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Photocatalytic Degradation and Mineralization of Reactive Textile Azo Dye Using Semiconductor Metal Oxide Nano Particles

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ABSTRACT – The textile industry consumes considerable amounts of water during the dying and finishing operations. Dyes extensively used are found to be toxic and considered to be resistant to biodegradation. In this work a detailed investigation of heterogeneous photocatalytic degradation of Navy blue HE2R **1** (NB), azo dye of reactive class is presented using UV/P-25TiO_2/ZnO_2/H_2O_2 process in aqueous suspension under 8W low-pressure mercury vapor lamp irradiation by using Semiconductor metal oxide nano particles. 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. The obtained results show that the employment of UV/P-25TiO_2/ZnO_2/H_2O_2 process and selection of optional operational parameters lead to complete decolorization and substantial mineralization of Navy blue HE2R **1** (NB) dye which is supported by showing decreases in Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) of the dye solution.

Keywords: Photocatalysis, Textile dye: Navy blue HE2R 1 (NB), Titanium dioxide, H_2O_2 , COD, TOC, ZnO, AOP, Mineralization.

1. INTRODUCTION

Azo dyes represent the largest class of textile dyes in industrial use. These reactive azo dyes are not easily amenable by conventional treatment methods due to their stability and non biodegradable nature. The colored wastewaters released by textile 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 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 [1]. Biological treatment methods have proven to be ineffective not only due to the resistance of azo dyes to aerobic degradation [2] but also due to the formation aromatic amines which are carcinogenic [3].

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 some selected azo dyes has been carried out using P-25 TiO_2 and Merck ZnO. Azo dyes which are selected for the present study are generally used in textile industry and are found to have serious health hazardous to aquatic organism as well as human beings. It is noteworthy that no studies about reactive azo dyes Navy Blue HE2R (NB) using photocatalytic degradation employing TiO_2/ZnO are found in literature. This is the first report on it. Study is also focused to extend the results obtained for the degradation of this dye to treat the real industrial textile effluents. Most of the published work is focused on the degradation of dyes using TiO_2. Literature reveals a few work on the application of ZnO for the degradation and decolorization of dyes based on spectrophotometer observations and no attention has been given till date to study mineralization of these dyes giving COD and TOC data. Therefore here a detailed study for the photocatalytic degradation and mineralization of NB dye has been carried out. In the present investigation, studies are carried out using very economic 8 W low pressure mercury vapour lamp giving very good degradation effectively in 5-6 hrs by employing various AOPs.

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To overcome the shortcomings in the existing treatment techniques research and development in innovative technologies during the last decade have shown that advanced oxidation processes (AOPs) have been applied for water purification effectively. These processes involve generation and subsequent reaction of $^{\cdot}OH$ hydroxyl radical by using the combination of powerful oxidizing agent and UV light. Many oxidation processes such as UV /TiO_2, UV /O_3, UV /H_2O_2, Photo-Fenton are currently employed for this purpose.

Currently, chemical methods such as advanced oxidation processes (AOPs) seem to be more promising for the treatment of textile industrial effluents [8]. Among the various advanced oxidation process (AOPs) heterogeneous photocatalysis on metal oxide semiconductor particles has been found to be very effective for removing the organic pollutants from wastewater [9-11]. The basic principle of heterogeneous photocatalysis using semiconductor oxide is well established [12] and can be briefly summarized in the following simplified processes. The photo-excitation of semiconductor particles promotes an electron from the valence band to the conduction band thus leaving an electron deficiency or hole in the valence band, in this way, electron/hole pairs are generated. Both reductive and oxidative processes can occur at/or near the surface of the photoexcited semiconductor particle. In aerated aqueous suspensions, oxygen is able to scavenge conduction band electrons forming superoxide ions ($O_2^{\cdot -}$) and its protonated form, the hydroperoxyl radical ($HO_2^{\cdot}$)

$O_2 + e^- \rightarrow O_2^{\cdot -}$ (1)

$O_2^{\cdot -} + H^+ \rightarrow HO_2^{\cdot}$ (2)

In this way, electron/hole recombination can be effectively prevented and lifetime of holes is prolonged. $HO_2^{\cdot}$ can lead to the formation of H_2O_2.

$HO_2^{\cdot} + e^- \rightarrow HO_2^-$ (3)

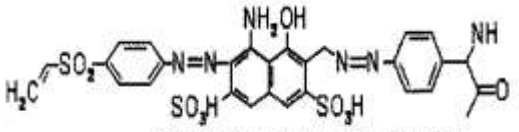
$HO_2^- + H^+ \rightarrow H_2O_2$ (4)

Photogenerated holes can react with adsorbed water molecules (or hydroxide anions) to give hydroxyl radicals:

$H_2O + h^+ \rightarrow HO^{\cdot} + H^+$ (5)

Or they can also be filled by an adsorbed organic donor. The whole process can end in complete mineralization of organic compounds. Further the addition of H_2O_2 to this heterogeneous system increases the concentration of $^{\cdot}OH$ radicals and it also inhibits electron hole recombination process at the same time and hence consequently increases the degradation rate dramatically. Keeping in view the concept of zero discharge and emerging strict environmental legislations for the disposal of wastewater in the rapidly developing countries, exhaustive research on photocatalytic treatment at laboratory scale and probing its suitability at an industrial level is a need of current research and development activities.

The aim of the present work is to investigate an effective and economical AOP for the degradation of azo dye of reactive class. Here we have undertaken detailed study on photo degradation of Navy Blue HE2R 1(NB) azo dye which is extensively used in textile industry and to the best of our knowledge; this is the first report on the photocatalytic degradation of this dye. We have employed UV/TiO_2/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.



Navy blue HE2R (Reactive Blue 172)

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),) Reactive textile dye Navy Blue HE2R (Reactive blue 172) was obtained from local textile industry, Solapur India. All chemicals were used in the form as received without further purification. The solutions were prepared in Millipore water.

2.2. Photoreactor

The experiments were carried out in batch immersion well photocatalytic reactor procured from ‘Scientific Aids and Instruments Corporation’ Chennai, India. (Refer Fig.1) The reactor consists of double wall immersion well made of quartz which was placed inside the glass reactor fitted with standard joint. The whole assembly of the reactor as procured from the manufacturer also consists of 8W low pressure mercury vapor lamp (peak emission at 254 nm) which was placed inside the immersion well. Water was circulated through the inlet & outlet provided by the reactor in order to maintain the constant temperature between 30 ± 1^0C.

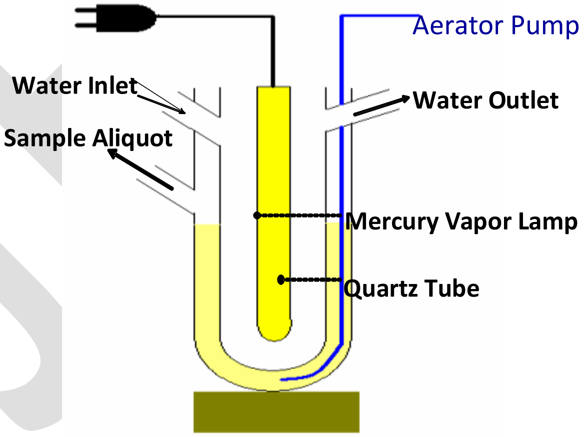


Fig. 1. Photoreactor

2.3 Procedure

The photodegradation of NB was carried out with different AOPs such as (i) UV (ii) UV/TiO_2 (iii) UV/TiO_2/H_2O_2 to identify the most suitable and economical process for complete decolorization and substantial mineralization of the dye. . Effect of various experimental parameters such as time of irradiation, 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 NB 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 NB solution was taken. The solution was agitated with the help of aeration pump and magnetic stirrer. To study the effect of time of irradiation photocatalytic degradation experiments were carried over the range of 3-8 hrs. Effect of catalyst concentration was studied by varying the amounts of TiO_2 L 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.

2.4 Analysis

Optical absorption spectrum for NB was determined by double beam Schimadzu UV- visible Spectrophotometer. The characterized wavelength of NB was found to be 610 nm which was used to monitor the decolorization and degradation of the dye. Chemical oxygen demand (COD) was measured by the dichromate reflux method [13] and total organic carbon (TOC) was measured using commercially available test kits (NONOCOLOR TOC 60) from Macherey–Nagel, Germany [14] to determine the mineralization of the dye solution under optimized conditions.

3. RESULTS AND DISCUSSION

The photo degradation of NB 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 time of irradiation (ii) Effect of catalyst concentration (iii) Effect of substrate concentration (iv) Effect of addition of H_2O_2

3.1.1 Effect of time of irradiation

The effect of time of irradiation on photocatalytic degradation of NB was studied over the range of 3-8 hours. Obtained results show that maximum degradation of NB can be achieved in first 3 hours. The minimum time of irradiation for maximum degradation was found to be 5 hours. Beyond this, the rate of degradation of NB is almost constant.

3.1.2 Effect of Catalyst Concentration

Effect of catalyst concentration was studied by varying the amounts of TiO_2 /ZnO ranging from 50 to 125 mg/250mL, in order to obtain an optimum catalyst concentration for the maximum photodegradation, which could save unnecessary use of excess of photocatalyst. For these studies the substrate concentration was kept constant ($2.5X10^{-5}$mol/L). Fig. 2. shows that the degradation efficiency increases up to 100mg/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 TiO_2 /ZnO particles. Hence the additional amount of catalyst is not involved in catalyst activities & the rate does not increase with an increase in the amount of catalyst [15]. Also at high TiO_2 concentrations particles aggregate this reduces the interfacial area between the reaction solution and the photocatalyst. Thus 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 TiO_2/ZnO. In the present investigation $_{100}$ mg of TiO_2 in 250mL of dye solution was found to be optimized dose for maximum degradation of NB.

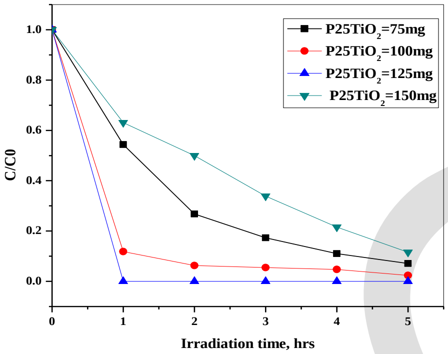


Fig.2. Optimization of Catalyst Concentration for the degradation of NB using P-25 TiO_2

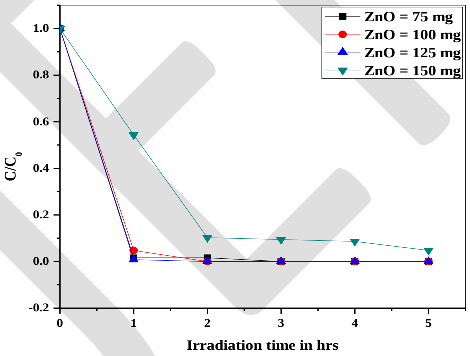


Fig.3. Optimization of Catalyst Concentration for degradation of NB using Merck ZnO

3.1.3 Effect of Substrate Concentration

The effect of substrate initial concentration on degradation of NB dye was studied at different concentrations varying from $1x10^{-5}$ 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.3, which shows that the degradation rate depends on the initial concentration of dye NB. The rate of degradation was found to increase with increasing concentration of NB up to 2.5×10^{-5} mol/L. Further increase of concentration decreases the rate of degradation. This may be explained on the basis that, on increasing the concentration of NB, 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 reached the catalyst surface. Hence, the production of hydroxyl and superoxide radicals are reduced [15]. 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 ·OH radical decreases. Consequently, the rate of reaction is retarded [16]. Hence in the present investigation the optimized substrate concentration of NB was found to be 2.5 x 10^{-5} mol/L.for P25 TiO_2

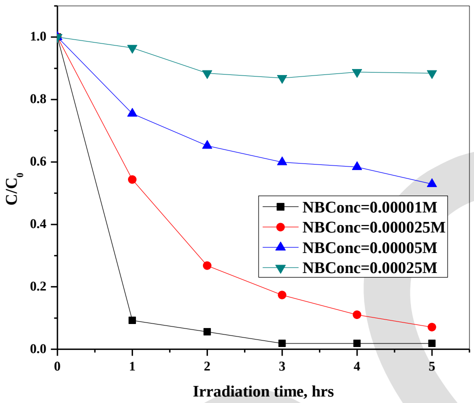


Fig. 4. Optimization of Substrate Concentration for degradation of NB using Degussa P-25 TiO_2

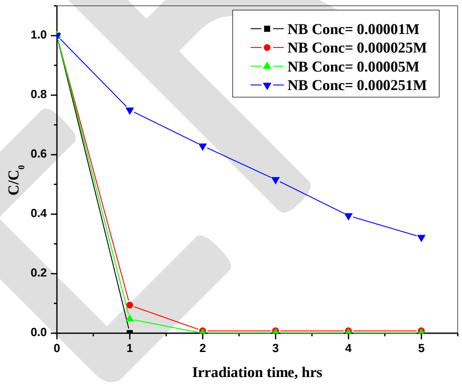
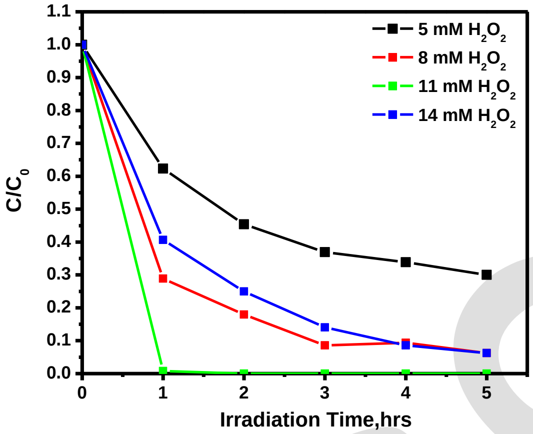


Fig.5. Optimization of Substrate Concentration for degradation of NB using Merck ZnO

3.1.4 Effect of addition of H_2O_2

The effect of addition of H_2O_2 to the system with optimized catalyst concentration and optimized initial substrate concentration was studied by varying the amount of H_2O_2 ranging from 0.175 g/250 mL to 0.475 g/250 mL. Fig.4 shows the variation in the photodegradation rate of NB for different amounts of H_2O_2. The highest rate of degradation was found for H_2O_2 = 0.375 g and beyond this the rate of degradation of NB was not significant. The addition of H_2O_2 to the heterogeneous system increases the concentration of ·OH radicals.



$$TiO_2\,(e^-) + H_2O_2 \rightarrow TiO_2 + OH^- + OH \quad (6)$$

Fig. 6. Optimization of Concentration of H_2O_2 using P-25 TiO_2

Being an electron acceptor, H_2O_2 does not only generate $^{\cdot}OH$ radicals but it also inhibits electron hole recombination process at the same time, which is one of the most important practical problems in using TiO_2 as photocatalyst. When the H_2O_2 concentration becomes high, the excess H_2O_2 consumes hydroxyl radicals and it performs like a hydroxyl radical scavengers [17].

$$H_2O_2 + {}^{\cdot}OH \rightarrow HO_2^{\cdot} + H_2O. \qquad (7)$$

When H_2O_2 was added, maximum degradation was achieved in the first hour only. Complete degradation was achieved in 2hrs. Thus in present investigation the optimized amount of H_2O_2 was found to be 0.375g/250mL. The photocatalytic degradation of NB using different AOPs such as (i) UV (ii) UV/TiO_2 (iii) UV/TiO_2/ZnO /H_2O_2 is shown in Fig 5. and the corresponding spectral changes observed for UV/TiO_2/ZnO/H_2O_2 process are depicted in Fig 6.

4.0 ESTIMATION OF 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 CO_2 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.

Table. 1. % Reduction in COD and TOC for degradation of NB

Name of the dye	% Reduction in COD		% Reduction in TOC		% degradation/ decolorization (By using UV-Spectrophotometer)	
	P-25 TiO_2	Merck ZnO	P-25 TiO_2	Merck ZnO	P-25 TiO_2	Merck ZnO
Navy Blue HE2R (NB)	85%	43.75%	65%	25%	92.91%	94.67%

In the selected dyes under study indicate that poor photocatalytic efficiency of P-25 TiO_2 than Merck ZnO. During photocatalytic experiments the observed changes in colour for the catalyst Degussa P-25 $TiO_{2.}$

Fig. 7. Decolorization of NB using Degussa P-25 TiO_2

Which clearly indicate the decolorization and degradation of NB dye. Graph 27 showed that Merck ZnO effectively degrade the dye only in 1 hr. In case of NB degradation, Merck ZnO was found to be best photocatalyst among all the three photocatalysts on the basis of UV-visible spectroscopic data. In case of Merck ZnO % decolorization was maximum but from COD and TOC data depicted in table 3. It was observed that P-25 TiO_2 is the most efficient photocatalyst because % reduction in COD and TOC was 85%

and 65% substantial mineralization achieved in P-25 TiO_2 while in case of Merck ZnO % deduction in COD and TOC is only 43.75% and 25%respectively indicate poor degree of mineralization.

On the basis of COD and TOC data P-25 TiO_2 was found to be the best photocatalyst han Merck ZnO. The order of photocatalytic efficiency was found to be P-25 TiO_2 > Merck ZnO > Merck TiO_2.

5. ACKNOWLEDGEMENTS

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6. CONCLUSIONS

The results obtained in the present study show the great efficiencies of advanced oxidation processes in removing diazo dyes which are resistant to other conventional treatment processes. This is the first report on the photocatalytic degradation of NB. The application of heterogeneous photocatalytic treatment using TiO_2 for the degradation of NB have 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 NB 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 to 85 % decrease in COD and 65 % decrease in TOC values resp. The observations of these investigations clearly demonstrated the importance of choosing the optimum degradation parameters which are essential for any practical application of photocatalytic oxidation process. Thus UV/TiO_2/H_2O_2 seems to be the most appealing choice for the complete degradation and substantial mineralization of NB and may be extended to treat real industrial wastewater.

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