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PHOTOCATALYTIC DEGRADATION OF REAL TEXTILE INDUSTRIAL EFFLUENT USING METAL OXIDES NANOPARTICALS

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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 GOV. The said effluent was collected from textile industry from Ichalkaranji, Maharashtra state was subjected to photocatalytic treatment using two different photocatalyst such as Degussa P-25 TiO_2 and Merck ZnO. GOV 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 brings out the degradation of GOV than Merck ZnO. Hence, the photocatalytic degradation was found to be fruitful treatment for degradation of real textile industrial effluent.

Keywords: AOPs, Photocatalyst, Degussa P-25, Merck ZnO

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1. 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 [1]. 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 [2].

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 wastewater from textile industries contains 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 organics and inorganics from water and wastewater before it releases into environment. The main objective of the present study is to find out effective method which can brings out complete mineralization and degradation of non-biodegradable and toxic organic compounds which are present in real textile effluents. For this purpose detailed study

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of various AOPs was carried out. Currently chemicals methods such as advance oxidation processes (AOPs) appear to be more promising for the treatment of textile industrial effluents [3]. Therefore photocatalytic experiments on the effluent (GOV) using different photocatalyst P-25 TiO_2 and Merck ZnO using various AOPs were studied. The aim of the present work is to find out best AOP by choosing best photocatalysts. Among various AOPs heterogeneous photocatalysis by using semiconductor metal oxide nanoparticles has been found to be very effective for removing organic pollutant from waste water [4-6]. For this it is essential to optimize catalyst concentration, comparisons of efficiencies of various photocatalyst and detection of inorganic ions as end products.

2. EXPERIMENTAL

2.1. Materials

TiO_2 was purchased from Degussa Pvt. Ltd. It having surface area is 50 m^2/g and particle size 11 nm as per the information provided by the manufacturer. ZnO is purchased from Merck pvt Ltd. Raw wastewater was collected from textile industry from Ichalkaranji located 40 km from Kolhapur from Maharashtra State, India. Wastewater was taken directly from outlet of textile industry. The physio-chemical parameters of the collected data is depicted in table 1 and color in Fig.1. Total Organic Carbon (TOC) was measured using commercially available test kits (NANO COLOR TOC 60) from Machery-Nagel, Germany.

Figure 1. Textile Industrial Effluent (GOV)

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2.2 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 compare 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[7] [7]. Total Organic Carbon (TOC) was measured using commercially available test kits (NANO COLOR TOC 60) from Machery-Nagel, Germany[8]. 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 PF11 for confirmation of degree of mineralization in real textile effluents.

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Table 1: Physicochemical parameters of Effluent (GOV)

Sr. no.	Name of the effluent	Parameters	Prevailing Range ppm
1	Effluent (GOV)	Colour	Dark brown
		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

2.3 Photocatalytic treatment for real textile effluents

The photocatalytic activity of Degussa P-25 & Merck ZnO was studied for the degradation of GOV. 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 aerator with constant speed. In a typical photocatalytic test performed at room temperature. In the said photocatalytic system different amount of Degussa P-25 TiO_2 and Merck ZnO has been separately used for the optimization of dose of Degussa P-25 TiO_2 and Merck ZnO. 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.

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Figure 2. Experimental set up for photocatalytic reaction

2.4 Mechanism of Heterogeneous Photocatalysis

The basic principles of heterogeneous photocatalysis using semiconductor metal oxide nanoparticles are well established and can be briefly summarized in the following simplified process. When the semiconductor nanoparticles is photo exited by light energy equal or greater than the band gap energy of semiconductor (eg.>3.2ev), it promotes an electron from valance band into conduction band and thus leaving a hole in valance band resulting in the formation of a positive hole (h^+) in valance band and an electron ($\bar{e}$) in the conduction band. The valance band holes act as powerful oxidants, whereas the conduction band electrons are good reluctant [9]. Both reductive and oxidative processes can occur at or near the surface of the photo excited semiconductor particle. In aerated aqueous suspension oxygen is able to scavenge conduction band electrons forming superoxide ions(O_2^-) by reduction and it gets protonated to form hydroperoxyl radical(HO_2) shown in Figure 3.

$$TiO_2 + hv \rightleftharpoons h^+_{vB} + \bar{e}_{cB} \qquad (1)$$

$$O_2 + \bar{e}_{CB} \rightarrow O^{\cdot -}_2 \qquad (2)$$

$$(O_2^-) + H_+ \rightarrow HO_2 \qquad (3)$$

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In this way electron/hole recombination can be effectively prevented and lifetime of holes gets prolonged.

The hydroperoxy radical lead to formation of H_2O_2 as

$$HO_2^{\cdot} + \bar{e} \rightarrow HO_2^- \quad (4)$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \quad (5)$$

While the photogenerated holes can oxidize either the organic molecules directly or can react with adsorbed water molecules to give hydroxyl radical $^{\cdot}OH$ [10].

$$H_2O + h_{v.b}^+ \rightleftharpoons HO_{ads}^{\cdot} + H_{ads}^+ \quad (6)$$

Thus the whole process can end in complete mineralization of organic compounds.

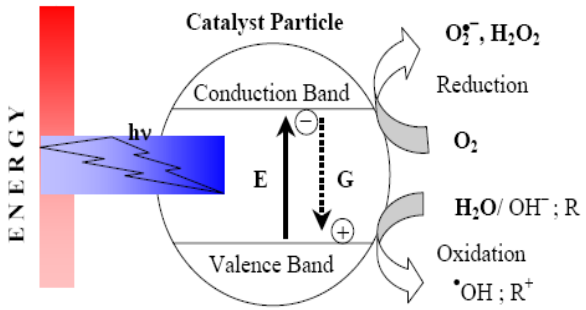

Figure 3. Mechanism on photocatalyst surface

3. RESULTS AND DISCUSSION

3.1 Optimization of Catalyst Degussa P-25 and Merck ZnO concentration

Effluent GOV was subjected for photocatalytic treatment using P-25 TiO_2 and Merck ZnO photocatalyst. The concentration of both catalyst were varied from 100 to 300 mg/250 mL diluted effluent in presence of UV, solutions were irradiated for 5, 8, 10, 12 hours. The obtained results are shown in table 2 and 3 for Degussa P-25 and Merck ZnO respectively.

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From the obtained values of COD graph was plotted as irradiation time in hrs Vs % reduction in COD for varied amount of catalyst which was summarized in Fig.4 for Degussa P-25 and Fig.5 for Merck ZnO. As the concentration of catalyst is increased, the number of pollutant molecules adsorbed increased owing to an increase in the number of TiO_2/ZnO particles. The density of particles in the area of illumination also increases and so the rate of degradation is enhanced. Above a certain level, the substrate molecules available are not sufficient for adsorption by the increased number of TiO_2/ZnO particles. Hence the additional catalyst amount is not involved in the catalytic activity and the rate does not increase with increase in the amount of catalyst [11]. Beyond a certain limit surface active sites also decreases due to aggregation of TiO_2 particles at high catalyst concentration. The surplus addition of catalyst makes the solution more turbid and turbidity impedes further penetration of light in the reactor[12]. Due to which there is reduction in degradation efficiency. Hence 200mg/250 mL was found to be optimized catalyst concentration for GOV using both the catalyst.

3.2 Detection of % Reduction in TOC

The value of % of reduction of COD is almost same for the Degussa P- 25 and and Merck ZnO for optimized condition. Therefore other parameters have been studied named as TOC. The total organic carbon (TOC) is defined as the amount of CO_2 liberated when an organic sample is totally oxidized. The TOC methodology is based on the transfer of all the carbon present in solution to CO_2. 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 evaluate the pollution level of an aqueous solution. The comparative evaluation of photocatalytic activity of Degussa P-25 and Merck ZnO from the observed TOC data which was shown in table 4. Suggested that Degussa P-25 TiO_2 exhibit better photocatalytic activity than Merck ZnO.

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Table 2. Optimization of catalyst concentration for GOV using P-25TiO_2

Time in 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 hr (Initial COD)	1600	0	1600	0	1600	0
5 hrs	1000	37.5	600	62.5	400	75
8 hrs	1000	37.5	400	75	200	47.5
10 hrs	800	50	8	87.5	400	75
12 hrs	800	50	8	87.5	600	62.5

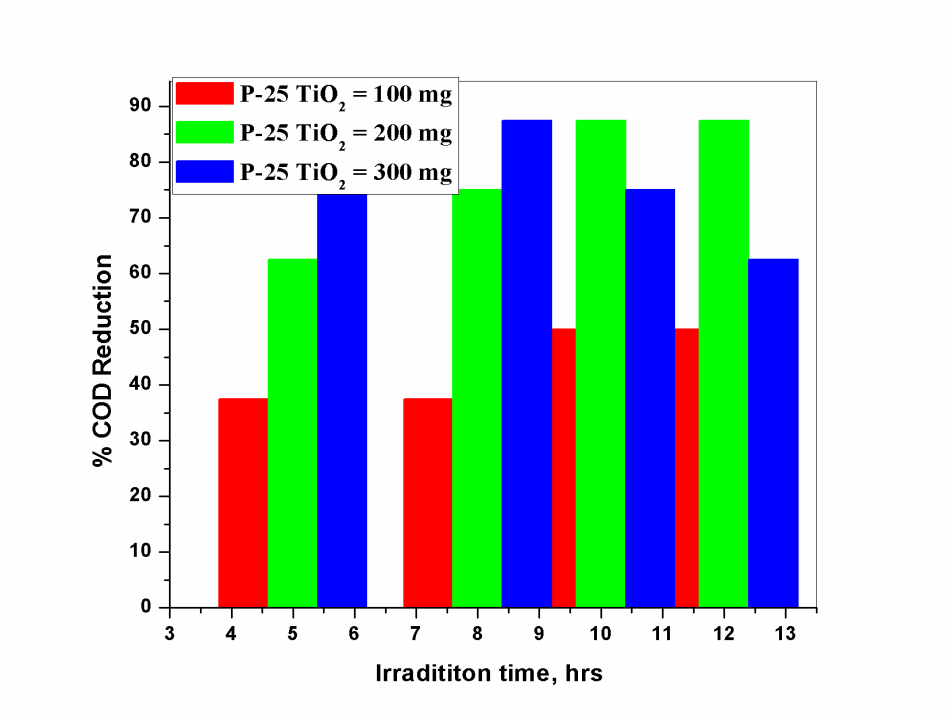

Figure. 4. Optimization of catalyst concentration using P-25 TiO_2 for the degradation of GOV

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Table 3. Optimization of catalyst concentration for GOV using Merck ZnO.

Time in hrs	Amount of Merck ZnO 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 hr (Initial COD)	1600	0	1600	0	1600	0
5 hrs	1000	37.5	800	50	400	75
8 hrs	1000	37.5	600	62.5	600	62.5
10 hrs	800	50	8	87.5	800	50
12 hrs	800	50	8	87.5	800	50

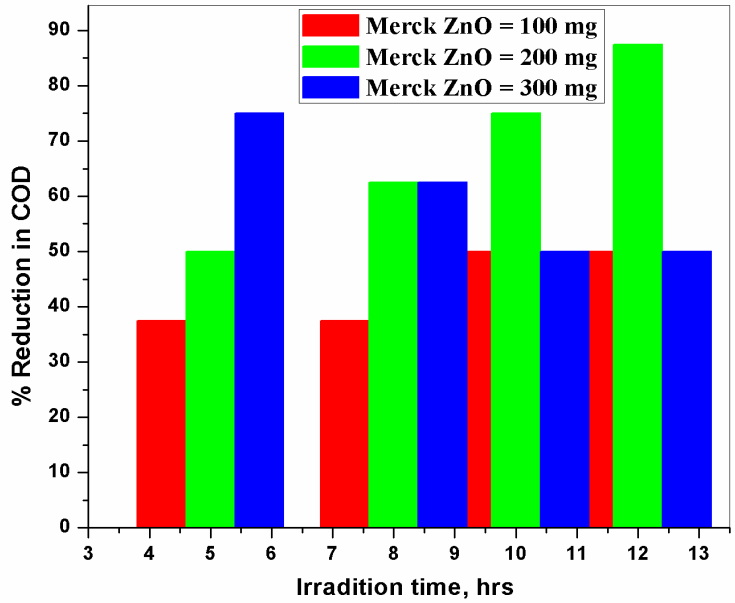

Fig. 5. Optimization of concentration of photocatalyst Merck ZnO for the degradation of Effluent (GOV)

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Table 4. % Reduction in TOC for GOV using Degussa P-25TiO_2 and Merck ZnO as photocatalysts.

Time in hrs	% Reduction in TOC			
	Degussa P-25 TiO_2		Merck ZnO	
	TOC in ppm	TOC in %	TOC in ppm	TOC in %
0 hr	375	100	375	100
5 hr	275	26.66	300	20
12 hr	175	53.33	250	33.36

The % reduction in TOC was found to be more in case of P-25 TiO_2 than Merck ZnO. Therefore degree of mineralization was found to be more by using Degussa P-25 TiO_2 compare to Merck ZnO. The TOC data suggests that Degussa P-25 $TiO_{2\ was}$ found to be the best photocatalyst for degradation as well as mineralization of GOV.

3.3 Detection of inorganic ions

To confirm the complete mineralization of GOV under investigation or the end products as inorganic ions such as sulphate, (SO_4^{2-}) Nitrate (NO_3^-), Nitrite (NO_2^-) and ammonium ion (NH_4^+) was quantitatively estimated after the completion of photocatalytic degradation reaction. In order to evaluate the degree of mineralization reached during the photocatalytic treatment the formation of inorganic is generally determined [13]. Inorganic ions were detected by using commercially available Viscolor rapid. Test kits from Machery Nagel, Germany using Degussa P-25 TiO_2 and Merck ZnO photocatalysts. The experimental results obtained for SO_4^{2-}, NO_3^-, NO_2^- and NH_4^+ as end products for photocatalytic degradation of GOV using photocatalyst DegussaP-25 TiO_2 and Merck ZnO investigation were summarized quantitatively in table 5.

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Table 5. Detection of end products as inorganic ions for degradation of GOV using photocatalysts Degussa P-25 TiO_2 and Merck ZnO.

Detection of ions	Initial value (ppm)	P-25 TiO_2		Merck ZnO	
		12 hrs (ppm)	24 hrs (ppm)	12 hrs (ppm)	24 hrs (ppm)
SO_4^{2-}	20	21	22	21	22
NO_3^-	4	4	11	5	5
NO_2^-	0	0	0	0.05	0.1
NH_4^+	0.5	2	1	1	0.5

According to literature, sulfur heteroatoms are converted into SO_4^{2-} ions [14]. From the result table 5 which suggests that GOV contains SO_4^{2-} as one of the end product which also indicates the effluent contents mixture of dyes which are having more sulphur heteroatom in their structure. Nitrogen is mineralized into, NH_4^+, NO_3^-, NO_2^- and N_2 [15]. The proportion depends mainly on the initial oxidation degree of nitrogen, the substrate structure and on irradiation time. NH_4^+ slowly undergo oxidation into nitrate [16]. Hence, increase in amount of NO_3^- was significantly more in GOV using Degussa P – 25 TiO_2 than Merck ZnO.

4.0 CONCLUSION

Heterogeneous photocatalysis was found to be very effective for significant degradation and mineralization of real textile industrial effluents such as GOV by using different photocatalysts such as Degussa P-25 TiO_2 and Merck ZnO. Optimization of catalyst concentration has been carried out on the basis of % reduction in COD for various doses of the Degussa P- 25 and Merck ZnO. 200mg/250 ml was found to be optimized catalyst concentration for GOV using both the catalyst. % Reduction in COD was almost same for both the photocatalyst. It was observed that % reduction in TOC was more in case of Degussa P-25 i.e. 53.33% and for Merck ZnO 33.36%. Mineralization of GOV was confirmed by formation of inorganic ions as end products. It confirms the degradation of GOV is more efficient by using Degussa P-25 than Merck ZnO.

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