

TREATMENT OF TEXTILE DYE WASTEWATER USING PHOTOCATALYTIC REACTOR

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ABSTRACT

This work was planned to investigate experimentally the removal of organic compounds from textile industrial wastewater by immobilized photocatalytic treatment, for its reuse in the same industry or for domestic purpose and irrigation. Now a days immobilized photocatalytic technique is used for the treatment of textile wastewater. Due to high photocatalytic activity and stability of titanium dioxide, it is generally used as a photocatalyst for the removal of organic compound. TiO₂ was immobilized by dipcoating technique. When dip-coating technique is applied, the operating region shifted from UV to visible. Sol-gel technique has been taken as one of the adaptable methods for the preparation of metal dipped nanocrystaline TiO₂. In this technique, the wavelength of the UV light and the amount of immobilized TiO₂ were negligible. Photocatalytic oxidation of the combined UV/TiO₂ catalyst excites the particles from the valance band to the conduction band having a forbidden energy zone value of 3.3 eV. The free hydroxyl radicals produced due to this excitation removes the organic compounds present in the dye wastewater by degradation. In the present work, we investigate in the operating conditions of catalyst concentration 100 mg/L, pH of 7 and at room temperature. Under these conditions, the degradation of about 80.5% of Congo red dye and 77.4% of T.blue SBL dye were achievable in 480 mins.

Key words: Photocatalytic treatment, Ultraviolet visible light, Industrial wastewater, Titanium dioxide.

INTRODUCTION

Dye wastewater pollutants are the major sources of environmental pollution. Textile wastewater introduces intensive colour and toxicity to aquatic systems. Dyes possess complex aromatic structure. Hence, conventional biological treatment methods are ineffective

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for decolourisation and degradation¹. Advanced oxidation processes (AOPs) have been successfully used as pretreatment methods to reduce the concentrations of toxic organic compounds that inhibit biological wastewater treatment process. Different types of homogeneous and heterogeneous AOPs have effectively degraded coloured aromatic compounds by the destructive oxidation of the dyes. Among heterogeneous AOPs, titanium dioxide (TiO₂) mediated photocatalytic oxidation appears to be a promising alternative, since the optical absorption of TiO_2 is the major advantage than other AOPs. Photodegradation involves the oxidation of organic pollutants where absorption of light is the driving force. TiO_2 has proved to be the best material for purification because it is readily available, cheap and chemically stable. TiO₂ semiconductor exists in three crystalline formsanatase, rutile and brookite. Among this anatase form of TiO_2 was found to be most effective for wastewater treatment². The combination of catalyst is also a very strong oxidizing agent. The combination of TiO₂, UV can create a very fast and efficient process for wastewater treatment by producing hydroxyl radicals. These electrons may form hydroxyl radicals, which can decompose organic compounds. With the use of dipping techniques, thin layer of TiO₂ were coated onto glass slides for testing the possibility of destroying benzoic acid and caffeine. Further, testing on greater thickness and light positions needed to be performed to further optimize the use of the catalyst and the reaction kinetics.

Mechanism of TiO₂

Photocatalytic oxidation by UV/TiO₂ or ZnO involves the oxidation of TiO_2/ZnO particles by UV light from valence band of the solid to the conduction band.

 $TiO_{2} + h\upsilon \rightarrow e^{-}_{CB} + h^{+}_{VB}$ $TiO_{2}(OH^{\bullet}) + H_{2}O + H^{+} \rightarrow TiO_{2}(OH^{\bullet}) + H^{+}$ $TiO_{2}(OH^{\bullet}) + R \rightarrow TiO_{2}(OH^{\bullet}) + RO + H^{-} + e^{-}$ $ZnO + h\upsilon \rightarrow e^{-}_{CB} + h^{+}_{VB}$

When a semiconductor such as catalyst absorbs photons the valence band electrons are excited to the conduction band. For this to occur, the energy of photon must exceed the band gap energy of the semiconductor. This excitation results in the formation of an electronic vacancy or positive hole at the valence band edge. This hole has a positive charge and reacts with the adsorbed water molecules on the surface of the solid producing the radical OH⁻ which has great potential oxidation of organic molecules. TiO₂ is a catalyst in the photocatalytic degradation of organic compounds due to its suitable band gap energy of 3.3 eV over a wide range of pH¹.



Fig. 1: Distribution of energy in bands

TiO₂ immobilization

Titanium (IV) isopropoxide mixed with glacial acetic acid in a beaker at 0°C. 1 g MgNO₃ is dissolved in water and was added drop wise and vigorously stirred for 1 hour using magnetic stirrer. The solution undergoes continuously stirring for another 1 hr to form a clear solution. The resulting solution was kept in dark for overnight and then solution was placed in an oven at a temperature of 70°C for gelation process for 12 hrs. Later, the gel was dried and calcined at 600°C. The prepared dipped TiO₂ nanoparticle is mixed with deionized water and poly vinyl alcohol (PVA) was subsequently added into the TiO₂ suspension, followed by mechanical stirring at 95°C for 1 hr. Then PVA/TiO₂/H₂O solution mixture rested in air to eliminate air bubbles and to cool the solution to room temperature. The obtained viscous solution mixture was coated onto a clean glass column and was allowed to evaporate overnight at room temperature.

EXPERIMENTAL

Material and methods

Collection of sample

The sample of textile dye wastewater was collected from dyeing industry located at SIPCOT, Perundurai, Erode District, Tamil Nadu.

Reagents and chemicals

The Congo red dye, T.blue SBL dye, Poly Vinyl Alcohol (PVA), Glacial acetic acid and titanium dioxide (TiO₂) were procured from S. D. Fine Chemical industry, Mumbai, India. All the chemicals are used for analytical reagent grade and employed directly without further purification. Distilled water was used in all experiments. Experimental studies were carried out in batch photocatalytic reactor of 1 L capacity at room temperature, which comprises of reactor vessel and UV lamp assembly. In this setup UV lamp was placed in an immersion tube, which is positioned in the reactor vessel containing the liquid to be irradiated. An electrical magnetic stirrer with magnetic bar was used continuously so that catalyst can be uniformly dispersed in the solution when the sample was degraded by UV light. The entire reactor was kept inside the UV inoculation chamber in order to guarantee maximum use of the radiation, to prevent the effect of external radiation and to maintain the temperature of the system. The reactor system temperature was maintained periodically and kept constant. The collected industrial sample is makeup and ensured that the complete hydrolysis is takes place. The concentration of sample dye before and after irradiation was determined using UV visible spectrophotometer.



Fig. 2: Photocatalytic reactor

In order to determine the concentration of the dye after treatment, a calibration curve was drawn by measuring the absorbance of dye solution of known concentrations. The calibration curve for the dye is shown below.



Fig. 3

The operating conditions of experiments are given in Table 1.

S. No.	Parameters	Value	
1.	Initial dye concentration	100 mg/L	
2.	TiO ₂ amount	0-120 mg/L	
3.	pH	2-10	
4.	Temperature	20-40°C	
5.	Irradiation time	up to 240 min	

Table 1: Operating conditions of experiments

Decolorization efficiency

Decolorization efficiency (DE) was calculated from a mathematical equation adapted from measurements of decolorization used before

$$DE = \frac{(Absorbance)_{o} - (Absorbance)_{t}}{(Absorbance)_{o}} \times 100$$

where, (Absorbance)_o = Absorbance before irradiation (Absorbance)_t = Absorbance at time t

To check the validity of the previous equation for used textile industrial wastewater, the photodegradation percentage of the dye was followed spectrophotometrically, by a comparison of the absorbance at specified interval of times, with a calibration curve accomplished by measuring the absorbance, at known wavelengths, with different concentrations of the dye solution.

RESULTS AND DISCUSSION

Effect of dye concentration

Experiments were conducted at initial dye concentration as 100 mg/L constant both Congo red dye and T. blue SBL dye. The degradation of organic compounds reduction with process time is increase shown in Fig. 3, 4 and 5. When the time is increased to dye concentration decrease extremely. The rate of degradation depends on the formation of OH radicals. There occurs the replacement of adsorbed OH positions by dye ions which results in reduced generation of OH radicals. On account of the fact these OH radicals react with the dye containing aromatic compounds in the textile wastewater.

Effect of catalyst dosage

The dosage of catalyst (anatase) was varied with the concentration of dye as constant to find the optimum dosage. The photocatalytic degradation experiments were carried out under the UV light by varying the amount of anatase dosage from 40 mg to 95 mg and the irradiation time was fixed for 8 hrs when the amount of anatase dosage was increased in the wastewater, degradation efficiency was slightly increased up to photocatalyst dosage of 70 mg. The photodegradation rate was slightly reduced beyond the 70 mg of photocatalyst dosage. Excess catalyst reduces the amount of photo energy being transferred in the medium due to opacity offered by catalyst particles. An amount of 70 mg/100 mL of photocatalyst was used for the subsequent photocatalytic degradation experiments.



Fig. 3: Effect of dye concentration



Fig. 4: Effect of dye concentration (with TiO₂)



Fig. 5: Effect of dye concentration (without TiO₂)

Effect of irradiation time

The required duration for the complete photocatalytic treatment of organic compounds in the textile wastewater was studied based on the duration of catalyst irradiation to the light source. The catalyst irradiation time was varied from 1 to 8 hrs under the UV light source for the dosage of 45 mg of photocatalyst into 100 mL of textile wastewater. In the present study highest degradation efficiency was observed. When the irradiation of photocatalyst was continued till 8 hrs under UV light source and the organic compound removal efficiency as 80.5% of Congo red dye and 77.4% of T.blue SBL dye. The photocatalyst and the result obtained are shown in Table 2.

Time (sec.)	AOPs with UV/ TiO ₂		UV Degradation with TiO ₂		UV Degradation without TiO ₂	
	Congo red	T.Blue SBL	Congo red	T.Blue SBL	Congo red	T.Blue SBL
60	95.25	93.47	91.6	90.25	87.0	84.32
120	90.5	88.75	85.8	84.8	80.5	79.8
180	86.42	77.25	80.0	79.31	70.24	63.41
240	80.27	70.0	71.2	69.8	60.5	58.75
300	72.51	66.25	65.3	60.0	53.9	41.6
360	69.0	61.5	56.8	55.3	42.0	39.62

Cont...

Time (sec.) -	AOPs with UV/ TiO ₂		UV Degradation with TiO ₂		UV Degradation without TiO ₂	
	Congo red	T.Blue SBL	Congo red	T.Blue SBL	Congo red	T.Blue SBL
420	60.31	57.29	50.15	42.1	33.21	23.25
480	59.52	55.5	42.0	39.1	22.6	19.5

Effect of UV light intensity

The absorption spectra of Congo red dye and T.blue SBL dye were studied at different times of irradiation. The effect of variation of light intensity on the degradation efficiency was also investigated. The result indicates that degradation efficiency increases in the light intensity will increase the number of photons striking per unit area of photocatalyst.

CONCLUSION

This work is terminates that the overall degradation percentage of Congo red dye and T.blue SBL dye in textile wastewater by photocatalytic treatment on using TiO_2 as catalyst is 80.5% and 77.4%. The TiO_2 catalyst is immobilized by dip-coating method. The problem of this work is degradation with TiO_2 as photocatalyst is that of being slow compared with conventional treatment methods but it has benefit not leaving toxic by sludge. The percentage degradation is measured for the different concentration of sample solution. Since the photocatalytic reactor is used for the treatment process the UV light is submerged inside the reactor. The percentage removal of the dye is directly proportional to the intensity of the UV light radiation. In this process, the combination of TiO_2 catalyst and UV visible radiation is the best oxidizing agent. It produces free hydroxyl radicals for the effective decomposition of pollutants present in the dye wastewater.

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