

PROCESS DEVELOPMENT FOR CONTINUOUS FLOW PHOTOCATALYTIC DEGRADATION OF TEXTILE DYES

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Abstract – Advanced oxidation processes (AOPs) are widely used for the removal of recalcitrant organic constituents from industrial and municipal wastewater.

This study mainly focused the use of TiO₂ and ZnO catalysts for removal of textile dyes. Synthesis of TiO₂ and ZnO photo catalysts was done by sol-gel method. These catalysts were used to obtain enhanced photo catalytic action and were coated on glass beads to improve the photo catalytic activity. The synthesized beads were examined using SEM, FTIR and XRD. Synthesized photocatalysts were examined extensively for their photocatalytic activities with Crystal Violet (CV), Direct Red Dye (DR), Textile industry Effluent (TIE) and mixture of dyes (CV+DR, CV+DR+TIE) at various concentrations (50ppm, 100ppm). The photocatalytic degradation of CV, DR, TIE, CV+DR and CV+DR+TIE dyes solution (100mg/L and 50mg/L) using TiO₂ and ZnO were investigated under UV light irradiation (λ=254nm). Photocatalytic studies revealed that the TiO₂ has shown much higher photocatalytic activity than the ZnO catalyst. The photocatalytic activity of the TiO₂ catalyst follows the order: Crystal Violet of 50 ppm (82.84%) > Textile Industry Effluent (78.72%) > Direct Red Dye of 50 ppm (78.69%) > Direct Red Dye of 100 ppm (75.12) > Crystal Violet of 100 ppm (73.38). The photocatalytic activity of the ZnO catalyst follows the order: Crystal Violet of 50 ppm (78.1%) > Textile Industry Effluent (75.3%) > Direct Red Dye of 50 ppm (73.98%) > Direct Red Dye of 100 ppm (71.24) > Crystal Violet of 100 ppm (70.29).

Key Words: Crystal Violet (CV), Direct Red Dye (DR), Textile Industry Effluent (TIE), Photocatalytic studies, TiO₂, ZnO, Textile Dyes

1.INTRODUCTION

Textile Effluents need to be treated before discharging them into water bodies because of Toxicity polluting the environment. In past years, conventional biological and physical treatment methods (adsorption, ultrafiltration, coagulation etc.) have been used to remove organic pollutants. These methods are not efficient and cost effective for wastewaters containing high concentrations of more toxic pollutants. This requires some novel techniques to transfer the highly toxic pollutants chemically into benign species. [1,2]

Advanced oxidation processes (AOP) became a promising technology in the recent years, since they are most efficient, cheap, and eco-friendly in the degradation of any kind of toxic pollutants. AOPs generate hydroxyl radical, a strong oxidant, which can completely degrade or mineralize the pollutants nonselective into harmless products. In this process no by-products and sludge are formed [3,4,7].

Heterogeneous catalysts such as UV-light/ TiO₂/ZnO are used for Photocatalytic degradation has attracted increasing attention as cleaner and greener technology for removal of toxic organic and inorganic pollutants in water and wastewater. [5,6].

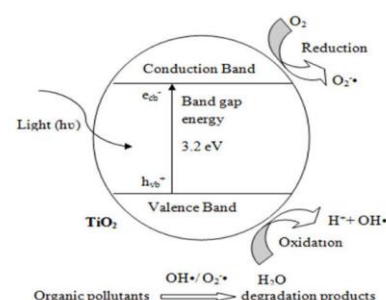
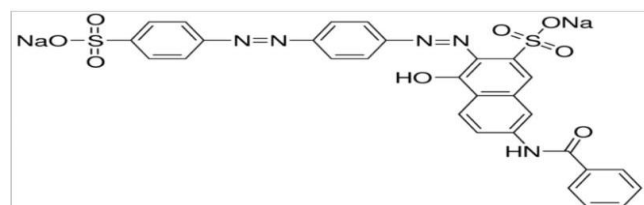


Figure 1.1 : Schematic diagram of an irradiated TiO₂ particle.

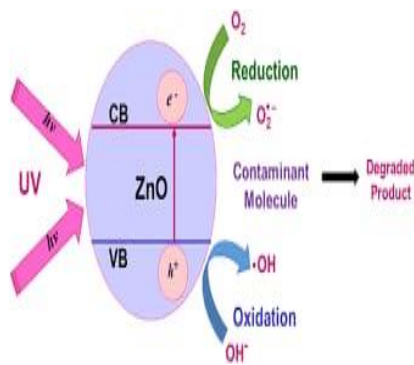


Figure 1.2: Schematic diagram of an irradiated ZnO particle.

Crystal Violet in water

Crystal Violet (CV), a triphenylmethane dye, has been extensively used in human and veterinary medicine as a biological stain, as a textile dye in textile processing industries and also used to provide a deep violet color to paints and printing ink.

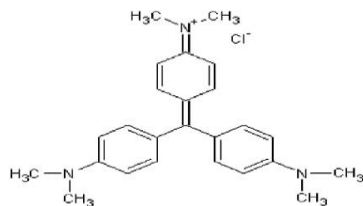


Fig. 1.3 Chemical structure of Crystal Violet

Direct Red in water: Direct red, a toxic sulphonated azo-based dye, known for its carcinogenic nature and toxicity towards animal and humans is selected as a synthetic model dye solution for experimentation which is widely used in many industries. It has double azo linkage along with sulphonic acid group, makes the dye easily soluble in water.

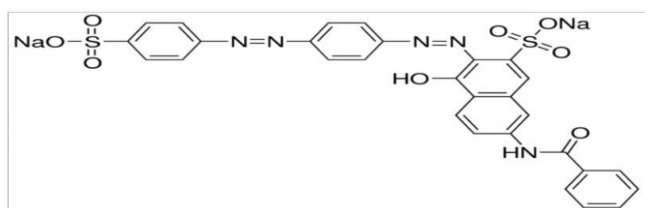


Fig. 1.4 Chemical structure of Direct Red

In this project crystal violet and direct red and textile Industrial dye effluent are consider. For Degradation using immobilized TiO₂ and ZnO catalyst on glass beads using UV-light in continuous reactor.

2. Materials & Methods:

Materials: Hydrofloruric Acid (5 wt%, purchased from Sigma Aldrich), Titanium (IV) isopropoxide (97%, purchased

from Sigma Aldrich), Ethanol (96%, from Sigma Aldrich), Hydrochloric Acid (98%, from Molychem), Zinc Acetate Dihydrate (98%, purchased from Avra), Sodium Carbonate from Avra, Crystal Violet, Direct Red, (from Atul industries) Glass Beads, (Avra) Distilled Water, Textile Industry Effluent (Area of Siricilla, Telangana).

Methods:

2.1 Coating of TiO₂ photocatalyst on glass beads: Before coating of glass beads, the glass beads were etched in Hydrofluoric acid (40% pure), for 24hrs and washed with demineralized water and dried in the oven for 2hrs at 105^oc. Now the catalyst was prepared using the sol-gel method [11,12]. Sample A was prepared using Titanium Isopropoxide (98% pure) and Ethanol (99% pure) with 1:4 ratio and stirred for 30minutes. Use 25ml of Hydrochloric Acid (98%pure) as Sample B. Add Sample B to Sample A drop wise and stir well until a light orange colored gel solution formed. Immerse the glass beads into the prepared gel for 30 minutes. The immersed glass beads were dried in the hot air oven at 105^oc for 1hr and calcinated for 2hrs at 450^o C. This procedure continued for further times of coatings [10,11,12].



Fig 2.1. TiO₂ catalyst coated on glass beads

2.2. Coating of ZnO photocatalyst on glass beads:

The glass beads were etched in Hydrofluoric acid (40% pure), for 24hrs before coating. The beads were then washed with demineralized water and dried in the oven for 2hrs at 105^oc. Using sol-gel method the catalyst was prepared.

Sample A was prepared using 2.2 grams of Zinc Acetate Dihydrate, 50ml of Distilled water prepared and stirred for 30 minutes. Sample B was prepared using 1.06 grams of Sodium Carbonate and 50 ml of Distilled water and stirred for 30 minutes. Sample B was added drop wise to Sample A under stirring until a white transparent gel is formed. The glass beads were immersed in the gel for 30minutes. Later the beads were dried in oven at 105^oc for 2hr and calcinated for 4hrs at 450^o C. This procedure was repeated for further number of coatings on glass beads.



Fig 2.2. ZnO catalyst coated on glass beads

3. Characterization Techniques;

The coated glass beads were characterized through scanning electron microscope (SEM), Fourier Transform Infrared (FTIR) and X-Ray Diffraction (XRD).

Scanning Electron Microscope (SEM)

SEM is used to detect the information about the sample's surface morphology, topography and composition. The electron beam is generally scanned in a scan pattern, and the beam's position is combined with the detected signal to produce an image.

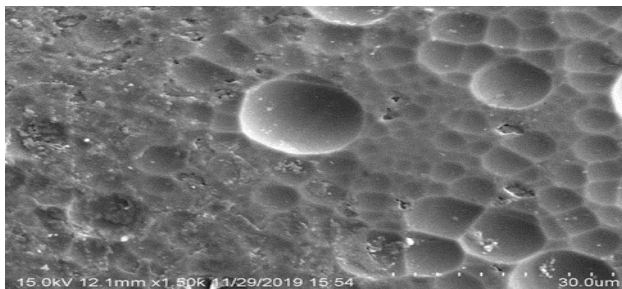


Fig 3.1a .SEM image before coating of catalyst on glass beads

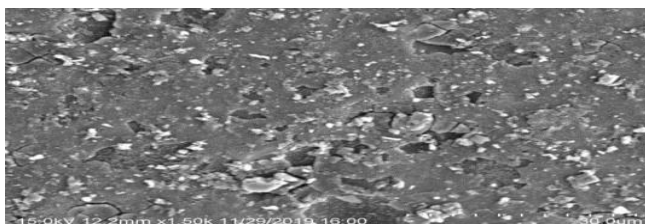


Fig 3.1b .SEM image after coating of catalyst on glass beads

Fourier Transform Infrared (FTIR)

The FTIR analysis method uses infrared light to scan test samples and observe chemical properties. Each molecule or chemical structure will produce a unique spectral fingerprint, making FTIR analysis a great tool for chemical identification.

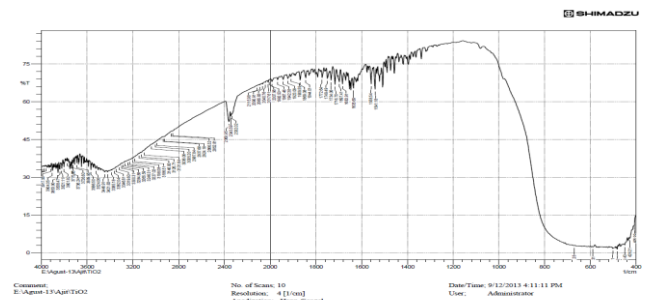


Fig 3.2 FTIR of TiO₂

X-Ray Diffraction (XRD)

Powder X-ray diffraction technique is useful in catalyst characterization and to investigate both qualitative and quantitative phase changes. It gives the information about the crystallinity of the specific components and allows identification of ensemble size of the components in the catalyst.

The XRD pattern of nano catalyst (TiO₂) showed the presence of three main peaks at $2\theta = 25.3^\circ(101)$, 26.1° , and 37.0° , which should be an attributive indication of anatase TiO₂. On the other hand, minor diffraction peaks appeared at $2\theta = 27.5^\circ(110)$ and 31.5° , which should correspond to rutile TiO₂. The results were in agreement with its mineral composition being an anatase to rutile ratio of 83:17

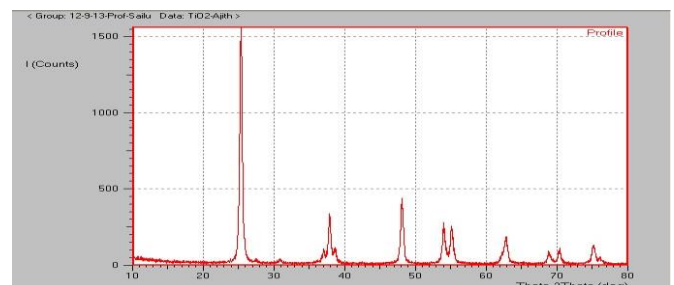


Fig 3.3a: XRD photograph of (TiO₂) catalyst

XRD of ZnO:

The peaks pointed out at 2θ values of can be associate with (100),(002), (101), (102), (110),(103) and (112), respectively, correspond to hexagonal zinc item phase of ZnO which are in good .The average ZnO nanoparticles size of 30 nm can be estimated by Scherrer's formula .

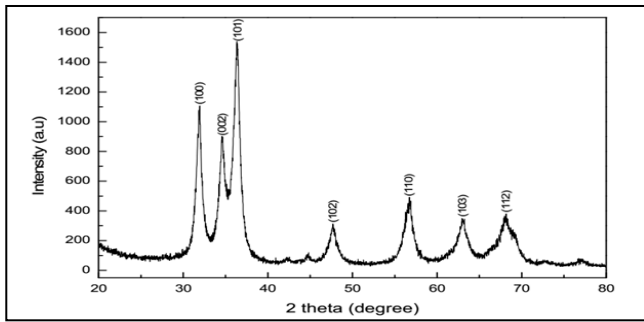


Fig 3.3b: XRD photograph of (ZnO) catalyst

4. Experimental Setup:

Photocatalytic degradation of textile dye effluents was performed in the continuous reactor system as shown in Fig.4.1, which consists of a cylindrical borosilicate glass reactor (with an effective volume of 275 Cm³). The TiO₂ and ZnO coated glass beads were placed in the reactor setup. The UV-C light (of 254 nm) is placed in the provision such a way that the UV light located in the middle of the reactor. The reactor covered to restrict natural light from entering. Peristaltic pump is used to transfer the treating solution or effluent into the reactor. Inlet and outlet of the reactor are connected such a way that the fluid passing through closed loop continuous reactor. The flow rate of the system adjusted to 20 lt/hr in clockwise direction [9,10].



Fig. 4.1. Experimental Setup

5. RESULTS AND DISCUSSION:

The dye effluent is treated in the reactor for three hours and samples were drawn every hour. The concentration of dye determined spectrophotometrically to find out concentration at respective times. Percentage of degradation calculated and compared the degradation against time. Industrial textile dye effluent Initial and final samples are also analyzed for chemical oxygen demand using open reflux method.

$$\% \text{Degradation} = \frac{[c]_i - [c]_f}{[c]_i} \times 100$$

The Degradation of Crystal Violet Using TiO₂:



Fig.5.1a. Degradation of Crystal Violet without



Fig.5.1b. Degradation of Crystal Violet with Catalyst TiO₂

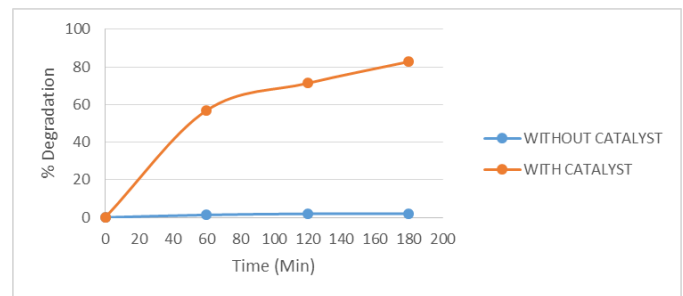


Fig. 5.2. % Degradation Vs time of CV 50ppm

Fig 5.2 shows the degradation of dye studied with and without catalyst, it is found that there is a remarkable difference. In case of Crystal Violet of 50ppm, it showed about 82.84% degradation with catalyst in other hand degradation limited to approximately 1.98% in the absence of catalyst.

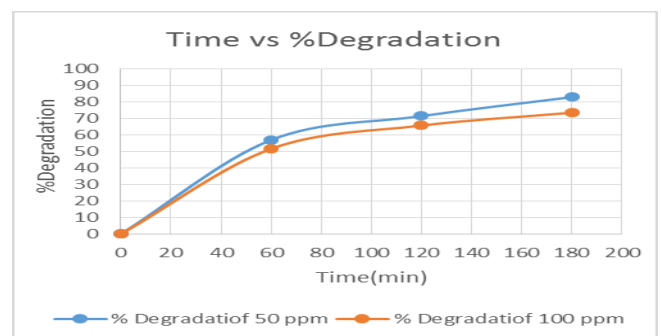


Fig. 5.3a. %Degradation of crystal violet dye 50ppm and 100ppm using TiO₂.

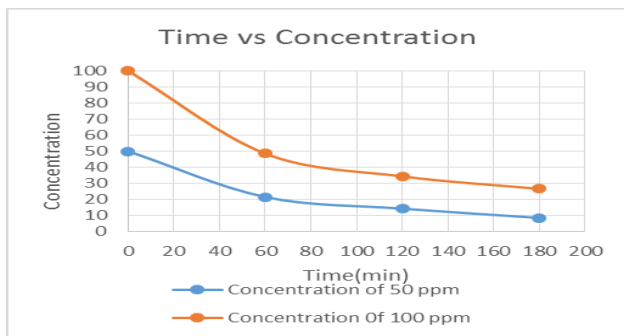


Fig 5.3b. Concentration Vs Time for 50ppm and 100 ppm CV with TiO₂

Fig 5.3a&b. shows the Difference between two concentrations (50ppm, 100ppm) of Crystal Violet %degradation is at 50ppm 82.84% and at 100ppm 73.3%. In terms of concentration 50ppm is reduced to 8.58 ppm and 100ppm to 26.62ppm after 3hours of experiment using TiO₂.

The Degradation of Direct Red Using TiO₂:



Fig. 5.4 Initial and final samples of Direct Red Dye using TiO₂

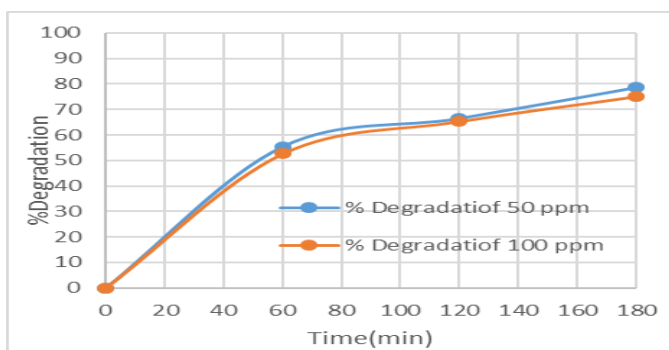


Fig. 5.5 a. Degradation of 50ppm and 100ppm direct red dye using TiO₂

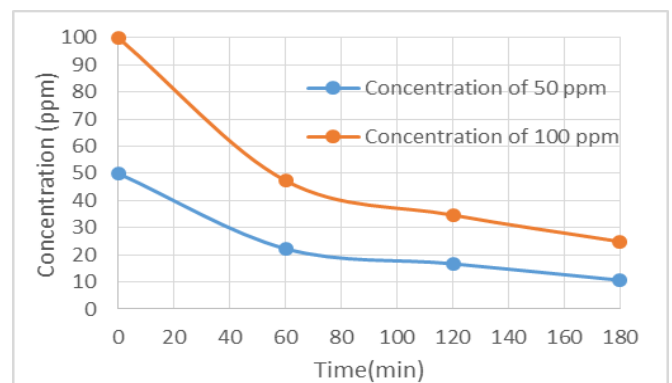


Fig 5.5b. Concentration Vs Time for 50ppm and 10 ppm direct red dye with TiO₂

Fig 5.5a&b. shows the difference between two concentrations (50ppm, 100ppm) of Direct Red %degradation is at 50ppm 78.69% and at 100ppm 75.12%. In terms of concentration 50ppm to 10.65ppm and 100ppm to 24.28ppm after 3hours of experiment using TiO₂.

The Degradation of Crystal Violet Using ZnO:



Fig.5.6. Degradation of Crystal Violet with Catalyst ZnO

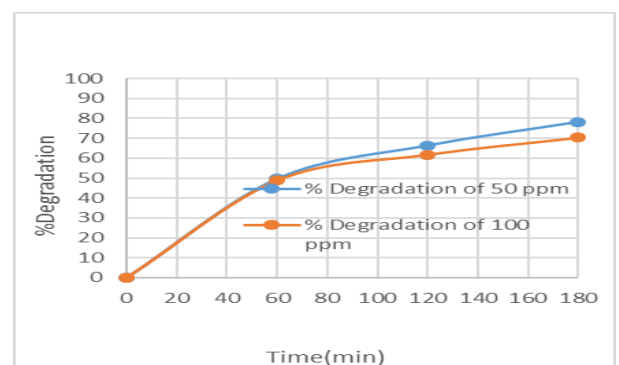


Fig. 5.7a. %Degradation of crystal violet dye 50ppm and 100ppm using ZnO

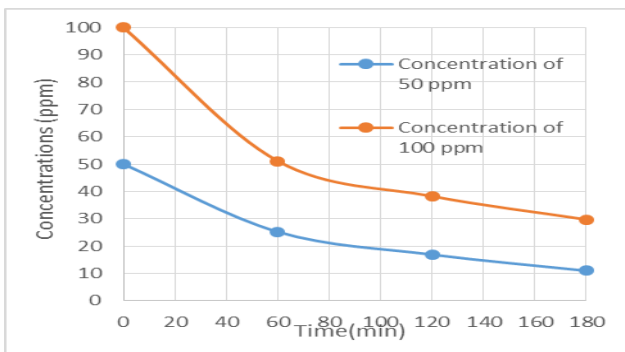


Fig 5.7b. Concentration Vs Time for Crystal violet dye 50ppm and 100 ppm

The fig 5.7a&b shows the Difference between two concentrations (50ppm, 100ppm) of crystal violet %degradation is at 50ppm 78.1% and at 100ppm 70.29%. In terms of concentration 50ppm to 10.95 ppm and 100ppm to 29.71ppm after 3hours of experiment using ZnO .

The Degradation of Direct Red Using ZnO



Fig. 5.8 Initial and final samples of Direct Red Dye using ZnO

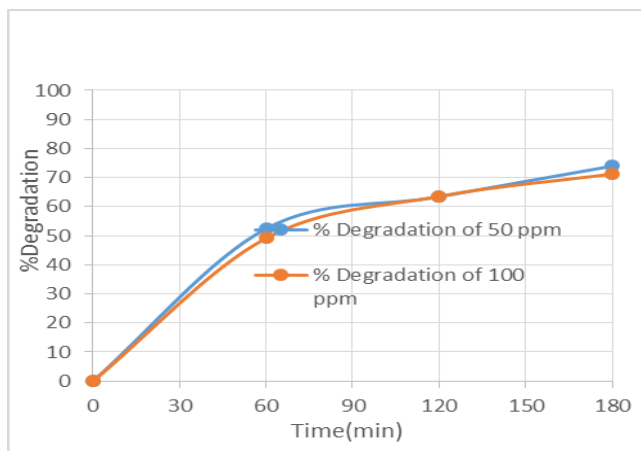


Fig. 5.9 a. Degradation of 50ppm and 100ppm direct red dye

Using ZnO catalyst

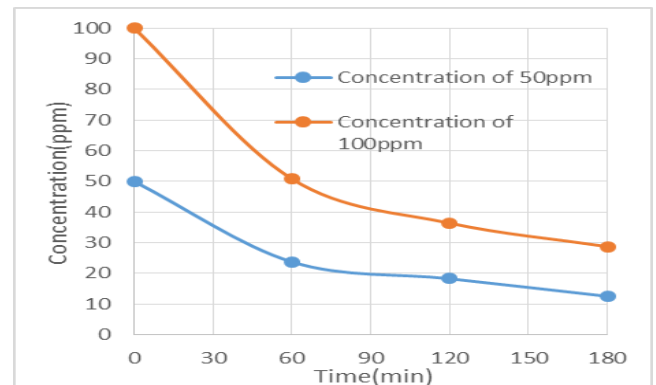


Fig 5.9b. Concentration Vs Time for Direct red dye 50ppm and 100 ppm with ZnO catalyst

The fig 5.9a&b. Shows it was observed the Difference between two concentrations (50ppm, 100ppm) of Direct Red %degradation is at 50ppm 73.98% and at 100ppm 70.16%. In terms of concentration 50ppm to 13ppm and 100ppm to 28.76ppm after 3hours of experiment using ZnO.

Textile Industrial Effluent using TiO₂ /ZnO:

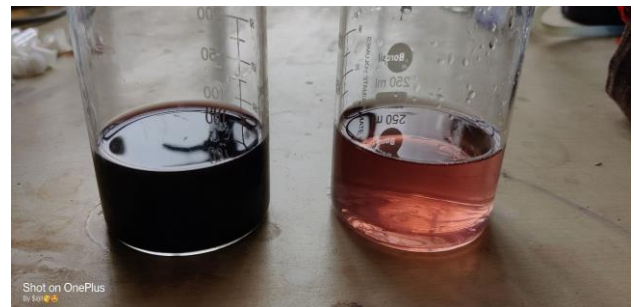


Fig 5.10.Textile Industry Effluent degradation initial and final sample

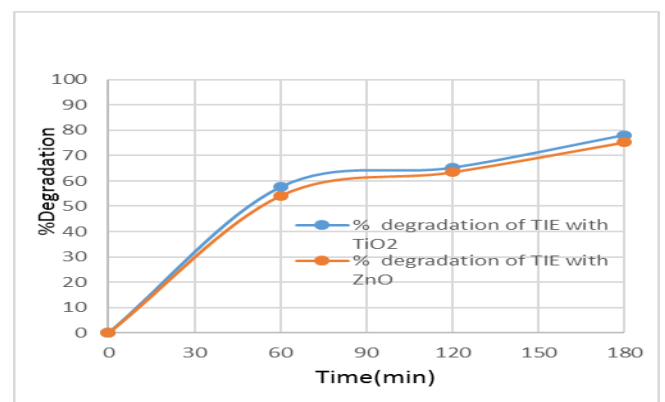


Fig.5.10a.Degradation of Textile Industry Effluent degradation using TiO₂&ZnO

The fig.5.10a. Using TiO_2 It was observed the Industrial Dye effluent %degradation is 78% after 3hours of experiment. In terms of concentration reduced from 10,640ppm to 2264ppm.and using ZnO It was observed the Industrial Dye effluent %degradation is 75% after 3hours of experiment and concentration reduced from 10640ppm to 2628ppm.

Mixed dyes with Textile Industrial Effluent using TiO_2 :



Fig.5.11. Initial and final samples of Dye mixtures analysis

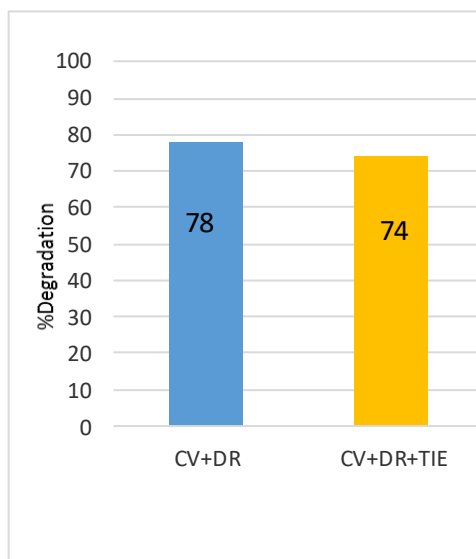


Fig .5.11.a. Degradation for Dye mixture with TIE using TiO_2

The fig.5.11a. shows It was observed the combined mixtures of dyes with textile Industrial Dye effluent %degradation is (CV+DR) 78% and (CV+DR+TIE) is 74% after 3hours of experiment using TiO_2 . Concentration of (CV+DR) is reduced from 100ppm to 22 ppm and COD removal of (CV+DR+TIE) is reduced from 10824 ppm to 2790ppm.

Mixed dyes with Textile Industrial Effluent using ZnO:

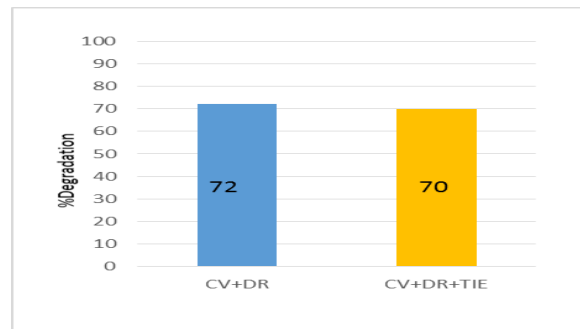


Fig.5.11b. Degradation of Dye mixture using ZnO

The fig 5.11b. Shows it was observed the combined mixtures of dyes with textile Industrial Dye effluent %degradation is (CV+DR) 72% and (CV+DR +TIE) is 70% after 3hours of experiment using ZnO. Concentration of (RO+RB) is reduced from 100ppm to 28ppm and COD removal of (CV+DR+TIE) is reduced from 10824ppm to 3175ppm.

6. Kinetics:

The reaction rate for the photo catalytic reactions is independent of hydroxyl concentrations Therefore a pseudo first-order kinetic model was used to fit the experimental data.

$$\frac{-dc}{dt} = kC \text{ COH}^{*..(1)}$$

By the pseudo-secondary hypothesis (i.e the COH^* can be considered), the rate expression (1) can be simplified to fit an equation following the first order kinetics,

$$\frac{-dc}{dt} = kC$$

Integrating the above equation; from 'C₀' to 'C' on the left hand side, and '0' to 't' on the right;

$$\int_{c_0}^c \frac{1}{C} dc = -k \int_0^t dt$$

$$\ln(C/C_0) = -k\tau$$

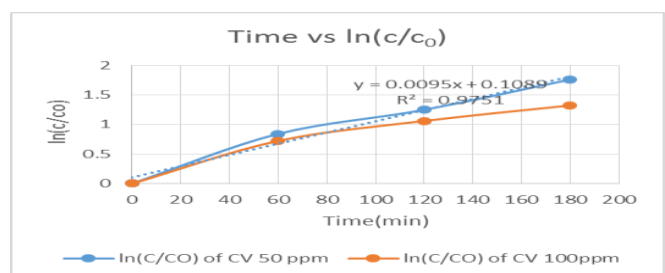


Fig .6.1. Time Vs ln (C/C₀) for CV using TiO_2

The kinetics of degradation of the dyes followed first order rate the rate constant k values are

S. No	Dye Name	Rate constant (K)
1	Crystal Violet using TiO ₂	0.0095
2	Direct Red Dye using TiO ₂	0.0082
3	Crystal Violet using ZnO	0.0082
4	Direct Red Dye using ZnO	0.0071

Discussion:

For 50ppm of crystal violet dye was treated for 180min and the degradation found without catalyst degradation is less (1%) when it is compared to with catalyst (83%).

In the presence of UV light and catalyst textile dyes can be degraded because it produce more hydroxyl radicals to degrade the compounds. Damodar and Swaminathan, 2008 found In continuous micro reactor the Degradation of crystal violet (10mg/L) and 400 min of run time and degradation achieved was 93%.

Because of light intensity and availability of active catalyst surface for dye adsorption as well as for hydroxyl radical generation (Damodar and Swaminathan, 2008).

When compared to ZnO catalyst TiO₂ gives more degradation due to band gap energy which is less in TiO₂ (3.2ev) whereas in ZnO (3.4ev). Degradation is slightly reduced for higher concentration because light intensity and active surface area may not be sufficient.

Industrial dye effluent treated Compared to individual dyes degradation is less when the combination of dyes are used. The catalyst was reused for 7 times.

Sapkal et al., 2012 treated 1000ppm of textile effluent by photoelectrocatalysis and found COD removal of 69% for 200 to 400nm wavelength within 3 h at room temperature. However in our case COD removal was 85% for TiO₂ catalyst and 82% using ZnO catalyst. The integral linear transform, $\ln(C/C_0)$ as a function of degradation time follows first order reaction kinetics.[13]

Zucca et al., 2012 found that the catalyst immobilized lignin peroxidase-like metalloporphines keeps a significant part of its catalytic activity during multi-cycle employment. This is

very important for large-scale applications to treat textile dye pollutant where classical photocatalysis or filtration approach not able to resolve it completely.[14]

7. CONCLUSIONS

The degradation of Crystal Violet dye without catalyst is 1.98% whereas with catalyst- 82.84%.

The degradation of Crystal Violet of 50 ppm (82.84%) > Direct Red Dye of 50 ppm (78.69%)> Textile Industry Effluent (78%) >Direct Red Dye of 100 ppm (75.12)>Crystal Violet of 100 ppm (73.38) using TiO₂ catalyst.

The kinetics of degradation of the dyes followed first order rate and rate constants for MB, BD and TIE are 0.0135, 0.007, and 0.0112 respectively.

The degradation of Crystal Violet of 50 ppm (78.1%) > Textile Industry Effluent (75.3%) Direct Red Dye of 50 ppm (73.98%)>Direct Red Dye of 100 ppm (71.24)>Crystal Violet of 100 ppm (70.29) using ZnO catalyst.

Photocatalytic performance for combination mixed dyes also studied and found that catalyst showed efficient results in degrading multiple dyes at a time.

CV+DR (75.5%); CV+DR +TIE (78.8%) for TiO₂, CV+DR (70.4%); CV+DR +TIE (75.8%) for ZnO.

The kinetics of degradation of the dyes followed first order rate and rate constants for CV, DR using TiO₂, CV, DR using ZnO are 0.0095, 0.0082, 0.0082, 0.0071 respectively.

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