

Heterogeneous Photocatalytic Decolorization of Brown NG by TiO₂ –UV Process

Khatamian, Maasoomeh[†]; Daneshvar, Nezameddin; Sabaee, Soodabeh*

Faculty of Chemistry, University of Tabriz, Tabriz, I.R. IRAN

ABSTRACT: *The photocatalytic decolorization of aqueous solutions Brown NG, a commercial textile dye, was studied using titana Degussa P-25 as a catalyst for the first time. The experiments were carried out in a batch reactor with the use of artificial light sources (UV-C). The effects of various process variables on decolorization performance of the process have been investigated. The photodegradation of Brown NG was enhanced by the addition of proper amounts of hydrogen peroxide, but it was inhibited by ethanol. Inhibiting effect of ethanol showed that hydroxyl radicals play a significant role in the photodegradation of the dye. In addition, the decolorization efficiency increased with decrease in pH, which implies that the pH is a very important parameter in dye adsorption. The efficiency is inversely related to the dye concentration. Results of TOC analysis show that the organic compounds were degraded, too.*

KEY WORDS: *Photocatalysis, Degradation, TiO₂, Decolorization, Textile wastewater, Brown NG.*

INTRODUCTION

Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger. About 1-20% of total world production of dyes is lost during the dyeing process and is released in the textile effluents. Approximately 50-70 % of dyes are azo compounds [1-5].

Colored textile effluents contain persistent dyestuffs, many of which are reported to be toxic and carcinogenic [6]. Direct discharge of these effluents can cause formation of toxic aromatic amines under anaerobic conditions in the receiving media, and contaminate the soil and ground water,

therefore, necessitating proper treatment before discharge into the environment [7].

Advanced Oxidation Process (AOPs) have demonstrated their usefulness in the purification of industrial wastewater, achieving a total or partial mineralization of organic pollutants [8-10]. Recent developments of Advanced Oxidation Processes (AOPs), have led to new improvements of the oxidative degradation of the organic compounds. In this process the solution is illuminated with UV irradiation in the presence of a suitable photocatalyst, Mainly TiO₂ [11-13]. The TiO₂ Photocatalyst

* To whom correspondence should be addressed.

† E-mail: mkhatamian@yahoo.com

1021-9986/10/3/21

7/\$/2.70

Archive of SID

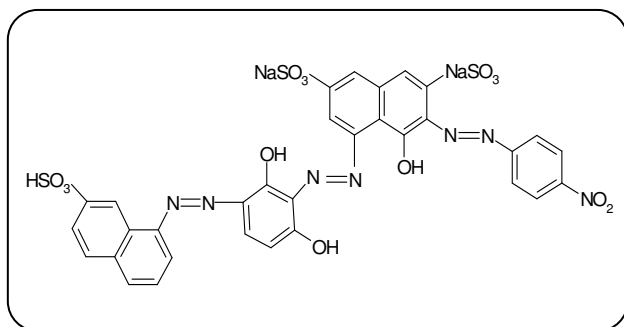


Fig. 1: Structure of Brown NG (C.I. no.502).

Mainly absorbs UV light of which the wavelength is lower than 400nm, and catalyzed the decomposition of organic compounds by including red-ox reaction [14]

TiO₂ in its anatase form is the most widely used because of its high photocatalytic activity, availability and chemical / photocorrosion stability in all reaction conditions [15-20].

In this research for the first time, we investigate the influence of various parameters on photocatalytic decolorization of a commercial azo dye, Brown NG, which is widely used in the textile and curriery industries by a heterogeneous photocatalytic process (UV/TiO₂ and UV / TiO₂ / H₂O₂). In particular, the effect of system parameters (TiO₂ amount, initial concentration of dye and solution pH) on the dye decolorization was examined, also organic compounds degradation was confirmed by TOC analysis.

The enhancing effect of H₂O₂ and inhibiting influence of ethanol was investigated too.

EXPERIMENTAL SECTION

Reagents

Degussa P-25 TiO₂ (70:30) % (w/w) anatase to rutile with an average particle size of 21nm was used as photocatalyst.

The hydrogen peroxide solution (30%), sulfuric acid, sodium hydroxide and ethanol were obtained from Merck, Brown NG was obtained from Boyak Saz. (Iran) and used without further purification. Its structure is given in Fig. 1.

Photoreactor and light source

Irradiation was performed in a batch photoreactor of 500 mL in volume with a mercury lamp Philips 30W (UV-C). It is indicated in Fig. 2.

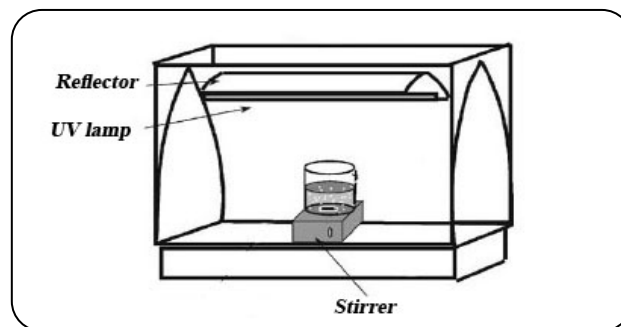


Fig. 2: The scheme of batch photoreactor.

Procedure

All photocatalytic activity experiments were carried out in a batch photoreactor with a mercury lamp 30W. A known volume of the dye solution was taken in the reactor. Predetermined amount of TiO₂ was added, and the solution was stirred using a magnetic stirrer. For equilibration in the dark before exposing the reactor assembly to the light. pH of solution was adjusted by adding H₂SO₄ and NaOH, dropwise. pH value was measured by pH meter (744 Ω Metrohm). Otherwise, the experiments were carried at the original pH of solution. The progress of photocatalytic decolorization was monitored by measuring the absorbance of the solution samples with UV-Vis spectrophotometer (Perkin-Elmer 5502) at λ_{max} = 450.5 nm. In the case of photocatalytic experiments, the samples were centrifuged to separate out TiO₂ particles. The removal efficiency of the dye was calculated by Eq. (1):

$$\text{Removal efficiency: } X = 100 \times ((C_0 - C) / C_0) \quad (1)$$

Where C₀ is the initial dye concentration and C is the concentration of Brown NG at time t. Dissolved Organic Carbon (DOC) in dye solution was measured with a Skaar Formacs^{HT} TOC / TN Carbon Analyzer.

RESULTS AND DISCUSSION

Spectral changes of brown NG observed during photodestruction

The progress in the absorbance spectrum of the dye solution during the reaction was monitored with initial 20 ppm dye concentration and 150 ppm catalyst concentration. The changes in the absorption spectra of Brown NG solutions during the decolorization times are shown in Fig. 3a.

Archive of SID

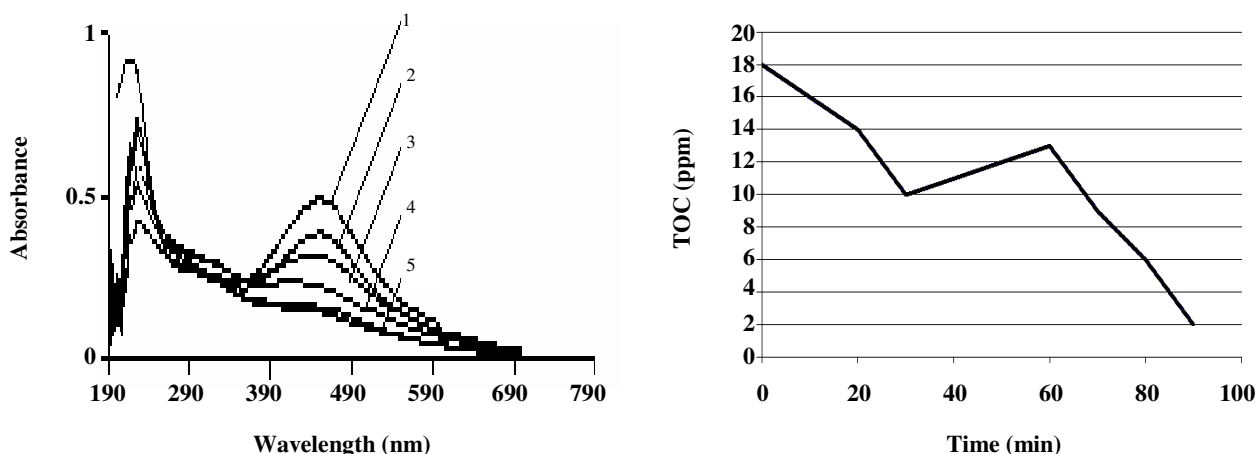


Fig. 3: Degradation of Brown NG (20 ppm) in aqueous TiO_2 dispersion ($[\text{TiO}_2] = 150 \text{ ppm}$) irradiated with a mercury lamp light at pH neutral, a) UV-Vis spectra changes at times: (1) zero, (2) 15 min, (3) 30 min, (4) 45, (5) 60 min, b) TOC analysis at several times.

The decrease of the absorption peak of brown NG at 450.5 nm in Fig. 3a. indicates a rapid decolorization of azo dye with no new absorption peaks appearing during the reaction. TOC analysis (Fig 3b) shows that organic compounds decrease in the first 30 min, the possible reason for this behavior is that the dye molecules are mainly adsorbed on the adsorbent sites to make high concentration environment around the nano TiO_2 particles. In the second 30 min, azo dye degraded to N_2 and organic residue of dye so concentration of carbon is increased. In the last 30 min nearly complete mineralization of organic compounds has happened.

These support the hypothesis that intermediate products formed during the decolorization are also successfully degraded towards complete mineralization [12].

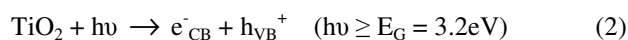
Effect of UV irradiation and TiO_2 particles

Fig. 4 shows the effect of UV irradiation and TiO_2 particles on photodegradation of brown NG, It can be seen from the figure that in the presence of both TiO_2 and UV light, the dye was degraded at the irradiation time of 80 min. For the same experiment, the reaction vessel was exposed to UV radiation in the absence of TiO_2 . It was noticed that efficiency of reaction was 35 % that is corresponding to photolysis of Brown NG in the presence of UV irradiation.

Results for experiments carried out with TiO_2 only, show that there was no observable loss of dye and the removal of Brown NG was negligible in the absence of UV radiation. These experiments show that both UV light

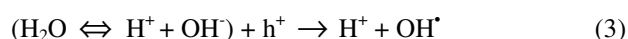
and TiO_2 were needed for the effective destruction of Brown NG. The mechanism of dye degradation under UV/ TiO_2 has been described, involving the steps shown in Eqs. (2) – (8).

Two oxidative agents can be considered: the photoproducted holes h^+ and/or OH^\bullet radicals, which are known as strongly active and degrading but non-selective agents. Actually, holes are the initial oxidizing agents generated by photoabsorption of efficient UV-photons by titania.

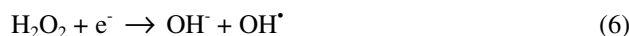


Subsequently, OH^\bullet radicals can be generated by various reactions

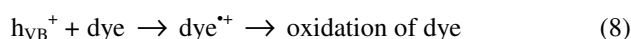
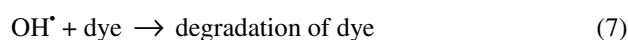
1. Oxidation of water by holes



2. Transient formation of hydroperoxide radicals



In this mechanism, the dye is degraded both in the bulk solution, through reaction with hydroxyl free radicals, and on the surface of the solid, reacting with the photogenerated holes [16].



Archive of SID

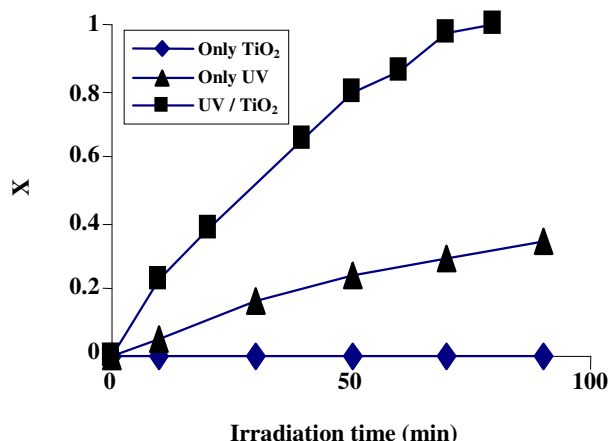


Fig. 4: Effect of UV light and TiO₂ on photocatalytic degradation of Brown NG. [Brown NG]₀ = 20 ppm, [TiO₂] = 150 ppm, pH neutral.

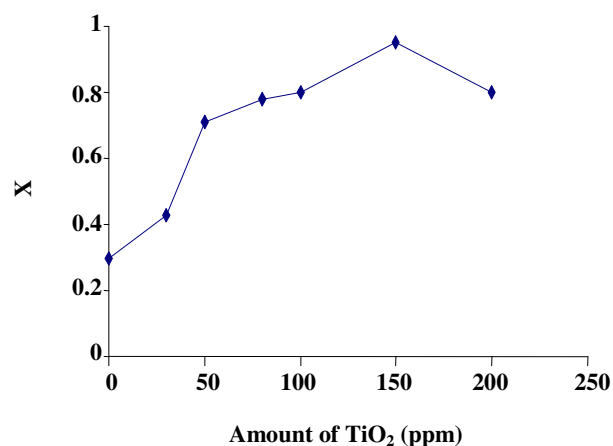


Fig. 6: Effect of amount of TiO₂ on photodegradation efficiency of Brown NG at irradiation time of 60 min. [Brown NG]₀ = 20 ppm, pH neutral.

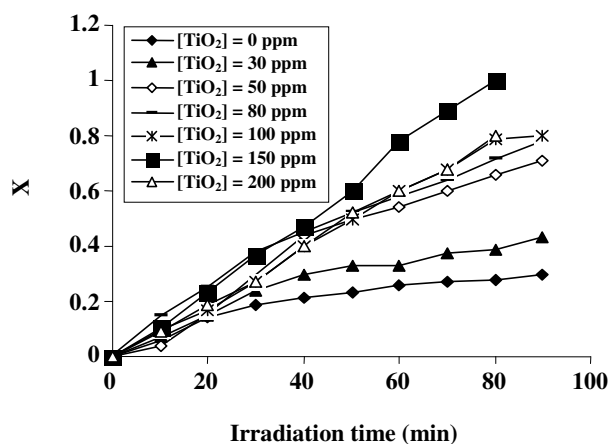


Fig. 5: Effect of the amount of TiO₂ on photodegradation efficiency of Brown NG. [Brown NG]₀ = 20 ppm, pH neutral.

Effect of TiO₂ concentration

To determine the effect of concentration of TiO₂ on decolorization rate of Brown NG, a series of experiments were carried out by varying the amount of TiO₂ from 30 ppm to 200 ppm. It was noticed that the best results were obtained when the concentration of TiO₂ in solution was 150 ppm (Figs. 5, 6).

The photodegradation efficiency, increased with an increase in the amount of photocatalyst, reaches the higher value catalyst amount (150 ppm) and then decreases.

The turbidity of the solution above 150 ppm reduced the light transmission through the solution, while below this level the adsorption on TiO₂ surface and the absorption of light by TiO₂ were the limiting factors.

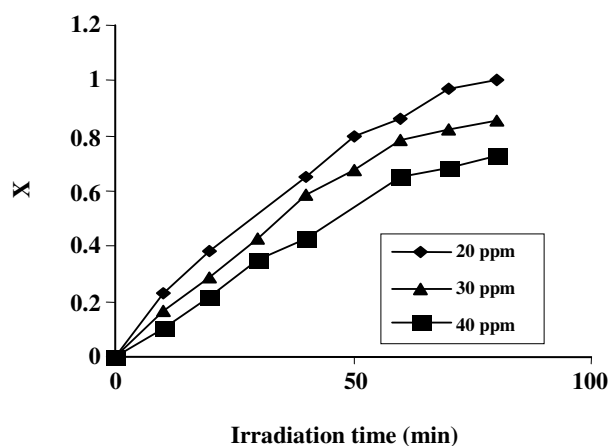


Fig. 7: Effect of the initial Brown NG concentration on photodegradation efficiency. [TiO₂] = 150 ppm, pH neutral.

Catalyst amount has both positive and negative impact on the photodecomposition rate. The increased amount of catalyst increases the quantity of photons absorbed and consequently the degradation rate.

Initial dye concentration

The effect of initial dye concentration on the decolorization efficiency was investigated by varying the initial concentration from 20-40 ppm at constant catalyst concentration (150 ppm).

As seen in the Fig. 7, decolorization efficiency is inversely affected by the dye concentration. This negative effect can be commented as follows; as the dye concentration is increased, the equilibrium adsorption of dye on the

Archive of SID

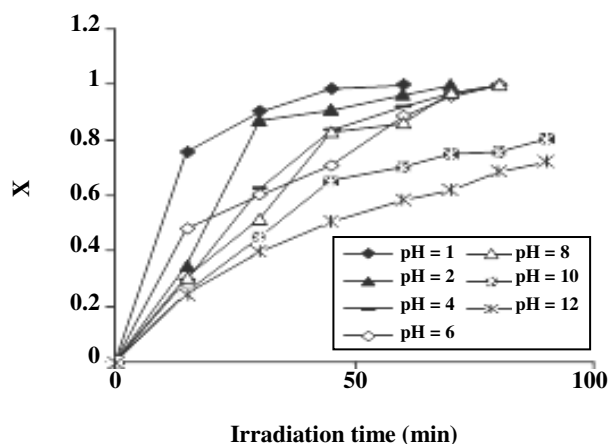
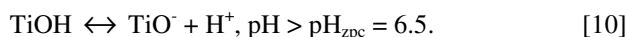
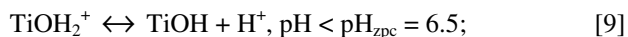


Fig. 8: Effect of pH on photodegradation efficiency of Brown NG at different irradiation times. [Brown NG] = 20 ppm, [TiO₂] = 150 ppm.

catalyst surface active site increases, hence competitive adsorption of OH[•] on the same sites decreases that means a lower formation rate of OH[•] which is the principle oxidant indispensable for a high degradation efficiency. On the other hand, considering Beer Lambert law, as the initial dye concentration increases, the path length of photons entering the solution decreases, which result in lower photons absorption on catalyst particle, and consequently lower photocatalytic reaction rates [12].

Effect of pH

The amphoteric behavior of titania influences the surface charge of photocatalyst [7]. The role of pH on the photocatalytic degradation rate was studied in a pH range in solutions containing 150 ppm TiO₂ and 20ppm azo dye. The experiments were performed at the same time. Best degradation was obtained with pH = 1. Degradation of organic compounds exhibited different behaviors depending on pH studied. The zero point charge pH (pH_{zpc}) for TiO₂ (Degussa P-25) is 6.5, according to the following equilibria:



Therefore catalyst surface was positively charged at acidic medium and negatively at basic medium. It was observed that increasing pH of the solution resulted in decreasing of the decolorization rate of brown NG. Since the dye has sulfonate groups in its structure, which are negatively

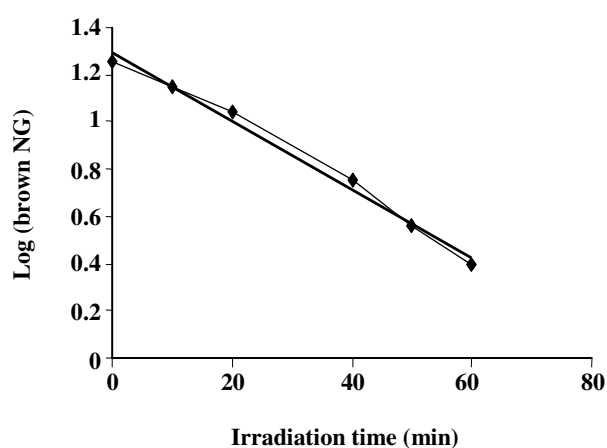


Fig. 9: Relationship between log [Brown NG] and irradiation time on photocatalytic degradation of Brown NG. [Brown NG]₀ = 20ppm, [TiO₂] = 150 ppm, pH neutral.

charged, the acidic solution favors adsorption of the dye onto TiO₂ surface. Thus, decolorization efficiency increased. At this pH there is also formation of OH radicals which react with dye molecules and increase the decolorization level [10, 11].

Photocatalytic kinetics of TiO₂/UV process

The decolorization of the dye solution showed that the destruction of the dyes occurred. Azo dyes are characterized by nitrogen double bonds (-N=N-). They contain at least one and up to four azo groups usually attached to two radicals of which at least one but usually both are aromatic groups. The color of azo dyes is determined by the azo bonds and their associated chromophores and auxochromes.

Azo bonds are the most active bonds in azo dye molecules, which are labile to be oxidized by positive hole or hydroxyl radical or reduced by electron in the conduction band. The reactions of azo bonds lead to decoloration of dyes [22].

The decolorization of brown NG reaction was observed to be a function of time.

The plot log [dye] versus irradiation time for brown NG was linear suggesting that photodegradation reaction approximately follows the first order kinetics (Fig. 9).

Rate constant ($K=1.44 \times 10^{-2} \text{ min}^{-1}$) was estimated from the slope of the log [dye] versus time plot in the optimized conditions.

Archive of SID

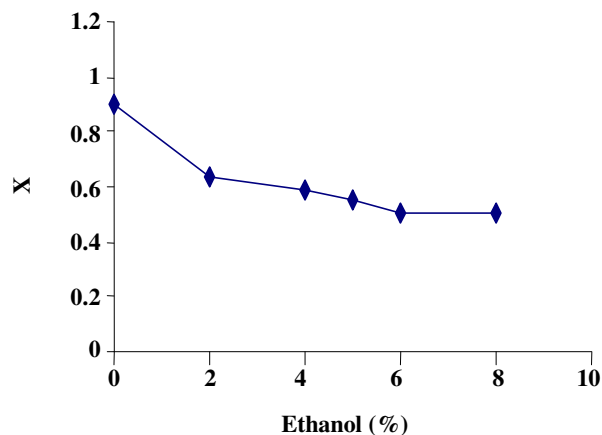


Fig. 10: Inhibitory effect of ethanol on photodegradation efficiency of Brown NG at the irradiation time of 90 min. $[Brown\ NG]_0 = 20\text{ppm}$, $[TiO_2] = 150\text{ ppm}$, pH neutral.

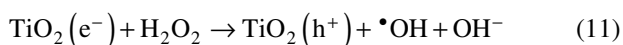
Addition of ethanol

Alcohols such as ethanol are commonly used to quench hydroxyl radicals. Fig. 10. shows that small amounts of ethanol inhibited the photocatalytic degradation of Brown NG [21]. This result shows that hydroxyl radicals play a major role in the UV/TiO₂ process. The retarding effect of EtOH in this system can be explained by $\cdot OH$ competitive reactions with EtOH and Brown NG. The rate constant of reaction between hydroxyl radicals and ethanol is $1.9 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ [22,23].

Effect of hydrogen peroxide addition on the performance of UV/TiO₂ pair

H₂O₂ exhibits triplet effect to increase oxidation rates of organic molecules in photocatalytic process:

1. As a strong oxidant, it scavenges conduction band electrons which are excited by irradiation of the catalyst and generates highly oxidative $h_{\nu B}^+$ on catalyst surface [17]:



2. H₂O₂ reacts with the electrons which are emitted from valence band of the photocatalyst to generate hydroxyl radicals and hydroxyl anions while inhibiting the $e^-/h_{\nu B}^+$ recombination process [17]:



3. H₂O₂ may also be split photocatalytically to produce hydroxyl radicals directly [15]:

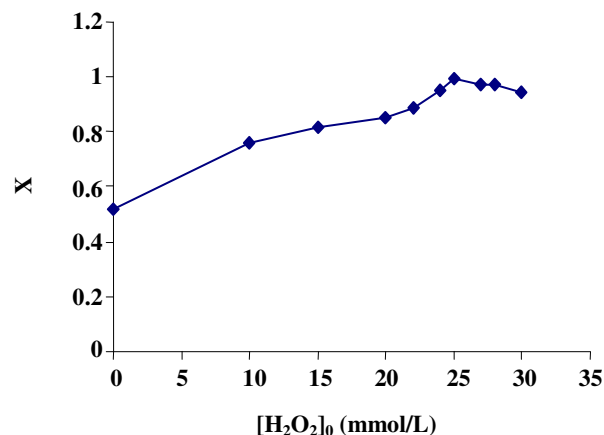
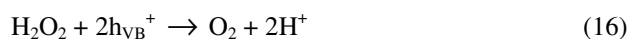
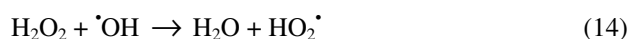


Fig. 11: Effect of H₂O₂ addition on photodegradation efficiency of Brown NG in UV/TiO₂ process at the irradiation time of 40 min. $[Brown\ NG]_0 = 20\text{ppm}$, $[TiO_2] = 150\text{ ppm}$, pH neutral.

It should be taken into consideration that photocatalytic oxidation will be inhibited via reaction of excess H₂O₂ with $\cdot OH$ radicals and $h_{\nu B}^+$ [17]:



These inhibition reactions are controlled by H₂O₂ concentration. Effect of hydrogen peroxide concentration on the degradation of Brown NG in the UV/TiO₂/H₂O₂ system was studied at different hydrogen peroxide concentrations. Results are given in Fig. 11. The degradation rate of Brown NG increased with increasing H₂O₂ concentration up to 25 mmol/l, but above it, degradation rate decreased. The higher reaction rates after the addition of peroxide were attributed to the increase in the concentration of hydroxyl radical. Eqs. (11)-(13). But at high dosage, H₂O₂ is a powerful $\cdot OH$ scavenger [21-23]. Eq. (13).

CONCLUSIONS

The result of our study showed that UV/TiO₂ process could be used for removal of Brown NG, successfully. TiO₂ and UV light had a negligible effect when they were used on their own. A correlation between the adsorption of dye onto photocatalyst material and the rate of degradation has been found. The results indicate that the degradation was obviously affected by the initial concentration of azo dye. pH influences both the photocatalyst surface and dye chemical structure. We also

Archive of SID

conclude that optimal amount of photocatalyst was 150ppm with dye concentration of 20 ppm. Decolorization of Brown NG after selection of desired operational parameters could be achieved in about 60 min, while complete degradation of dye occurred in about 90 min. The photodegradation rate could be increased by proper addition of hydrogen peroxide, but it was inhibited by ethanol. These results suggest that UV-irradiated TiO₂ may be considered as an adequate process for the degradation and detoxification treatment of diluted colored textile wastewater.

Acknowledgment

The authors are grateful to university of Tabriz Research Council for the financial support of this research.

Received : May 15, 2008 ; Accepted : May 3, 2010

REFERENCES

- [1] Yuan S., Sheng Q., Zhang J., Chen F., Anpo M., Zhang Q., Synthesis of La³⁺ Doped Mesoporous Titania with Highly Crystallized Walls, *Microporous and Mesoporous Materials* **79**, p. 93 (2005).
- [2] Konstantinou I.K., Albanis T.A., TiO₂-Assisted Photocatalytic Degradation of Azo Dyes in Aqueous Solution: Kinetic and Mechanistic Investigations: A Review, *Appl. Catal. B. Environ.* **49**, p. 1 (2004).
- [3] Aguedach A., Brosillon S., Morvan J., Lhadi E.K., Influence of Ionic Strength in the Adsorption and During Photocatalysis of Reactive Black 5 Azo Dye on TiO₂ Coated on Non Woven Paper with SiO₂ as a Binder, *Journal of Hazardous Materials*, **150**, p. 250 (2008).
- [4] Aguedach A., Brosillon S., Morvan J., Lhadi E.K., Photocatalytic Degradation of Azo-Dyes Reactive Black 5 and Reactive Yellow 145 in Water Over a Newly Deposited Titanium Dioxide, *Applied Catalysis B: Environmental*, **57**, p. 55 (2005).
- [5] Grzechulska J., Morawski A.W., Photocatalytic Decomposition of Azo-Dye Acid Black 1 in Water Over Modified Titanium Dioxide, *Applied Catalysis B: Environmental*, **36**, p. 45 (2002).
- [6] Golka K., Kopps S., Myslak Z.W., Carcinogenicity of Azo Colorants: Influence of Solubility and Bioavailability, *Toxicol. Lett.*, **151**, p. 203 (2004).
- [7] Swaminathan K., Sandhya S., Sophia A.C., Pachhade K., Subrahmanyam Y.V., Decolorization and Degradation of H-Acid and Other Dyes Using Ferrous-Hydrogen Peroxide System, *Chemosphere*, **50**, p. 619 (2003).
- [8] Esplugas S., Gimenez J., Contreras S., Pascual E., Rodriguez M., Comparison of Different Advanced Oxidation Processes for Phenol Degradation, *Water Research*, **36**, p. 1034 (2002).
- [9] Bhatkhande D.S., Kamble S.P., Sawant S.B., Pangarkar V.G., Photocatalytic and Photochemical Degradation of Nitrobenzene Using Artificial Ultraviolet Light, *Chemical Engineering Journal*, **102**, p. 283 (2004).
- [10] Akyol A., Yatmaz H.C., Bayramoglu M., Photocatalytic Decolorization of Remazol Red RR in Aqueous ZnO Suspensions, *Applied Catalysis B: Environmental*, **54**, p. 19 (2004).
- [11] Moon J., Yun C.Y., Chung K.W., Kang M., Yi J., Photocatalytic Activation of TiO₂ Under Visible Light Using Acid Red 44, *Catal. Today*, **87**, p. 77 (2003).
- [12] Muruganandham M., Swaminathan M., Photocatalytic Decolourisation and Degradation of Reactive Orange 4 by TiO₂-UV Process, *Dyes and Pigments*, **68**, p. 133 (2006).
- [13] Soutsas K., Karayannis V., Poullos I., Riga A., Ntampeglitis K., Spiliotis X., Papapolymerou G., Decolorization and Degradation of Reactive Azo Dyes Via Heterogeneous Photocatalytic Processes, *Desalination*, **250**, p. 345 (2010).
- [14] Kusvuran E., Gulnaz O., Irmak S., Atanur O.M., Yavuz H.I., Ebratur O., Comparison of Several Advanced Oxidation Processes for the Decolorization of Reactive Red 120 Azo Dye in Aqueous Solution, *Journal of Hazardous Materials B* **109**, p. 85 (2004).
- [15] Higarashi M.M., Jardim W.F., Remediation of Pesticide Contaminated Solid Using TiO₂ Mediated by Solar Light, *Catalysis Today*, **76**, 201 (2002).
- [16] Tanaka K., Reddy K.S.N., Photodegradation of Phenoxyacetic Acid and Carbamate Pesticides on TiO₂, *Applied Catalysis B: Environmental*, **39**, p. 305 (2002).
- [17] Irmak S., Kusvuran E., Ebratur O., Degradation of 4-Chloro-2-Methylphenol in Aqueous Solution by UV Irradiation in the Presence of Titanium Dioxide, *Applied Catalysis B: Environmental*, **54**, p. 85 (2004).

Archive of SID

- [18] Khatamian M., Hashemian S., Sabaee S., Preparation and Photo-Catalytic Activity of Nano-TiO₂-ZSM-5 Composite, *Mater. Sci. in Semicond. Process*, Available Online 9 December (2010).
- [19] Shankar M.V., Cheralathan K.K., Banumathi Arabindoo, Palanichamy M., Murugesan V., Murugesan, Enhanced Photocatalytic Activity for the Destruction of Monocrotophos Pesticide by TiO₂ / H β , *Journal of Molecular Catalysis A: Chemical*, **223**, p. 195 (2004).
- [20] Zhu C., Wang L., Kong L., Yang X., Wang L., Zheng S., Chen F., Zhi F.M., Zong H., Photocatalytic Degradation of Azo Dyes by Supported TiO₂ + UV in Aqueous Solution, *Chemosphere*, **41**, p. 303 (2000).
- [21] Behnajady M.A., Modirshahla N., Shokri M., Photodestruction of Acid Orange 7 (AO7) in Aqueous Solutions by UV / H₂O₂: Influence of Operational Parameters, *Chemosphere*, **55**, p. 129 (2004).
- [22] Daneshvar N., Salari D., Khataee A.R., Photocatalytic Degradation of Azo Dye Acid Red 14 in Water on ZnO as an Alternative Catalyst to TiO₂, *J. Photochem. Photobiol. A: Chemistry*, **162**, p. 317 (2004).
- [23] Daneshvar N., Salari D., khataee A.R., Photocatalytic Degradation of Azo Dye Acid Red 14 in Water: Investigation of the Effect of Operational Parameters, *J. Photochem. Photobiol. A: Chemistry*, **157**, p. 111 (2003).