

UV Assisted Photocatalytic degradation of Azo dye in Textile Effluent by Advanced Oxidation Processes Using TiO₂ Nanoparticles

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To Cite this Article

Manjusha Kulkarni , UV Assisted Photocatalytic degradation of Azo dye in Textile Effluent by Advanced Oxidation Processes Using TiO₂ Nanoparticles”, *Journal of Science and Technology*, Vol. 07, Issue 05,-July 2022, pp117-130

Article Info

Received: 26-05-2022

Revised: 18-06-2022

Accepted: 20-07-2022

Published: 30-07-2022

Abstract:

In the present investigation the photocatalytic degradation studies of Orange G (azo dye) employing Advanced Oxidation Processes (AOP) in aqueous suspension under 8W low-pressure mercury vapor lamp irradiation is demonstrated. The optimization of various experimental parameters such as effect of catalyst concentration, effect of substrate concentration, effect of addition of H₂O₂ is thoroughly investigated. Additionally, the obtained results indicates that the employment of AOPs process and selection of the operational parameters led to a complete degradation and substantial dye mineralization supported by the values of the reduction in Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) of the treated dye solution.

Keywords: Azo dye, TiO₂, Photocatalysis, AOPs, COD, TOC

Introduction

Water one of the basic five elements of nature is the most essential component of life. In fact, it formulates/ is the bedrock of origin and evolution of life on our very planet earth. Since the last century, due to rapid industrialization, our planet has witnessed an adverse climatic change. This has led to frequent scanty rainfalls and severe droughts in many parts of the world. Consequently, the quantum/amount of potable water is rapidly decreasing round the globe. This has threatened the very existence and survival of human beings and livestock's. r. In developing

countries the industrial sector is one of the major consumers of the available water resource. Particularly, the chemical industries and more specifically the dyestuff industries demand a bigger share of this water source. The untreated waste waters from such dyestuff industries are one of the major pollutants of the natural water resources and pose a threat not only to the aquatic flora and fauna but also to human beings. In this context, the reuse/recycling of the available water gains prime importance [1-5].

The textile industries are major consumers of water with an average water consumption of 160 Litres per kg of the finished product [6-8]. Large amounts of dyes are produced annually and applied in many different industries, including the textile, paper, leather, cosmetic, pharmaceutical and food industries [9]. The waste waters from such industries often contain synthetic dyes and pigments which lead to water pollution. Therefore, it is very essential to treat/remove these effluents before being discharged into the natural water bodies. Most of the azo dyes are highly toxic, often resistant to biodegradation. As these dyes enter the human body, they get split into the respective aromatic amines by liver enzymes and intestinal flora finally leading to cancers [10-12]. Various generic methods like biological, physical and chemical are being explored and employed, for the remediation of these azo dyes but these methods have their own limitations. Chemical processes are important alternatives when biological treatments are not capable to abate both the color and COD from textile wastewaters. Advanced oxidation processes (AOPs) are powerful remediation treatments/techniques to destroy such lethal pollutants in water. Amongst, all the AOPs heterogeneous photocatalysis employing TiO_2 catalyst has been found to be the most promising treatment process. These processes offer the degradation of persistent organic pollutants. [13-18]. In order 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 to AOPs, semiconductor mediated photocatalysis with H_2O_2 ranks the foremost due to its ability to photosensitize and completely mineralize a wide range of azo dyes. [19]. Recent advances in AOP technologies for the degradation of industrial wastewater pollutants generally enclosed with seven areas viz. artificial neural networks (ANNs), sustainability, plasma activation, catalyst structures, AOP-Bioremediation, and membrane-based AOPs. In spite of advances in AOPs, a number of challenges still continue to exist namely lack of appropriate ANN modeling structures, impractical spatial and temporal scales of and membrane fouling in membrane-based AOPs [20]. This heterogeneous TiO_2 photo

catalytic method has been found an economical and efficient way for the advanced oxidation treatment of textile industry waste water [21].

Advanced oxidation process

AOPs generally involve generation and subsequent reaction of hydroxyl radical ($\cdot\text{OH}$) by using the combination of powerful oxidizing agent and UV light. Advanced Oxidation Process produce in situ reactive free radical mainly the hydroxyl radical ($\cdot\text{OH}$) by means of different reacting systems [23-26].

The complete mineralization of most of the organic matter is possible when the hydroxyl radical is the main oxidant species present in the solution. 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 [27] Photocatalytic degradation of azodyes ORG (Orange g dye) was found to be depend on the parameters like catalyst concentration, substrate concentration, oxidant concentration etc. [28]. *S Krishnan et al.* has described advanced oxidation processes currently used for the remediation of water and wastewater. It also provides the cost estimation of installing and running an AOP system. The costs are separated into three categories: capital, operational, and operating & maintenance [29].

2. Experimental

Material and Methods

Analytical Grade (A.R.) reagents were used throughout the present studies. The following chemicals were purchased from various companies. The different photocatalysts used were TiO_2 purchased from Merck Pvt. Ltd., Germany. Degussa Titanium dioxide TiO_2 (AR grade: mixture of anatase A) of band gap = 3.2 eV, was purchased from Degussa Pvt. Ltd.(surface area is $50 \text{ m}^2/\text{g}$ and particle size 11 nm) H_2O_2 (30%, w/w, Merck), Reactive Textile dyes, Orange G (ORG) was obtained from textile industry from Kolhapur and Echalkaranji, India. In order to quantify COD - HgSO_4 , AgSO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, Ferroin indicator (from SRL), H_2SO_4 (96% pure, from SDFine chemicals), Total organic carbon (TOC) was measured using commercially available test kits (NONOCOLOR TOC 60) from Macherey–Nagel, Germany. All the chemicals were used in the form as received without further purification. The solutions were prepared in millipore water.

General procedure:

Photocatalytic degradation of azo dyes

The experiments were carried out in batch immersion well photocatalytic reactor. The reactor was equipped with UV lamp which is 8 W low pressure mercury vapour lamp of maximum wavelength 254 nm. It is located axially and held in a quartz immersion tube. Water was circulated through the outlet and inlet tubes provided by reactor to maintain the constant temperature between 303 ± 2 °K. The total volume of photoreactor was 250 ml. Air was bubbled through the reaction solution from the bottom using aerator with constant speed. The hydrolyzed dye solutions were magnetically stirred. The azo dye which is selected for study is a very useful model compound for photocatalytic degradation studies. In the present study of heterogeneous photocatalysis, we have tested the photocatalytic activity of two different semiconductor nanoparticles namely Merck TiO₂, Degussa P-25 TiO₂ as photocatalyst on the degradation of Orange G (ORG) azo dye. The degradation of Orange G dye on ZnO/TiO₂ photocatalyst was found to be in accordance with the Network Kinetic Model, and the calculated equilibrium constant and activation energies of the ZnO/TiO₂ thin film photocatalyst are 20.02 and 16.16 kJ/mol [30].

ORG is an acid azo dye, and its molecular structure is shown in Figure 1. This dye causes chromosomal damage, and clastogenic activity as inimitable toxic effects [31]. Therefore, water conservation and their purification technique should be an absolute priority for researchers to fight for this crisis [32-34].

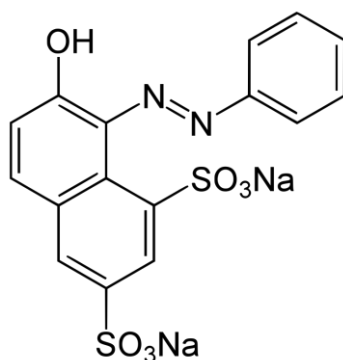


Fig.1. molecular structure of Orange g dye

3. Results and Discussion

Photocatalytic degradation of Orange G (ORG):

The photocatalytic ability of the photocatalysts Merck TiO₂ and P-25 TiO₂ on the photodegradation of Orange G (ORG) dye in an aqueous solution under visible light illumination was investigated using various optimization conditions.

Optimization of catalyst concentration

The effect of catalyst concentration was studied by varying the concentration of photocatalysts Merck TiO₂ and P-25 TiO₂ from 75 to 150 mg/250mg of Orange G (ORG) in order to obtain an optimum catalyst concentration for maximum degradation of ORG dye. For this the substrate concentration was kept constant (2.5×10^{-5} mol/L). From the experimental results a graph was plotted as irradiation time in hours Vs C/C₀ for various concentrations of both catalysts. Results are summarized in fig.2 & fig.3. which show that the optimum catalyst concentration of Merck TiO₂ and P-25 TiO₂ for ORG dye degradation was found to be 125 mg/250 ml for both the catalysts.

Optimization of catalyst concentration

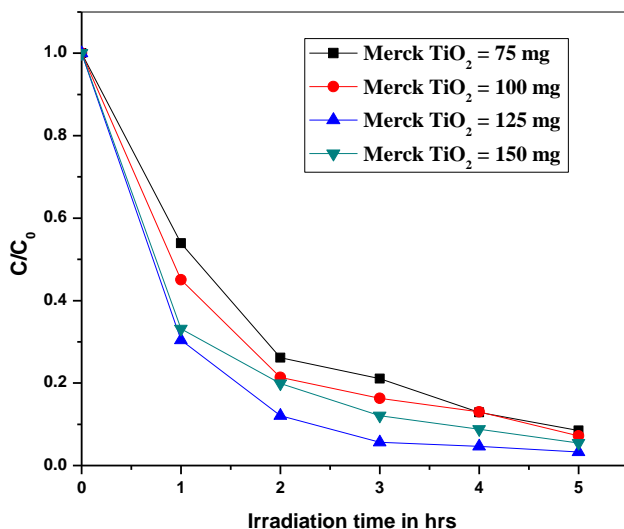


Fig. 2. Optimization of catalyst conc. of ORG using Merck TiO₂

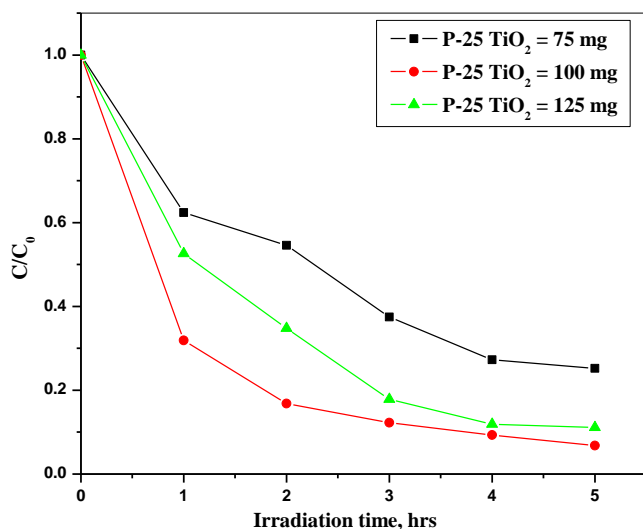


Fig. 3. Optimization of catalyst conc. of ORG using P-25 TiO₂

Fig. 2 & 3 show that the degradation efficiency increases up to 125 mg/250mL of the dye solution, above which it shows reduction in degradation efficiency. Beyond this dose the substrate molecules available are not sufficient for adsorption by the increased number of TiO₂ particles indicating that the additional amount of catalyst is not involved in catalytic activity and hence does not increase the rate of dye degradation. [35]. Also, at high TiO₂ concentrations the number of active sites on the catalyst surface decreases. The surplus addition of catalyst makes the solution more turbid and the reduction in degradation efficiency may be due to the reduction in penetration of light with surplus amount of TiO₂. In the present investigation 125 mg of TiO₂ in 250 ml of dye solution was found to be optimized dose for maximum degradation of ORG for both catalysts.

Optimization of substrate concentration

The effect of substrate concentration on degradation of Orange G (ORG) dye was studied with constant catalyst loading of 100mg/250ml. The effect of substrate concentration on degradation of Orange G (ORG) dye was studied with constant catalyst loading of 100 mg/250 ml.

The effect of substrate initial concentration on degradation of Orange G dye was studied at different concentrations varying from 1×10^{-5} to 2.5×10^{-4} mol/L since the pollutant concentration is a very important parameter in water treatment. Experimental results are presented in Fig.4 & Fig.5., which shows that the degradation rate depends on the initial concentration of dye ORG.

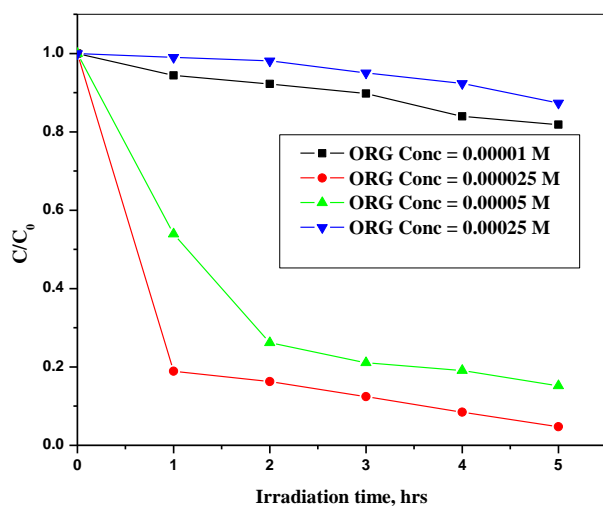


Fig. 4. Optimization of substrate conc. of ORG using Merck TiO₂

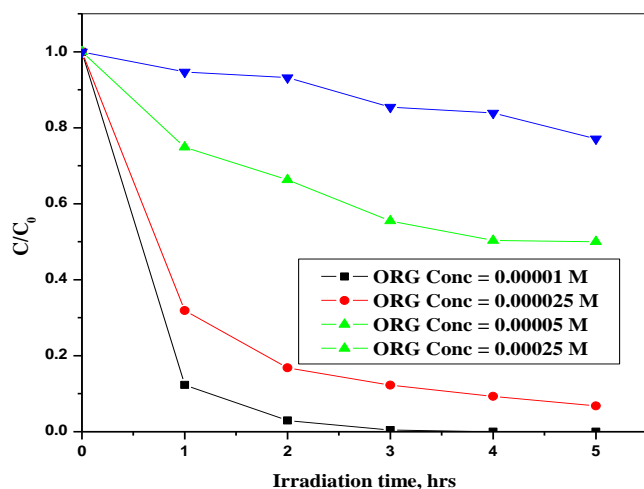


Fig. 5. Optimization of substrate conc. of ORG using P-25 TiO₂

From graph it was observed that rate of degradation of ORG using Merck TiO₂ increases with increases in substrate concentration from 1×10^{-5} to 2.5×10^{-5} mol/L. The rate of degradation of ORG became maximum at 2.5×10^{-5} mol/L and by further increase in substrate concentration from 5×10^{-5} to 2.5×10^{-4} mol/L the rate of degradation of ORG decreases.

The rate of degradation was found to increase with increasing concentration of Orange G upto 2.5×10^{-5} mol/L for Merck TiO₂. Further increase of concentration decreases the rate of degradation. This may be explained on the basis that, on increasing the concentration of Orange

G, the reaction rate increases as more molecules of the dye are available for degradation. Also, with an increase in dye concentration, the solution becomes more intense colored and the path length of photons entering the solution is decreased thereby fewer photons reach the catalyst surface. Hence, the productions of hydroxyl and superoxide radicals are reduced. Therefore, the photodegradation efficiency is reduced. Moreover, at the higher concentration, the number of collisions between dye molecules increases whereas the number of collisions between dye molecules and $\cdot\text{OH}$, radical decreases. Consequently, the rate of degradation is retarded [36]. Hence in the present investigation the optimized substrate concentration of Orange G was found to be 2.5×10^{-5} mol/L for Merck TiO_2 and 1×10^{-5} mol/L for P-25 TiO_2 . Hence the optimized concentration for degradation of ORG using Merck TiO_2 was found to be 2.5×10^{-5} mol/L.

Above graph indicated that by using P-25 TiO_2 catalyst the degradation rate of ORG was found to be decrease continuously from 1×10^{-5} to 2.5×10^{-4} mol/L. Hence the optimized substrate concentration for degradation of ORG using P-25 was found to be 1×10^{-5} mol/L.

Effect of addition of H_2O_2

The photocatalytic degradation for ORG in presence of hydrogen peroxide by using various photocatalyst Merck TiO_2 , P-25 TiO_2 have been shown in Fig. 6 and Fig. 7 for respective catalysts.

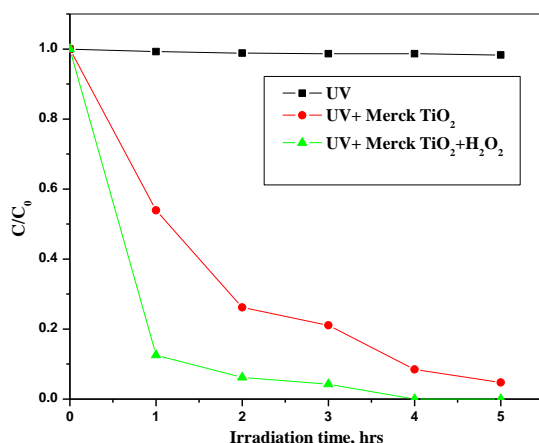
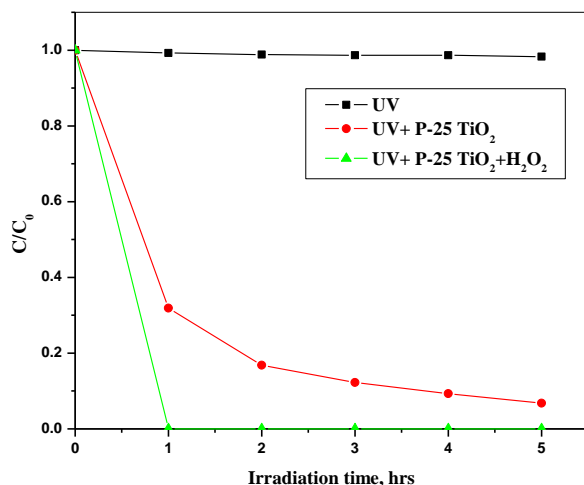


Fig. 6. Comparison of various AOPs in ORG using Merck TiO₂**Fig. 7.** Comparison of various AOPs in ORG using P-25TiO₂

The addition of optimum amount of H₂O₂ was found to enhance the degradation rate of the azodye ORG under study using various photocatalysts. This is because H₂O₂ plays a dual role in photocatalytic reaction, acting as electron acceptor as it accepts a photogenerated electron from conduction band and thus promotes the charge separation and generation of ·OH radicals but high doses of H₂O₂ act as powerful radical scavenger. Hence addition of optimum amount of H₂O₂ is very essential.

Determination of % reduction in Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC)

The COD is widely used as an effective technique to measure the organic strength of wastewater. The test allows measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic matter to the CO₂ and water. The COD of the dye solution was estimated before and after the treatment under optimized conditions. The reduction in the COD and TOC values of the treated dye solution indicates the mineralization of dye molecules along with color removal.

Photocatalytic degradation of ORG using Degussa P-25 TiO₂ as photocatalyst was carried out separately. Then after removal of catalyst from filtration the COD was measured by closed dichromate reflux titrimetric method [37] and TOC by commercially available test kits (NANOCOLOR TOC 60) from Machery-Nagel Germany. From this data initial and final COD

and TOC were noted. By using this data the percentage reduction in COD and TOC of ORG dye were calculated and summarized in Table No. 1.

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

Name of the dye	% Reduction in COD		% Reduction in TOC		% Degradation	
	Merck TiO ₂	P-25 TiO ₂	Merck TiO ₂	P-25TiO ₂	Merck TiO ₂	P-25TiO ₂
Orange G (ORG)	42.20%	72.13%	19.4%	58.44%	85.34%	93.19%

Comparison of various photocatalyst on degradation of Orange G (ORG)

The experiments were carried out to check the photocatalytic efficiency of two different photocatalysts namely Merck TiO₂, Degussa P-25 TiO₂. The comparisons of degradation rate for the decomposition of ORG dye in the presence of two different types of photocatalysts are summarized in Fig. 8.

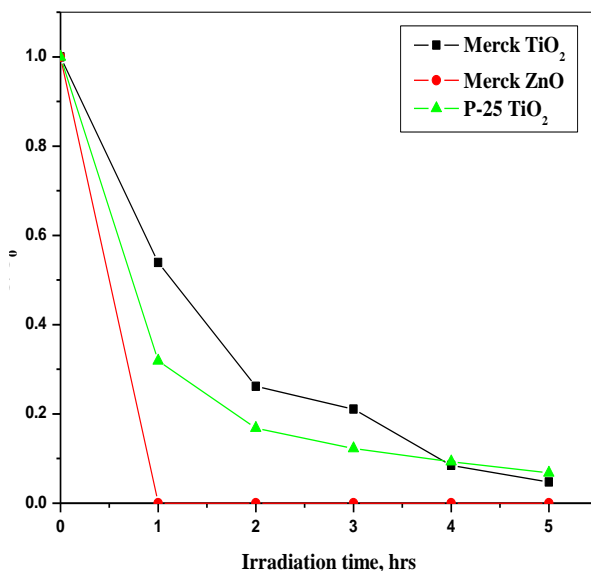


Fig.8. Comparison of efficiency of different photocatalysts

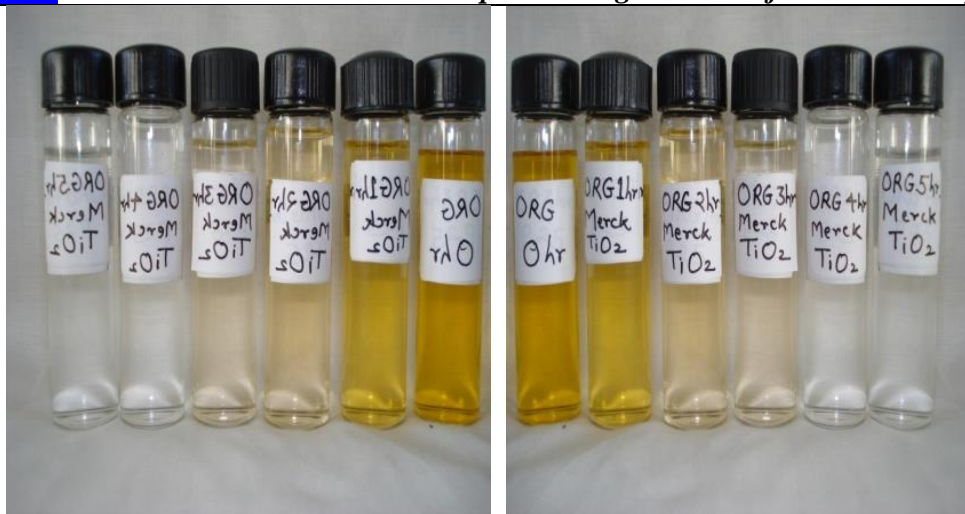


Fig. 9. Colour changes during Degradation of ORG

The colour change observed during the experiments from 0-5 hrs by using these catalysts is depicted in Fig. 9 for Merck TiO_2 and P-25 TiO_2 . It has been shown that P-25 TiO_2 showed better degradation efficiency than Merck TiO_2 . % Reduction in COD and TOC data suggest that substantial mineralization achieved only by using P-25 TiO_2 . Hence, P-25 TiO_2 was found the best photocatalyst than Merck TiO_2 .

Observed order of photocatalytic efficiency in case of ORG dye was P-25 $\text{TiO}_2 >$ Merck TiO_2 .

Conclusions

The results obtained in the present study led to the following conclusions

- The order of enhancement for degradation of the selected azodyes ORG using various photocatalysts were found to be in the order $\text{UV} + \text{TiO}_2 + \text{H}_2\text{O}_2 > \text{UV} + \text{TiO}_2 > \text{UV}$. Thus, among the various AOPs selected and tested, $\text{UV} + \text{TiO}_2 + \text{H}_2\text{O}_2$ was found to be the best AOP which effectively brought about the complete degradation and significant mineralization of selected azodye in a within a short period. We need to add time studies.
- The addition of optimum amount of H_2O_2 was found to enhance the degradation rate of the azodye ORG tremendously using various photocatalysts.
- % Reduction in COD and TOC was done to achieve maximum degradation of azo dye. P-25 TiO_2 was found to be more efficient than Merck TiO_2 .

- % Reduction in COD and TOC values after the photocatalytic treatment in ORG for P-25 TiO₂ was found to be 72.13% and 58.44% respectively. This clearly indicates that in case of P-25 TiO₂ the degree of mineralization of azodyes was found to be more significant than Merck TiO₂. The observed % reduction in COD and TOC data suggest that P-25 TiO₂ exhibits better photocatalytic activity than Merck TiO₂

Acknowledgements

Author is thankful to the Secretary of Gokhale Education Society and Principal of RNC Arts, JDB Commerce and NSC Science College, Nashik-Road for their constant support during the research work.

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