Sonochemical degradation of Basic Blue 41 dye assisted by nanoTiO$_2$ and H$_2$O$_2$

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Abstract

The sonolysis of Basic Blue 41 dye in aqueous solution was performed at 35 kHz using ultrasonic power of 160 W and aqueous temperature of $25 + 1\,^\circ C$ within 180 min. The TiO$_2$ nanoparticles were used as a catalyst to assist the sonication process. The effect of experimental parameters such as pH, H$_2$O$_2$ concentration and initial dye concentration on the reaction were investigated. It was recognized that in lower pH values the dye removal rate decreased. However, dye removal increased via increase in H$_2$O$_2$ concentration and lowering the initial dye concentration. All intermediate compounds were detected by integrated gas chromatography–mass spectrometry (GC/MS) and also ion chromatograph (IC). During the decolorization, all nitrogen atoms and aromatic groups of Basic Blue 41 were converted to urea, nitrate, formic acid, acetic acid and oxalic acid, etc. Kinetic studies revealed that the degradation process followed pseudo-first order mechanism with the correlation coefficient (R^2) of 0.9918 under experimental conditions. The results showed that power ultrasound can be regarded as an appropriate tool for degradation of azo dyes to non-toxic end products.
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1. Introduction

There are many different classes of dyes, such as azo, antheraquinone, metal complex, azo metal complex and phythalocynanine, reflecting the chromosphere structures of their constituent molecules [1]. Azo dyes are the most important group of the synthetic colorants (60–70%) [2]. The azo group (−N=N−) characterizes them, in association with aromatic systems and auxochromes (−OH, −SO$_3$, etc.). These chemical groups are combined variously in dye molecules and in that way their bio-elimination from effluents has become an intricate matter. The diverse processes used for decolorization of dyes are based on physical or chemical methods. They include membrane filtration [3–5], electrochemical technology [6–8] and advance oxidation process (AOP) such as photochemical oxidation [9], photocatalysis [10–12] and ultrasonic wave [13–16].

The chemical and biological effects of ultrasonic were reported by Loomis in 1927 [17]. Ultrasonic wave spans the frequencies of roughly 18 kHz–10 MHz with associated acoustic wavelengths of 10–0.01 cm. The chemical effects of high intensity ultrasound arise from acoustic cavitations of liquids: this rapid formation, growth and implosive collapse of gas vacuoles generates short-lived (-ns), localized "hot spots" whose peak temperatures and pressures have been measured at 5000 K and 1000 atm, confirming earlier calculations (Fig. 1) [18,19].

Interior of collapsing gas bubbles (i.e., the core) in which very high temperatures and pressures exist. Under these conditions the solvent vapor inside the bubble undergoes pyrolysis reactions at the interface between the collapsing bubble and the bulk solvent, where high temperature and pressure gradients exist.

In aqueous solutions, the relative efficiency of non-volatile solutes to decompose thermally or scavenge radicals formed in the hot spot depends on their ability to accumulate at the gas/solution interface of the growing micro bubble and bulk solution at ambient temperature. Free radicals formed in the hot regions may diffuse to the bulk solution and react to yield products similar to those found in aqueous radiation chemistry.

Substrates such as phenol [20], chlorinated hydrocarbons [21], various aromatics [22,23] and dyes [1,24–26] are trans-

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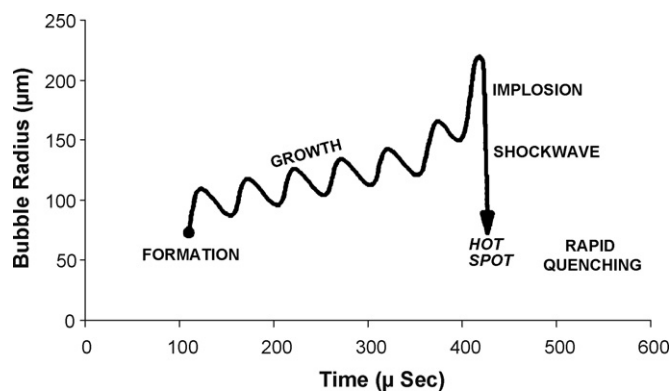 *E-mail address:* mahabbasi79@yahoo.com (M. Abbasi).

Fig. 1. Bubble growth and implosion in a liquid solution with ultrasonic irradiations [19]. With permission of susilk.

Fig. 2. SEM photographs of the TiO_2 surface ($\sim$100 nm).

formed into short chain organic acids, inorganic ions, CO, CO_2, and H_2O as the final products.

Two reaction mechanisms have been mainly proposed for sonodegradation. The first mechanism is pyrolysis in the cavitations of bubble which is expected to be the major reaction path for the degradation of polar compounds. The second mechanism is the generation of hydroxyl radicals in the cavitations bubble which subsequently oxidize the polar organic compounds [18].

The objective of this work is the evaluation of ultrasound irradiation applicability in decolorization of colored wastewaters. For this purpose, Basic Blue 41 (BB41) was chosen as a model dye as it is widely used in textile industry and cannot be quickly degraded. The sonication was performed by the assist of nanocatalyst and H_2O_2. Intermediate species were all detected via GC/MS and IC techniques. The process was optimized in terms of pH, H_2O_2 concentration and initial dye concentration. Finally, the kinetic investigation was done to find out the relevant mechanism.

2. Experimental

2.1. Chemicals

Basic Blue 41 [1-Amino-6-methoxybenzotiazole] was purchased from Fluka chemical company and used without further purification. Table 1 illustrates some characteristics of BB41. All other chemicals were prepared from Merck chemical company.

Titania nanoparticle (Degussaa P25) was utilized as a nanocatalyst. Its main physical data were as follows: average
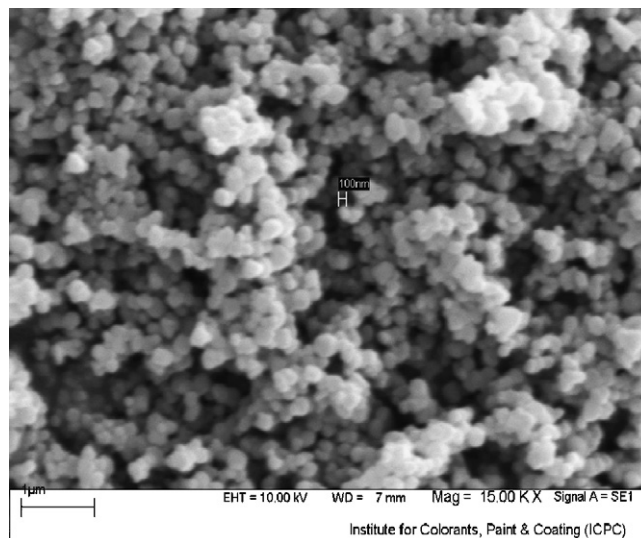
primary particle size around 100 nm, about 97% purity and 80:20 anatase to rutile ratio. In all of the experiments, constant concentration of nanocatalyst was used (0.2 gr l^{-1}). Fig. 2 displays scanning electron microscopy (SEM) image of Titania nonocatalyst which was captured by LEO 1455 VP scanning microscope.

2.2. Apparatus

The ultrasonic irradiation was produced using an ultrasonic bath (Bandelin electronic RK 255H, Germany) at 35 kHz and 160 W. The 150 ml cylindrical reactor was double-surrounded and the temperature was controlled via thermostate bath and water circulation system (LAUDA, RE 104, Germany).

Absorbance measurements were performed using PDA-Multispect Shimadzu 1501 spectrophotometer. Intermediate compounds were detected by gas chromatography coupled with mass spectrometry (GC 2010/MS, Shimadzu, Japan). The GC was equipped with a column (30 m × 0.25 mm) and column was operated for 2 min at a temperature of 80 °C, which was then increased to 280 °C at the rate of 15 °C min^{-1}.

Ion chromatograph (METROHM 761 Compact IC) was used to assay the appearance and quantity of formate, acetate, oxalate, sulfate and nitrate ions formed during the degradation and mineralization of the selected dyes applying a METROSEP anion dual 2 with 0.8 ml min^{-1} flow, 2 mM $NaHCO_3$/1.3 mM

Table 1
Characteristics of Basic Blue 41

Name and color index (C.I)	structure	λ_{max} (nm)	Molecular weight
Basic Blue 41; 11,105		617 nm	482.57 g mole^{-1}

Na$_2$CO$_3$ as eluent, temperature of 20 °C, pressure of 3.4 MPa and conductivity detector.

All pH measurements were made by a digital pH meter (Hack).

2.3. Experimental procedure

Dye degradation process was performed using 100 ml aqueous BB41 portion with desirable concentrations under constant stirring. The acidity of media was adjusted using dilute HCl and NaCl solutions. The experimental procedure was considered to be conducted in four different conditions.

1. BB41 degradation in the presence of H$_2$O$_2$ without sonication. In this case dye solution was contacted with various concentrations of hydrogen peroxide solution for 180 min to achieve the decolorization.
2. BB41 degradation in the presence of H$_2$O$_2$ and nano TiO$_2$ without sonication. Prepared dye solutions were contacted with H$_2$O$_2$, Then 0.01 gr of nano TiO$_2$ was suspended in each medium
3. BB41 degradation in the presence of only sonication. Prepared dye solutions were irradiated by ultrasound waves for 180 min.
4. BB41 degradation using nano TiO$_2$ and sonication. 0.01 gr of nano TiO$_2$ was suspended in each dye solutions and the resulted mixture was sonicated for 180 min.
5. BB41 degradation using Nano-TiO$_2$, Hydrogen peroxide and sonication. 0.01 gr of nano TiO$_2$ was suspended in each dye solution. To this, Hydrogen peroxide solutions with desirable concentrations were added. The whole solution was sonicated for 180 min.

3. Results and discussion

3.1. Sonocatalysis of Basic Blue 41

Sonochemical degradation of 15 mg/l of BB41 was carried out in the cylindrical jacketed glass cell described above. The BB41 showed maximum absorbance at 617 nm in aqueous medium (Fig. 3).

The variation of maximum dye absorption was monitored to study on the reaction progress. The percentage of removed dye in solution for each treatment can be given by

$$\text{Dye removal}(\%) = \frac{(C_0 - C)}{C_0} \times 100 \tag{1}$$

Where C_0 and C are initial dye concentration and dye concentration at time t (min), respectively. BB41 was destroyed after 180 min of sonolysis at 35 kHz with ultrasonic power of 160 W and liquid temperature of 25 °C (298 K) under various conditions. The experimental results for BB41 decolorization are depicted in Fig. 4.

In the case where only H$_2$O$_2$ was used to decompose BB 41, the decolorization occurred to the lower extent. The reason may be due to the insufficient amount of active radicals. Another case was performed via using hydrogen peroxide and suspended nano
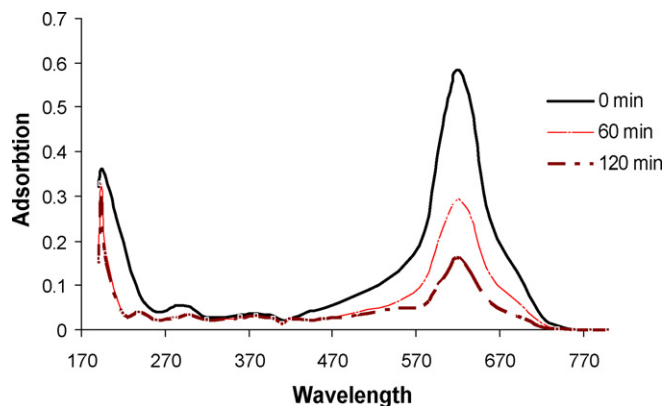

Fig. 3. Change in the absorption UV–visible spectra of BB41 during of Sonolysis: initial dye concentration: 15 mg/l, US: 35 kHz, H$_2$O$_2$ concentration: 250 mg/l and nano TiO$_2$:0.1 gr.

TiO$_2$ particles in the solution. In this case we observed a little more dye removal which could be attributed to the presence of nano catalyst in the medium.

In the aqueous solution, ultrasonic irradiation includes the formation of free radicals as a consequence of cavitation. The thermal decomposition of the water vapour and H$_2$O$_2$ in a cavitation bubble leads to the formation of HO$^\bullet$, H$^\bullet$ and HOO$^\bullet$ radicals. Scavenging of radicals in the bubble or at the interface increases the concentration of the oxidizing radicals. The radicals may also reach the liquid bubble interface and may pass into bulk solution where they can react with solutes [20]. So there would be an increase in degradation yield compared to the case where only hydrogen peroxide molecules were responsible for decolorization process.

In the presence of nano TiO$_2$, production of active radicals obeys two simultaneous mechanisms; homogeneous and heterogeneous. In the absence of nano TiO$_2$ the controlling mechanism would be homogeneous which produced less active radicals. As a result, decolorization of BB41 was significantly increased by addition of nano TiO$_2$.

The results revealed the efficiency of nano TiO$_2$ particles in degradation rate compared with large particle sized TiO$_2$
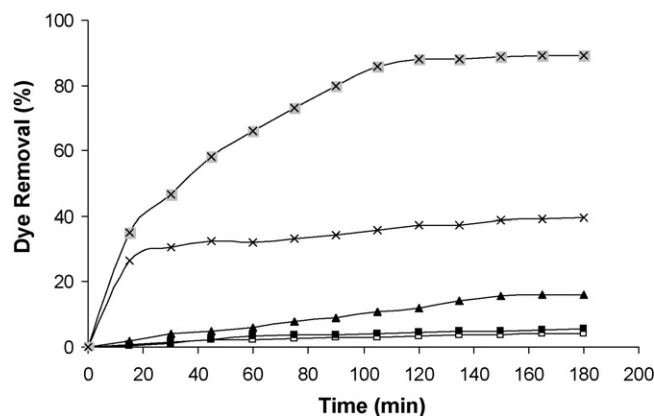

Fig. 4. Sonochemical degradation of Basic Blue 41 at 180 min by (□) H$_2$O$_2$ and without sonication, (■) nanoTiO$_2$ and H$_2$O$_2$ (▲) only US without nano TiO$_2$ and H$_2$O$_2$, (×) sonication and nano TiO$_2$, (☒) sonication, nano TiO$_2$ and H$_2$O$_2$.

Table 2
Intermediates identified by GC/MS and IC

Compounds	Analytical methods	
	GC/MS	IC
Benzaldehyde	*	
Formamide	*	
2-Propyn-1-ol	*	
Indene	*	
2,2,3,3-Tetramethylbutane	*	
Cyclopentanol	*	
1, 3-Benzodioxol-2-one	*	
2-Methoxy-2-methyl	*	
Pentadecanal	*	
2-Ethoxy-2,3-dihydro-3,3-dimethyl-methanesulfonate	*	
Acetic acid		*
Oxalic acid		*
Formic acid		*

[15]. The reason would be due to increased surface area of nano particles which provides more active sites to produce radicals.

However, the most ideal condition for dye degradation could be achieved by simultaneous usage of ultrasound, nano TiO$_2$ and H$_2$O$_2$ as it was expected from the theoretical aspect. Organic intermediates generated during the decolorization were all detected by GC/MS and IC. The chemical structures of relevant intermediates are displayed in Table 2.

3.2. Effect of initial dye concentration

Results showed that the decolorization efficiency decreased with the increasing of initial dye concentration. When the initial dye concentration was 15 mg/l, the decolorization efficiency reached 89.5% in 180 min, but when initial dye concentration enhanced to 240 mg/l, the decolorization efficiency declined to 33%. Plot of percentage dye removal against time is depicted in Fig. 5.

More concentrations of dye would provide interferences which inhibited degradation. The effect increased within the formation of more intermediate species.
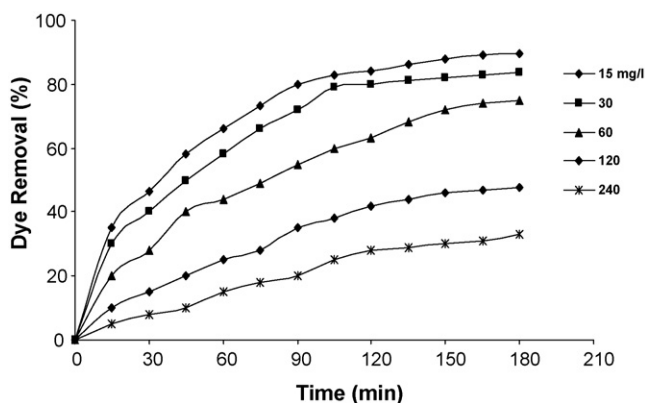
3.3. Effect of H$_2$O$_2$ concentration

One of the most popular advanced oxidation process (AOP) methods for decolorization of organic compounds is the oxidation with H$_2$O$_2$. Presence of Hydrogen peroxide is a key parameter for dye decomposition in AOP technique, depending on its concentration and nature of reductants. Hydrogen peroxide increases the formation rate of hydroxyl radicals in two ways. Firstly, the reduction of H$_2$O$_2$ at the conduction band would produce hydroxyl radicals. Secondly, the self-decomposition as a result of ultrasound irritation would also produce hydroxyl radicals. Generally, the decolorization rate of dye increases as the H$_2$O$_2$ concentration increases until an optimal concentration is achieved [27]. Recently, ultrasound irradiation was described as a possible generator of highly active $^\bullet$OH, HOO$^\bullet$ and H$^\bullet$ radicals [18]. However, at high concentration, H$_2$O$_2$ can also become a scavenger of valence bond holes and hydroxyl radicals causing less dye to be degradated. The resulting plots of percentage dye removal versus time implying the H$_2$O$_2$ effect are shown in Fig. 6.

The effect of ultrasonic irradiation combined with H$_2$O$_2$ is observed only when free radical attack is the controlling mechanism.

3.4. Effect of pH

pH of the solution is one of the most important parameters affecting the dye removal amount. The effect of varied initial pH values on the decolorization of BB41 during the sonocatalysis is presented in Fig. 7. It was revealed that the decolorization efficiency increased with the increase of pH. When pH was 4.5, the decolorization efficiency was found to be 51% after 180 min sonolysis while arising pH to 8, increased the decolorization efficiency to 89.5%. The effect of pH in the presence of TiO$_2$ for the degradation of dyes using advanced oxidation processes was investigated by others [27–29]. The point of zero charge (pzc) is at pH$_{pzc}$ 6.8 for the TiO$_2$ particles. As the pH of the system increases, the number of negatively charged sites increased. A negatively charged surface site on the TiO$_2$ favors the adsorption of dye cations due to the electrostatic attraction. So the degradation of dye was increased.
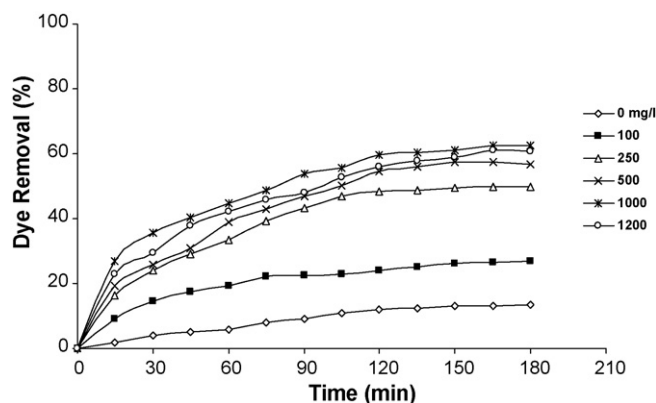

Fig. 5. Effect of initial dye concentration.

Fig. 6. Effect of H$_2$O$_2$ concentration: initial dye concentration: 15 mg/l, US: 35 kHz and nano-TiO$_2$:0.1 gr.
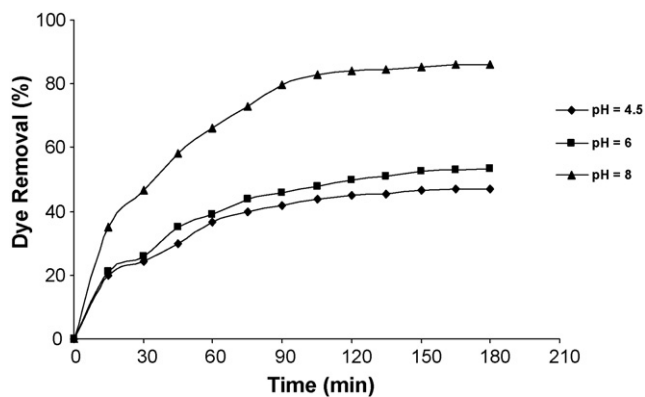
Fig. 7. Effect of pH: initial dye concentration: 15 mg/l, US: 35 kHz, H_2O_2 concentration: 250 mg/l and nano TiO_2:0.1 gr.

Table 3
Rate coefficients for sonochemical degradation of Basic Blue 41

H_2O_2 concentration (mg/l)	K_{obs} (min^{-1})	r^2
0	9×10^{-4}	0.9908
100	2.5×10^{-3}	0.9913
250	4.2×10^{-3}	0.9918
500	7.5×10^{-3}	0.9940
1000	9.9×10^{-3}	0.9896

4. Kinetics study

Results showed that degradation of BB41 by nanoTiO$_2$ and H$_2$O$_2$ assisted sonochemical process fitted appropriately by pseudo-first-order kinetics. The related regression coefficients are listed in Table 3.

The related kinetic model is shown as

$$\ln \frac{C}{C_0} = -kt \tag{2}$$

where C_0 and C are initial dye concentration and dye concentration at time t (min), respectively, t is sonolysis time (min) and k is the rate constant (min^{-1}). The linear fit between the ln A/A_0 and sonolysis time and different concentration of H$_2$O$_2$ can be approximated as pseudo-first-order model (Fig. 8).
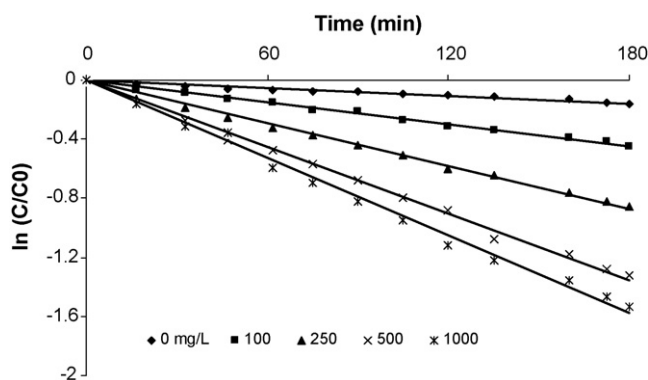

Fig. 8. Pseudo-first-order kinetic plots of BB41 degradation under ultrasound in the presence of TiO$_2$ nanoparticles (US + TiO$_2$) and deferent H$_2$O$_2$ concentration, initial dye concentration: 15 mg/l C_0 and C are initial dye concentration at time t (min).
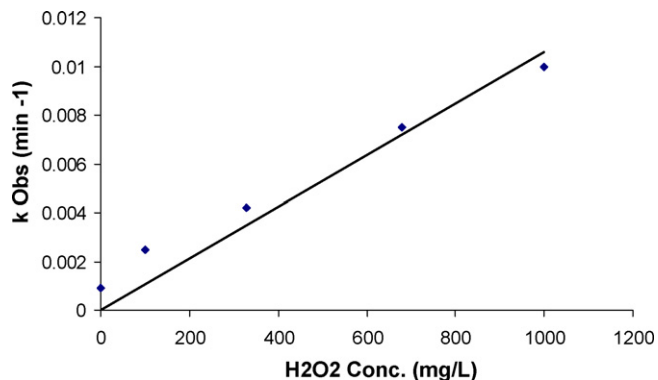

Fig. 9. The effect of H$_2$O$_2$ concentration on the observed first order rate constant.

The relationship between the observed rate constant and H$_2$O$_2$ concentration is shown in Fig. 9 and Table 3 which indicates that the pseudo-first-order rate constant is a linear function of H$_2$O$_2$ concentration.

5. Conclusion

The results obtained in this study show that H$_2$O$_2$ and nanocatalyst assisted sonolysis is an effective technique for the degradation of aqueous BB41 solutions. The decolorization was strongly depended on pH while efficient degradation of dye occurred in alkaline media. Higher dye removal could be attained using lower initial dye concentrations. H$_2$O$_2$ played an important role in degradation efficiency which could be well described via its varied concentration effect on response. Nanocatalysis serves as a substantial part that can be added to the reaction to reach desirable results. The major organic intermediates were detected by GC/MS while nitrate and sulphate ions, formic acid, acetic acid and oxalic acids were recognized by IC. The color decay correlated pseudo-first order model.

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