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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 Efluent1. The said Effluent1 was collected from textile industry from Echalkaranji; Maharashtra state was subjected to photocatalytic treatment using photocatalyst such as Degussa P-25 TiO_2. Efluent1 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 TiO_2 effectively brought out the degradation of Efluent1. Addition of optimum amount of H_2O_2 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 /O_3) or hydrogen peroxide (UV /H_2O_2) 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 /TiO_2) 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

TiO_2 purchased from Degussa Pvt. Ltd., contained surface area of 50 m^2/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)

Name of the effluent	Parameters	Prevailing range ppm
Efluent1	Colour	Dark brown
	pH	8.82
	COD	1600 ppm
	TOC	375 ppm
	Presence of inorganic ions	
	SO_4^{2-}	20-24 ppm
	NO_3^-	4-11 ppm
	NO_2^-	0-0.25 ppm
	NH_4^+	0.5-2 ppm

Fig. 1. Textile industrial efluent1

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 (to go to) for completion (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 $SO_4^{2-}, NO_3^-, NO_2^-$ & NH_4^+ 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 efluent1. 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 TiO_2 was used for the dose of Degussa P-25 TiO_2. Aliquots were taken out for 1 hr interval and filtered through 0.2 ìm 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 H_2O_2

One of the possible ways to increase the rate of reaction was to increase the concentration of ·OH radicals. H_2O_2 was widely used to increase the ·OH radical concentration by its addition to the heterogeneous system,

$$TiO_2(\bar{e}) + H_2O_2 \rightarrow TiO_2 + {}^{\cdot}OH + {}^{\cdot}OH \ldots\ldots\ldots\ldots (1)$$

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 H_2O_2 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 H_2O_2 concentration was raised to 0.5 ml.

Results and Discussion

Optimization of catalyst Degussa P-25 concentration

Efluent1 was subjected for photocatalytic treatment using P-25 TiO_2. The concentration of catalyst Degussa P-25 TiO_2 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 2. Optimization of catalyst concentration for Efluent1 using P-25TiO_2

Time (hrs)	Amount of P-25 TiO_2 in mg and their % reduction in COD value					
	100 mg		200 mg		300 mg	
	COD in ppm	COD in %	COD in ppm	COD in %	COD in ppm	COD in %
0	1600	0	1600	0	1600	0
5	1000	37.5	600	62.5	400	75.0
8	1000	37.5	400	75.0	200	47.5
10	800	50.0	8.00	87.5	400	75.0
12	800	50.0	8.00	87.5	600	62.5

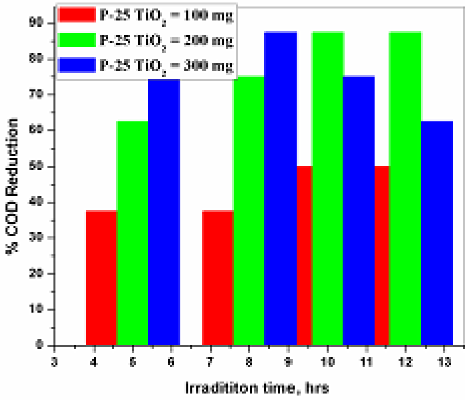

Fig.2. Optimization of catalyst concentration using P-25 TiO_2 for the degradation of efluent1

Fig. 2. concluded that optimized catalyst concentration was found to be 200mg/250 ml diluted effluent in case of Efluent 1using P-25 TiO_2.

Effect of addition of H_2O_2 on efluent1 Degussa P-25

In case of efluent1 by addition of H_2O_2 to photocatalytically treated reaction solution containing P-25 TiO_2 catalyst, the rate of degradation tremendously increased which could be observed from % reduction in COD data. The addition of H_2O_2 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 efluent1 using Degussa P-25TiO_2.

Table 3. Efluent1 reduction (%) in COD at the optimized catalyst concentration (200 mg) using P-25TiO$_2$ and P-25TiO$_2$ + H$_2$O$_2$ system

Time (hrs)	Reduction in COD TiO$_2$ COD in ppm	COD in %	Reduction in COD TiO$_2$ + H$_2$O$_2$ COD in ppm	COD in %
0	1600	0	1600	0
5	1000	37.5	1000	37.5
8	1000	37.5	800	50.0
10	800	50.0	600	62.5
12	400	75.0	200	87.5

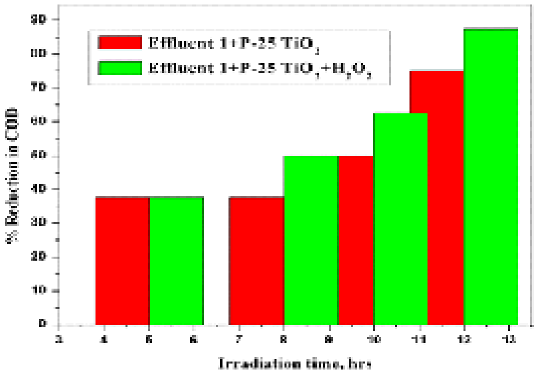

Fig. 3. Effect of addition of H$_2$O$_2$ to P-25 TiO$_2$ for the degradation of efluent1

Estimation of % reduction in total organic carbon (TOC)

TOC analysis seems to be more accurate and appropriate for evaluating the decontamination of polluted waters containing organics since it takes into account all the residual carbon containing metabolites. TOC directly evaluates the pollution level of an aqueous solution. The obtained results have been presented in table 4 for reduction (%) in TOC for the degradation of efluent1. The TOC data suggests that Degussa P-25 TiO$_2$ was found to be the best photocatalyst for degradation as well as mineralization of efluent1. Thus AOP using P-25 TiO$_2$ represents powerful treatment for degradation of efluent1.

Table 4. Reduction % in TOC for photocatalyst Degussa P-25

Time in hrs	% Reduction in TOC Degussa P-25 TiO2 TOC in ppm	TOC in %
0 hr	375	0
5 hr	275	26.66
12 hr	175	53.33

Detection of inorganic ions

To confirm the complete mineralization of wastewater, the end products such as sulphate (SO_4^{2-}), Nitrate (NO_3^-), Nitrite (NO_2^-) and ammonium ion (NH_4^+) 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 TiO$_2$ as a photocatalyst. The experimental procedures provided along with the test kits was followed for the quantitative determination of inorganic ions such as SO_4^{2-}, NO_3^-, NO_2^- & NH_4^+ 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 SO_4^{2-} , NO_3^- NO_2^- and NH_4^+ degradation but mineralization of efluent1 also achieved very effectively.

Table. 5. Detection of SO_4^{2-}, NO_3^- , NO_2^- and NH_4^+

Obs. No.	Detection of Inorganic ions	Degussa P-25 TiO$_2$ 0 hrs(ppm)	12 hrs (ppm)	24 hrs (ppm)
1	SO_4^{2-}	20	21	22
2	NO_3^-	4	4	11
3	NH_4^+	0.5	2	1
4	NO_2^-	0	0	0

The end products such as SO_4^{2-}, NO_3^-, NO_2^-, and NH_4^+ 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 Efluent1 under investigation might contain sulphur atom and it got converted into SO_4^{2-} as end product. Therefore in efluent1, 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

$$R-SO_3^- + OH \rightarrow R-OH + SO_3^- \ldots\ldots \quad (2)$$

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

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

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

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.

$$R-N=N-R^1 + H^\circ \rightarrow R-N=N\circ + R^1H \ldots (5)$$

$$R-N=N^\circ \rightarrow R^\circ + N\equiv N\ (N_2\uparrow) \ldots\ldots\ldots\ldots\ldots (6)$$

In the azo bonds each nitrogen atom is in its +1 oxidation state. This degree of oxidation favors the evolution of gaseous nitrogen $(N_2\uparrow)$ 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 ions by successive attacks of hydrogen species.

$$R-NH_2 + H^\circ \rightarrow R^\circ + NH_3 \ldots\ldots\ldots\ldots \quad (7)$$

$$NH_3 + H^+ \rightarrow NH_4^+ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

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 catalysts 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 nitrite 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 efluent1. As N-containing mineralization products obtained clearly indicated the photocatalytic treatment using UV/TiO_2 was effectively not only show degradation but mineralization of efluent1 also achieved very effectively.

The end products SO_4^{2-}, NO_3^-, NO_2^-, and NH_4^+ obtained from photocatalytic degradation of efluent1 confirms the substantial mineralization of azo dyes present in wastewater efluent1.

The result obtained from UV/TiO_2/H_2O_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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