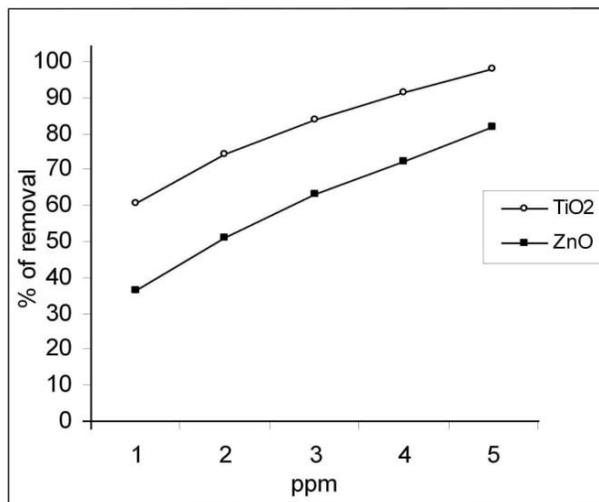


Fig.6. Effect of Photocatalyst dose

#### Effect of dye concentration

The concentration of semiconducting materials was increased with increasing a initial concentration of Methylene blue [28]. The equilibrium time is taken for the maximum removal of dye by increasing in photocatalyst. The equilibrium time was found to be 180 min for 10 mg/L to 50 mg/L of the MB dye concentration. The

removal of the dye is rapid in the initial stage of contact time and gradually decreases with time [29].

**Characterization of photocatalysts**

• **X ray Diffraction**

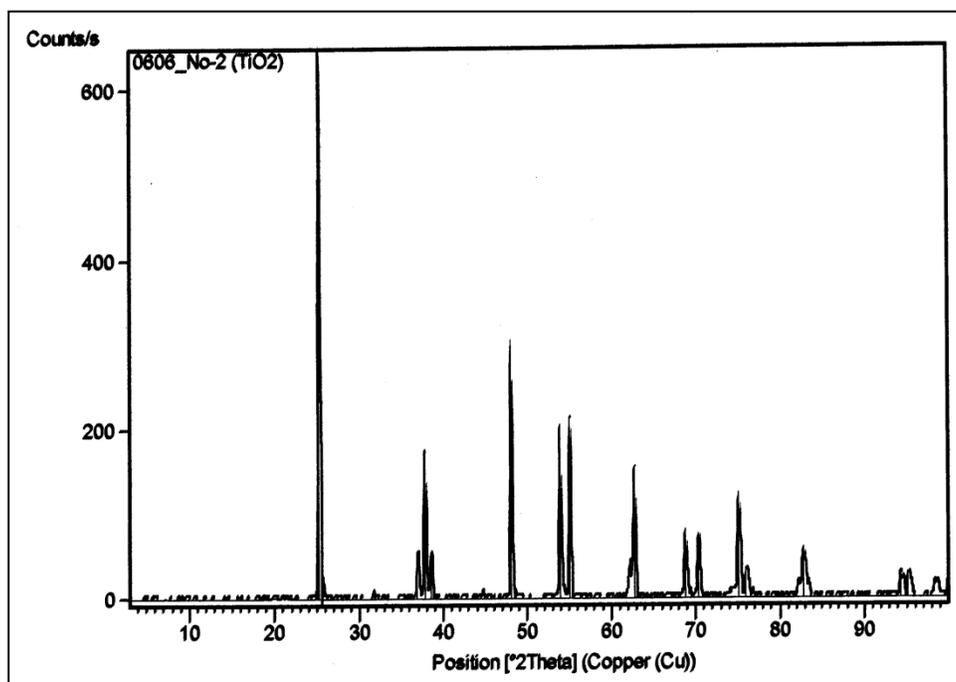
X ray diffraction of TiO<sub>2</sub> and ZnO was recorded by using Xray diffractometer (model-Xpert MPD Philips, Holland) using copper (Cu K $\alpha$ ) target. The d values obtained for TiO<sub>2</sub> and ZnO were 0.5764, 0.4706 correspond to 0.4583 and 0.4012 respectively. Table 1, indicates that after photocatalytic degradation particles size are increased [30]. The size of particle is determined by using equation 1.

$$D_{nm} = (K\lambda / \beta \cos\theta) \tag{1}$$

The X ray powder diffraction pattern of TiO<sub>2</sub> and ZnO was recorded at 2 $\theta$  angle. The percentage form was determined from the integrated intensity at 2 $\theta$  =25.25  $^\circ$ , 31.78  $^\circ$  the diffraction pattern shows a shift to 25.24  $^\circ$  and 36.38  $^\circ$  indicating the interrelation of surfactant ions in the ZnO. The d values obtained for TiO<sub>2</sub> and ZnO was 0.5764 nm, 0.4586 nm correspond to 0.4583 nm and 0.4012 nm respectively, before photocatalytic degradation. The sizes of the particles are nano size in nature. It indicates that after photcatlalytic degradation the sizes of particles are increased (Figures 7 and 8).

**Table 1.** Nano sized photocatlyst before and after treatment by using XRD

TiO <sub>2</sub>		ZnO	
Before	After	Before	After
0.458 nm	0.576 nm	0.401 nm	0.458 nm



**Fig. 7.** XRD diagram of TiO<sub>2</sub> semiconductor after irradiation

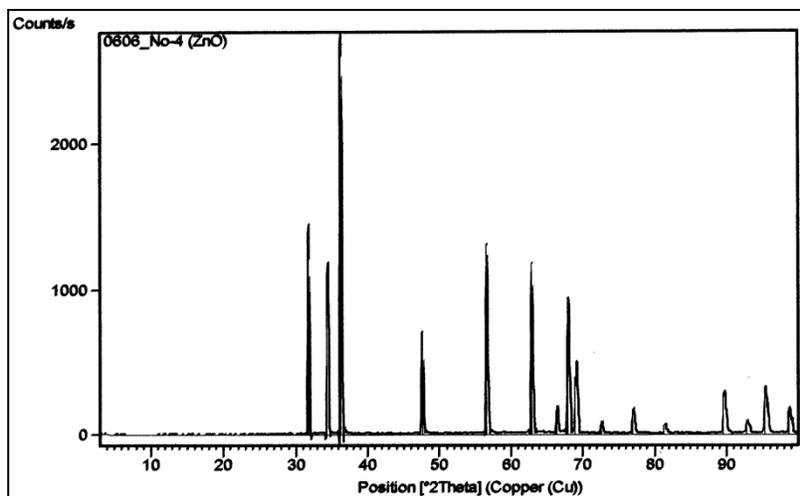


Fig.8. XRD diagram of ZnO semiconductor after irradiation

- SEM

The scanning electron microscopic (SEM) is the primary tool used for characterization of the surface morphology and fundamental physical properties of photocatalyst surface. It is useful for determining the particle size, shape, porosity, and appropriate size distribution of the TiO<sub>2</sub> and ZnO [31]. The SEM photograph was recorded by using Philips Netherland, (Model-SEM-EDAX XL-30). Scanning electron micrograph of semiconducting materials with MB (Figures 9 and 10) the degradation of TiO<sub>2</sub> and ZnO photocatalysts on the MB before and after degradation was observed. The SEM photographs show that particle size is increased after degradation. The surface texture was found rough and heterogeneous porous in nature before and after treatment. ZnO has a considerable number of pores where there is good possibility for dye to be trapped and adsorbed on these pores and it is a good sign for effective adsorption of dye MB.

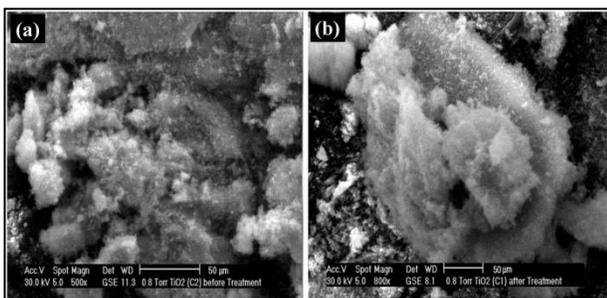


Fig. 9. SEM images of TiO<sub>2</sub> a) before treatment b) after treatment

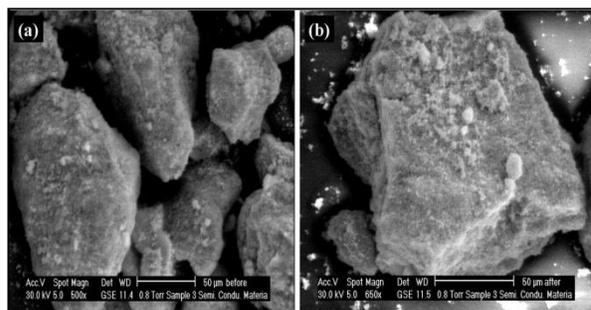


Fig.10. SEM images of ZnO c) before treatment d) after treatment

- EDX

Energy-dispersive X-ray spectroscopy (EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons or a beam of X-rays, is focused into the sample being studied of the TiO<sub>2</sub> film coated on the glass substrate (Figures 11 and 12). The figure shows 2 peaks around 3.7 and 4.1 keV. The intense peak is assigned to the bulk TiO<sub>2</sub> and the less intense one to the surface TiO<sub>2</sub>. The elemental composition of the TiO<sub>2</sub> film was found 65% Ti, 29% O, Si is 6% and Fe was 3% were the presence of TiO<sub>2</sub> was confirmed. For the ZnO it is found that Zn was 71%, O, 18.5%, C 10%.

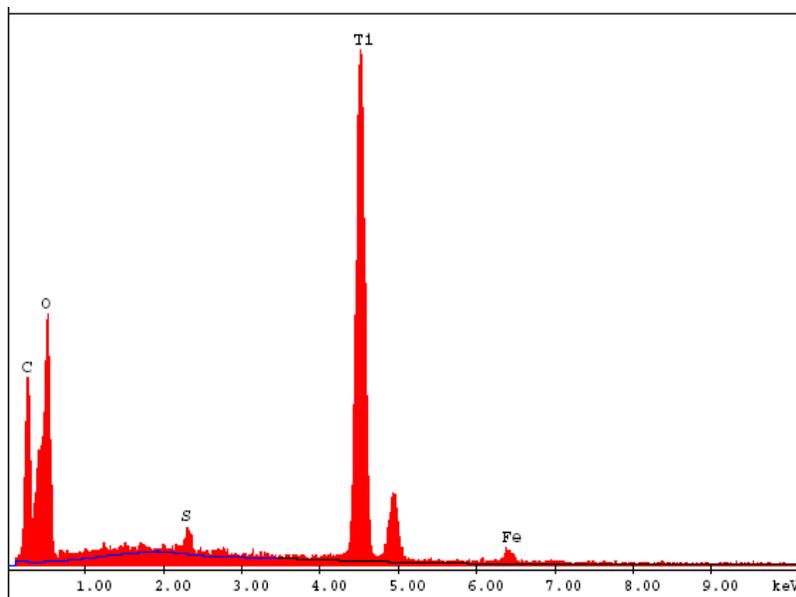


Fig. 11. EDX pattern of TiO<sub>2</sub>

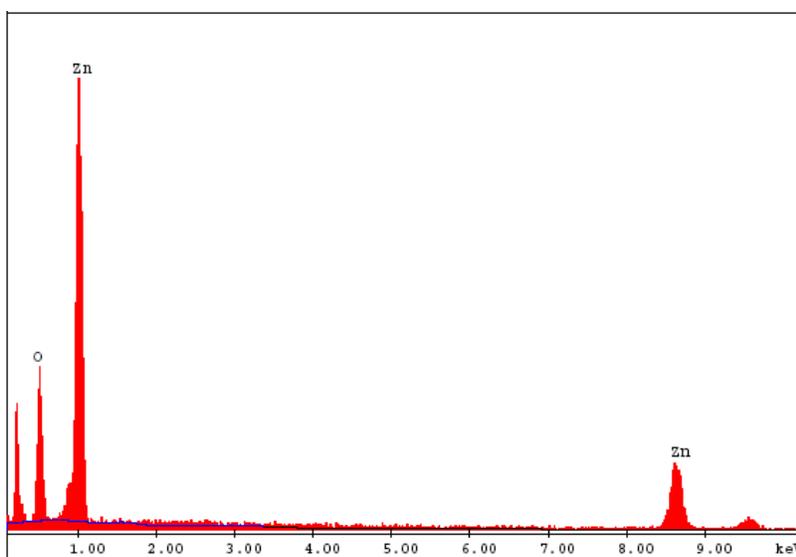


Fig. 12. EDX pattern of ZnO

#### • FT-IR

In order to investigate the surface characteristics of TiO<sub>2</sub> before and after treatment with methylene blue dye, Fourier transfer infrared (FTIR, Perkin-Elmer spectrophotometer) the range of 500-4000 cm<sup>-1</sup> was studied (Figures 13 and 14). The FTIR spectrum of TiO<sub>2</sub> before treatment shows that the peak positions are at 3875.12, 3016.77, 2341.66, 1313.57, 1205.55, 752.26 cm<sup>-1</sup>. The band at 3875.12 are due to NH<sub>2</sub>. While 3016.77 shows

OH carboxylic acid, 2341.66 are due to C≡C ring, 1313.17 shows CH<sub>2</sub> group and 1205.55 shows C-N amine group. The FTIR spectrum of TiO<sub>2</sub> after treatment on Methylene blue shows the peak at 3718.88, 2931.90, 2353.23, 1236.41 and 839.06 cm<sup>-1</sup>. The band at 3718.88 shows NH<sub>2</sub> group aliphatic and aromatic group, 2931.90 shows C-H, aliphatic group, 2353.23 shows C≡N nitrate group and 1236.41 cm<sup>-1</sup> shows that OR aromatic group.

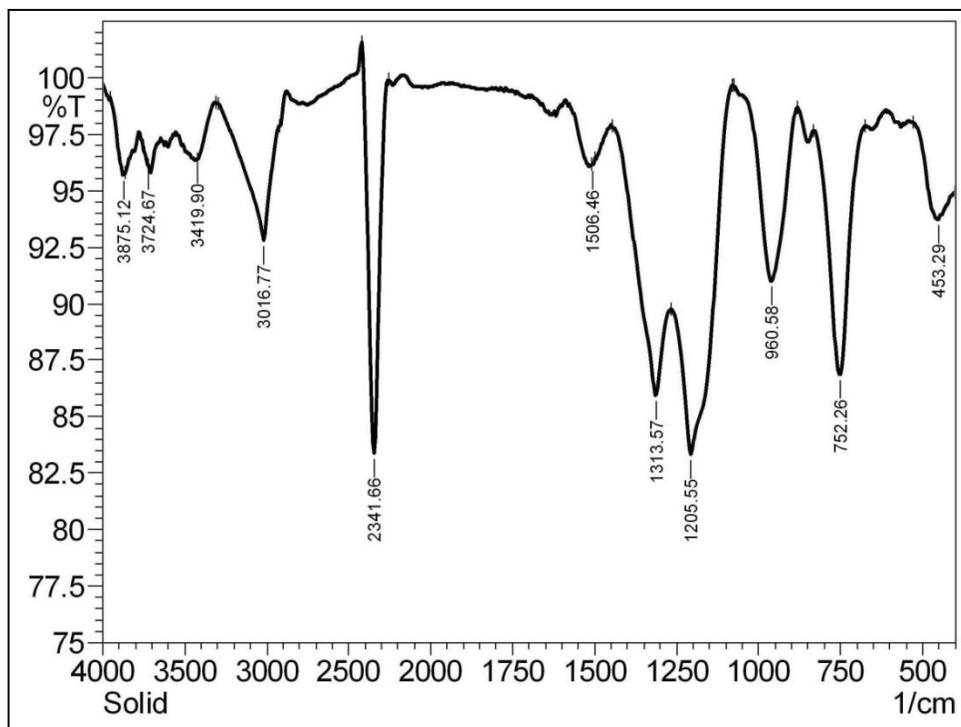


Fig. 13. FTIR spectra of TiO<sub>2</sub> on Methylene blue before photodegradation TiO<sub>2</sub>

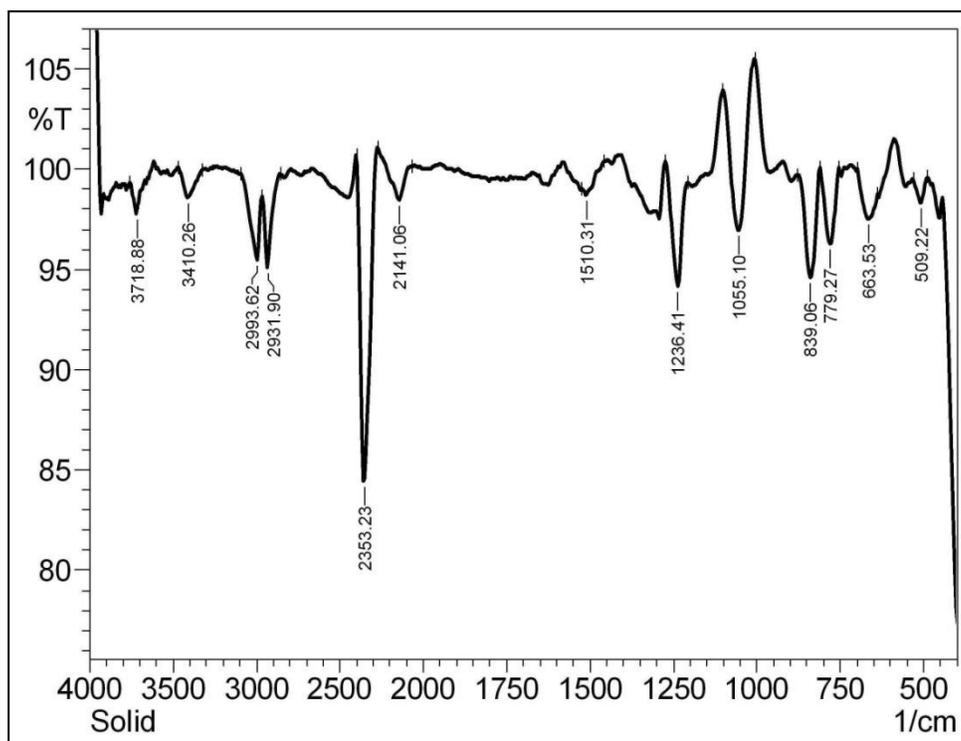


Fig. 14. FTIR spectra of TiO<sub>2</sub> on Methylene blue after photodegradation

- **Total organic carbon**

TOC is very important in detecting contaminants in drinking water, cooling water, water used in semiconductor manufacturing, and water for pharmaceutical use. Analysis may be made either as an online continuous measurement or a lab-based measurement. TOC is a highly sensitive, non-specific measurement of all organics present in a sample. It can be used to regulate the organic chemical discharge to the environment in a manufacturing plant. In addition, low TOC can confirm the absence of potentially harmful organic chemicals in water used to manufacture pharmaceutical products [32]. TOC is also of interest in the field of potable water purification due to disinfection of byproducts. Inorganic carbon poses little to no threat.

The basic principle for the quantization of total organic carbon relies on the destruction of organic matter present in the wastewater or sediment although there are a few non-destructive techniques identified in the literature that are currently under development. The destruction of the organic matter can be performed chemically or via heat at elevated temperatures. All carbon forms in the sample are converted to CO<sub>2</sub> which is then measured directly or indirectly and converted to total organic carbon or total carbon content, based on the presence of inorganic carbonates. These methods can either be quantitative or semi-quantitative depending on the process used to destroy the organic matter and it is used for detecting/quantifying the carbon present [33].

$$\text{Total Carbon} = \text{Inorganic Carbon} + \text{Organic Carbon} \quad (1)$$

TOC content can be measured directly or can be determined by difference if the total carbon content and inorganic carbon contents are measured. For soils and sediments where no inorganic carbon forms are present, Equation 1 becomes:

$$\text{Total Organic Carbon} = \text{Total carbon} - \text{Inorganic Carbon} \quad (2)$$

The basic principle for the quantization of total organic carbon relies on the destruction of organic matter present in the water or sediment although there are a few non-destructive techniques identified.

The degradation of dye was measured by TOC determination. Degree of mineralization was determined using a total organic carbon (TOC) analyzer. Samples consisting of 30ml aliquots were taken at different time intervals. A solution of 100 mg/L of methylene blue was prepared with the catalyst of 0.1 mg/L used. Results show that mineralization is a slow process, requiring longer time for a complete TOC elimination. After 120 minute total decolorisation is reached catalytically, whereas only 68% of TOC is removed by mineralization was observed. Total organic carbon reduction of MB with respect to time over the TiO<sub>2</sub> catalyst **Table 2**.

**Table 2.** Total organic carbon reduction of Methylene blue with respect to time over the TiO<sub>2</sub> photocatalyst.

Samples TOC (mg/L)	Before TOC (mg/L)	After TOC (mg/L)
Original solution	19.8	31.7
Solution after catalyzed for 30 min	15.4	26.4
10	13.7	18.3
20	14.6	17.2
40	21.8	36.7
50	24.7	40.8

- **COD**

The chemical oxygen demand test is widely used as an effective technique to measure the organic strength of wastewater. The test allows the measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic matter to CO<sub>2</sub> and water [34]. In the present work result of COD were taken as one of the parameter to judge the feasibility for photocatalysis

In this Experiment the dye solution (100ml) and the photocatalysts 0.05g l<sup>-1</sup> were taken in the reactor and exposed to UV light for 120 min. Dye sample of about 10 ml were taken out at regular interval from the test solution, centrifuge for 10-15 min and the adsorbance were recorded at 665 nm Comparison of the COD values of the initial dye concentration with ht irradiated solution

indicates that the COD values is substantially reduced. It is observed that the COD values decreases from 874 to 134 mg l<sup>-1</sup>(Figure 15).

The influence of the dye concentration on percentage of COD removal over photocatalyst TiO<sub>2</sub> and ZnO is shown in figure. It is clearly find that the percentage of COD reduction increases with increasing concentration of MB ions for the same irradiation time. Thus higher concentration of dye may need longer illustration time.

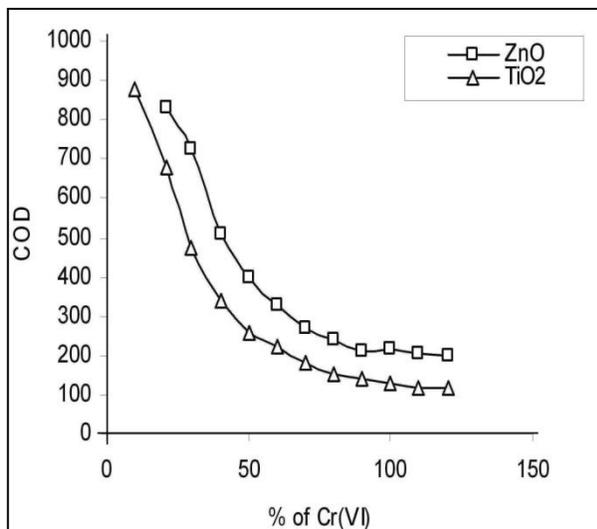


Fig. 15. Effect of Chemical Oxygen Demand

#### • Dark adsorption and photocatalytic deposition

Dark adsorption of MB was very low as compared to UV light. However, the trends of removal were similar. Percentage of degradation was found to decrease with increasing concentrations. Maximum removal of 56.4% was obtained in the dark adsorption. The adsorption value was decreased up to 12.6%. The anions were repelled by the negatively charged TiO<sub>2</sub> surface, thereby decreasing the overall adsorption value.

In absence of the whole scavenger, maximum deposition of 56.4% was obtained. Initially the removal for both was similarly increasing. The photocatalysis values were obtained for MB was 83.5% in the UV light (Figure 16). The results for MB deposition on TiO<sub>2</sub> surface are depicted. Deposition of MB was found to decrease with increasing concentration.

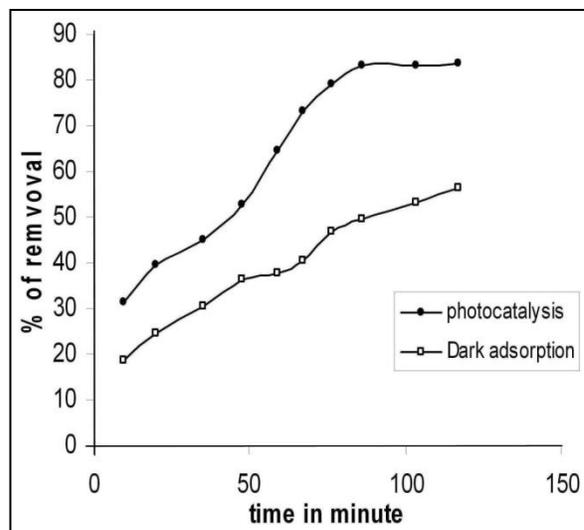


Fig. 16. Photocatalysis and dark adsorption of Methylene blue

## CONCLUSION

Photocatalytic degradation of Methylene Blue can be achieved by using photocatalysts TiO<sub>2</sub>, and ZnO. From this experiment it is possible to obtain decolorized water in a convenient time scale. The Experimental results indicates that the degradation process, TiO<sub>2</sub> /UV, ZnO/UV system is very effective compared with different natural and artificial adsorbent available. The rate of degradation of dye is found to be more at 0.5 g /L than in 1.0 g /L. of these two catalysts TiO<sub>2</sub> and ZnO, Titanium dioxide is more efficient catalyst than ZnO in the removal of Methylene Blue. In this system hundred percent of removal of dye is possible in a practical time scale.

By using XRD it is found that the size of the photocatalytic particles are increased after the dye reacted with these particles. SEM photographs show that the TiO<sub>2</sub> and ZnO have heterogeneous pores in nature as well as the surface is rough in nature. TOC is very useful technique for rapid analysis, often as quick as for a single sample TOC determination. Predictive accuracy for TOC was excellent. From the COD it was found that the COD has great potential of employing photocatalysis.

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