Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1087880

57 (2016) 17955–17962
August

Synergetic degradation of benzotriazole by ultraviolet and ultrasound irradiation

Chengqiang Wu*, Li Xu, Kangling Bian, Xiao Chen, Feng He

College of Biological and Environmental Engineering, Zhejiang University of Technology, 18 Chaowang Road, Hangzhou, P.R. China, Tel./Fax: +86 571 88871099; emails: wucq@zjut.edu.cn (C. Wu), 845828588@qq.com (L. Xu), biankangling@163.com (K. Bian), cx@zjut.edu.cn (X. Chen), fenghe@zjut.edu.cn (F. He)

Received 7 December 2014; Accepted 16 August 2015

ABSTRACT

The sonophotolytic degradation of benzotriazole (BTri) in aqueous solution was investigated in this study by combining ultrasound (20 kHz) and ultraviolet irradiation ($\lambda = 254$ nm). The ultrasound-caused pyrolysis was found to effectively promote the photochemical degradation of BTri and the corresponding synergetic effects were studied under different reaction conditions. Lower pH and higher ultrasonic power enhanced the BTri removal. However, the synergy between UV and US was much stronger at higher pH. The 15 min BTri removal at pH 3 was about four times of that at pH 9, while the synergy at pH 3 was nearly one-third of that at pH 9. The BTri removal increased with reaction time but the synergy decreased. Kinetics studies revealed that the degradation process followed the pseudo-first-order model.

Keywords: Benzotriazole; Removal; Synergy; Ultrasound; Ultraviolet light

1. Introduction

Benzotriazole (BTri) has been commonly used as an industrial chemical with versatile applications for technical and commercial production [1–3], which results in high entry of BTri into freshwater and marine environments [4,5]. BTri is highly polar and very mobile in the aquatic environment and it is stable against biological decomposition [6–9]. BTri with concentration higher than 100 mg/L can cause acute toxicity to prokaryotic and eukaryotic organisms [10]. Therefore, efficient treatment technologies for BTri wastewater are in high demand.

Advanced oxidation processes (AOPs) such as photochemical oxidation, photocatalysis, ultrasonic oxidation, ozone, hydrogen peroxide process, etc., have shown high efficiencies for destruction of refractory pollutants in wastewater [11–14]. Particularly, UV photolysis could be an efficient treatment method for BTri degradation in wastewater due to its high photochemical sensitivity [15]. With UV irradiation, different transient species can be generated: e^-_{ap} (photoionization), radicals generated by bond homolysis or bond heterolysis, etc. [16,17]. The photochemical degradation pathway of BTri can be summarized in Fig. 1 [18–20].

After receiving photon energy, BTri is at an excitation state and, therefore N–N bond fission and N–NH bond scission occur from the S1 (π, π*) state to produce diazoimine (Step 1 in Fig. 1), which is unstable at temperatures higher than 110 K. Diazoimine is then converted to carbene photochemically or thermally

---

*Corresponding author.

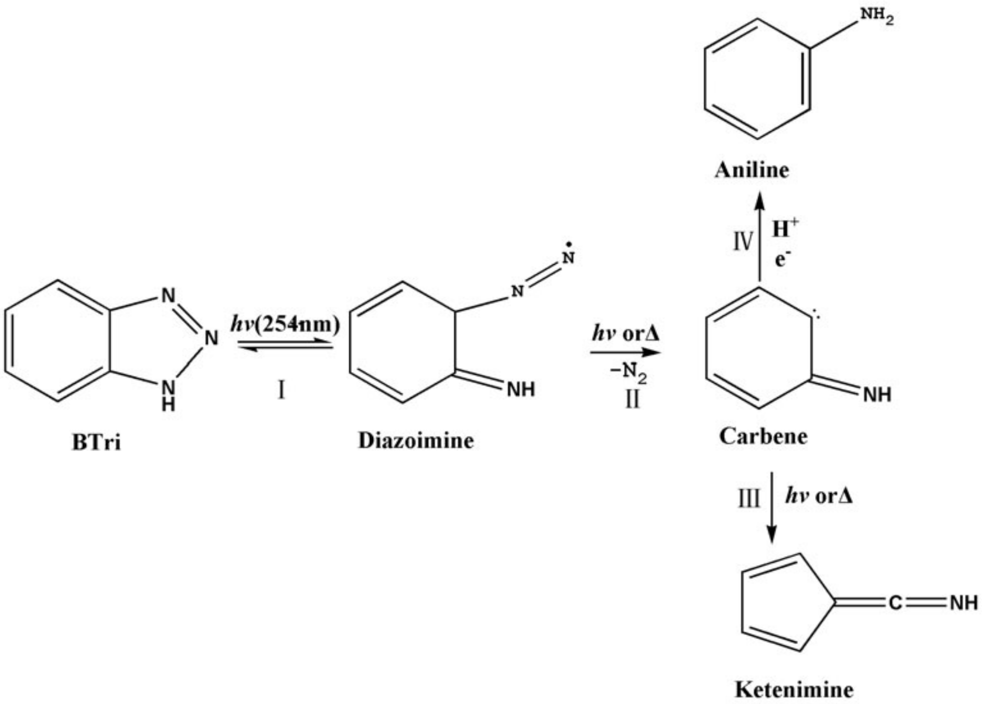

Fig. 1. Photochemical degradation pathway of Benzotriazole.

(Step 2). Carbene may undergo a photochemical or thermal rearrangement to generate ketenimine (Step 3). On the other hand, carbene is capable of abstracting hydrogen to form aniline (Step 4). Moreover, hydroxyl radical ($HO^{\cdot}$) might also be generated during photolysis of BTri through various pathways, which may induce radical oxidation.

In order to effectively utilize UV light and obtain higher degradation efficiency, other techniques, such as H_2O_2, TiO_2 film/electrode, and ultrasound (US), have been jointly used with UV light [19,21–26]. It is reported that a synergistic effect of ultrasound and visible light irradiations existed in degrading organics [23–25]. A synergy factor of 2.5 based on pseudo-first-order reaction rate constant (k_{obs}) was reported for degradation of azo dye reactive black 5 by US/UV/Fe^{3+}, along with enhanced organic detoxification and mineralization [26]. However, there are few literatures on degradation of BTri by combining UV light with other techniques such as ultrasound.

Ultrasound (US) can produce an oxidative environment via acoustic cavitation due to the formation and subsequent collapse of microbubbles, which generates localized, transient high temperatures (≥5,000 K) and pressures (≥1,000 atm) [27]. For sonodegradation, two main reaction mechanisms have been proposed [28]. The first mechanism is pyrolysis in the cavitations of bubble which is expected to be the major reaction pathway for the degradation of nonpolar compounds. The second mechanism is the generation of hydroxyl radicals in the cavitations of bubble which subsequently oxidize the polar organic compounds. The pyrolysis effect produced by US might accelerate photochemical degradation of BTri, especially through reaction Steps of 2 and 3 as described in Fig. 1. Therefore, we hypothesize that combining UV and US (i.e. UV–US) could significantly enhance the photochemical degradation of BTri.

The objective of this study was to identify and quantify the synergistic effect between US and UV in BTri degradation. The effects of reaction parameters on BTri removal by UV–US were also evaluated. Additionally, the kinetics of BTri degradation by UV–US was investigated.

2. Experimental

2.1. Chemicals

1H-Benzotriazole (>99.5% purity) was purchased from Wuxi Haishuo Biology Co., Ltd. Sodium hydroxide (>96% purity) was obtained from Hangzhou Xiaoshan Chemical Reagent factory. Sodium hydroxide solution was used to dissolve benzotriazole. Acetonitrile (HPLC grade) was obtained from Fisher Chemical Company. The solution pH was adjusted with sodium hydroxide or hydrochloric acid solution. All aqueous solutions were prepared using deionized water.

2.2. Apparatus

A bath system for ultrasonic experiments was adopted [29]. The ultrasonic device was an ultrasonic cleaning machine QH-250 (Heat Systems-W cm-ultrasonics, 20 kHz). The sonophotochemical degradation of BTri was performed in a single double-surrounded cylindrical photoreactor ($D = 90$ mm, $H = 150$ mm) as shown in Fig. 2. The volume of the reaction solution was 200 ml. An 18-W UVC lamp with a major emission wavelength of 253.7 nm was used as the light source for the degradation experiments. The reaction temperature inside the reaction vessel was controlled at 25 ± 1℃ via a thermostate bath and water circulation system.

2.3. Analytical methods

BTri in aqueous solutions was subjected to UV irradiation with and without ultrasonic irradiation. Absorbance measurements were performed using a UV–vis spectrophotometer (Meipuda UV-3200, Shanghai, China). The concentration of BTri was determined using a high-performance liquid chromatography (HPLC 1200, Agilent) equipped with a Hiqsil C18 ODS column (4.6 mm × 150 mm) and a UV detector (G1314B). The mobile phase was 30% acetonitrile and 70% water with a flow rate of 0.8 ml min^{-1}. The wavelength of the UV detector was set at 259 nm. All pH measurements were made using a digital pH meter (PHSJ-4A).

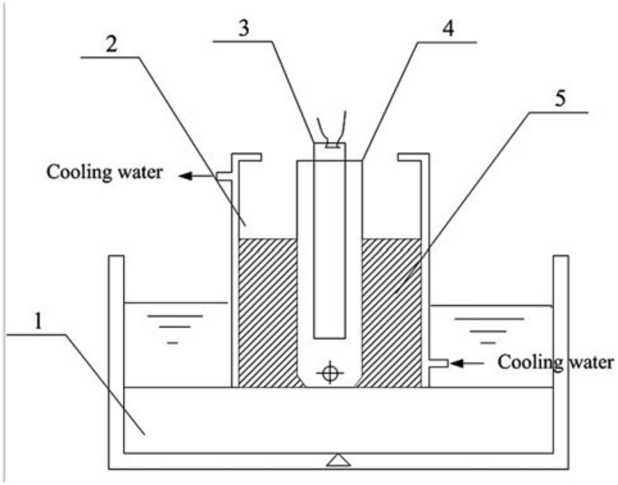

Fig. 2. Diagram of photosonochemical reactor.
Notes: (1) ultrasonic device, (2) photoreactor, (3) UV light, (4) quartz sleeve, and (5) BTri solution.

3. Results and discussion

3.1. Sonophotochemical degradation of BTri

Sonophotochemical degradation of BTri was carried out in the cylindrical jacketed glass cell as described above. The BTri showed maximum absorbance at 259 nm in aqueous medium and the change of maximum adsorbance at 268 nm was monitored on the reaction progress (Fig. 3). After 30 min of sonophotolysis, most BTri were decomposed with a rapid decrease in absorbance peak. As revealed in Fig. 4, BTri was largely decomposed into four to five products. It was reported that BTri could be decomposed into phenazine, aniline, and 2,6-diethylaniline by UV irradiation [30,31].

The peak area of BTri on high-performance liquid chromatography was monitored to study the degradation progress. The BTri removal for each treatment is given by Eq. (1):

$$\text{BTri removal}\,(\%) = (C_0 - C)/C_0 \times 100\% \tag{1}$$

where C_0 and C are initial BTri concentration and BTri concentration at time t (min), respectively.

As shown in Fig. 5, BTri was completely destroyed after a reaction time of 120 min by UV–US, while BTri degradation by UV irradiation was 88.11% and BTri degradation by US was negligible. Therefore, photolysis is the major reaction pathway for degradation of BTri, while pyrolysis and radical oxidation caused by US cannot effectively degrade BTri. As a result, Step 1 in the BTri photochemical degradation pathway (Fig. 1) is very critical for its decomposition. Step 1 was accomplished after BTri receiving protons from UV light and the next steps (i.e. Steps 2 and 3) could go thermally. Since pyrolysis caused by US can speed up these steps, combining US with UV induced more rapid and complete BTri degradation.

3.2. Effect of pH

Solution pH is one of the most important parameters affecting BTri removal as pH affects the form of BTri in aqueous phase. The BTri dissociation equilibrium is given in Eq. (2):

$$\text{BTri} \rightleftharpoons \text{BTri}^- + \text{H}^+ \quad (\text{p}K_\text{a} = 8.2 - 8.8) \tag{2}$$

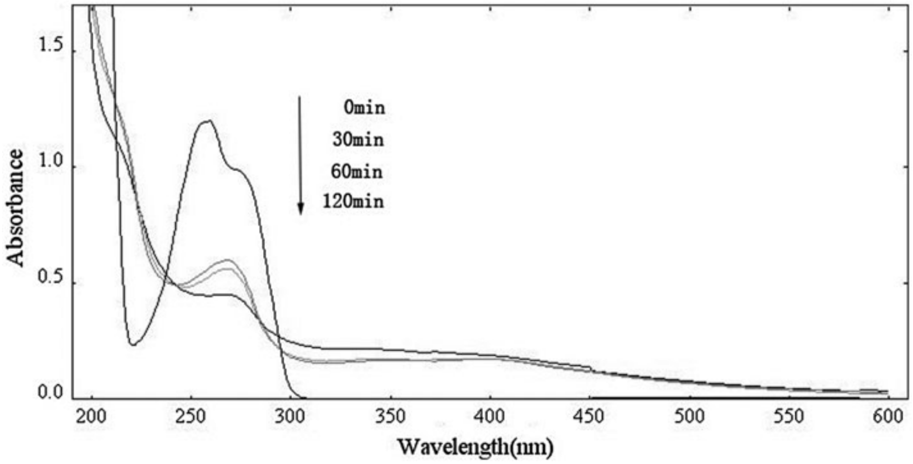

Fig. 3. Change of the UV–vis spectra during BTri sonophotolysis (Reaction conditions: [BTri] = 23 mg/L, US: 20 kHz, UV:18 W, pH 3.0).

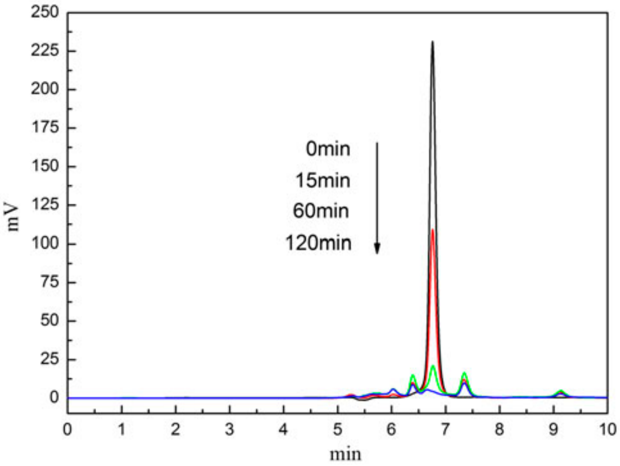

Fig. 4. HPLC chromatograms depicting eluted peaks at different photosonochemical reaction times ([BTri] = 23 mg/L, US: 20 kHz, UV: 18 W, pH 3.0).

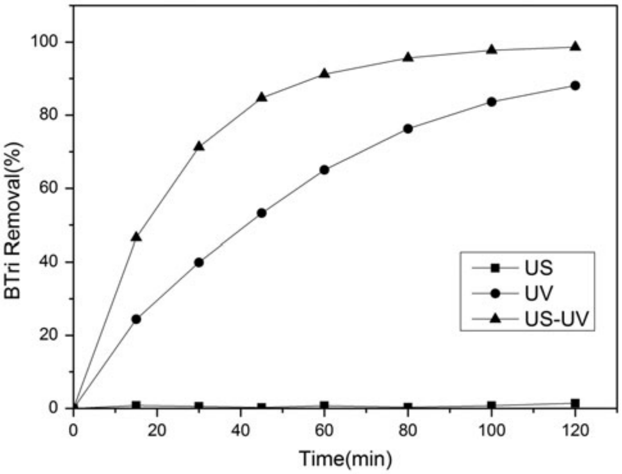

Fig. 5. Degradation of BTri with time by UV, US, and UV–US ([BTri] = 23 mg/L, US: 20 kHz, US power :250 W, UV:18 W, pH 3.0).

The effect of pH ranging from 3 to 9 on the degradation of BTri by UV–US is presented in Fig. 6(a). The results indicate that degradation of BTri is pH dependent and a lower pH is beneficial for the degradation reaction. The BTri removal reached 98.59% at pH 3 and smoothly decreased to 94.63% with the increase in pH from 3 to 7. When the solution pH further increased from 7 to 9, BTri removal significantly decreased to 74.74%. These results are in accordance with the previous findings that BTri was effectively removed from wastewater at $pH < 7$ by UV treatment [29]. Since the pK_a of BTri is 8.2–8.8 [1,15], BTri exists mainly as dissociated form at pH higher than pK_a. It was reported that the non-dissociated form of BTri was much more photoreactive than the dissociated one [15]. Indeed, the degradation of BTri by UV in our study was much more efficient at pH lower than 7 where BTri was present as the non-dissociated form (Fig. 6(b)). Therefore, lower pH was beneficial for UV absorption, which is the first and the limiting step for BTri degradation by UV–US. As a result, lower pH promoted the BTri degradation by UV–US. We note that the degradation of BTri by US was negligible at pHs ranging from 3 to 9. Since BTri removal by UV–US is much higher than that by UV, there exists a synergetic effect between UV and US for BTri degradation, which will be further discussed.

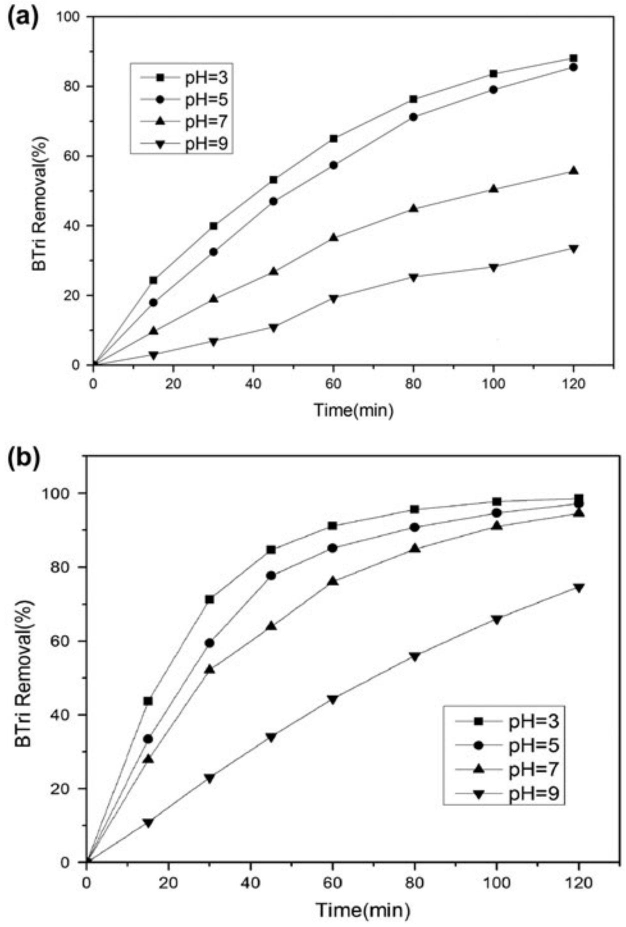

Fig. 6. Effect of pH on BTri degradation by UV–US and UV ([BTri] = 23 mg/L, US: 20 kHz, US power: 250 W, UV: 18 W).

3.3. Effect of ultrasonic power

Fig. 7 shows the change of BTri removal with the variation of US power at pH 3. The BTri removal at 120 min was only 83.37% when the ultrasonic power was 50 W, which is comparable to that without using any ultrasonic power. An increase in ultrasonic power from 50 to 100 W dramatically increased the BTri removal to 96.93%. Further increasing the ultrasonic power to 250 W only mildly enhanced the BTri removal to 98.59%. Therefore, BTri degradation is dependent on the acoustic intensity and the higher the ultrasonic power, the better the BTri removal. With the increase in ultrasound power, the pyrolysis caused by ultrasound is strengthened, which can promote Steps 2 and 3 of the BTri photochemical degradation. This promotion was most effective at US power ranging from 50 to 100 W but decreased after 100 W, which indicates pyrolysis caused by US is not linear but rather flat out at high US power. Ultrasound may also enhance mass transfer in the liquid phase [32], which can enhance the BTri removal. In addition, increasing US power produces more highly reactive primary radicals such as HO$^•$ and H$^•$ [31], which can contribute to BTri degradation. However, this contribution should be limited since US itself cannot effectively degrade BTri.

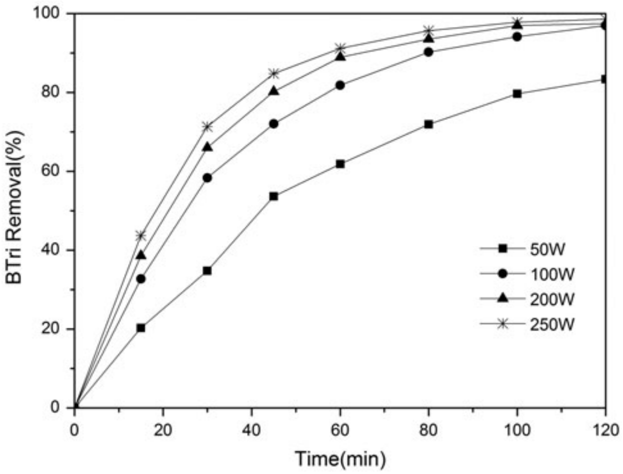

Fig. 7. The influence of ultrasonic power on the degradation of BTri by UV–US ([BTri] = 23 mg/L, US: 20 kHz, UV: 18 W, pH 3.0).

3.4. Synergy of US and UV

Fig. 8 shows the synergy (*S*) of sonophotolytic degradation of BTri at different pH. The synergism between the photolysis and sonolysis was determined using BTri removal. The synergy (*S*) is defined as

$$S = [R_{\text{US-UV}} - (R_{\text{US}} + R_{\text{UV}})]/(R_{\text{US}} + R_{\text{UV}}) \times 100\% \quad (3)$$

where R_{US} and R_{UV} are BTri removal by US and UV, respectively, $R_{\text{US-UV}}$ is BTri removal by the combination of UV and US (i.e. UV–US).

If *S* is greater than 0, there exist synergistic effects between UV and US. As shown in Fig. 8, synergistic effects are present at any pH throughout the whole reaction process. The synergy *S* is closely related to pH and reaction time, and increased with increasing pH and decreased with reaction time. For example, at *t* = 15 min, the *S* at pH 3, 7, and 9 was 84.7, 185.2, and 264.4%, respectively.

Although a higher BTri removal by UV–US was obtained at lower pH, the synergy between UV and US was much stronger at higher pH. The 15-min BTri

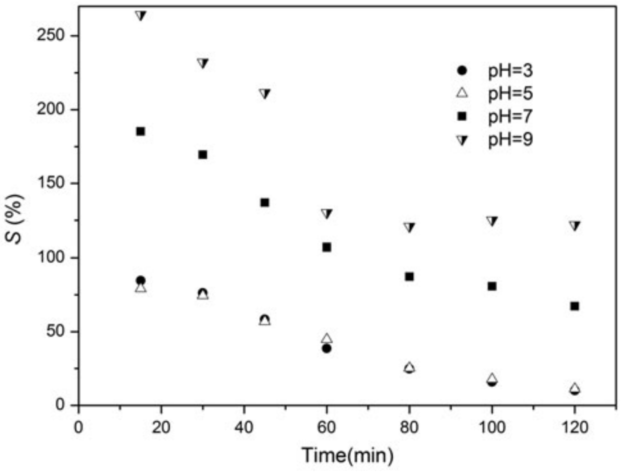

Fig. 8. Synergy of BTri degradation by UV–US as a function of reaction time and pH ([BTri] = 23 mg/L, US: 20 kHz, US power: 250 W, UV: 18 W).

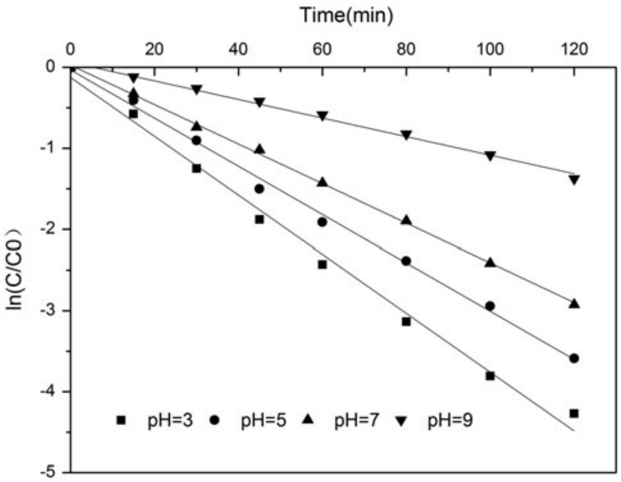

Fig. 9. First-order kinetic plots of BTri degradation by UV–US at different ([BTri] = 23 mg/L, US: 20 kHz, US power: 250 W, UV: 18 W).

removal at pH 3 was about four times of that at pH 9, while the synergy at pH 3 was only one-third of that at pH 9.

When pH was lower than 5, the synergy was kept almost constant and was hardly influenced by pH. As previously reported [15], the absorbance of BTri solution at 254 nm was constant at pH lower than 5 and the BTri was predominantly present as non-dissociated form. The higher synergy of UV–US at pH > 5 indicates that US is more effective in promoting the degradation of dissociated form of BTri. This may be explained by the fact that the dissociated form of BTri is less photoreactive than the non-dissociated form. Since Steps 2 and 3 of the photodegradation of BTri can be either promoted by UV or heat, the pyrolysis provided by US becomes more important at higher pH where the dissociated BTri is less photoreactive. Actually, because the decrease in R_{UV} with the increase in pH from 5 to 9 is much more dramatic than the decrease in $R_{\mathrm{UV–US}}$ as shown in Fig. 6(b) and R_{US} is almost negligible, the S significantly increases with this pH increase based on Eq. (3). In addition, the synergy S decreases with time at any pH. This can be explained by the fact that the increase in $R_{\mathrm{UV–US}}$ with time is slower than the increase in R_{UV} at later stage (Fig. 6), which results in the decrease in S based on Eq. (3).

Ma et al. [23] investigated the decomposition of an azo dye in aqueous solution by combining ultrasound and visible light and a synergistic effect was observed. The degradation of benomyl by the sonophotocatalytic system was greatly higher than that by the photocatalytic system [24]. The sonophotodegradation of 2,4,6-trichlorophenol (TCP) in a homogeneous aqueous system was also investigated and the synergy between US and UV was only as high as 12.22% [25], which is far lower than that observed in our study. Therefore, for the degradation of different organics by UV–US, the synergistic effect between UV and US commonly exists but the degree varies.

Table 1
Rate constants for the degradation of BTri by UV–US

The pattern of radiation	pH value	k_{obs} (min^{-1})	r^2	$t_{1/2}$ (min)
US/UV	3	3.61×10^{-2}	0.992	19.17
US/UV	5	2.97×10^{-2}	0.996	23.31
US/UV	7	2.44×10^{-2}	0.999	28.44
US/UV	9	1.15×10^{-2}	0.992	60.44
UV	3	1.79×10^{-2}	0.999	38.62
UV	5	1.64×10^{-2}	0.994	42.29
UV	7	0.69×10^{-2}	0.994	99.59
UV	9	0.36×10^{-2}	0.980	192.56

3.5. Kinetics study

The degradation of BTri by UV–US and UV can be well fitted by pseudo-first-order reaction kinetics. The related kinetic model is shown as Eq. (4):

$$\ln C/C_0 = -kt \tag{4}$$

where C_0 and C are initial BTri concentration and BTri concentration at time t (min), respectively, t is sonophotolysis time (min), and k is the rate constant (min^{-1}). The linear relationship between the $\ln C/C_0$ and reaction time at different pH is shown in Fig. 9 and the related regression coefficients are listed in Table 1.

The calculated k_{obs} at pH 3 for BTri degradation by UV–US is three times as much as that at pH 9. Therefore, BTri reduction was enormously affected by pH. Moreover, the k_{obs} of 3.61×10^{-2} min^{-1} by UV–US is twice as much as that of 1.79×10^{-2} min^{-1} by UV (k_{obs} from US is almost 0), which indicated the obvious synergetic effect between UV and US.

4. Conclusion

In this paper, we studied the synergetic degradation of benzotriazole by ultraviolet and ultrasound irradiation. There was an obvious synergistic effect between UV and US on the degradation of benzotriazole. The synergy of UV and US strongly depended on the pH and reaction time. Higher BTri removal by UV–US could be obtained at lower pH, while the synergy of UV and US was much stronger at higher pH. With reaction time going, BTri removal increased but the synergy decreased. Moreover, the BTri degradation was also affected by ultrasonic power, and higher ultrasonic power could greatly increase BTri removal. The BTri degradation process was well fitted by pseudo-first-order model. The synergetic effect appears to relate to photochemical degradation of BTri degradation. US could accelerate the decomposition of intermediates from photochemical processes via pyrolysis. Further experiments should be performed to further explore the BTri degradation mechanism.

Acknowledgment

This work is supported by the Natural Science Foundation of Zhejiang Province (Y5110141).

References

[1] S. Weiss, J. Jakobs, T. Reemtsma, Discharge of three benzotriazole corrosion inhibitors with municipal wastewater and improvements by membrane bioreactor treatment and ozonation †, Environ. Sci. Technol. 40 (2006) 7193–7199.

[2] D. Voutsa, P. Hartmann, C. Schaffner, W. Giger, Benzotriazoles, Alkylphenols and Bisphenol A in Municipal Wastewaters and in the Glatt River, Switzerland, Environ. Sci. Pollut. Res. 13(5) (2006) 333–341.

[3] J. Kim, T. Isobe, G. Malarvannan, A. Sudaryanto, K. Chang, M. Prudente, S. Tanabe, Contamination of benzotriazole ultraviolet stabilizers in house dust from the Philippines: Implications on human exposure, Sci. Total Environ. 424 (2012) 174–181.

[4] D.S. Hart, L.C. Davis, L.E. Erickson, T.M. Callender, Sorption and partitioning parameters of benzotriazole compounds, Microchem. J. 77 (2004) 9–17.

[5] H. Janna, M.D. Scrimshaw, R.J. Williams, J. Churchley, J.P. Sumpter, From dishwasher to tap? xenobiotic substances benzotriazole and tolyltriazole in the environment, Environ. Sci. Technol. 45 (2011) 3858–3864.

[6] T. Reemtsma, S. Weiss, J. Mueller, M. Petrovic, S. González, D. Barcelo, F. Ventura, T.P. Knepper, Polar pollutants entry into the water cycle by municipal wastewater: A European perspective, Environ. Sci. Technol. 40 (2006) 5451–5458.

[7] W. Giger, C. Schaffner, H.E. Kohler, Benzotriazole and tolyltriazole as aquatic contaminants. 1. Input and occurrence in rivers and lakes †, Environ. Sci. Technol. 40 (2006) 7186–7192.

[8] A. Kloepfer, M. Jekel, T. Reemtsma, Occurrence, sources, and fate of benzothiazoles in municipal wastewater treatment plants, Environ. Sci. Technol. 39 (2005) 3792–3798.

[9] K.J. Woodcroft, C.D. Webb, M. Yao, A.C. Weedon, J.R. Bend, Metabolism of the P450 mechanism-based inhibitor N-benzyl-1-aminobenzotriazole to products that covalently bind with protein in Guinea pig liver and lung microsomes: Comparative study with 1-aminobenzotriazole, Chem. Res. Toxicol. 10(5) (1997) 589–599.

[10] D.A. Pillard, J.S. Cornell, D.L. DuFresne, M.T. Hernandez, Toxicity of benzotriazole and benzotriazole derivatives to three aquatic species, Water Res. 35(2) (2001) 557–560.

[11] G.G. Ying, R.S. Kookana, D.W. Kolpin, Occurrence and removal of pharmaceutically active compounds in sewage treatment plants with different technologies, J. Environ. Monit. 11 (2009) 1498–1505.

[12] A. Rehorek, M. Tauber, G. Gubitzb, Application of power ultrasound for azo dye degradation, Ultrason. Sonochem. 11 (2004) 177–182.

[13] D.B. Mawhinney, B.J. Vanderford, S.A. Snyder, Transformation of 1H-benzotriazole by ozone in aqueous solution, Environ. Sci. Technol. 46 (2012) 7102–7111.

[14] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, Catal. Today 53 (1999) 51–59.

[15] R. Andreozzi, V. Caprio, A. Insola, G. Longo, Photochemical degradation of benzotriazole in aqueous solution, J. Chem. Technol. Biotechnol. 73 (1988) 93–98.

[16] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, J. Chem. Rev. 93 (1993) 671–698.

[17] H.D. Burrows, M. Canle L, J.A. Santaballa, S. Steenken, Reaction pathways and mechanisms of photodegradation of pesticides, J. Photochem. Photobiol. B 67 (2002) 71–108.

[18] H. Shizuka, H. Hiratsuka, M. Jinguji, H. Hiraoka, Photolysis of benzotriazole in alcoholic glass at 77 K, Phys. Chem. 91 (1987) 1793–1797.

[19] Y. Ding, C. Yang, L. Zhu, J. Zhang, Photoelectrochemical activity of liquid phase deposited TiO_2 film for degradation of benzotriazole, J. Hazard. Mater. 175 (2010) 96–103.

[20] P.A. Wender, S.M. Touami, C. Alayrac, U.C. Philipp, Triazole photonucleases: A new family of light activatable DNA cleaving agents, J. Am. Chem. Soc. 118 (1996) 6522–6523.

[21] P. Strauel, Destruction of photographic developer solution by a UV/H_2O_2 oxidation process, International Conference on Oxidation Technologies for Water and Wastewater Treatment, Goslar, Germany, 12 May 1996.

[22] L. Lhomme, S. Brosillon, D. Wolbert, Photocatalytic degradation of a triazole pesticide, cyproconazole, in water, J. Photochem. Photobiol. A 188 (2007) 34–42.

[23] C.Y. Ma, J.Y. Xu, X.J. Liu, Decomposition of an azo dye in aqueous solution by combination of ultrasound and visible light, Ultrasonics 44 (2006) e375–e378.

[24] J.H. Park, Photochemical degradation and toxicity reduction of methyl 1-[(butylamino)carbonyl]-1H-benzimidazol-2-ylcarbamate in agricultural wastewater: Comparative study of photocatalysis and sonophotocatalysis, Desalination 249(2) (2009) 480–485.

[25] C.G. Joseph, G.L. Puma, A. Bono, Y.H. Taufiq-Yap, D. Krishnaiah, Operating parameters and synergistic effects of combining ultrasound and ultraviolet irradiation in the degradation of 2,4,6-trichlorophenol, Desalination 276 (2011) 303–309.

[26] T. Zhou, T.T. Lim, X. Wu, Sonophotolytic degradation of azo dye reactive black 5 in an ultrasound/UV/ferric system and the roles of different organic ligands, Water Res. 45(9) (2011) 2915–2924.

[27] K.S. Suslick, Sonochemistry, in: Kirk-Othmer Encyclopedia of Chemical Technology, vol. 26, fourth ed., Wiley & Sons, New York, NY, 1998, pp. 517–541.

[28] P. Chowdhury, T. Viraraghavan, Sonochemical degradation of chlorinated organic compounds, phenolic compounds and organic dyes—A review, Sci. Total Environ. 407 (2009) 2474–2492.

[29] L.J. Hem, T. Hartnik, R. Roseth, G.D. Breedveld, Photochemical degradation of benzotriazole, J. Environ. Sci. Health A 38(3) (2003) 471–481.

[30] Y.S. Liu, G.G. Ying, A. Shareef, R.S. Kookana, Photolysis of benzotriazole and formation of its polymerised photoproducts in aqueous solutions under UV irradiation, Environ. Chem. 8 (2011) 174–181.

[31] B. Neppolian, A. Doronila, F. Grieser, M. Ashokkumar, Simple and efficient sonochemical method for the oxidation of arsenic(III) to arsenic(V), Environ. Sci. Technol. 43 (2009) 6793–6798.

[32] M.T. Taghizadeh, R. Abdollahi, Sonolytic, sonocatalytic and sonophotocatalytic degradation of chitosan in the presence of TiO_2 nanoparticles, Ultrason. Sonochem. 18 (2011) 149–157.