Photocatalytic Degradation of Real Textile Industrial Effluent under UV Light Catalyzed by Metal Oxide Nanoparticles

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Abstract
The domestic use and industrial activity, especially in developing countries, produce large amount of wastewater. This wastewater when disposed into natural channels may lead to high pollution risk. There are different methods for wastewater treatment one of them is Advanced Oxidation Processes (AOPs), still it has some limitations. The present work has been concentrated on the degradation of real textile industrial effluent named as Effluent1. The said Effluent1 was collected from textile industry from Echalkaranji; Maharashtra state was subjected to photocatalytic treatment using photocatalyst such as Degussa P-25 TiO₂. Effluent1 was analyzed before and after the treatment for their physiochemical parameters like color, COD, TOC and presence of inorganic ions. Throughout the study it was observed that Degussa P-25 TiO₂ effectively brought out the degradation of Effluent1. Addition of optimum amount of H₂O₂ to the heterogeneous photocatalytic treatment was found to enhance the degradation of real textile effluents to a large extent. Hence, the photocatalytic degradation was found to be fruitful treatment for degradation of real textile industrial effluent as well as by adding oxidant the photocatalytic degradation has been enhanced.

Key words: AOPs, COD, Degussa P-25, Photocatalyst, TOC

Introduction
Since, water is one of the fundamental requirements of life and any undesired addition of chemical substances lead to its contamination and make it unfit for human use, the quality of this valuable resource (water) will directly influence the normal life of human being.

The growth of the world’s population and industry has increased the demand for water supply. The domestic use and industrial activity, especially in developing countries, produce large amount of wastewater. This wastewater when disposed into natural channels may lead to high pollution risk.

Large amounts of dyes are produced annually and applied in many different industries, including the textile, paper, leather, cosmetic, pharmaceutical and food industries (Zee & Villaverde 2005). Synthetic dyes and pigments released into the environment mainly in the form of wastewater effluents by textile, leather and printing industries causes severe water pollution.

Thus, increase in industrialization significantly demands the removal of organic or inorganic substances at ppm or ppb level from industrial wastewater. The typical industries that discharge toxic organic compounds and pollute the nearby aquatic environment are those of chemical, refinery, dye, textile etc (Brown & De Vito 1993). There are large numbers of textile industries all over India. The total production capacity is expected to increase two to three times a year with an aim to achieve 10% of the global market share. Though this progress will be of great benefit to Indian economy, it will impose substantial threat to the environment and the quality of the living conditions especially in the vicinity of textile industries.

Approximately 30-40 cubic meter of wastewater is being discharged per ton of hide’s process waste water from textile industries containing toxic and non-biodegradable constituents which are not eco-friendly. Hence, there is urgent need to develop suitable and cost effective
technology for the treatment of various effluents from dye house. Reviewing of established treatment technologies and need for AOPs for the complete degradation of organic and inorganic substances from water and wastewater before it is released into the environment. AOPs classified under homogeneous photocatalysis such as photolytically induced oxidation with ozone (UV /O3) or hydrogen peroxide (UV /H2O2) are found to be uneconomical in industrial wastewater application. (Legrini et al. 1993, Schivello 1997, Vincenzo et al. 2006). The utilization of metal salt Fe (II) as Fenton’s reagent requires pH control and produces the problem of sludge generation that may cause waste disposal problem (Pignatello et al. 2006). Thus, among the various AOPs heterogeneous photocatalysis using metal oxide semiconductor as catalyst (UV /TiO2) has been found to be very promising for degradation of toxic and bio-resistant organic pollutants from industrial wastewater (Aleboyed et al. 2003).

Methodology

Materials

TiO2 purchased from Degussa Pvt. Ltd., contained surface area of 50 m2/g and particle size of 11 nm as per the information provided by the manufacturer. Raw wastewater was collected from the textile industry from Echalkaranji located 40 km from Kolhapur, Maharashtra State, India. The physico-chemical data of the collected water are presented in Table 1 and Fig. 1. Total organic carbon (TOC) was measured using commercially available test kits (NANO COLOR TOC 60) from Machery-Nagel, Germany.

Table 1. Physicochemical parameters of effluent (efluent1)

<table>
<thead>
<tr>
<th>Name of the effluent</th>
<th>Parameters</th>
<th>Prevailing range ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efluent1</td>
<td>Colour</td>
<td>Dark brown</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>8.82</td>
</tr>
<tr>
<td></td>
<td>COD</td>
<td>1600 ppm</td>
</tr>
<tr>
<td></td>
<td>TOC</td>
<td>375 ppm</td>
</tr>
<tr>
<td></td>
<td>SO4²⁻</td>
<td>20-24 ppm</td>
</tr>
<tr>
<td></td>
<td>NO3⁻</td>
<td>4-11 ppm</td>
</tr>
<tr>
<td></td>
<td>NO2⁻</td>
<td>0-0.25 ppm</td>
</tr>
<tr>
<td></td>
<td>NH₄⁺</td>
<td>0.5-2 ppm</td>
</tr>
</tbody>
</table>

Chemical oxygen demand (COD)

COD is defined as the oxygen equivalent of the organic matter content of the wastewater that is susceptible to oxidation by a strong oxidizing agent. It is one of the most rapid and reliable methods of estimating the strength of any wastewater and offers huge advantage over the biochemical oxygen demand (BOD) as it takes a very short period of time (2-3 hrs) as compared to the 5-7 days duration required for the BOD test. Further the BOD test is much more susceptible to interference due to various factors as compared to the COD test. In the present investigation the COD of the textile effluent was determined in accordance with the procedure given in the standard methods of analysis as closed dichromate reflux titrimetric method (Franson 1989). Total Organic Carbon (TOC) was measured using commercially available test kits (NANO COLOR TOC 60) from Machery-Nagel, Germany (Dominguiz et al. 2005).

To determine the mineralization of real textile effluent under optimized conditions, % reduction in TOC of before and after decolorization was calculated. Estimation of inorganic ions as end product was quantitatively estimated using commercially available Viscocolor from Machery Nagel, Germany. The experimental procedures provided along with the test kits was followed for the quantitative determination of inorganic ions such as SO4²⁻ , NO3⁻ , NO2⁻ & NH₄⁺ in ppm by using photometer for confirmation of degree of mineralization in real textile effluents.
Photocatalytic treatment for real textile effluents

The photocatalytic activity of Degussa P-25 was studied for the degradation of effluent1. The photocatalytic reaction system included a 500ml cylindrical glass reactor inside equipped with a UV illumination source (254 nm), which was located axially in a quartz immersion tube. A circulating water jacket was employed to cool the irradiation source. Air was bubbled through the reaction solution from the bottom using an aerator with constant speed in a typical photocatalytic test performed at room temperature. In this photocatalytic system different amount of Degussa P-25 TiO₂ was used for the dose of Degussa P-25 TiO₂. Aliquots were taken out for 1 hr interval and filtered through 0.2 μm filter paper. After filtration, determining and quantifying the individual constituents of the textile effluents under study, gross parameters like COD, TOC and concentration of inorganic ions were measured.

Effect of addition of H₂O₂

One of the possible ways to increase the rate of reaction was to increase the concentration of OH radicals. H₂O₂ was widely used to increase the OH radical concentration by its addition to the heterogeneous system, 

\[ \text{TiO}_2 (\text{e}^-) + \text{H}_2\text{O}_2 \rightarrow \text{TiO}_2 + \cdot\text{OH} + \cdot\text{OH} \ldots \ldots \ldots \ldots (1) \]

Hydrogen peroxide is considered to have two functions in the process of photocatalytic degradation. It accepts a photogenerated electron from a conduction band and thus promotes the charge separation and it also forms OH radicals according to equation (1). However at high concentration of H₂O₂ it also acts as scavenger.

From the experiments conducted by varying the hydrogen peroxide concentration from 0.3 to 0.6 ml per 250 ml of the diluted effluent, the best results were obtained when H₂O₂ concentration was raised to 0.5 ml.

Results and Discussion

Optimization of catalyst Degussa P-25 concentration

Effluent1 was subjected for photocatalytic treatment using P-25 TiO₂. The concentration of catalyst Degussa P-25 TiO₂ varied from 100 to 300 mg/250 ml. From the obtained values of COD a graph was plotted as irradiation time in hrs Vs % reduction in COD for varied amount of catalyst which has summarized in Fig.2.

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Amount of P-25 TiO₂ in mg and their % reduction in COD value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amount of P-25 TiO₂ in mg and their % reduction in COD value</td>
</tr>
<tr>
<td></td>
<td>100 mg</td>
</tr>
<tr>
<td>0</td>
<td>COD in ppm</td>
</tr>
<tr>
<td>5</td>
<td>1000</td>
</tr>
<tr>
<td>8</td>
<td>1000</td>
</tr>
<tr>
<td>10</td>
<td>800</td>
</tr>
<tr>
<td>12</td>
<td>800</td>
</tr>
</tbody>
</table>

Fig. 2. Optimization of catalyst concentration using P-25 TiO₂ for the degradation of effluent1

Effect of addition of H₂O₂ on effluent1 Degussa P-25

In case of effluent1 by addition of H₂O₂ to photocatalytically treated reaction solution containing P-25 TiO₂ catalyst, the rate of degradation tremendously increased which could be observed from % reduction in COD data. The addition of H₂O₂ to said system showed increase in % reduction in COD, which was indicative of decrease in organic strength in turn substantial mineralization of the effluent. Results obtained had been depicted in Table 3 and Fig. 3 for effluent1 using Degussa P-25TiO₂.
Table 3. Efluent1 reduction (%) in COD at the optimized catalyst concentration (200 mg) using P-25TiO₂ and P-25TiO₂ + H₂O₂ system

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Reduction in COD</th>
<th>Reduction in COD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TiO₂ COD in ppm</td>
<td>TiO₂ + H₂O₂ COD in ppm</td>
</tr>
<tr>
<td>0</td>
<td>1600</td>
<td>1600</td>
</tr>
<tr>
<td>5</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>8</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>10</td>
<td>800</td>
<td>600</td>
</tr>
<tr>
<td>12</td>
<td>400</td>
<td>200</td>
</tr>
</tbody>
</table>

Fig. 3. Effect of addition of H₂O₂ to P-25 TiO₂ for the degradation of efluent1

Detection of inorganic ions

To confirm the complete mineralization of wastewater, the end products such as sulphate (SO₄²⁻), Nitrate (NO₃⁻), Nitrite (NO₂⁻) and ammonium ion (NH₄⁺) were quantitatively estimated after the completion of photocatalytic degradation of efluent1 using commercially available Viscolor Test Kits procured from Machery Nagel, Germany using P-25 TiO₂ as a photocatalyst. The experimental procedures provided along with the test kits was followed for the quantitative determination of inorganic ions such as SO₄²⁻, NO₃⁻, NO₂⁻ & NH₄⁺ in ppm by using photometer PF11 which confirmed the degree of mineralization in synthetic real textile effluents.

The experimental results obtained for efluent1 under investigation are summarized quantitatively in Table 5 for SO₄²⁻, NO₃⁻, NO₂⁻ and NH₄⁺ degradation but mineralization of efluent1 also achieved very effectively.

Table 5. Detection of SO₄²⁻, NO₃⁻, NO₂⁻ and NH₄⁺

<table>
<thead>
<tr>
<th>Obs. No.</th>
<th>Detection of Inorganic ions</th>
<th>Degussa P-25 TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0 hrs (ppm)</td>
</tr>
<tr>
<td>1</td>
<td>SO₄²⁻</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>NO₃⁻</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>NH₄⁺</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>NO₂⁻</td>
<td>0</td>
</tr>
</tbody>
</table>

The end products such as SO₄²⁻, NO₃⁻, NO₂⁻, and NH₄⁺ obtained from photocatalytic degradation of efluent1 confirms the substantial mineralization of azo dyes present in wastewater (efluent1).
Evaluation of sulphate ions

Literature revealed that the dyes containing sulfur atoms were mineralized into sulfate ions (Ioannis et al. 2004). The wastewater Effluent1 under investigation might contain sulphur atom and it got converted into $SO_4^{2-}$ as end product. Therefore in effluent1, after photocatalytic treatment, the presence of $SO_4^{2-}$ ions was found in the range of 20-25 ppm.

$SO_4^{2-}$ was the initial product directly resulting from the initial attack on sulfonyl groups. The release of $SO_4^{2-}$ ions could be due to an initial attack by OH radicals as shown below

$$R - SO_2^- + OH^- \rightarrow R - OH + SO_2^- \quad (2)$$
$$SO_2^- + OH^- \rightarrow SO_3^{2-} + H^+ \quad \ldots \ldots \ldots \ldots (3)$$

The hydrogen atom H could subsequently react with hydroxyl radicals to form water (Daneshvar et al. 2005).

$$OH + H^+ \rightarrow H_2O \quad \ldots \ldots \ldots \ldots (4)$$

Evolution of nitrogen-containing final products

Puzenat et al. showed the first example of N$_2$ evolution in aqueous photocatalytic degradation of N-containing pollutants in Congo Red and Amaranth dye. The formation of N$_2$ in azo dyes could be shown as follows.

$$R - N - N - R^\prime + H^+ \rightarrow R - N - N^* + R^\prime H \quad \ldots \ldots \ldots \ldots (5)$$
$$R - N = N^* \rightarrow R^* + N = N (N_2f) \quad \ldots \ldots \ldots \ldots (6)$$

In the azo bonds each nitrogen atom is in its +1 oxidation state. This degree of oxidation favors the evolution of gaseous nitrogen (N$_2f$) as shown above. N$_2$ evolution constitutes the ideal case for a decontamination reaction involving totally innocuous nitrogen containing final product. Nitrogen ions mineralize into, , and (Hurum & Agrios 2003).

$NH_4^+$ appears as the primary product with respect to in $NH_3$ case of amine compounds. The nitrogen atoms in the amino-groups of the dyes can lead to $NH_4^+$ ions by successive attacks of hydrogen species.

$$R - NH_2^+ + H^+ \rightarrow R^* + NH_3 \quad \ldots \ldots \ldots (7)$$
$$NH_3 + H^+ \rightarrow NH_4^+ \quad \ldots \ldots \ldots \ldots (8)$$

When nitrogen is present in -3 oxidation state in amino group, it spontaneously evolves as $NH_4^+$ with the same oxidation state and then $NH_4^+$ slowly undergoes oxidation into nitrate (Tanaka et al. 2000).

The amount of $NH_4^+$ was obtained in the range of 0.5 to 1 ppm in both catalysis which was less, while nitrate $NO_3^-$ ions were found in the range of maximum 5 ppm in P-25 TiO$_2$ and less 1-2 ppm in Merck ZnO. The amount of nitrate obtained was negligible.

The amount of $NH_4^+$ was less as compared to $NO_3^-$ ion. This might be due to as a result of $NH_4^+$ undergoing oxidation to $NO_3^-$ and $NO_2^-$ (Chun et al. 2001). No significant $NO_2^-$ ions were detected after the photocatalytic degradation of effluent1. As N-containing mineralization products obtained clearly indicated the photocatalytic treatment using UV/TiO$_2$ was effectively not only show degradation but mineralization of effluent also achieved very effectively.

The end products $SO_4^{2-}$, $NO_3^-$, $NO_2^-$, and $NH_4^+$ obtained from photocatalytic degradation of effluent confirms the substantial mineralization of azo dyes present in wastewater effluent1.

The result obtained from UV/TiO$_2$/H$_2$O$_2$ treatment process, made it the most appealing choice for complete degradation and substantial mineralization of real textile effluents at laboratory scale, which can be successfully extended to industrial scale.

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