



Photo and Electrocatalytic Treatment of Textile Wastewater and Its Comparison

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ABSTRACT :

Electrochemical and photochemical techniques have been proved to be effective for the removal of organic pollutants in textile wastewater. The present study deals with degradation of synthetic textile effluents containing reactive dyes and assisting chemicals, using electro oxidation and photo catalytic treatment. The influence of various operating parameters such as dye concentration, current density, supporting electrolyte concentration and lamp intensity on TOC removal has been determined. From the present investigation it has been observed that nearly 70% of TOC removal has been recorded for electrooxidation treatment with current density 5 mA/dm², supporting electrolyte concentration of 3 g/L and in photocatalytic treatment with 250 V as optimum lamp intensity nearly 67% of TOC removal was observed. The result indicates that electro oxidation treatment is more efficient than photocatalytic treatment for dye degradation.

Keywords : TiO₂/UV, Electro oxidation, Photocatalysis, Organic pollutant, Textile effluent

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1. Introduction

With rapidly growing population and increasing reports on adverse effects on the environment, its conservation has become a major concern. The strategies for environmental protection in industry generally include processes for waste treatment as well as development of new processes or products, which have less or no harmful effects on the environment. Pollutants from several origins have ecological problem since degradation of these pollutants are slow and conventional treatment methods in most cases are ineffective.¹⁾ Textile wastewater contains many variety of dyes and added chemicals which pose a serious threat to the environment in the form of liquid waste.²⁾ Dyeing and finishing processes in the textile industries leads to the main pollution in textile waste water. It has

been estimated that more than 700,000 tons of the dyes are used of which over 15-20% are left in the effluent during dyeing process.³⁾ The main pollutants are highly suspended solids, heat, colour, acidity, chemical oxygen demand and other compounds.⁴⁾

Advanced oxidation process such as electrochemical technique and photochemical techniques have an important role to play in both types of strategies. A wide range of organic pollutants is observed in industrial and municipal wastewater. Some of these compounds (both synthetic organic chemicals and naturally occurring substances) have adverse impact on biological treatment systems due to their resistance to biodegradation and toxic effects on microbial processes.⁵⁾ Advanced oxidation processes (AOPs) have been successfully used as pretreatment methods to reduce the concentrations of toxic organic compounds that inhibit biological wastewater treatment processes.

Different types of homogeneous and heterogeneous AOPs have effectively degraded coloured aromatic

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compounds by the destructive oxidation of the dyes. Among heterogeneous AOPs, titanium dioxide (TiO_2)-mediated photo catalytic oxidation appears to be a promising alternative, since the optical absorption of TiO_2 is the major advantage than other AOPs. Photocatalytic treatment is an effective technology for the degradation of organic pollutant present in the synthetic dye house effluent as reported earlier.⁶⁾ Photo degradation involves the oxidation of organic pollutants where absorption of light is the driving force. Titanium dioxide has proved to be the best material for purification because it is readily available, cheap and chemically stable.¹⁾ TiO_2 semiconductor exists in three crystalline forms—anatase, rutile, and brookite. Among this anatase form of titanium dioxide was found to be most effective for wastewater treatment.⁷⁾ Application of photocatalysis using semiconductor appears to be most attractive because conventional oxidation methods for the decomposition of hazardous compounds to non-hazardous compound are ineffective,^{1, 8-12)} due to the complex structure of organic dyestuffs.¹³⁻¹⁶⁾ Photocatalysis becomes more advantageous because of the fact that semiconductors are: (i) cost effective, (ii) nontoxic, (iii) have large surface area, (iv) broad absorption spectra with high absorption coefficient, (v) shows properties which can be altered by size reduction, doping, sensitizers etc., (vi) has provision for multielectron transfer process and (vii) capable for extensive use without significant loss of photocatalytic activity.¹¹⁾

2. Mechanism of Photocatalytic Treatment of Organic Pollutants

The basic degradation mechanism of organic pollutants using UV/ TiO_2 is shown in scheme 1. Ultra-band gap energy is supplied to the semiconductor particle as an input due to which valence band (VB) electrons get promoted to the conduction band (CB) along with charge separation. Electrons in conduction band and valence band settle on the surface of the TiO_2 semiconductor and involve in oxidation reduction reaction. Oxygen molecule takes up the electron from the conduction band of the semiconductor since the CB of TiO_2 and reduction potential of oxygen are isoenergetics.^{17,18)} In the absence of oxygen photocatalytic activity is nearly suppressed. Photocatalysis process widely uses TiO_2 semiconductor powders; the recombination between the electron and holes becomes prominent

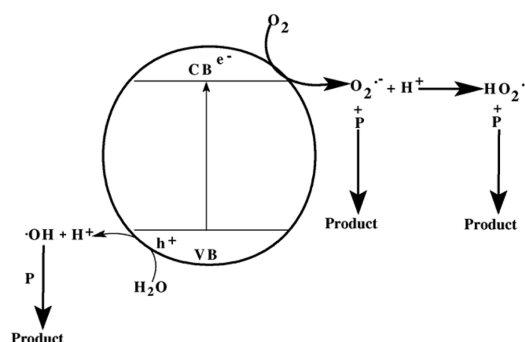
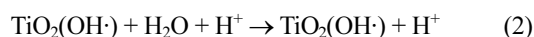
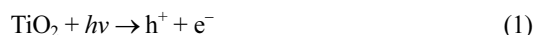


Fig. 1. Basic degradation mechanism of organic pollutants using UV/ TiO_2 .¹⁾

which reduces the efficiency of photocatalytic process. For an effective photocatalytic process the charge carriers should be separated as much as possible which can be achieved by photocatalysis or photoelectrolysis.¹⁹⁻²³⁾ The schematic representation of the mechanism associated with photocatalytic treatment of organic pollutant using UV/ TiO_2 is depicted in Fig. 1.

Decomposition of organic contaminants is mediated by a series of radical reactions initiated by the active oxygen species formed on the surface of TiO_2 crystal.⁶⁾ Thus TiO_2 photo catalysis is effective for the degradation of the wide range of organic pollutants in water.



The present study examined the treatment of synthetic textile effluent by means of electrooxidation method and photochemical degradation using UV/ TiO_2 as photocatalyst. The effect of various operating parameter such as current density, supporting electrolyte concentration, effluent concentration, lamp intensity were studied and compared.

3. Experimental Methods

3.1. Photocatalytic treatment

Experimental studies were carried out in batch photoreactor 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. The reactor consists of cylindrical quartz tube with low pressure mercury pump on the inner part, peristaltic pump was used to ruffle the reaction mixture continuously in to the photoreactor. The photoreactor was filled with 800 ml of the effluent and treated for TOC reduction, to maintain a constant output UV light was turned on 30 minutes before the start of the experiment. 1 g of commercially available TiO_2 powder was mixed to the effluent. In order to achieve a homogenous solution, the reaction mixture was sonicated for 20 min followed by magnetic stirring for another 30 min. The photoreactor was continuously purged with air to have adequate O_2 concentration in the reaction medium. From the photocatalytically treated sample 10 ml was taken periodically and subjected to TOC estimation. The experimental setup of photocatalytic reactor can be found elsewhere.

The photonic efficiency ζ can be calculated based on the equation²⁴⁾ below

$$\zeta(\%) = \frac{\Delta\text{TOC} \times \Delta t^{-1} \times V \times E_m}{A \times I_0} \times 100 \quad (4)$$

Where ΔTOC is the total moles of TOC removed per unit volume (mol/L), Δt treatment time (s), V is the volume of irradiated waste water (800 ml), E_m the mean energy of 1 mol of photons with $\lambda_m=357.5$ nm, A the total irradiated surface area of the photoreactor and I_0 is the incident intensity of UV lamp. Synthetic dye solution was prepared by mixing 100 mg/L of reactive red dye (powder) in water and kept for 24 hrs before start of the experiment to ensure complete hydrolysis of the dye. The concentration of synthetic dye effluent before and after irradiation was determined using UV-vis spectrophotometer.

3.2. Electrochemical method

Experiments were conducted in batch electrochemical reactor. The setup consists of electrolysis cell which has provision for insertion of electrode. Electrolysis was carried under galvanostatic condition which is used to measure the amount of charge passed through the solution. Commercially available RuO_2 , PbO_2/Ti , (titanium substrate insoluble anodes) TSIA were employed as anodes and stainless steel (SS) as cathode respectively. A known concentration of the synthetic effluent of about 800 ml was used for each experiment. The pollutant concentrations were esti-

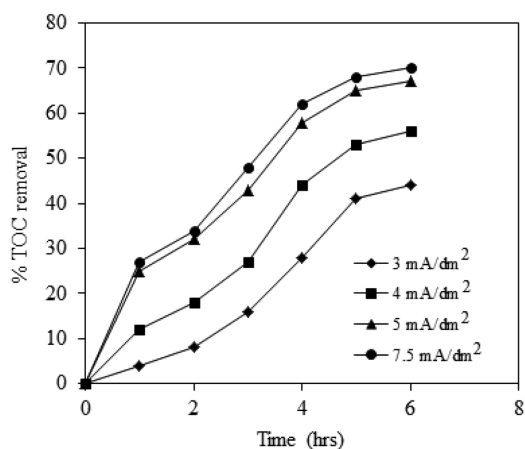


Fig. 2. Effect of current density on pollutant degradation with time, Initial concentration: 1000 ppm; NaCl: 3 g/L.

mated in terms of TOC. Samples were collected at regular intervals of time for TOC estimation.

4. Results and Discussion

4.1. Electrochemical treatment

4.1.1. Effect of current density

Experiments were carried out at five different current densities keeping the other parameters constant. TOC was found to be reducing with the increase in current density. This was due to increase in the formation of hypochlorite ion which enhances the dye degradation, which is similar to direct oxidation using hypochlorite.²⁵⁾ Beyond current density of 5 mA/dm² there was no significant removal of TOC removal as depicted in Fig. 2. Further increase in current density generates heat and it may not be effective for the oxidation process.

4.1.2. Effect of supporting electrolyte

Dye degradation is much regulated by a small amount of supporting electrolyte. The concentration of the supporting electrolyte is preferred to be minimum which varies from 0.01 to 1.0 M. Since it will reduce the movement of the electroactive species due to electric field and detain the interfacial potential difference.²⁶⁾ This is due to the increase in generation of hypochlorite ion produced by the supporting electrolyte. The generated hypochlorite ions act as main oxidizing species for the degradation of dye present in the effluent with sodium chloride as supporting electro-

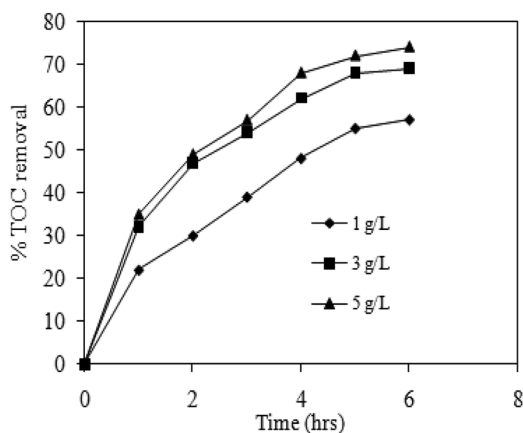


Fig. 3. Effect of supporting electrolyte concentration on pollutant degradation with time. C.D: 5 A/dm²; NaCl: 3 g/L.

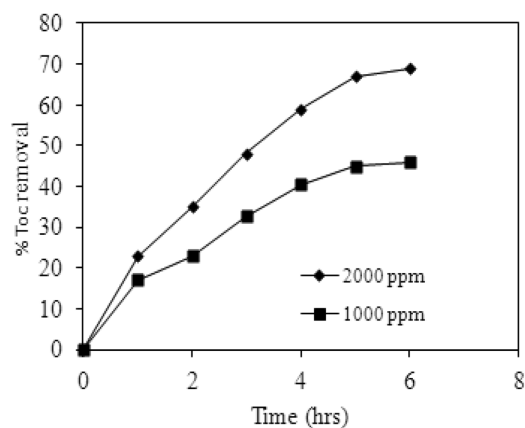


Fig. 4. Effect of dye concentration with reaction time; C.D 5 mA/dm²; NaCl: 3 g/L.

lyte. The presence of chloride ion promotes the rate of dye degradation. Chloride ion enhances the dye degradation rate while ions like sulphate and carbonate shows the reverse effect. The desirable properties of solution for electrochemical degradation may be obtained by using sodium chloride as supporting electrolyte, since in case of other supporting electrolytes some ions may react with the electrode or their products. Thus use of reliable supporting electrolyte enhances degradation performance and is also imperative to sustain the ionic strength.²⁷⁾ TOC removal increases with increase in the supporting electrolyte concentration from 1 to 3 g/L of NaCl. Further increase in concentration to 5 g/L increase in TOC removal is insignificant, hence 3 g/L is considered as optimum condition as shown in Fig. 3.

4.1.3. Effect of dye concentration

Experiments were conducted at two varying dye concentrations i.e., 1000 ppm and 2000 ppm. The variation of TOC reduction with the process time is given in Fig. 4. The dye degradation was faster under dilute conditions. When the dye concentration is increased to 2000 ppm dye degradation decreases extremely, since the rate of degradation depends on the formation of $\cdot\text{OH}$ radicals. There occurs the replacement of adsorbed OH^- position by dye ions which results in reduced generation of $\cdot\text{OH}$ radicals. On account of the fact these $\cdot\text{OH}$ radicals react with the dye containing aromatic compounds in the textile effluent.²⁸⁾ The ratio of hypochlorite ion generated decreases with increase in the effluent concentration

from 1000 to 2000 ppm, leading to decrease in the rate of dye degradation.

4.1.4. Photochemical Reactor

Experiments have been carried out in photocatalytic reactor covering a wide range of operating parameters. In the present study three UV-lamp intensity of 8 V, 125 V, 250 V have been used to study the effect of pollutant degradation with time. For each experiment 800 ml of the dye house effluent was taken and to maintain uniform concentration, air was circulated throughout the process. Samples were collected periodically and estimated for TOC. The rate of degradation in photo catalytic technique is highly influenced by the lamp intensity; it increases with increasing lamp intensity. Fig. 5 shows the effect of

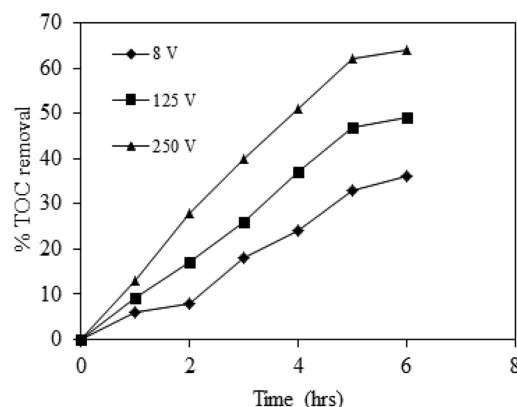


Fig. 5. Effect of lamp intensity with reaction time; concentration: 1000 ppm; NaCl: 3 g/L.

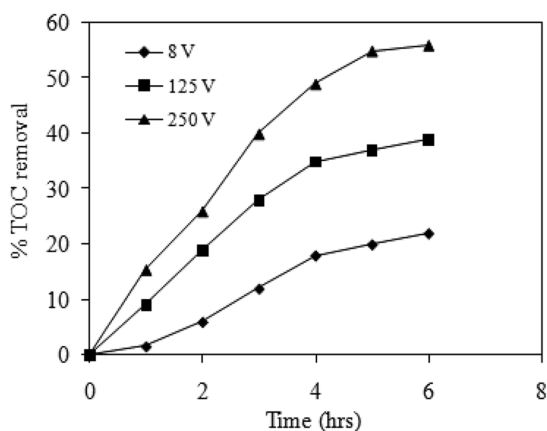


Fig. 6. Effect of lamp intensity with reaction time; concentration: 2000 ppm; NaCl: 3 g/L.

lamp intensity on dye degradation with 1000 ppm concentration. Lamp intensity of 250 V gave nearly 67% TOC removal which was in agreement with the electrochemical treatment. For the effluent concentration of 2000 ppm, TOC removal was less than the 67% which is shown in Fig. 6. With increase in the concentration of the effluent, the ratio of organic compounds present in the effluent will be more which may not degrade as effectively as in lower concentrations. This is due to the inhomogeneous nature of the organic compounds which leads to decrease in the TOC removal.

4.1.5. Comparison between the performance of electrochemical and photochemical methods

Electrochemical treatment of synthetic dye with different current densities and concentrations was compared with the photocatalytic treatment with varied lamp intensities. The electrochemical treatment gave an improved result than photocatalytic treatment for lamp intensity of 8 and 125 V. However photocatalytic treatment at lamp intensity of 250 V was in par with electrochemical treatment at the operating conditions of 1000 ppm concentration and current density 5 mA/dm² as shown in Fig. 7.

When we critically analyze the performance of the treatment employed for the dye degradation, it was found that in terms of rapidity; the photocatalytic reaction was found to be much rapid compared to electrochemical treatment. However, electrochemical treatment seems to be a cleaner process than photocatalysis, since the latter process involves TiO₂ catalyst

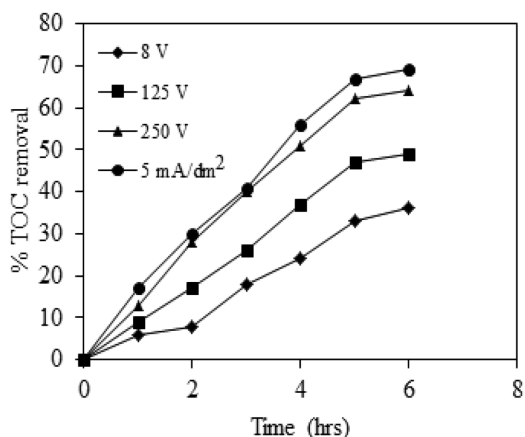


Fig. 7. Comparison of % TOC removal for photochemical and electrochemical treatment; Conc: 1000 ppm; NaCl: 3 g/L; Current density: 5 mA/dm².

in the reaction mixture which must be treated in an environmentally acceptable manner. Hence electrochemical method can be considered to be more efficient for dye degradation in terms of simplicity and cost.

5. Conclusions

Degradation of the textile wastewater containing reactive groups using TiO₂ heterogeneous photocatalytic and electrochemical treatment was effective in terms of TOC removal of nearly 70%. Throughout the reaction pH of the effluent was not found to change from the neutral condition. With increases in the lamp intensity % TOC removal also increases. Lamp intensity of 250 V was found to be at par with the electrochemical method. However one of the most important disadvantages of photocatalytic degradation with TiO₂ as photocatalyst is that the quantum yield is less and catalyst must be removed after treatment, which is a secondary pollutant. Hence it can be concluded that electrochemical treatment can be used efficiently for dye degradation than the photocatalytic treatment.

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