



Process Development for Photocatalytic Degradation of Reactive Dyes in Wastewater

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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 photocatalysts was done by sol-gel method. These catalysts were used to obtain enhanced photocatalytic action and were coated on glass beads to improve the photocatalytic activity. The synthesized beads were examined using SEM, FTIR and XRD. Synthesized photocatalysts were examined extensively for their photocatalytic activities with Reactive Orange (RO), Reactive Blue (RB), Textile industry Effluent (TIE) and mixture of dyes (RO+RB, RO+RB +TIE) at various concentrations (50ppm, 100ppm). The photocatalytic degradation of RO, RB, TIE, RO+RB and RO+RB +TIE dyes solution (100mg/L and 50mg/L) using TiO₂ and ZnO were investigated under UV light irradiation ($\lambda=254\text{nm}$). 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: Reactive Orange of 50 ppm (80.98%) > Reactive Blue dye of 50 ppm (77.17%) > Reactive Orange dye of 100 ppm (74.98%) > Reactive blue of 100 ppm (72%). The photocatalytic activity of the ZnO catalyst follows the order: Reactive Orange of 50 ppm (75.12%) > Reactive Blue dye of 50 ppm (73.98%) > Reactive Blue dye of 100 ppm (71%) > Reactive Orange of 100 ppm (70%).

Key words: Reactive Orange (RO), Reactive Blue (RB), Textile Industry Effluent (TIE), Photocatalytic studies, TiO₂, ZnO, Textile Dyes.

1. INTRODUCTION

Water is the core of sustainable development, but became a limited resource. Due to increase in population and changes in the climate have given rise to an alarming decline of freshwater resources and their availability, thus posing a major challenge worldwide. The frequency and intensity for droughts have drastically increased over the last 35 years due to global warming effect.

India being the one of the top countries in textile manufacturing, it is estimated that more than 1 million textiles were thrown away every year. Even though nearly 100 per cent of clothing is recyclable, about 75 to 85% of textile waste ends up in landfills or is incinerated instead of being reused, thereby polluting the environment.

Therefore, these wastewaters need to be treated before discharging them into water bodies. 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].

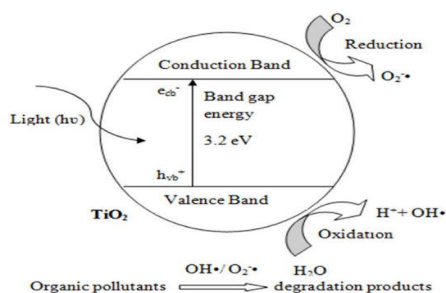


Figure 1.1: Schematic diagram of an irradiated TiO₂ particle.

Similar reactions for ZnO

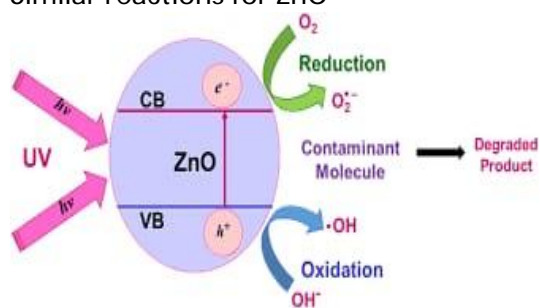


Figure 1.2: Schematic diagram of an irradiated ZnO particle.

Reactive Orange dye in water

Reactive orange (RO), a triphenylmethane dye, has been extensively used in human and veterinary medicine as a biological stain, as a textile dye in textile processing industries. Crystal Violet effects on health and the environment are mainly associated with corneal and conjunctiva irritation, skin and airway damage, renal and respiratory insufficiency, carcinogenic or clastogenic alterations and disturbance of aquatic ecosystem.

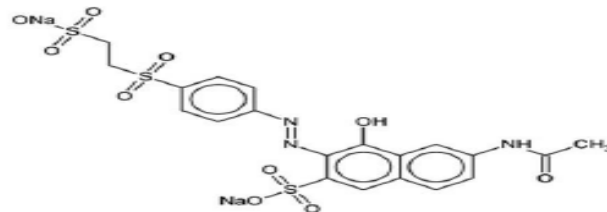


Figure: 1.3 Chemical structure of Reactive Orange dye.

Reactive Blue dye in water

Reactive Blue, 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. Ingestion of significant amount of this dye results in gastro-intestinal discomfort producing nausea and vomiting. It also has harmful effect on skin and eyes.

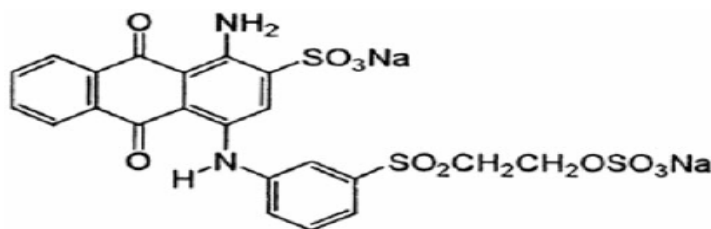


Figure : 1.4 Chemical structure of Reactive Blue dye.

2.MATERIALS & METHODS

Materials: Hydrofluoric 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, Reactive Orange, Reactive Blue, (Atul industries)Textile Industry Effluent(from siricilla area) Glass Beads (from Avra)Distilled Water.

Methods

2.1 Coating of TiO₂ catalyst 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 105⁰c. Now the catalyst was prepared using the sol-gel method .

Sample A was prepared using Titanium Isopropoxide (98% pure) and Ethanol (99% pure) with 1:4 ratio and stirred for 30 minutes. 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 105⁰c for 1hr and calcinated for 2hrs at 450° C. This procedure continued for further number of coatings.[10,11].



Figure 2.1a Beads before catalyst coating.



Figure 2.1b. Beads after TiO₂ catalyst coating.

2.2. Coating of ZnO catalyst 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 105⁰c. 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 30 minutes. Later the beads were dried in oven at 105⁰c for 2hr and calcinated for 4hrs at 450° C. This procedure was repeated for further number of coatings on glass beads.



Figure 2.1c. Beads after ZnO catalyst coating.

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.

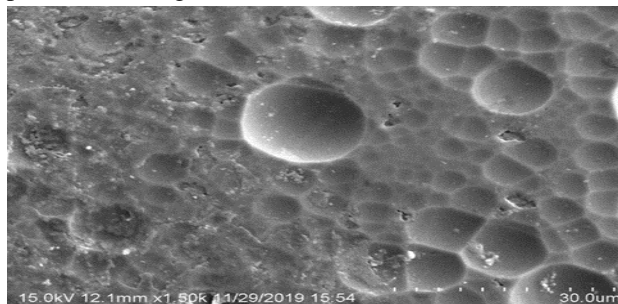


Figure 3.1a .SEM image before coating of catalyst on glass beads

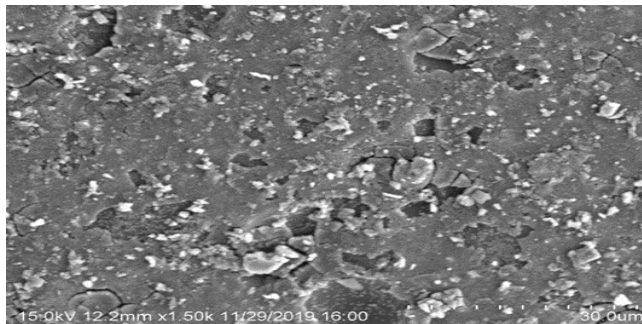


Figure 3.1b .SEM image after coating of catalyst on glass beads

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.

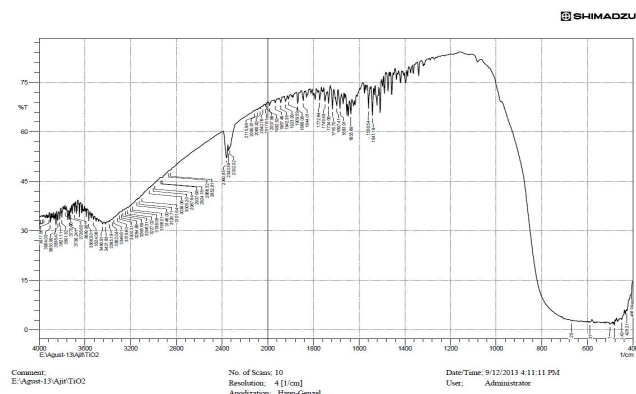


Figure 3.2 FTIR of TiO₂

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.

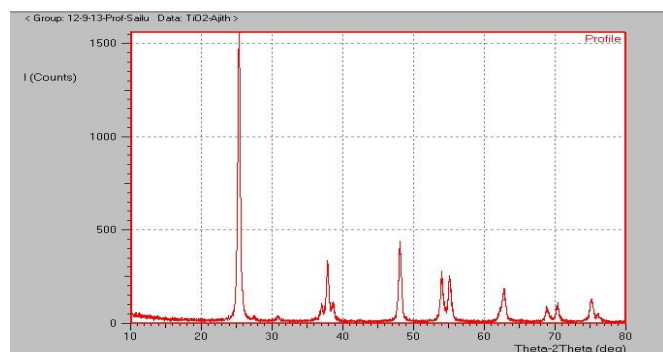


Figure 3.3a: XRD photograph of (TiO₂) catalyst

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 agreement with the literature values (JCPDS card

no.36-1451).The average ZnO nanoparticles size of 30 nm can be estimated by Scherrer's formula (Ganesh *et al.*,2012). $D = \lambda / (\beta \cos\theta)$, where $k = 0.9$, λ is the X-ray wavelength (1.5405980 \AA), β is the full width at half maximum of and θ is the Bragg diffraction angle of the diffraction peaks

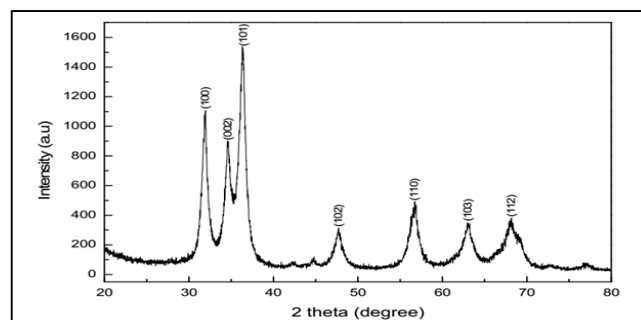


Figure 3.3b: XRD photograph of (ZnO) catalyst

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 Cm^3). 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 [8,9].



Figure 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 Reactive Orange Using TiO₂



Figure 5.1. Initial and final samples of Reactive orange dye

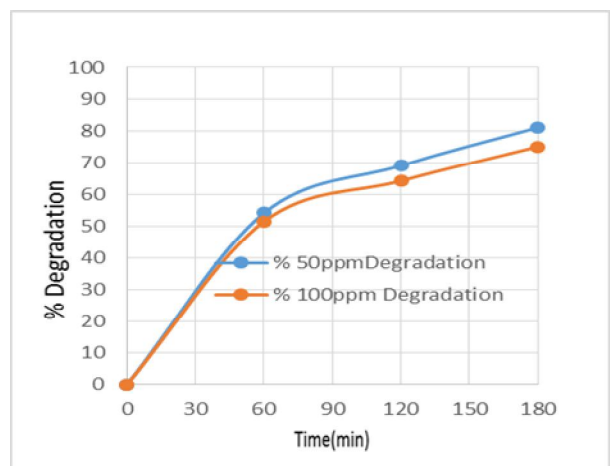


Figure 5.1 a. Degradation of 50ppm and 100ppm Reactive orange dye using TiO₂ catalyst.

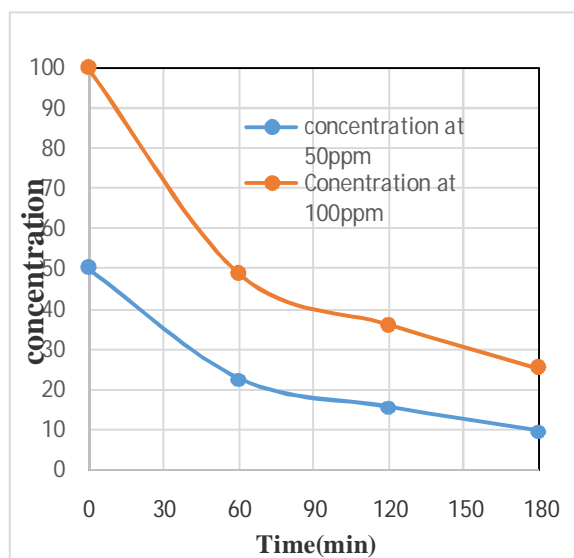


Figure 5.1b. Concentration Vs Time for 50ppm and 100ppm Reactive orange dye using TiO₂ catalyst.

The fig 5.1a&b shows the Difference between two concentrations (50ppm, 100ppm) of Ractive orange %degradation is at 50ppm 80.98% and at 100ppm 75%. In terms of concentration 50ppm is reduced to 9.31 ppm and 100ppm to 25.02ppm after 3hours of experiment using TiO₂.

The Degradation of Reactive Blue Using TiO₂:



Figure 5.2. Initial and final samples of Reactive blue dye

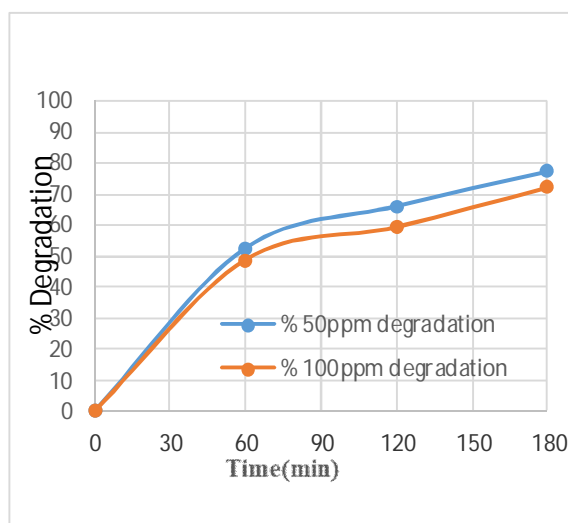


Figure 5.2a. Degradation of 50ppm and 100ppm Reactive blue dye using TiO₂ catalyst.

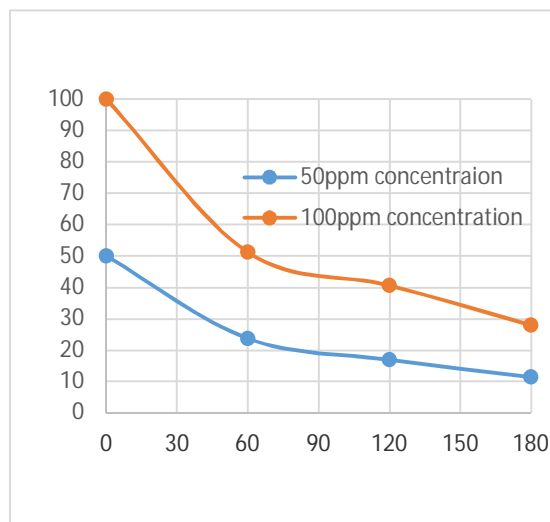


Figure 5.2b. Concentration Vs Time for 50ppm and 100ppm Reactive blue dye using TiO₂ catalyst.

The fig 5.2a&b shows the Difference between two concentrations (50ppm, 100ppm) of Direct Red %degradation is at 50ppm 77.17% and at 100ppm 72 %. In terms of concentration 50ppm to 11.41ppm and 100ppm to 28ppm after 3hours of experiment using TiO₂.

The Degradation of Reactive Orange Using ZnO:

Figure 5.3. Initial and final samples of Reactive orange dye



The fig 5.3a&b shows the Difference between two concentrations (50ppm, 100ppm) of Ractive orange %degradation is at 50ppm 75.12% and at 100ppm 71%. In terms of concentration 50ppm is reduced to 12.44 ppm and 100ppm to 29ppm after 3hours of experiment using ZnO.

The Degradation of Reactive Blue Using ZnO:



Figure 5.4. Initial and final samples of Reactive blue dye

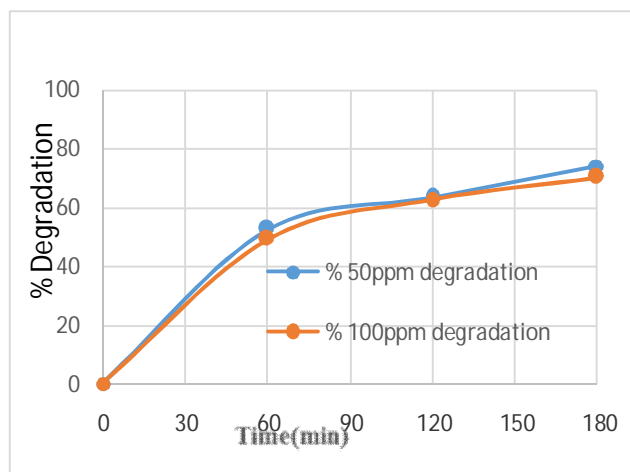


Figure . 5.3 a. Degradation of 50ppm and 100ppm Reactive orange dye using ZnO catalyst.

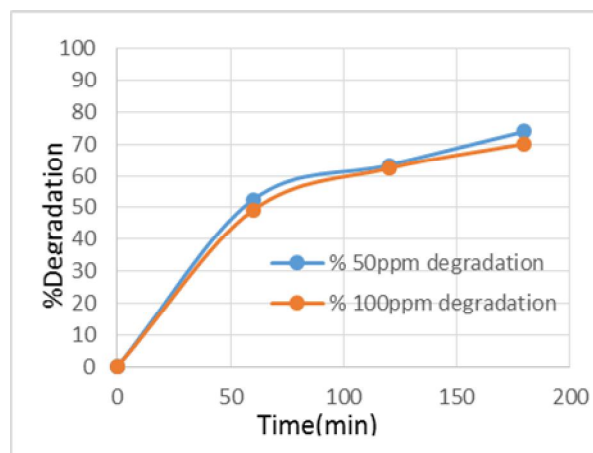


Figure 5.4a. Degradation of 50ppm and 100ppm Reactive blue dye using ZnO catalyst

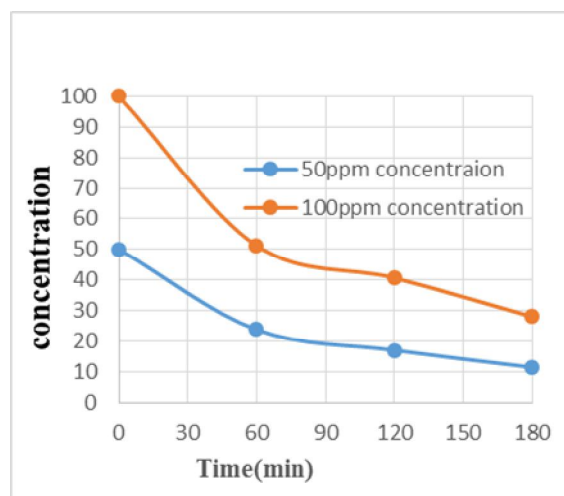


Figure 5.3b. Concentration Vs Time for 50ppm and 10 ppm Reactive orange dye using ZnO catalyst.

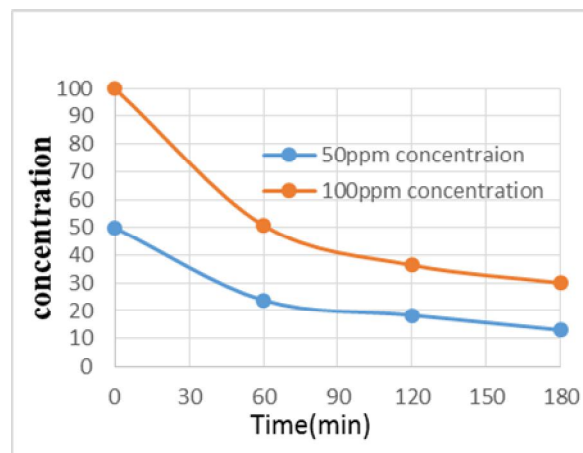


Figure 5.4b. Concentration Vs Time for 50ppm and 10 ppm Reactive blue dye using ZnO catalyst.

The fig 5.4a&b. shows the Difference between two concentrations (50ppm, 100ppm) of Reactive blue %degradation is at 50ppm 73.98% and at 100ppm 70.5%. In terms of concentration 50ppm to ppm 13.01and 100ppm to 28.95ppm after 3hours of experiment using ZnO.



Figure 5.5. Textile Industry dye Effluent degradation before after the experiment using TiO_2 & ZnO

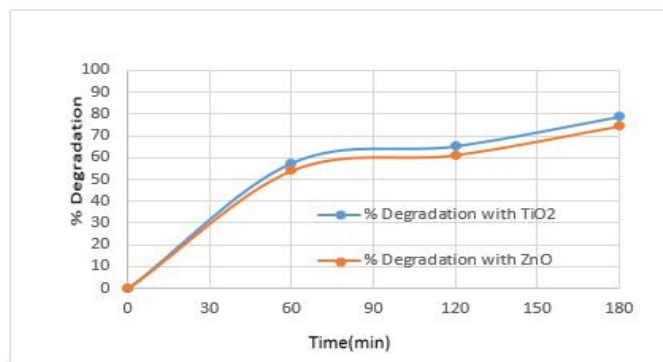


Figure 5.5a. Degradation of Textile Industry Effluent degradation using TiO_2 & ZnO .

The fig .5.5a. 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 (RO +RB) with Textile Industrial Effluent using TiO_2 :



Figure 5.6. Initial and final samples of Dye mixtures analysis

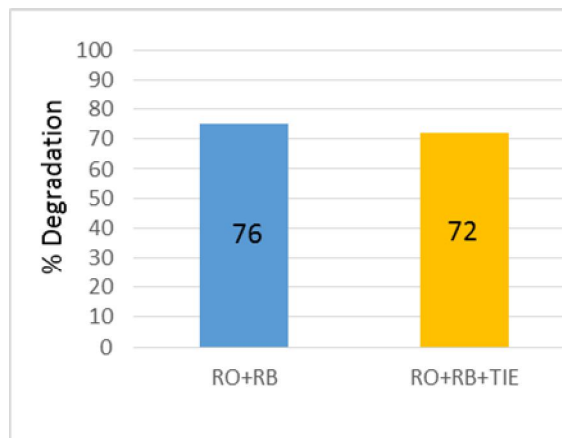


Figure 5.6a. Degradation for Dye mixture with TIE using TiO_2

The fig .5.6a. shows It was observed the combined mixtures of dyes with textile Industrial Dye effluent %degradation is (RO+RB) 76% and (RO+RB+TIR) is 72% after 3hours of experiment using TiO_2 . Concentration of (RO+RB) is reduced from 100ppm to 24 ppm and COD removal of (RO+RB+TIR) is reduced from 10720 ppm to 2975ppm.

Mixed dyes (RO+RB) with Textile Industrial Effluent using ZnO :

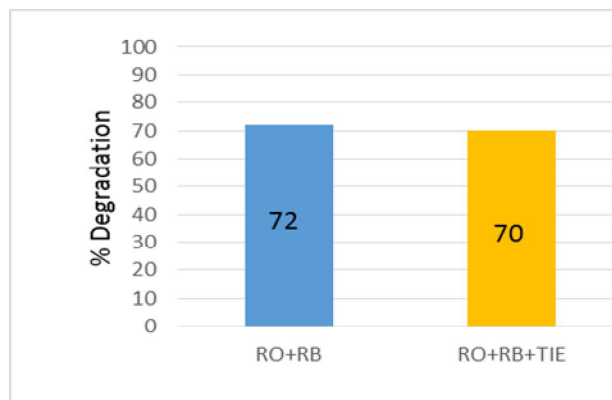


Figure .5.7. Degradation of Dye mixture using ZnO

The fig 5.7. Shows it was observed the combined mixtures of dyes with textile Industrial Dye effluent %degradation is (RO+RB) 72% and (RO+RB +TIR) is 70% after 3hours of experiment using ZnO . Concentration of (RO+RB) is reduced from 100ppm to 28ppm and COD removal of (RO+RB+TIR) is reduced from 10720ppm to 3216ppm.

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.

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

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; concentration from 'C0' to 'C' and time from '0' to 't'.

$$\int_{C_0}^C \frac{1}{C} dC = -k \int_0^t dt$$

$$\ln(C/C_0) = -k_t$$

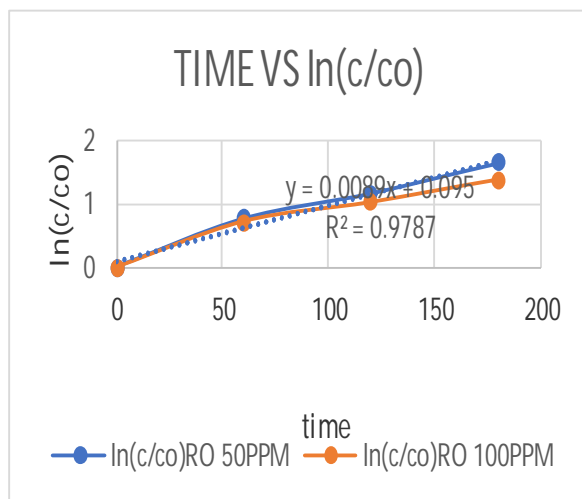


Figure 6.1. Time Vs ln (C/C₀) for RO using TiO₂

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

Dyes name	ppm	With TiO ₂ K values	With ZnO K values
Reactive orange	50	1.65	1.39
Reactive orange	100	1.38	1.22
Reactive blue	50	1.47	1.24
Reactive blue	100	1.23	1.17

Discussion: In the presence of UV light and catalyst textile dyes can be degraded because it produce more hydroxy radicals to degrade the compounds.

Because of light intensity and availability of active catalyst surface for dye adsorption as well as for hydroxyl radical generation.

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.

7. CONCLUSIONS

The degradation of individual effluents has been studied using TiO₂ catalyst and found that percentage of degradation of different dyes is found to be in given order. For Reactive Orange of 50 ppm (80.98%) > Textile Industry Effluent (78.72%) > Reactive Blue Dye of 50 ppm (77.17%) > Reactive Orange of 100 ppm (74%) > Reactive Blue Dye of 100 ppm (72%).

The degradation of individual effluents has been studied using ZnO catalyst and found that percentage of degradation for Reactive Orange of 50 ppm (75.12%) > Textile Industry Effluent (75.3%) > Reactive Blue Dye of 50 ppm (73.98%) > Reactive Orange of 100 ppm (71%) Reactive Blue Dye of 100 ppm (70%).

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

RO+RB (76%); RO+RB+TIE (72%) for TiO₂, RO+RB(72%); RO+RB+TIE (70%) for ZnO.

The kinetics of degradation of the dyes followed first order rate and rate constants for RO and RB (50ppm, 100ppm) using TiO₂ are 1.65, 1.38, 1.47, and 1.23 respectively.

The kinetics of degradation of the dyes followed first order rate and rate constants for RO (50ppm, 100ppm), RB (50ppm, 100ppm) using ZnO are 1.39, 1.22, 1.24, and 1.17 respectively.

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