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Photocatalytic purification of textile wastewater using P-25 TiO_2 and Merck ZnO metaloxide 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. 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. There are different methods for wastewater treatment. Currently chemical methods such as advance oxidation processes (AOPs) appear to be more promising for the treatment of textile industrial effluents. The present work has been concentrated on the degradation of real textile industrial effluent 2 (ARV). The said effluent was subjected to photocatalytic treatment using different photo catalysts. The effluent 2 (ARV) was analyzed before and after the treatment for their physiochemical parameters, COD, TOC and presence of inorganic ions. Throughout the study it was observed that, Degussa P-25 TiO_2 nanoparticles effectively brings out the degradation of effluent 2 (ARV) than Merck ZnO nanoparticles. 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, Effluent.

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I. INTRODUCTION

The 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. Approximately 30-40 cubic meter of wastewater is being discharged 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 organic and inorganic pollutants 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 of various AOPs was carried out. Currently chemical methods such as advance oxidation processes (AOPs) appear to be more promising for the treatment of textile industrial effluents [1].

II. MATERIAL AND METHODS

TiO_2 was purchased from Degussa Pvt. Ltd., having the surface area of 50 m^2/g and particle size 11 nm as per the information provided by the manufacturer. ZnO was purchased from Merck Pvt Ltd. Raw wastewater was collected from textile industry from Echalkaranji 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 are 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.

Fig.1. Textile Industrial Effluent 2 (ARV)

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 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 [2]. Total Organic Carbon (TOC) was measured using commercially available test kits (NANO COLOR TOC 60) from Machery-Nagel, Germany [3]. To determine the mineralization of real textile effluent under optimized conditions, % reduction in TOC of effluent 2 (ARV) 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.

Table. 1. Physicochemical parameters of Effluent 2 (ARV)

Sr. no.	Name of the effluent	Parameters	Prevailing Range ppm
1	Effluent 2 (ARV)	Colour	Dark Green
		pH	8.85
		COD	272 ppm
		TOC	200 ppm
		Presence of inorganic ions	
		SO_4^{2-}	163-200 ppm
		NO_3^-	5-17 ppm
		NO_2^-	0-0.25 ppm
		NH_4^+	0.5-15 ppm

Photocatalytic treatment for real textile effluents:

The photocatalytic activity of Degussa P-25 & Merck ZnO was studied for the degradation of effluent 2 (ARV). 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.

Heterogeneous Photocatalysis:

The basic principle 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 reductant [4]. 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 by reduction and it gets protonated to form hydroperoxyl radicalas shown in Figure2.

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

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

$$(O_2^-) + H_+ \rightarrow HO_2^{\cdot} \quad (3)$$

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 .OH [5].

$$H_2O + h^+_{vb} \rightleftharpoons HO^{\cdot}_{ads} + H^+_{ads} \quad (6)$$

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

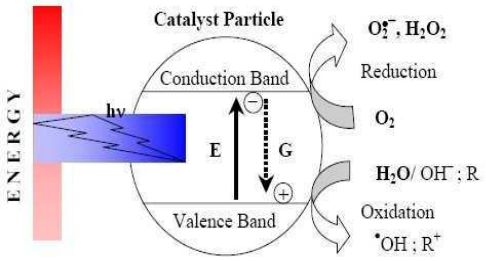

Fig.2. Mechanism on photocatalyst surface

III. RESULT AND DISCUSSION

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

Effluent 2 (ARV) was subjected for photocatalytic treatment using P-25 TiO_2 and Merck ZnO photocatalysts. The concentration of both catalysts were varied from 100 to 300 mg/250 , diluted effluent in presence of UV, solutions were irradiated for 5, 8, 10, 12 hours. The obtained results are shown in table 2 for Degussa P-25. 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.3 for Degussa P-25. As the concentration of catalyst is increased, the number of pollutant molecules absorbed are 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 [6]. Beyond a certain limit surface active sites also decreases due to aggregation of TiO_2 particles at high concentration. The surplus addition of catalyst makes the solution more turbid and turbidity impedes further penetration of light in the reactor [7]. Due to which there is reduction in degradation efficiency. Hence 200mg/250 mL was found to be optimized catalyst concentration for effluent 2 (ARV) using both the photocatalystsDegussa P-25 TiO_2 and Merck ZnO.

Table 2: Optimization of catalyst concentration for effluent 2 (ARV) using P-25 TiO_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%
0hr (Initial COD)	272	0	272	0	272	0
5 hrs	232	14.7	112	58.82	24	91.17
8 hrs	184	32.35	64	76.47	48	81.45
10 hrs	184	32.35	32	88.23	48	81.45
12 hrs	128	52.94	24	91.17	56	79.41

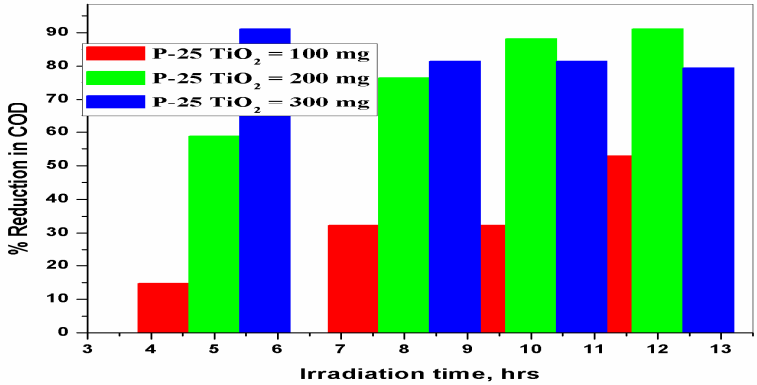

Fig 3: Optimization of catalyst concentration for effluent 2 (ARV) using P-25 TiO_2

Effect of addition of H_2O_2 on effluent 2 (ARV) using both photocatalysts:
Effect of addition of H_2O_2 on effluent 2 (ARV) using both photocatalysts at the optimized concentration of H_2O_2 were depicted in following tables 3 and Fig.4 using photocatalyst Degussa P-25 TiO_2 and table 4 and Fig.5 for photocatalyst Merck ZnO respectively.

Table3. Effect of addition of H_2O_2 on Effluent 2 (ARV) using P-25TiO_2 catalyst.

Time in hrs	Reduction in CODP-25 TiO_2		Reduction in CODP-25 TiO_2 + H_2O_2	
	COD in ppm	COD in %	COD in ppm	COD in %
0	272	0	272	0
5	112	58.82	32	88.23
8	64	76.47	24	91.17
10	32	88.23	24	91.17
12	24	91.17	16	94.11

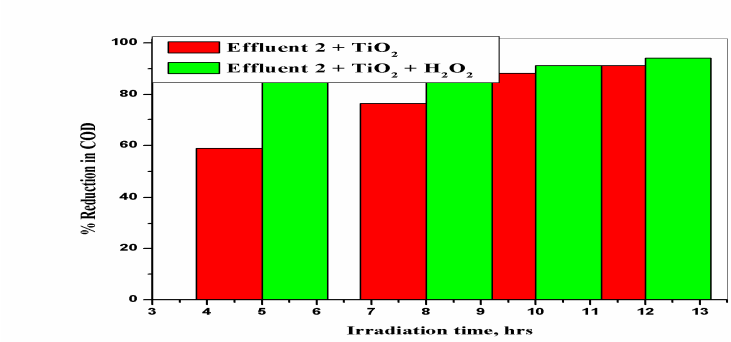

Fig 4. Effect of addition of H_2O_2 to P-25 TiO_2 for the degradation Effluent 2 (ARV)

Table. 4. Effect of addition of H_2O_2 on effluent 2 (ARV) using Merck ZnO catalyst

Time in hrs	Reduction in COD (ZnO)		Reduction in COD (ZnO + H_2O_2)	
	COD in ppm	COD in %	COD in ppm	COD in %
0	272	0	272	0
5	128	52.94	56	79.41
8	96	64.70	56	79.41
10	64	76.70	48	82.35
12	56	79.41	48	82.35

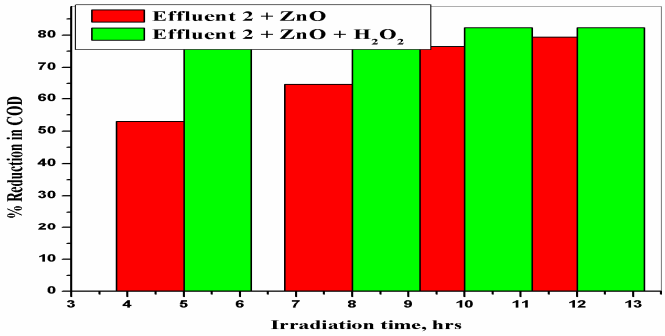

Fig 5. Effect of addition of H_2O_2 to Merck ZnO for degradation of Effluent 2 (ARV)

By addition of H_2O_2 in effluent 2 (ARV) in case of P-25 TiO_2, the photocatalytic activity was found to be enhanced tremendously. There is increase in % reduction in COD upto 94.11% shown in table 5 indicating significant decrease in organic strength present in effluent 2 (ARV). Almost complete mineralization of organic matter present in effluent 2 (ARV) was observed. Addition of H_2O_2 to Merck ZnO in case of effluent 2 (ARV) also showed increase in % reduction of COD upto 82.35% which is also depicted in table 5. Above results indicate greater activity P-25 TiO_2 as compare to Merck ZnO.

Table 5. Comparison of different photocatalysts on photodegradation of effluent 2 (ARV)

Time in hrs	% Reduction in COD							
	P-25 TiO_2		P-25 TiO_2 + H_2O_2		Merck ZnO		Merck ZnO + H_2O_2	
	COD in ppm	COD in %	COD in ppm	COD in %	COD in ppm	COD in %	COD in ppm	COD in %
0	272	100	272	100	272	100	272	100
5	112	58.82	32	88.23	128	52.94	56	79.41
8	64	76.47	24	91.17	96	64.70	56	79.41
10	32	88.23	24	91.17	64	76.47	48	82.35
12	24	91.17	16	94.11	56	79.41	48	82.35

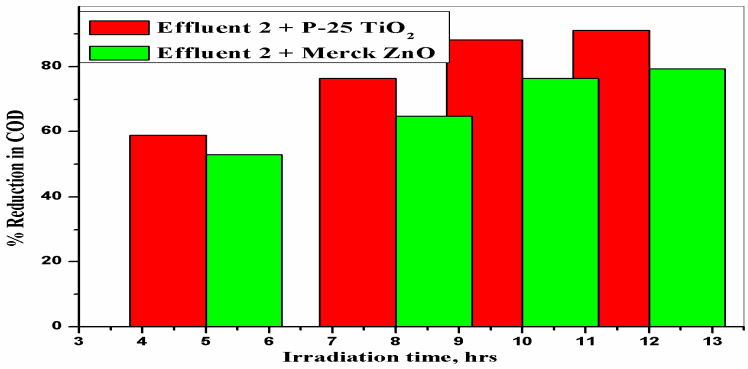

Fig. 6. Comparisons of various photocatalysts for the degradation of Effluent 2 (ARV)

The decrease in organic pollutant strength upon addition of H_2O_2 can be depicted in Fig. 4 & 5. Which clearly indicates H_2O_2 caused effective mineralization of pollutants resulting in 94.11% decrease in the Chemical Oxygen Demand (COD) which effectively brings out mineralization of pollutants present in effluent 2 (ARV). Out of the two AOPs system P25 TiO_2 + H_2O_2 found to be more efficient than ZnO + H_2O_2 system. On the basis of % reduction in COD, order of photodegradation efficiencies of various AOP was found to be

P25 TiO_2 + H_2O_2>ZnO + H_2O_2> P-25TiO_2>ZnO.

Detection of % Reduction in TOC :

The value of % of reduction of COD is almost same for the Degussa P- 25 and Merck ZnO at 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. Fig.6 indicates greater activity of P-25 TiO_2 as compare to Merck ZnO and the comparative evaluation of photocatalytic activity of Degussa P-25 and Merck ZnO from the observed TOC data which was shown in table 6., suggested that Degussa P-25 exhibit better photocatalytic activity than Merck ZnO .

Table 6.% Reduction in TOC for effluent 2 (ARV) using Degussa P-25TiO_2 and Merck ZnO as photocatalysts.

Name of Effluents	Time in hrs	% Reduction in TOC P-25 TiO_2		% Reduction in TOC Merck ZnO	
		TOC in ppm	TOC in %	TOC in ppm mg/L	TOC in %
Effluent 2 (ARV)	0 hr	8	0	8	0
	5 hr	6	25	7	12.5
	12 hr	1	87.5	4	50.0

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 comparative evaluation of photocatalytic activity of P-25 and Merck ZnO from the observed TOC data shown in table 6 suggests that P-25TiO_2 exhibit better photocatalytic activity than Merck ZnO. The % reduction in TOC is 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 P-25 TiO_2 compared to Merck ZnO. The maximum % reduction in TOC found for effluent 2 (ARV) was significantly reduced to 87.5% at 12 hrs indicating the almost complete mineralization of effluent 2 (ARV) has occurred by using Degussa P-25 TiO_2. Thus P-25 TiO_2 was found to be the best photocatalyst for degradation as well as mineralization of real textile effluents.

Detection of inorganic ions: To confirm the complete mineralization of effluent 2 (ARV) 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 formations of inorganic ions are generally determined [8]. 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 effluent 2 (ARV) using photocatalysts Degussa P-25 TiO_2 and Merck ZnO investigation were summarized quantitatively in table 7.

Table 7. Detection of end products as inorganic ions for degradation of ARV using photocatalysts Degussa P-25 TiO_2 and Merck ZnO.

		P-25 TiO_2		**Merck ZnO**	
Detection ions	**Initial Value (ppm)**	**12 hrs (ppm)**	**24hrs (ppm)**	**12 hrs (ppm)**	**24hrs (ppm)**
SO_4^{2-}	163	176	194	183	192
NO_3^-	5	12	17	9	12
NO_2^-	0	0.10	0.10	0.25	0.25
NH_4^+	15	7	1	0.5	0.5

According to literature, sulfur heteroatoms are converted into SO_4^{2-} ions [9]. From the result table7. which suggests that effluent 2 (ARV) contains SO_4^{2-} as one of the endproduct 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[10]. The proportion depends mainly on the initial oxidation degree of nitrogen, the substrate structure and on irradiation time. NH_4^+ slowly undergoes oxidation into nitrate [11-13]. Hence, increase in amount of NO_3^- was significantly more in effluent2 (ARV) using Degussa P – 25 TiO_2 than Merck ZnO. In case of effluent 2 (ARV), it was found that initial ion original amount of NH_4^+ in original effluent was found to be 15 ppm (high) and after photocatalytic treatment it decreases 0.5 to 7 ppm. It was interesting to note that amount of NO_3^- ion found in effluent 2 (ARV) was significantly greater 5-17 ppm in both catalysts. The amount of NH_4^+ was less as compare to NO_3^- ion in effluent 2 (ARV) indicates that this is due to more and more NH_4^+ oxidizes converts into NO_3^- and NO_2^- . Thus degree of mineralization increases. This observation was found to be supportive. On the basis of TOC data it was observed complete mineralization was achieved in effluent 2(ARV).

IV. CONCLUSIONS

Heterogeneous photocatalysis was found to be very effective for significant degradation and mineralization of real textile industrial effluents such as effluent 2 (ARV) 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 effluent 2 (ARV) using both the photocatalysts. % Reduction in COD was almost same for both the photocatalysts. It was observed that % reduction in TOC was more in case of Degussa P-25 i.e. 87.5 % and for Merck ZnO was only 50 %. Mineralization of effluent 2 (ARV) was confirmed by formation of inorganic ions as end products. It confirms the degradation of effluent 2 (ARV) is more efficient by using Degussa P-25 than Merck ZnO.

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