# Heterogeneos Photocatalytic Decolorization of Brown NG by $TiO_2$ –UV Process

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**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, $TiO_2$, 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 $TiO_2$ [11-13]. The $TiO_2$ Photocatalyst

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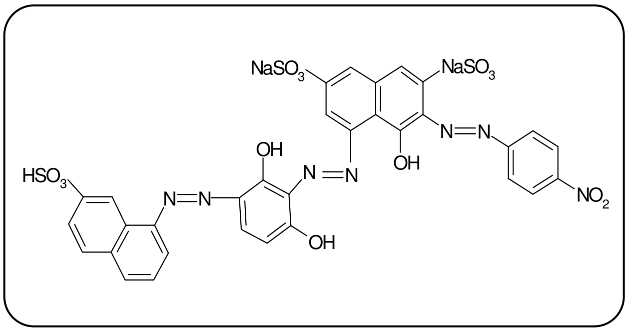

Fig. 1: Structure of Brown NG (C.I. no.502).

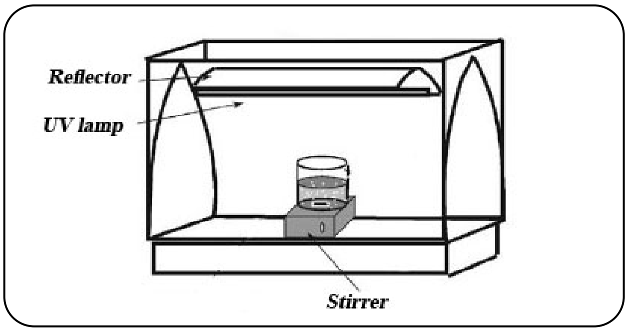

Fig. 2: The scheme of batch photoreactor.

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]

$TiO_2$ 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/$TiO_2$ and UV / $TiO_2$ / $H_2O_2$). In particular, the effect of system parameters ($TiO_2$ 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 $H_2O_2$ and inhibiting influence of ethanol was investigated too.

## EXPERIMENTAL SECTION

### Reagents

Degussa P-25 $TiO_2$ (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.

### 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 $TiO_2$ 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 $H_2SO_4$ and NaOH, dropwise. pH value was measured by pH meter (744 Ω Metrohm). Oherwise, 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 $\lambda_{max}$ = 450.5 nm. In the case of photocatalytic experiments, the samples were centrifuged to separate out $TiO_2$ particles. The removal efficiency of the dye was calculated by Eq. (1):

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

Where $C_0$ 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.

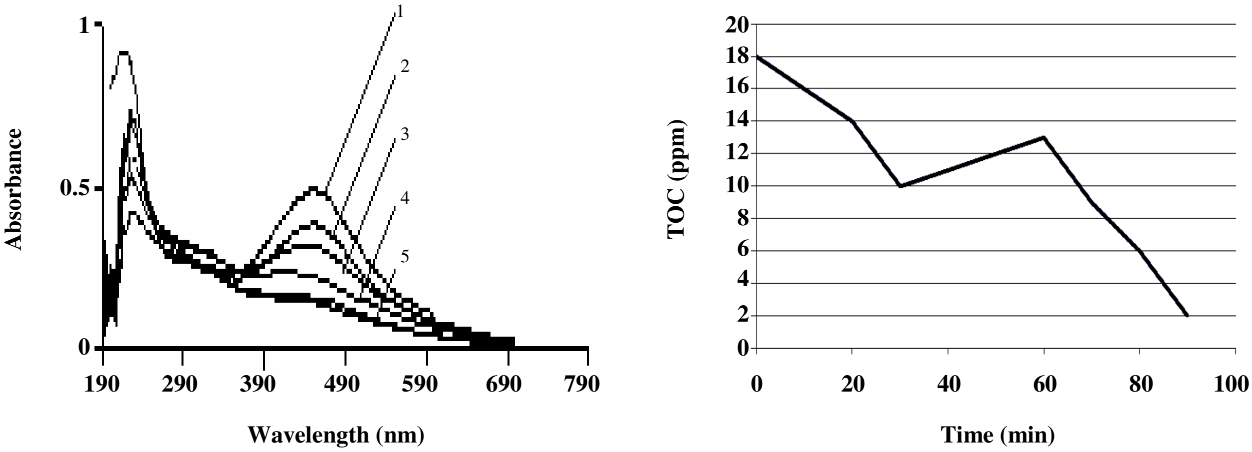

***Fig. 3: Degradation of Brown NG (20 ppm) in aqueous $TiO_2$ dispersion ($[TiO_2]$ = 150 ppm) irradiated with a mercury lamp light at pH neutral ,a) UV-Vis spectra changes at times: (1) zero, (2) 15 min, (3) 30 min, (4) 45, (5) 60 min, b)TOC analysis at several times.***

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) showes 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 photoproduced 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 titana.

$$TiO_2 + h\upsilon \longrightarrow e^-_{CB} + h_{VB}^+ \quad (h\upsilon \geq E_G = 3.2eV) \qquad (2)$$

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

1. Oxidation of water by holes

$$(H_2O \Leftrightarrow H^+ + OH^-) + h^+ \longrightarrow H^+ + OH^\bullet \qquad (3)$$

2. Transient formation of hydroperoxide radicals

$$O_2\bullet- + H^+ \longrightarrow HO_2^\bullet \qquad (4)$$

$$2HO_2^\bullet \longrightarrow H_2O_2 + O_2 \qquad (5)$$

$$H_2O_2 + e^- \longrightarrow OH^- + OH^\bullet \qquad (6)$$

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].

$$OH^\bullet + dye \longrightarrow \text{degradation of dye} \qquad (7)$$

$$h_{VB}^+ + dye \longrightarrow dye^{\bullet +} \longrightarrow \text{oxidation of dye} \qquad (8)$$

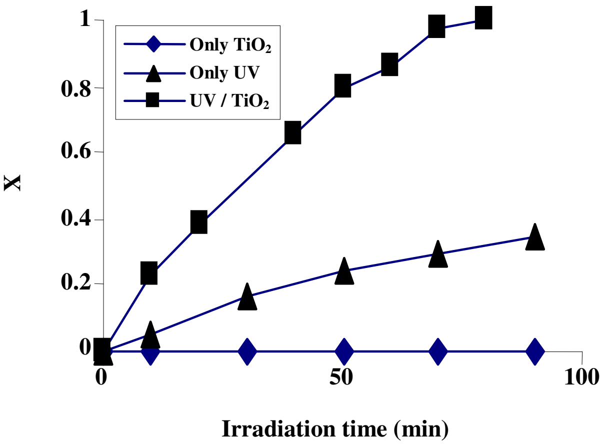

*Fig. 4: Effect of UV light and $TiO_2$ on photocatalytic degradation of Brown NG. [Brown NG]$_0$ = 20 ppm, [$TiO_2$] = 150ppm, pH neutral.*

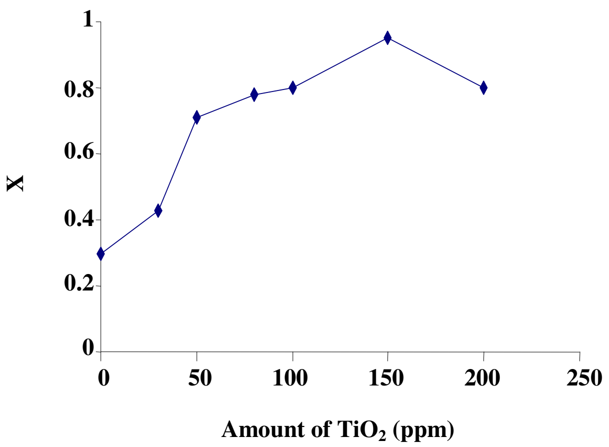

*Fig. 6: Effect of amount of $TiO_2$ on photodegradation efficiency of Brown NG at irradiation time of 60 min. [Brown NG]$_0$ = 20 ppm, pH neutral.*

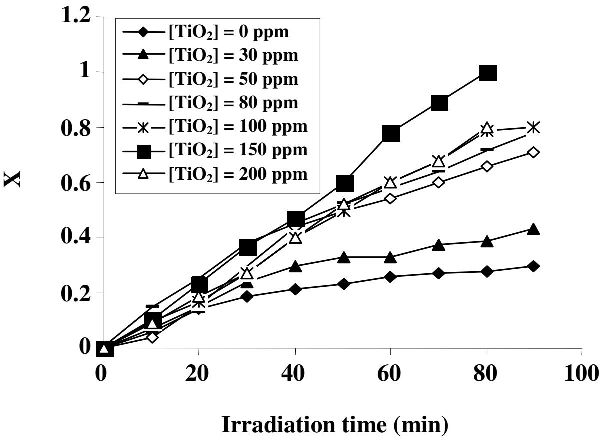

*Fig. 5: Effect of the amount of $TiO_2$ on photodegradation efficiency of Brown NG. [Brown NG]$_0$ = 20 ppm, pH neutral.*

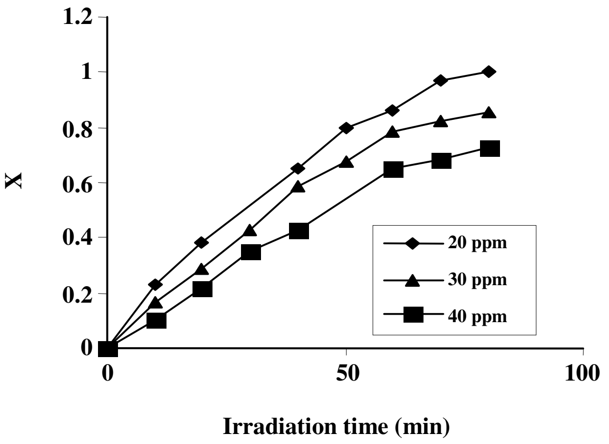

*Fig. 7: Effect of the initial Brown NG concentration on photodegradation efficiency. [$TiO_2$] = 150 ppm, pH neutral.*

### *Effect of $TiO_2$ concentration*

To determined the effect of concentration of $TiO_2$ on decolorization rate of Brown NG, a series of experiments were carried out by varying the amount of $TiO_2$ from 30 ppm to 200 ppm. It was noticed that the best results were obtained when the concentration of $TiO_2$ 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 $TiO_2$ surface and the absorption of light by TiO2 were the limiting factors. 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

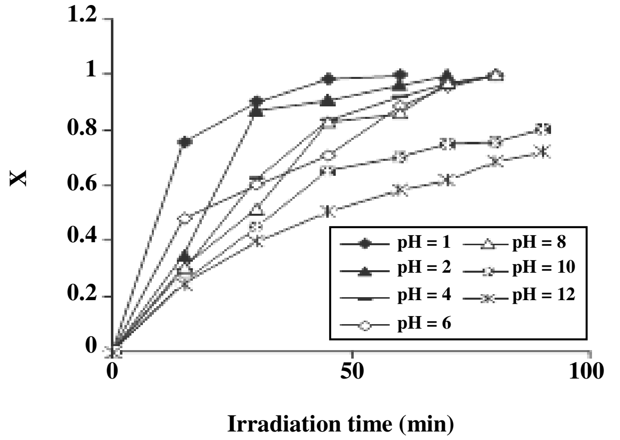

*Fig. 8: Effect of pH on photodegradation efficiency of Brown NG at different irradiation times. [Brown NG] = 20 ppm, [TiO$_2$] = 150 ppm.*

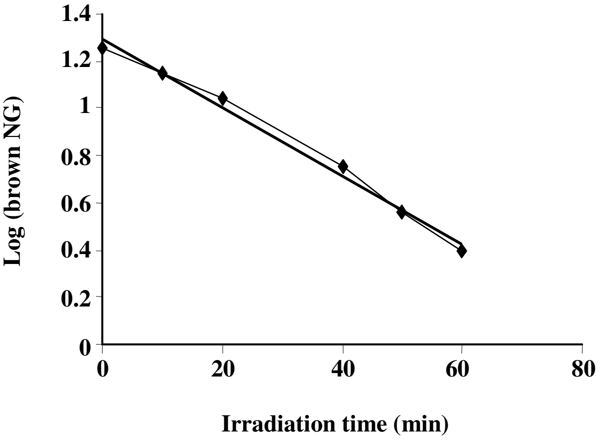

*Fig. 9: Relationship between log [Brown NG] and irradiation time on photocatalytic degradation of Brown NG. [Brown NG]$_0$ = 20ppm, [TiO$_2$] = 150 ppm, pH neutral.*

catalyst surface active site increases, hence competitive adsorption of $OH^\bullet$ on the same sites decreases that means a lower formation rate of $OH^\bullet$ 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 titana 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 $TiO_2$ 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 $TiO_2$ (Degussa P-25) is 6.5, according to the following equilibria:

$$TiOH_2^+ \leftrightarrow TiOH + H^+, pH < pH_{zpc} = 6.5; \qquad [9]$$

$$TiOH \leftrightarrow TiO^- + H^+, pH > pH_{zpc} = 6.5. \qquad [10]$$

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 charged, the acidic solution favors adsorption of the dye onto $TiO_2$ 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 TiO$_2$/ 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 ($K=1.44\times10^{-2}$ $min^{-1}$) was estimated from the slope of the log [dye] versus time plot in the optimized conditions.

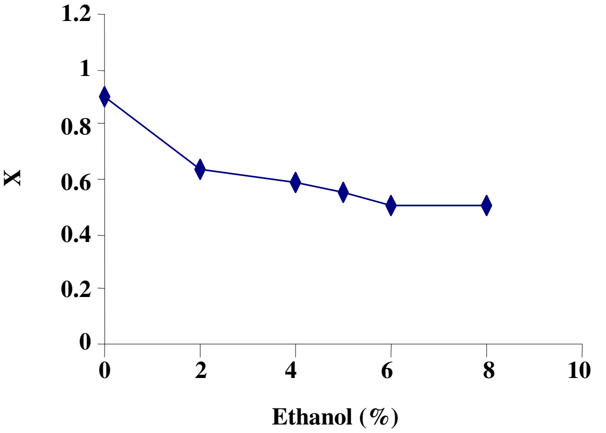

*Fig. 10: Inhibitory effect of ethanol on photodegradation efficiency of Brown NG at the irradiation time of 90 min. [Brown NG]$_0$ = 20ppm, [$TiO_2$] = 150 ppm, pH neutral.*

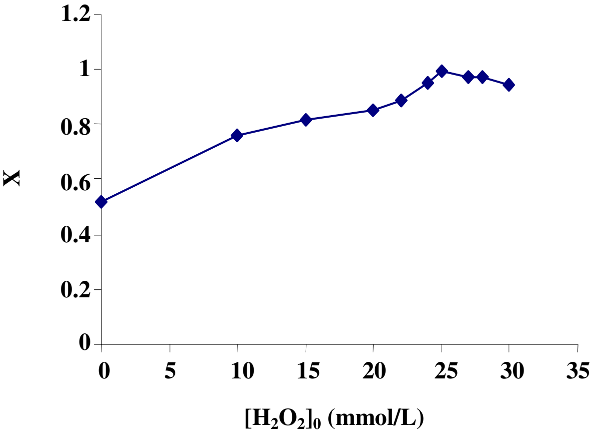

*Fig. 11: Effect of $H_2O_2$ addition on photodegradation of efficiency of Brown NG in UV/TiO2 process at the irradiation time of 40 min. [Brown NG]$_0$ = 20ppm, [$TiO_2$] = 150 ppm, pH neutral.*

### *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/$TiO_2$ process. The retarding effect of EtOH in this system can be explained by $^{\bullet}OH$ competitive reactions with EtOH and Brown NG. The rate constant of reaction between hydroxyl radicals and ethanol is $1.9 \times 10^9$ $M^{-1}s^{-1}$ [22,23].

### *Effect of hydrogen peroxide addition on the performance of UV/$TiO_2$ pair*

$H_2O_2$ 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 exited by irradiation of the catalyst and generates highly oxidative $h_{VB}^+$ on catalyst surface [17]:

$$TiO_2(e^-) + H_2O_2 \rightarrow TiO_2(h^+) + {}^{\bullet}OH + OH^- \qquad (11)$$

2. $H_2O_2$ reacts with the electrons which are emitted from valence band of the photocatalyst to generate hydroxyl radicals and hydroxyl anions while inhibiting the $e^-/h_{VB}^+$ recombination process [17]:

$$H_2O_2 + e_{CB}^- \rightarrow {}^{\bullet}OH + OH^- \qquad (12)$$

3. $H_2O_2$ may also be split photocatalytically to produce hydroxyl radicals directly [15]:

$$H_2O_2 + h\upsilon \rightarrow 2{}^{\bullet}OH \qquad (13)$$

It should be taken into consideration that photocatalytic oxidation will be inhabited via reaction of excess $H_2O_2$ with $^{\bullet}OH$ radicals and $h_{VB}^+$ [17]:

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \qquad (14)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \qquad (15)$$

$$H_2O_2 + 2h_{VB}^+ \rightarrow O_2 + 2H^+ \qquad (16)$$

These inhibition reactions are controlled by $H_2O_2$ concentration. Effect of hydrogen peroxide concentration on the degradation of Brown NG in the UV/$TiO_2$/$H_2O_2$ system was studied at different hydrogen peroxide concentrations. Results are given in Fig. 11. The degradation rate of Brown NG increased with increasing $H_2O_2$ 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, $H_2O_2$ is a powerful $^{\bullet}OH$ scavenger [21-23]. Eq. (13).

## CONCLUSIONS

The result of our study showed that UV/$TiO_2$ process could be used for removal of Brown NG, successfully. $TiO_2$ 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 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 $TiO_2$ may be considered as an adequate process for the degradation and detoxification treatment of diluted colored textile wastewater.

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