Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1041050

57 (2016) 9318–9324
April

Taylor & Francis
Taylor & Francis Group

Decolorization of Direct Blue 71 using UV irradiation and ultrasound in the presence of TiO_2 catalyst

Nese Ertugay[a,*], Filiz Nuran Acar[b]

[a]*Faculty of Engineering, Civil Engineering Department, Erzincan University, Erzincan, Turkey, Tel. +90 446 2240088; Fax: +90 446 2240077; email: nertugay@erzincan.edu.tr*
[b]*Faculty of Engineering, Environmental Engineering Department, Atatürk University, Erzurum, Turkey*

Received 24 April 2014; Accepted 2 March 2015

ABSTRACT

The sono, photo, and sonophotocatalytic degradations of Direct Blue 71 (DB71) in the presence heterogeneous TiO_2 catalyst were studied at 20 kHz using ultrasonic (US) power of 95 W and aqueous temperature of 20°C for 20 min. The effects of various operational parameters such as the concentration of the dye, pH, and amounts of catalysts on the sonochemical degradation were also investigated. Sonochemical degradation of DB71 was strongly affected by initial substrate concentration, amounts of catalysts, and pH. Acidic pH was favored for the sonocatalytic degradation of DB71 using catalysts. The hybrid technique of sonocatalytic degradation was compared with the individual techniques of catalysis, sonolysis, and photocatalysis. The US degradation of dye was enhanced by catalyst addition. The structure and morphology of the catalyst were investigated using scanning electron microscopy and X-ray diffraction pattern.

Keywords: Ultrasound; Sonocatalysis; Cavitation; Catalyst; Advanced oxidation

1. Introduction

Textile and other industrial dyes constitute one of the largest groups of organic compounds that represent an increasing environmental danger [1]. Anthropogenic dyes, such as azo dyes produced from textile and other industries, have low biodegradability under aerobic conditions leading to concern over industrial discharges [2]. Some azo dyes and degradation products such as aromatic amines are highly carcinogenic. If these effluents are released into the environment without treatment, they pose a threat to the ecosystem [3]. The treatments of these pollutants involve chemical, physical, and biological methods, in which advanced oxidation processes (AOPs) such as sonolysis, radiolysis, and photocatalysis have emerged as useful methods for mineralizing organic compounds in aqueous media. All these processes which produce hydroxyl radicals ($^{\cdot}OH$) as the primary oxidant assist in environmental remediation [4]. Recently, ultrasonic (US) irradiation and UV applications of semiconductor materials mediated by suitable catalysts (sonocatalysis) and (photocatalysis) have been receiving attention as a promising technique for the treatment of hazardous organic pollutants in wastewater. Sonolysis can convert ideally the organic pollutants to carbon dioxide and water or convert them to compounds which are less harmful than the original pollutants. Ultrasound can be used alone or in conjunction with other techniques. However, the degradation rate is slow

---

*Corresponding author.

compared to other established methods [5,6]. Several efforts to enhance the efficiency of AOPs through forming hybrid systems consisting of two or more processes, such as sonophotocatalysis, have been made by many research groups during the last years [7]. The use of insoluble particles (heterogeneous catalysis) such as metallic oxides, mixtures of metals, and nano-sized TiO_2, are even more promising in accelerating sonochemical reactions [8]. The combination of US with TiO_2 photocatalyst degrades the target pollutant by an additional generation of hydroxyl radicals through both band gap excitation of TiO_2 and sonolytic splitting of water molecules. The important advantage of this combination process is that US continuously cleans the photocatalyst and is useful in maintaining its reactivity over longer irradiation times. The following description is widely accepted as the mechanism for photocatalytic degradation of organic pollutants over TiO_2 system [9,10]:

Reactions involved in photcatalysis:

$$TiO_2 + hv \rightarrow h_s^+ + e_s^- \tag{1}$$

$$OH_s^- + h_s^+ \rightarrow OH_s^{\bullet} \tag{2}$$

$$OH_s^{\bullet} + OH_s^{\bullet} \rightarrow (H_2O_2)_s \tag{3}$$

$$(H_2O_2)_s + h_s^+ \rightarrow (HO_2^{\bullet})_s + H_{aq}^+ \tag{4}$$

$$(HO_2^{\bullet})_s + h_s^+ \rightarrow O_2 + H_{aq}^+ \tag{5}$$

$$OH_s^{\bullet} + (RH_2)_{aq} \rightarrow (RH^{\bullet})_{aq} + OH_s^- + H_{aq}^+ \tag{6}$$

$$OH_s^{\bullet} + e_s^- \rightarrow OH_s^- \tag{7}$$

$$(H_2O_2)_s + e_s^- \rightarrow OHO_s^- + OHO_s^- \tag{8}$$

$$OH_s^{\bullet} + (RH^{\bullet})_{aq} \rightarrow OH_s^- + R_{aq} + H_{aq}^+ \tag{9}$$

$$(RH^{\bullet})_{aq} \rightarrow R_{aq} + e_s^- + H_{aq}^+ \tag{10}$$

$$O_2 + e_s^- \rightarrow O_2^- \tag{11}$$

Reaction involved in sonolysis:

$$H_2O +)))) \rightarrow H^+ + HO^{\bullet} \tag{12}$$

$$H_2O +))))) \rightarrow 1/2H_2 + 1/2H_2O_2 \tag{13}$$

$$H_2O_2 + H^+ \rightarrow H_2O + HO^{\bullet} \tag{14}$$

where e^- is electron, h^+ is hole, and OH^- is the hydroxide ion adsorbed on the TiO_2 surface [11,12].

The aim of our work was to study the decoloration of Direct Blue 71 (DB71) by low (20 kHz) US irradiation, and to enhance their decoloration by the addition of TiO_2 catalyst. Efforts have been made to characterize the catalyst and to elucidate the effects of initial dye concentration, addition of H_2O_2, solution pH, and the catalyst loading. Besides, the coupled US process, such as US/H_2O_2 [13,14], US/TiO_2 [15,16], US/TiO_2/H_2O_2 [13], US/ZnO, US/ZnO/H_2O_2 [17], UV/TiO_2 [16], US/UV [18], and US/UV/TiO_2 [9], increases the decomposition efficiency and reduces the time required for removing the pollutants. The main objective of this study was to investigate the degradation of DB71 by the combining procedure and different catalysts. DB71 is a water-soluble substantive dye and has many applications in cotton, cellulose, polyester, silk, leather, and paper dyeing [19].

2. Experimental

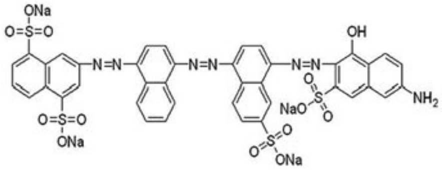
2.1. Apparatus and methods

The chemical structure and some characteristics of DB71 dye are given in Table 1. The average size of TiO_2 nanoparticles was computed using scanning electron microscopy (SEM) which was captured by Quanta FEG 450 Scanning Microscope. A typical SEM image of TiO_2 particles is shown in Fig. 1. DB71 was purchased from Aldrich. Original pH of the model solution was measured as ~5.50. P-25 TiO_2 was obtained from Degussa Corporation and used as received. Hydrogen peroxide (30% w/w) was purchased from Riedel-de Haën.

The US irradiation was produced using an US bath (Cole Parmer US Processor) at 20 kHz and 750 W. The ultrasound probe was immersed into the solution at a depth of approximately 3 cm within a 250 mL DB71 sample in a 500 mL glass reactor with cooling jacket. The experiment was carried out using amplitude level 90%. The power level (Watts) was measured 95 W using Powmet-230 Power Meter. UV irradiation was provided by two $44\ W\ m^{-2}$ lamps (Pen-Ray, $\lambda_{max} = 254$ nm) that were located in the center of the reactor. The reaction temperature of 20 ± 2°C was maintained by circulating water. The experimental setup for US and UV irradiations is shown in Fig. 2.

Samples were withdrawn and filtrated through a 0.45 μm membrane filter and then the supernatant was analyzed. The absorbance of the sample was measured by a spectrophotometer (UV-160A Shimadzu) at 587 nm which corresponds to the maximum absorbance of DB71. The concentration of DB71 in samples was calculated using a standard curve of DB71. In the experiment of pH effect, H_2SO_4 was used to control

Table 1
Characteristics of Direct Blue 71

Name	Structure	λ_{max} (nm)	Molecular weight (g mol^{-1})
Direct Blue 71		587	1,029.9

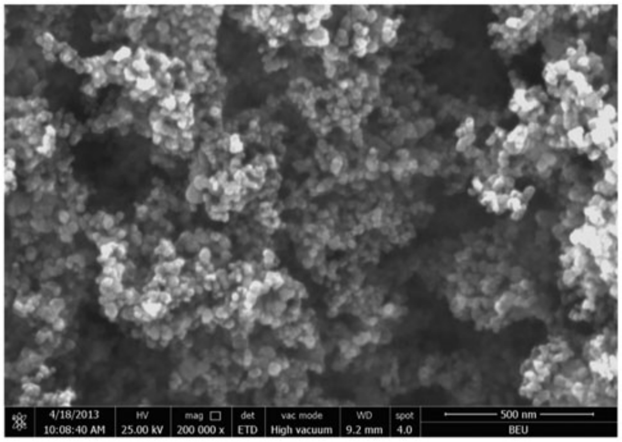


Fig. 1. SEM images of TiO_2 catalyst.

the pH. Stock dye solutions were prepared by dissolving 1 g of DB71 dye in 1 L of deionized water. For experiments without US, the reactor was stirred at 100 rpm during the experiment.

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

$$\text{Dye removal } (\%) = \frac{C_0 - C}{C_0} \times 100 \qquad (15)$$

where C_0 and C are initial dye concentration and dye concentration at 20 min, respectively.

3. Results and discussion

3.1. Decolorization with ultrasound of DB71 under different experimental conditions

3.1.1. Effect of catalyst dose

From an economical point of view, in any degradation process the catalyst concentration is considered as one of the most important parameters that should be investigated. In order to determine the optimum concentration of TiO_2 catalyst on the sonocatalysis of DB71 decolorization, a series of decolorization experiments was conducted by varying the initial concentration of catalyst TiO_2 in the range from 0 to 1 g L^{-1}

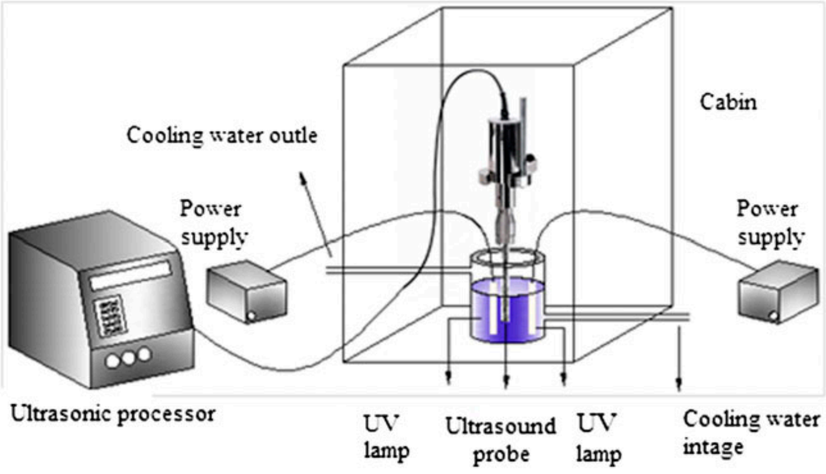


Fig. 2. Experimental setup.

(Fig. 3). The degradation rate of DB71 dye with the addition of 0.1 g L^{-1} catalyst is slightly higher than the degradation of DB71 dye using US alone. As the catalyst dosage increased from 0 to 1 g L^{-1}, the decolorization yield increased from 23 to 74% for DB71 dye. This may be caused by the increase in the number of TiO_2 micro particles, resulting in an increase in the number of photons absorbed and the number of dye molecules adsorbed [20], and surface area of nanoparticles which provides more active sites to produce radicals. It is commonly accepted that the presence of TiO_2 particles in US treatment enhances the cavitation phenomenon as the micro bubbles tend to break up into smaller ones resulting in the increase in the total number of regions of high temperature and pressure [21].

3.1.2. Effect of pH

The pH had a great effect on the sonocatalytic degradation of dye. Fig. 4 shows higher catalytic activity obtained at an initial solution pH of 2.5. Decolorization rate was 74% at pH 2.5, whereas decolorization rate decreased to 28% at pH 5.5. As a conclusion, pH favored the degradation of various types of organic dyes [22]. DB71 molecule has an amine group that can be protonated at low pH. This protonated DB71 is easier to be degraded under acidic conditions. The degradation rate was found to increase with oxidation potential of ·OH radical in the acidic medium [23].

The surface charge of TiO_2 particles and the adsorption of dye on the surface vary by changing the pH. The interpretation of pH effects on the efficiency of dye removal is a very difficult task. This is due to the multiple roles of pH on the ionization state of the surface, ·OH radical formation, agglomeration of particles, and the specification of dye and products. The acidic solution favors adsorption of the dye molecules onto TiO_2 surface due to the change in the specification of the dye [24].

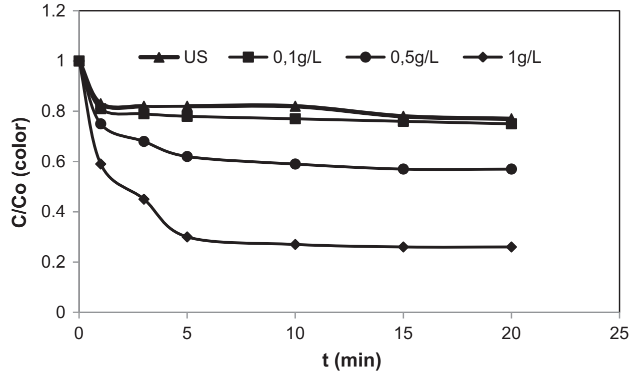


Fig. 3. The effect of catalyst concentration on sonochemical degradation of DB71 (C_0 = 100 mg L^{-1}, pH = 2.5, power = 95 W, and T = 20°C).

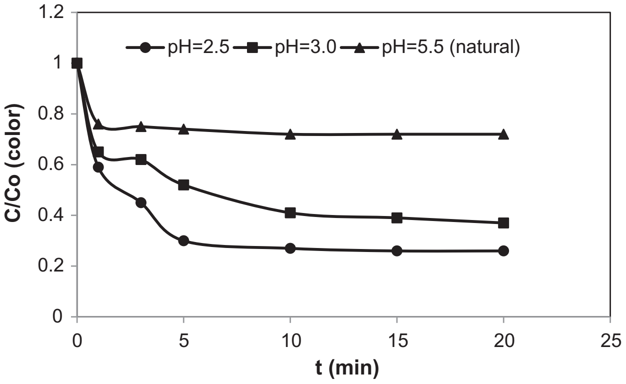


Fig. 4. Effect of pH on sonochemical degradation of DB71 (C_0 = 100 mg L^{-1}, TiO_2 = 1 g L^{-1}, power = 95 W, and T = 20°C).

3.1.3. Effect of initial dye concentration

The decolorization efficiency of the heterogeneous catalyst as a function of initial dye concentration was also investigated by changing the concentration of DB71 solution from 50 to 200 mg L^{-1}. As shown in Fig. 5, the decolorization efficiency of DB71 decreased with increase in the initial concentration of DB71. The increase in initial concentration of the dye from 50 to 200 mg L^{-1} decreased the decolorization efficiency from 100 to 44%. A possible reason of the experimental observation could be the high initial concentration of dye solution which caused more degradation to take place to achieve the same level of degradation [25]. Also, the deactivation of the catalyst with increase in initial dye concentration could be ascribed that the same amount of the ·OH radicals generated in the reaction system was insufficient to oxidize more dye molecules. As a result, the activity of the catalyst was found to decrease with initial dye concentration [22]. However, higher concentrations might also cause excessive adsorption of the dye molecules onto the surface of TiO_2 powder on the TiO_2 sonocatalyst to limit its efficiency. Also, mutual screens between DB71 molecules and TiO_2 particles increased with increase in the initial dye concentration. These two phenomena could hinder TiO_2 particles absorbing heat and energy released from the acoustic cavitation and also disturbed the transmission of ultrasound [25].

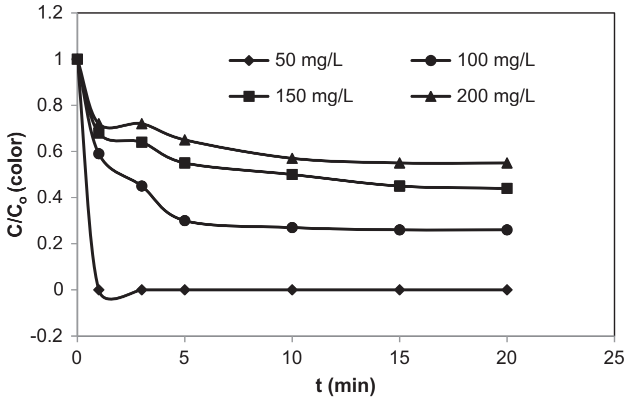


Fig. 5. Effect of initial dye concentration on sonochemical degradation of DB71 (pH = 2.5, $TiO_2 = 1\ g\ L^{-1}$, power = 95 W, and $T = 20$°C).

3.2. Effect of H_2O_2 and TiO_2 on decolorization with ultrasound of DB71

One of the most popular AOP methods for decolorization of organic compounds is the oxidation with H_2O_2. Presence of H_2O_2 is a key parameter for dye decomposition in AOP technique, depending on its concentration and nature of reductants. In the case where only H_2O_2 and US were used to decompose DB71, the decolorization occurred to the lower extent. This could be due to the insufficient amount of active radicals. Another case was performed via using H_2O_2 and suspended nano TiO_2 particles in the solution. In this case, we observed more dye removal which could be attributed to the presence of nano catalyst in the medium (Fig. 6). In the aqueous solution, US irradiation includes the formation of free radicals as a consequence of cavitation. The thermal decomposition of the water vapor and H_2O_2 in a cavitation bubble leads to the formation of $HO^{\bullet}$, $H^{\bullet}$, and $HOO^{\bullet}$ radicals. The radicals may also reach the liquid bubble interface and may pass into bulk solution where they can react with solutes. In the presence of TiO_2 catalyst, 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 DB71 was significantly increased by the addition of TiO_2 catalyst [26]. However, the most ideal condition for dye degradation could be achieved by simultaneous usage of ultrasound, nano TiO_2, and H_2O_2, as it was expected from the theoretical aspect. As shown in Fig. 6, the color removal of DB71 after 20 min was 55% (US/H_2O_2), 74% (US/TiO_2), and 84% ($US/TiO_2/H_2O_2$), respectively.

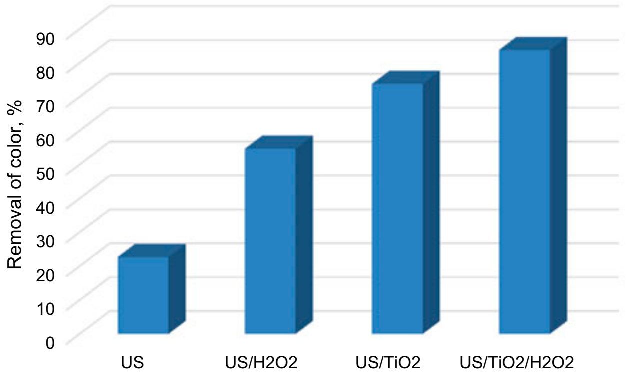


Fig. 6. Concentration of dye remaining by heterogeneous sonocatalytic degradation of DB71 ($C_0 = 100\ mg\ L^{-1}$, $TiO_2 = 1\ g\ L^{-1}$, $H_2O_2 = 75\ mg\ L^{-1}$, power = 95 W, pH = 2.5, $T = 20$°C, and $t = 20$ min).

3.3. Effect of TiO_2 and H_2O_2 on decolorization with UV and US/UV of DB71

To evaluate the photocatalytic and sonophotocatalytic activities of the composite catalyst, decolorization of DB71 was carried out under different processes. The results in Fig. 7 also show that photolysis and sonophotolysis processes show limited efficiency in the DB71 color removal. The added TiO_2 increased the degradation efficiency in both UV and US/UV processes. However, H_2O_2 addition decreased color removal because excessive doses of H_2O_2 prevent fragmentation of the radical and show the reaction interference effect [27]. While the color removal was about 47% with UV oxidation, UV/TiO_2 and UV/H_2O_2 oxidation were 78 and 42.4%, respectively, and was 84% in $US/UV/TiO_2$.

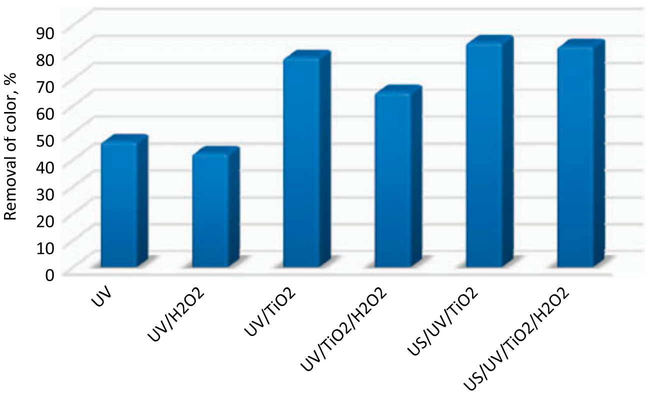


Fig. 7. Removal of color by heterogeneous photocatalytic and sonophotocatalytic oxidations of DB71 ($C_0 = 100\ mg\ L^{-1}$, $TiO_2 = 1\ g\ L^{-1}$, $H_2O_2 = 75\ mg\ L^{-1}$, pH = 2.5, $T = 20$°C, and $t = 20$ min).

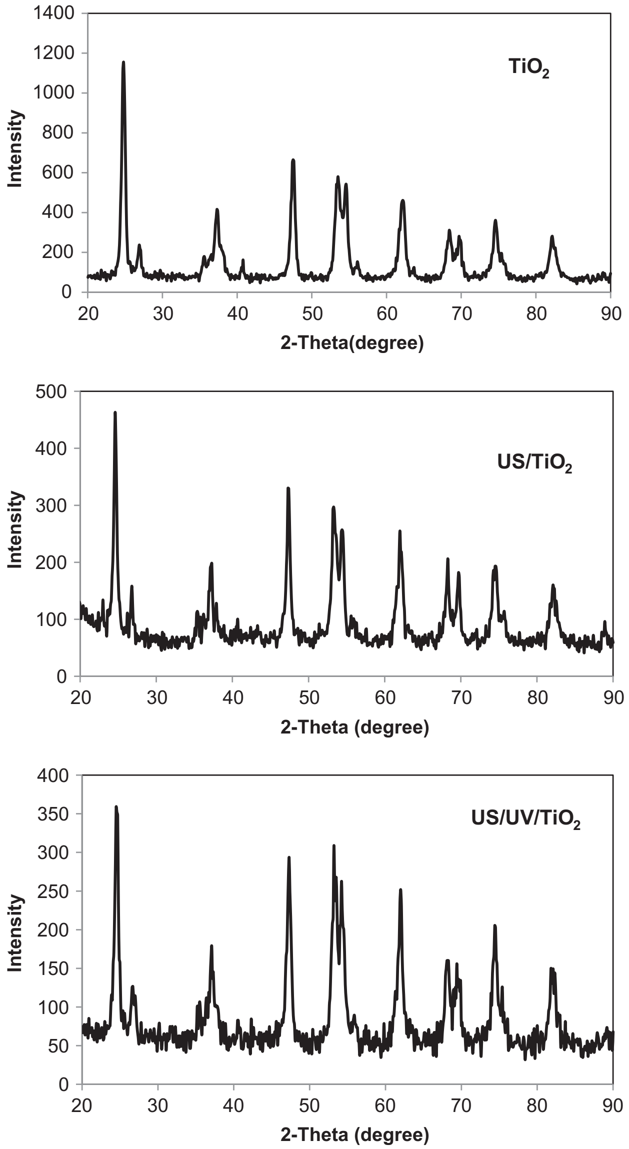


Fig. 8. XRD patterns of TiO_2 catalyst (a) TiO_2 alone, (b) US/TiO_2, and (c) US/UV/TiO_2.

3.4. Catalyst characterization

X-ray diffraction (XRD) patterns of the fresh and used catalyst samples are shown in Fig. 8. The patterns were scanned from 10° to 90° (2θ) at a scanning rate. Fig. 8 shows XRD patterns of the catalyst sample and were quite similar to those of the used one, pointing out that the crystalline catalyst structure was not affected during the sonophotocatalytic treatment. Catalyst was reduced to smaller particles by US and US/UV treatments, and as a result of this, a decrease was seen in peak values. All the above discussion shows that the material was not destructed after reaction [28].

4. Conclusions

This study investigated the sono and photocatalytic oxidations of DB71 and evaluated the decolorization efficiency of US, UV, US/H_2O_2, US/TiO_2, UV/TiO_2, UV/H_2O_2, US/UV/TiO_2, and other combination systems. The removal of DB71 was very low by sonication alone. The presence of catalyst and H_2O_2 enhanced decolorization removal of DB71. In the presence of TiO_2 and H_2O_2, the decolorization efficiency followed the order $US/UV/TiO_2 > US/TiO_2/H_2O_2 > US/UV/TiO_2/H_2O_2 > UV/TiO_2 > US/TiO_2 > UV/TiO_2/H_2O_2 > US/H_2O_2 > UV/TiO_2$. The maximum removal of DB71 84% was observed in US/UV/TiO_2 system at pH 2.5, TiO_2 1 g L^{-1}, 100 mg L^{-1} DB71 for 20 min reaction time.

The extent of removal depends on the operating conditions employed such as catalyst dosage, initial dye concentration, and solution pH. The removal of dye increases with the increase in concentration of the catalyst, while the removal percentage was decreased with the increase in initial concentration. But, the decolorization efficiency decreased with the increase in pH. The study has shown that ultrasound is quite effective for decomposing azo dyes when applied in the presence of additives—TiO_2, H_2O_2, and UV.

References

[1] R.S. Juang, S.H. Lin, P.Y. Hsueh, Removal of binary azo dyes from water by UV-irradiated degradation in TiO_2 suspensions, J. Hazard. Mater. 182 (2010) 820–826.
[2] T.M. Elmorsi, Y.M. Riyad, Z.H. Mohamed, H.M.H. Abd El Bary, Decolorization of Mordant red 73 azo dye in water using H_2O_2/UV and photo-Fenton treatment, J. Hazard. Mater. 174 (2010) 352–358.
[3] M.A. Behnajady, N. Modirshahla, M. Shokri, B. Vahid, Design equation with mathematical kinetic modeling for photooxidative degradation of C.I. Acid Orange 7 in an annular continuous-flow photoreactor, J. Hazard. Mater. 165 (2009) 168–173.
[4] H. Wang, J. Niu, X. Long, Y. He, Sonophotocatalytic degradation of methyl orange by nano-sized Ag/TiO_2 particles in aqueous solutions, Ultrason. Sonochem. 15 (2008) 386–392.
[5] S.G. Anju, S. Yesodharan, E.P. Yesodharan, Zinc oxide mediated sonophotocatalytic degradation of phenol in water, Chem. Eng. J. (2012) 84–93.
[6] D. Lin, J. Wang, X. Li, H. Liu, Effect of ultrasonic frequency on the structure and sonophotocatalytic property of CdS/TiO_2 nanocomposite, Mater. Sci. Semicond. Process. 15 (2012) 152–158.
[7] E. Hapeshi, I. Fotiou, D. Fatta-Kassinos, Sonophotocatalytic treatment of ofloxacin in secondary treated effluent and elucidation of its transformation products, Chem. Eng. J. 224 (2013) 96–105.
[8] Z. Eren, N.H. Ince, Sonolytic and sonocatalytic degradation of azo dyes by low and high frequency ultrasound, J. Hazard. Mater. 177 (2010) 1019–1024.

[9] F. Ahmedchekkat, M.S. Medjram, M. Chiha, A. Mahmoud Ali Al-bsoul, Sonophotocatalytic degradation of Rhodamine B using a novel reactor geometry: Effect of operating conditions, Chem. Eng. J. 178 (2011) 244–251.

[10] H.Y. Xu, Z. Zheng, G.J. Mao, Enhanced photocatalytic discoloration of acid fuchsine wastewater by TiO_2/schorl composite catalyst, J. Hazard. Mater. 175 (2010) 658–665.

[11] A. Kaur, V. Agarwal, Sonophotocatalytic degradation of monocrotophos pesticides using immersion well reactor, Int. J. Appl. Eng. Res. 18 (2013) 2067–2074.

[12] T.L. Villarreal, R. Gómez, M. González, P. Salvador, A kinetic model for distinguishing between direct and indirect interfacial hole transfer in the heterogeneous photooxidation of dissolved organics on TiO_2 nanoparticle suspensions, J. Phys. Chem. B. 108 (2004) 20278–20290.

[13] P. Nalini Vijaya Laxmi, P. Saritha, N. Rambabu, V. Himabindu, Y. Anjaneyulu, Sonochemical degradation of 2chloro-5methyl phenol assisted by TiO_2 and H_2O_2, J. Hazard. Mater. 174 (2010) 151–155.

[14] D.B. Voncina, A. Majcen-Le-Marechal, Reactive dye decolorization using combined ultrasound/H_2O_2, Dyes Pigm. 59 (2003) 173–179.

[15] C.H. Wu, Photodegradation of C.I. Reactive Red 2 in UV/TiO_2-based systems: Effects of ultrasound irradiation, J. Hazard. Mater. 167 (2009) 434–439.

[16] S. Kaur, V. Singh, Visible light induced sonophotocatalytic degradation of Reactive Red dye 198 using dye sensitized TiO_2, Ultrason. Sonochem. 14 (2007) 531–537.

[17] J. Gao, R. Jiang, J. Wang, P. Kang, B. Wang, Y. Li, K. Li, X. Zhang, The investigation of sonocatalytic activity of Er^{3+}: $YAlO_3/TiO_2$–ZnO composite in azo dyes degradation, Ultrason. Sonochem. 18 (2011) 541–548.

[18] S. Wang, Q. Gong, J. Liang, Sonophotocatalytic degradation of methyl orange by carbon nanotube/TiO_2 in aqueous solutions, Ultrason. Sonochem. 16 (2009) 205–208.

[19] J. Saien, A.R. Soleymani, Degradation and mineralization of Direct Blue 71 in a circulating upflow reactor by UV/TiO_2 process and employing a new method in kinetic study, J. Hazard. Mater. 144 (2007) 506–512.

[20] C.Y. Chen, M.C. Cheng, A.H. Chen, Photocatalytic decolorization of Remazol Black 5 and Remazol Brilliant Orange 3R by mesoporous TiO_2, J. Environ. Manag. 102 (2012) 125–133.

[21] Z. Cheng, X. Quan, Y. Xiong, L. Yang, Y. Huang, Synergistic degradation of methyl orange in an ultrasound intensified photocatalytic reactor, Ultrason. Sonochem. 19 (2012) 1027–1032.

[22] A.H. Alwash, A.Z. Abdullah, N. Ismail, Zeolite Y encapsulated with Fe–TiO_2 for ultrasound-assisted degradation of amaranth dye in water, J. Hazard. Mater. 233–234 (2012) 184–193.

[23] S.K. Tang, T.T. Teng, A.F.M. Alkarkhi, Z. Li, Sonocatalytic degradation of Rhodamine B in aqueous solution in the presence of TiO_2 coated activated carbon, APCBEE Procedia 1 (2012) 110–115.

[24] N. Ghows, M.H. Entezari, Exceptional catalytic efficiency in mineralization of the reactive textile azo dye (RB5) by a combination of ultrasound and core–shell nanoparticles (CdS/TiO_2), J. Hazard. Mater. 195 (2011) 132–138.

[25] A.Z. Abdullah, P.Y. Ling, Heat treatment effects on the characteristics and sonocatalytic performance of TiO_2 in the degradation of organic dyes in aqueous solution, J. Hazard. Mater. 173 (2010) 159–167.

[26] M. Abbasi, N.R. Asl, Sonochemical degradation of Basic Blue 41 dye assisted by nanoTiO_2 and H_2O_2, J. Hazard. Mater. 153 (2008) 942–947.

[27] M.Yalılı Kılıç, K.Kestioğlu, Endüstriyel Atıksuların Arıtımında İleri Oksidasyon Proseslerinin Uygulanabilirliğinin Araştırılması (The investigation of applicability advanced oxydation processes in removal of industrial waste water), Uludağ Üniversitesi Mühendislik-Mimarlık Fakültesi Dergisi 13(1) (2008) 67.

[28] C. Pan, Y. Zhu, New type of $BiPO_4$ oxy-acid salt photocatalyst with high photocatalytic activity on degradation of dye, Environ. Sci. Technol. 44 (2010) 5570–5574.