APPLICATION OF AOP FOR AM DYE USING NANO MATERIALS, Au AND γ - Fe_2O_3 MODIFIED TiO_2 NANO COMPOSITES

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Abstract: In the present investigation we have shown the photocatalytic degradation of azo dye using Advance Oxidation Process in presence of different metal oxide nanoparticles &. Au & γ-Fe_2O_3 modified TiO_2 Nano composites. We report here the photocatalytic degradation studies on Amaranth (AM) dye as a representative of the class of azo dye using UV+TiO_2/ZnO and UV+TiO_2/ZnO+H_2O_2 processes in aqueous suspension under 8W low-pressure mercury vapor lamp irradiation. This azodye is widely used in food industry and released into the eco system by the food industrial effluents. It is found to be carcinogenic, posing serious danger to the aquatic and human life. Environmental Protection Agency (EPA) declared Amaranth dye as a priority pollutant. Hence, we focus our study on degradation of Amaranth dye using various AOPs. Here we also report the optimization of various experimental parameters such as effect of catalyst concentration, effect of substrate concentration, effect of addition of H_2O_2. Obtained results are very encouraging. By addition of H_2O_2 the rate of photodegradation is dramatically increases. The obtained result shows that the employment of UV+TiO_2/ZnO and UV+TiO_2/ZnO+H_2O_2 processes and selection of operational parameters led to a complete degradation and substantial dye mineralization supported by the values of the % reduction in Chemical Oxygen Demand (COD) ~ 86.2 % and Total Organic Carbon (TOC) ~ 55% of the treated dye using DP25 TiO_2 & also testified by using γ-Fe_2O_3 NPs attached TiO_2,which shows a remarkable 95% degradation of the azodye in 15 minutes of UV exposure. Furthermore, we extend our study to treat real industrial effluent using nanomaterial for effective degradation and mineralization of hazardous pollutants.

Index Terms: Amaranth dye, TiO_2, Photocatalysis, Nano composites, AOP.

1. Introduction

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, cosmetics, pharmaceutical and food industries [1]. Among the 10,000 different dyes and pigments available azo dyes constitute over 50% of all textile dyes used in industry [2]. Most of them are toxic to aquatic organisms [3] and are non biodegradable. Dyes, phenols, pesticides, detergents and other chemical products are disposed of directly into the environment without an effective treatment strategy [4,5,6]. The colored wastewater released by textile or food industry effluent pose a potential environmental hazard to ecosystem and must be treated before being discharged into the natural water bodies. Till today no economical and technically fit solution for the effective degradation and mineralization of the hazardous, organic compounds present in textile/food industry effluents is available. Various generic methods like physical, biological and chemical are being explored and employed however they have their own limitation as the physical methods like adsorption on activated carbon, reverse osmosis etc. do not lead to complete mineralization, rather they simply transfer the pollutants from one phase to another causing secondary pollution [7]. Biological

treatment generally by means of activated sludge [8,9] , in adequate conditions [10]. Biological treatment methods have proven to be ineffective not only due to the resistance of azo dyes to aerobic degradation [11] but also due to the formation aromatic amines which are carcinogenic [12].

Therefore in the last decade, attention has been focused on treatment technologies that lead to the complete destruction of the dye molecules. Among these treatments Advanced Oxidation Processes (AOPs) have emerged as powerful remediation treatments to destroy refractory pollutants in water. Among all the AOPs heterogeneous photocatalysis has been found to be the most promising treatment process for the degradation of various dyes at lab scale. But to extend this process to treat real textile industrial effluent, more focused and detailed study is the need of current research and development activities. In comparison with other AOPs semiconductor mediated photocatalysis with H_2O_2 ranks the foremost due to its ability to photosensitize the complete mineralization of wide range of organic pollutants without production of harmful by-products.

Therefore, in the present study a detailed study on the heterogeneous photocatalytic degradation of Amaranth selected azo dye has been carried out using P-25 TiO_2 and Merck ZnO and Au & γ-Fe_2O_3 modified TiO_2 Nano composites. We have employed UV/TiO_2/ZnO/H_2O_2 processes for complete decolorization and substantial decreases of Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) of dye solution under optimized conditions of experimental parameter.

2. Experimental

2.1. Reagent and Chemicals

TiO_2 (LR grade Merck with 99 % purity: mixture of anatase and rutile) of band gap = 3.2 eV, H_2O_2 (30%, w/w, Merck),) Amaranth Dye is obtained from local Food industry, Solapur India. All chemicals were used in the form as received without further purification. The solutions were prepared in Millipore water.

2.2. Procedure

. Effect of various experimental parameters such as catalyst concentration, substrate concentration and addition of H_2O_2 was carried out to arrive at optimized experimental conditions. For that, from the stock solution of AM of concentration 0.01 mol/L, various solutions of desired concentrations were prepared in millipore water. The photodegradation experiments were carried out in photoreactor in which 250 mL of AM solution was taken. The solution was agitated with the help of aeration pump and magnetic stirrer. The effect of catalyst concentration was studied by varying the amounts of TiO_2/ZnO from 75 to 150 mg. To study the effect of substrate concentration, the photocatalytic degradation experiments were carried out at optimized catalyst concentration.. For each experiment, aliquot was taken out after every one hour with the help of syringe, which was then filtered through 0.2 μm, 13 mm diameter millipore disc and analyzed for its concentration with Schimadzu UV-visible Spectrophotometer to study the decolorization and degradation. The degree of mineralization of the dye was confirmed by COD and TOC analysis.

2.3 Analysis

Optical absorption spectrum for AM was determined by double beam Schimadzu UV- visible Spectrophotometer. The characterized wavelength of AM was found to be 625 nm which was used to monitor the decolorization and degradation of the dye. Chemical oxygen demand (COD) was measured by the dichromate reflux method and total organic carbon (TOC) was measured using commercially available test kits (NONOCOLOR TOC 60) from Macherey–Nagel, Germany [13] to determine the mineralization of the dye solution under optimized conditions.

3. Result and Discussion

The photo degradation of AM was carried out with different AOPs such as (i) UV (ii) UV/ TiO_2/ZnO (iii) UV/ TiO_2/ZnO /H_2O_2 to identify the most suitable and economical process for complete decolorization and substantial mineralization of the dye.

3.1 Optimization of various experimental parameters

(i) Effect of catalyst concentration (ii) Effect of substrate concentration (iii) Effect of addition of H_2O_2

3.1.1. Optimization of catalyst concentration

The effect of catalyst concentration on degradation of Amaranth dye (AM) were investigated by using different photocatalyst Degussa P-25 TiO_2 and Merck ZnO by employing the amount of catalyst concentration ranging from 75 to 150 mg/250 mL of dye solution. For these studies the substrate concentration was kept constant 2.5 x 10^{-5} mol/L for throughout the experiments.

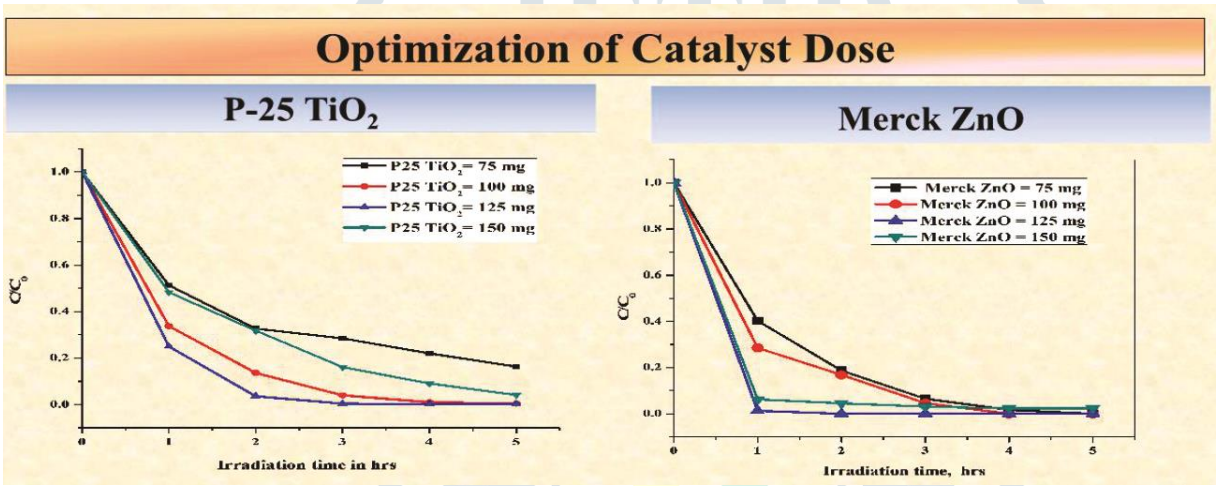

Figure 1: Optimization of catalyst concentration for degradation of AM using P-25 TiO_2

Figure 2: Optimization of catalyst concentration for degradation of AM using Merck ZnO.

3.3.1 (C1) P-25 TiO_2

Experiments performed with different concentrations of Degussa P-25 TiO_2 showed that the photodegradation efficiency increases with increase in a Degussa P-25 TiO_2 concentration upto 125mg and then decreases by increasing concentration of catalyst concentration. The most effective decomposition of Amaranth (AM) was observed with 125mg of Degussa P-25 TiO_2 catalyst in 2 hr only. Hence optimized catalyst concentration for degradation of AM using Degussa P-25 TiO_2 was found to be 125mg.

3.3.1. (C2) Merck ZnO

The rate of degradation of AM increases with increase in the amount of catalyst from 75-125mg and then further increase in catalyst concentration of Merck ZnO the rate of degradation of AM decreases. The degradation of AM effectively took place by using 125mg of Merck ZnO in one hour only hence 125 mg was found to be optimized catalyst concentration in case of Merck ZnO for degradation of AM.

3.1.2 Optimization of substrate concentration.

To optimized the substrate concentration of Amaranth dye using various catalysts Degussa P-25 TiO_2 and Merck ZnO. The initial substrate concentration of Amaranth varies from 1 x 10^{-5} to 2.5 x 10^{-4} mol/L with constant catalyst loading of 100 mg/250 mL.

Obtained result shows that optimized substrate concentration was found to be 1 x 10^{-5} mol/L for effective degradation of AM dye using Degussa P-25 TiO_2 as well as Merck ZnO.

3.1.3. Effect of addition of H_2O_2

Addition of optimized amount of H_2O_2 was shown to increase the degradation rate of Amaranth dye (AM) in presence of various photocalyst using P-25 TiO_2 and Merck ZnO have been summarized in figure 3 and figure 4 respectively. Addition of H_2O_2 to the various AOPs made the degradation much faster and could degrade the dye only in couple of hours. Degradation of AM was found to be increase in the order

UV/TiO_2 / ZnO+H_2O_2 > UV/TiO_2 / ZnO > UV.

Figure 3 and 4 Comparison of various AOPs in AM using P-25 TiO_2 and Merck ZnO respectively

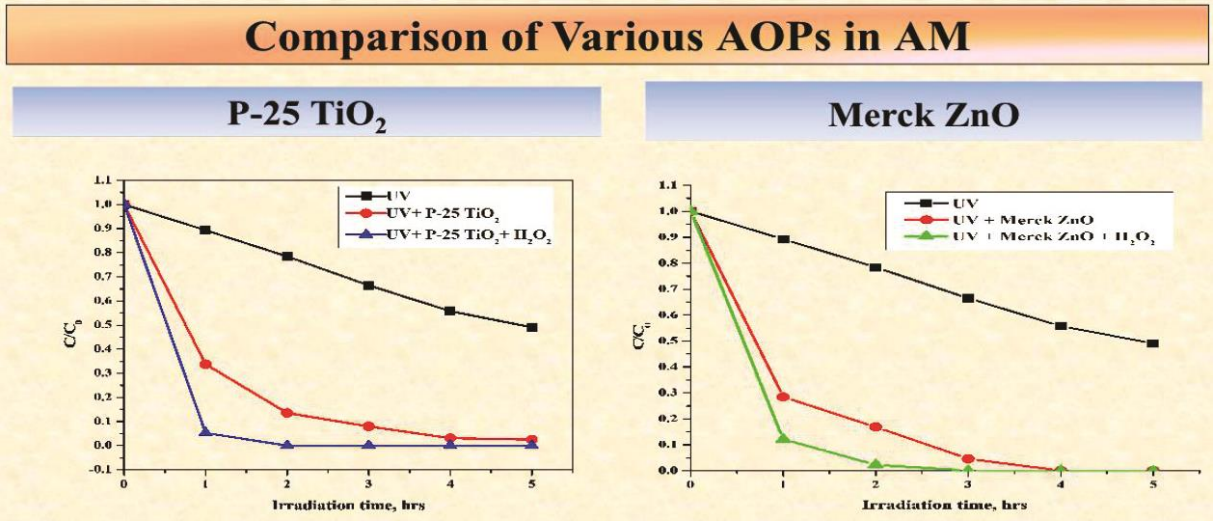

Figure 3 **figure 4**

3.1.4. Comparison of X- Ray Diffraction and TEM image of (a) TiO_2 and (b) Au and γ-Fe_2O_3 modified TiO_2 nanoparticles (NPs)

in Figure 5 and Figure 6.

A modified sol-gel route was employed to synthesize Au and γ-Fe_2O_3 modified TiO_2 nanoparticles (NPs).X-ray diffraction, Raman studies showed Au and γ-Fe_2O_3 alongwith Anatase TiO_2 phase. TEM studies showed TiO_2 nano composite particles of size 10-12 nm.γ-Fe_2O_3 NPs attached TiO_2, a remarkable 95% degradation of the azodye in 15 minutes of UV exposure.

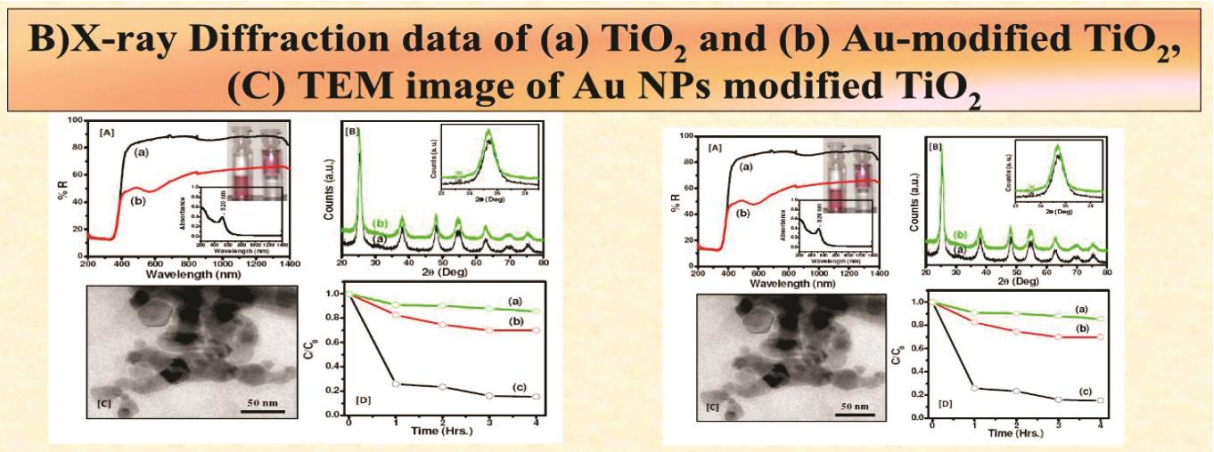

Figure 5 **Figure 6**

3.1.4. Determination of % reduction in Chemical Oxygen Demand (COD) and TOC for the degradation of AM dye

The photocatalytic degradation of AM using Degussa P-25 and Merck ZnO photocatalyst were carried out separately. Then after filtration of catalyst initial COD was noted before the treatment. Then % reduction in COD was calculated. TOC of AM before and after photocatalytic treatment using P-25 TiO_2 and Merck ZnO was measured using commercially available test kits (NANO COLOR TOC 60) from Machery-Nagel, Germany and experimental results obtained are used to calculate % reduction in TOC. Thus % reduction in COD and TOC which was obtained from experiments are summarized in table No. 1

Table 1: % Reduction in COD and TOC for degradation of AM

Name of the dye	% Reduction in COD		% Reduction in TOC		% degradation	
Amaranth (AM)	P-25 TiO_2	Merck ZnO	P-25 TiO_2	Merck ZnO	P-25 TiO_2	Merck ZnO
	86. 66	53.33	64%	32%	91.40%	100%

3.1.5. Comparison of various photocatalyst on degradation of AM

The photocatalytic activity of two different commercially available photocatalyst like Degussa P-25 TiO_2 and Merck ZnO was tested for the degradation of Amaranth dye. From the experimental UV-Visible absorbance data the graph was plotted irradiation time in hrs Vs C/Co using the two photocatalysts on degradation of AM was summarized in figure 7. The actual observed decolorization of the dye using various catalysts can be shown in figure 8. for P-25 TiO_2.

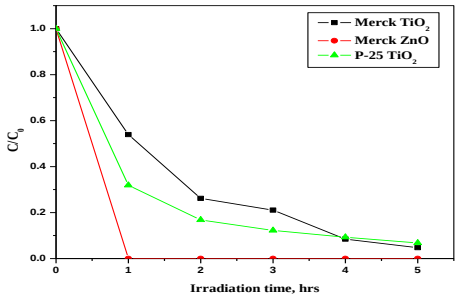

Figure 7: Comparison of efficiencies of different photocatalyst for the degradation of AM

It has been observed that the degradation of AM proceeds much more rapidly in case of Merck ZnO as compared with P-25 TiO_2. But reduction in % COD and TOC data of AM was 86.66 % and 64% respectively by using P-25 TiO_2 and 53.33% and 32% in case of Merck ZnO. Suggest that substantial mineralization along with degradation observed in P-25 TiO_2 and not in Merck ZnO. On the basis of COD and TOC data P-25 TiO_2 was found to be the best photocatalyst among the other

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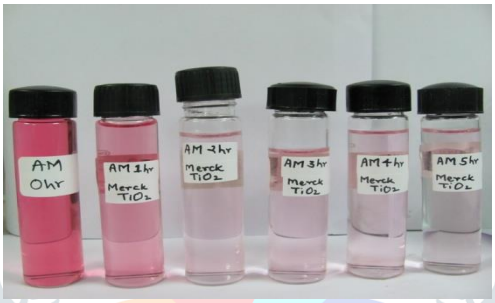

Figure 8. decolorization of AM using P-25 TiO_2

4. Conclusions

The results obtained in the present study show the great efficiencies of advanced oxidation processes in removing azo which is resistant to other conventional treatment processes. Simple UV irradiation could not achieve significant degradation of AM but Heterogeneous photocatalysis (UV + TiO_2 /ZnO + H_2O_2) was found to be extremely favorable and achieve almost nearly 100% degradation of AM The application of heterogeneous photocatalytic treatment using TiO_2 for the degradation of AM has been found to be promising process. Further addition of H_2O_2 to the above system made the degradation much faster and could degrade the dye only in couple of hours. Degradation of AM was found to increase in the order UV < UV/TiO_2 < $UV/TiO_2/H_2O_2$. The employment of $UV/TiO_2/H_2O_2$ process led to complete decolorization and substantial mineralization upto 86.66 % decrease in COD and 64 % decrease in TOC values respectively using $DP25TiO_2$. Thus $UV/TiO_2/ZnO$ +H_2O_2 seems to be the most appealing choice for the complete degradation and substantial mineralization of AM also by using γ-Fe_2O_3 NPs attached TiO_2, a remarkable 95% degradation of the azodye in 15 minutes of UV exposure was observed.

5. References

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