Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1089196

57 (2016) 18168–18174
August

Contribution of hydroxyl radicals to the degradation of Acid Orange 7 by fly ash under ultrasonic irradiation

Guoting Li*, Yanmin Feng, Binbin Wang, Minduo Wang

Department of Environmental and Municipal Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450011, China, Tel. +86 371 69127436; Fax: +86 371 65790239; emails: liguoting@ncwu.edu.cn (G. Li), 15038286924@163.com (Y. Feng), huashuiwangbinbin@163.com (B. Wang), 1461570603@qq.com (M. Wang)

Received 12 January 2015; Accepted 24 August 2015

ABSTRACT

Ultrasonic irradiation (US) alone usually has comparatively low ultrasonic degradation efficiency for limited organic pollutants. In this research, fly ash, an industrial waste from thermal power plant, was used to assist ultrasonic degradation of Acid Orange 7, a common dye pollutant. The decolorization efficiency within 60 min by US alone, fly ash adsorption alone and the combined process were of 3.8, 41.5, and 76.7%, respectively. The contribution of hydroxyl radicals was investigated systematically by indirect iso-propanol quenching method. Although more dyes were degraded by hydroxyl radicals in fly ash-assisted US than in US alone, the contribution percentage of hydroxyl radicals in the former system was much lower than that in the latter system, being 24.8 and 53.4%, respectively. The results showed that pH had significant impact on the degradation efficiency of dye due to its influence on generation of hydroxyl radicals. The coexistence of chloride, sulfate, and nitrate anions inhibited the contribution of hydroxyl radicals. In comparison to fly ash, diatomite and tourmaline were capable of facilitating the generation of more OH radicals, while kaoline actually reduced the contribution percentage of hydroxyl radicals.

Keywords: Degradation; Hydroxyl radicals; Contribution percentage; Ultrasonic irradiation; Fly ash

1. Introduction

Advanced oxidation processes (AOPs) are defined as technologies to employ highly reactive hydroxyl radicals as the main oxidative species for the breakdown of organic contaminants [1,2]. Along with several decades of development, AOPs have been applied for degradation of a large variety of organic pollutants in wastewater treatment. As one of the AOPs, ultrasound technology is extensively used in laboratories, food industry, municipal sludge treatment plants, and cleaning applications across the commercial and industrial sectors [3]. The ultrasonic reactions depend upon the ultrasound-induced cavitation bubbles, and the implosion of these bubbles could generate localized temperatures and pressures on the order of 5,000 K and hundreds of atmospheres, respectively. Consequently, thermal dissociation of water vapor into reactive hydroxyl radicals and other radicals occurs as the following equations [2,4,5]:

$$H_2O \rightarrow H^{\cdot} + OH^{\cdot} \quad (1)$$

---

*Corresponding author.

$$O_2 \rightarrow 2{}^{\bullet}O \qquad (2)$$

$${}^{\bullet}O + H_2O \rightarrow 2HO^{\bullet} \qquad (3)$$

$$H^{\bullet} + O_2 \rightarrow HO^{\bullet} + O \qquad (4)$$

Although the parent pollutants can be degraded effectively and efficiently by ultrasonic irradiation (US), the polar degradation intermediates such as low-molecular-weight organic acids generally accumulate due to their slow degradation rate [6]. Recently, some materials have been employed as catalyst to enhance the overall remediation efficiency of sonochemical degradation [7]. The degradation performance of ultrasonication can be accelerated by the presence of heterogeneous catalyst as nucleus [3]. If the size of catalyst particle is in the same order of magnitude as the resonance size of cavitation bubbles, these catalysts could act as cavitation nucleus [8]. As a byproduct of coal combustion in power stations, large quantities of fly ashes are produced annually, which has to be dumped into landfills. Most recently, fly ash has shown great potential for the remediation of organic pollutants. For instance, Wang et al. investigated the sonochemical treatment of fly ash and subsequent application for enhanced dye adsorption [9]. The sonochemical-treated fly ash significantly increased the adsorption capacity. Fly ash consists of particles in a wide range of sizes, and hydroxyl radicals could be generated by fly ash under US. Hence, in this study, fly ash from a thermal power plant was employed to assist the degradation of organics by US. An azo dye, Acid Orange 7 (AO7), was used as the target pollutant subjected to the combined degradation process.

In addition, the contribution of hydroxyl radicals in sonochemical degradation is still not clear, although it has been investigated in some studies [6,10]. Alcohols are commonly used to study the oxidation mechanism of hydroxyl radicals (OH radicals) in AOPs through quenching method [11–13]. One of the alcohol 1-butanol is considered as a radical scavenger for the gaseous region or the interfacial region of the collapsing bubbles [10,14]. Similarly, iso-propanol (ISP) can scavenge hydroxyl radicals and it is often used as the quencher of hydroxyl radicals to evaluate the production and contribution of hydroxyl radicals [11,13,15]. The inhibitive effect of ISP on the oxidation processes can be indicated by the decline in reaction rate constants. Therefore, in this study, the contribution of hydroxyl radicals in AO7 degradation was investigated by comparing the decolorization efficiencies and reaction rates between with and without the addition of ISP. The effects of solution pH, coexisting anions, and natural minerals on the contribution of hydroxyl radicals in fly ash-assisted ultrasonic degradation of AO7 were investigated.

2. Materials and methods

2.1. Materials and apparatus

AO7 and kaoline was purchased from Beijing Chemical Reagents Company. AO7 was selected as a model pollutant and used without further purification. Fly ash was collected from Xinli electric power plant located in Zhengzhou City (Henan province, China). Diatomite was provided by Linjiang Meston Powdery Materials Co. Ltd (Jilin Province, China). Tourmaline was obtained from Mianyang Renzhiqi Novel Materials Co. Ltd (Sichuan Province, China).

2.2. Degradation of AO7 by fly ash under US

Degradation of AO7 by fly ash-assisted US was carried out in a conical flask. The effective volume of the conical flask was 500 mL and 400 mL of AO7 solution (10 mg/L) was added. The dosage of fly ash was 3 g in 400 mL AO7 solution and solution pH was maintained at 7.0 unless otherwise stated. Sonication was performed in a 40 kHz ultrasonic cleaning bath (AS3120A, Tianjin Aotesai Instrument Co., China). The water-circulating unit was used to control water bath temperature. In the alcohol quenching tests, the dosage of ISP was 0.05 mol/L. Natural minerals such as diatomite, tourmaline, and kaoline were used under same conditions as a comparison to better understand the contribution of hydroxyl radicals.

2.3. Analyses

The concentration of AO7 was determined by measuring the maximum absorbance at a fixed wavelength (484 nm), which corresponded to the maximum absorption wavelength, using an UVmini-1240 spectrophotometer (Shimadzu, Japan). Samples were collected and filtered through a 0.45 μm membrane before analyzing.

The decrease in apparent rate constant (pseudo-first-order) K_{app} resulted from ISP quenching can be used to indicate the contribution and contribution percentages of hydroxyl radicals, which was calculated as the following equation [11,15]:

$$\text{Contribution } K_{\mathrm{app}} = K_{\mathrm{app}} - K_{\mathrm{app}} \text{ (quenching)} \qquad (5)$$

$$\text{Contribution percentage} = (1 - K_{\text{app}}\,(\text{quenching})/K_{\text{app}}) \times 100\% \tag{6}$$

The pseudo-first-order kinetics of the three processes was simulated as:

$$\ln{(C_0/C)} = K_{\text{app}}t \tag{7}$$

where C is the dye concentration at time t, C_0 is the initial dye concentration, and K_{app} is the apparent first-order rate constant.

3. Results and discussion

3.1. Degradation of AO7 by fly ash under US

US is one of the typical AOPs and hydroxyl radicals are expected to be predominant for the decolorization of AO7. As presented in Fig. 1, the decolorization efficiency by US and fly ash adsorption alone achieved 3.8 and 41.5% at 60 min, respectively. For fly ash-assisted US, the efficiency reached 76.7%, which is much higher than the other two processes. Fly ash adsorption alone could not generate hydroxyl radicals, while US is capable of producing a number of oxidizing species such as hydroxyl radicals and hydrogen peroxide [6,16]. The above results indicate that the contribution of hydroxyl radicals might be prevailing for the dye degradation by the combined process.

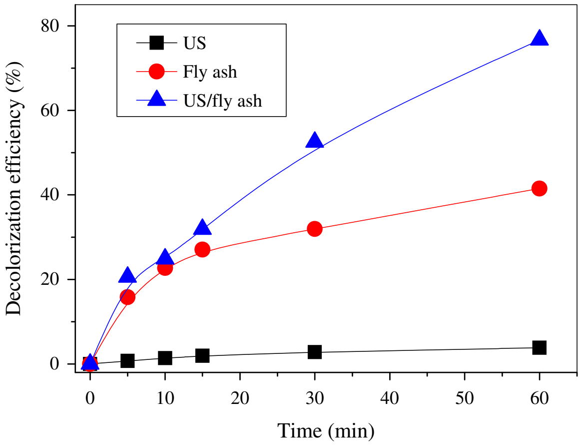

Fig. 1. Decolorization of AO7 by US, fly ash adsorption (fly ash), and fly ash under ultrasonic irradiation (US/fly ash).

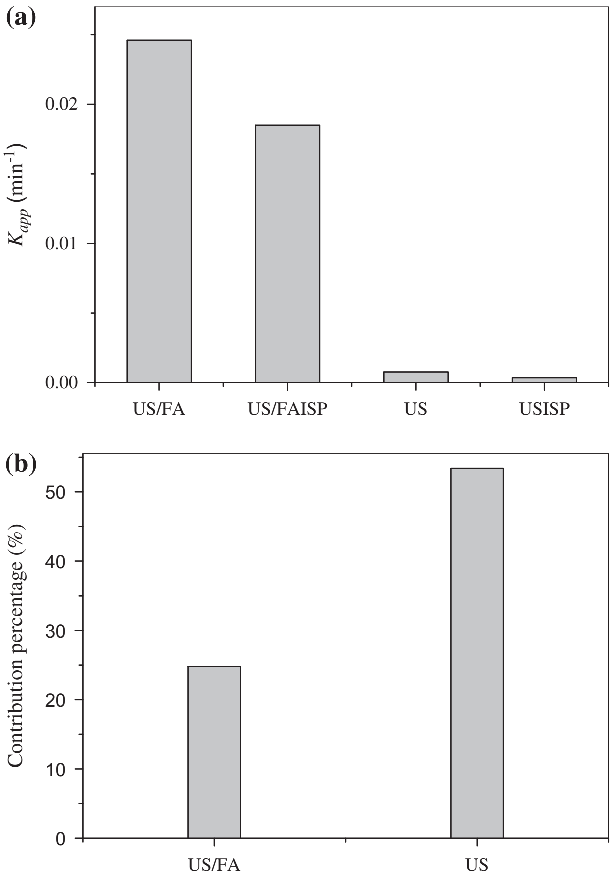

Fig. 2. The K_{app} (a) and contribution percentages of hydroxyl radicals (b) for AO7 degradation in US alone and the combined process (US/FA).

The effect of hydroxyl radicals on US alone and the combined process (US/FA) was examined by ISP quenching method, which is illustrated in Fig. 2. As presented in Fig. 2(a), the K_{app} in the combined process achieved 0.0246 min^{-1} (R^2 = 0.99), while it decreased to 0.0185 min^{-1} (R^2 = 0.97) in the presence of ISP. The K_{app} contributed by hydroxyl radicals was of 0.0061 min^{-1} in the combined process. As a comparison, the K_{app} in US decreased from 7.55×10^{-4} min^{-1} to 3.52×10^{-4} min^{-1} after adding quenching agent, which means that contribution K_{app} of hydroxyl radicals was of 4.03×10^{-4} min^{-1}. Judging from the K_{app} decrease by ISP quenching in US and the combined process, the increased amount of hydroxyl radicals was generated by US when fly ash was introduced. As a result, the combined process could be regarded as a sonocatalytic process where more hydroxyl radicals were involved in the degradation of AO7 than US alone. Nakui and co-workers also found in previous study that coal ash accelerated phenol degradation and the authors claimed it was attributed by the increase in hydroxyl radicals [17]. Meanwhile, as presented in Fig. 2(b), the contribution percentage of hydroxyl radicals in the combined process and US process are of 24.8 and

53.4%, respectively. Obviously, the K_{app} decrease is better to indicate the effect of hydroxyl radicals more accurately than contribution percentage.

3.2. Effect of solution pH on the contribution of hydroxyl radicals

Solution pH conditions could influence the charge property of AO7 and fly ash particles, and even the degradation performance by US was expected to be dependent on solution pH as well. The effect of solution pH on the production and contribution of hydroxyl radicals was investigated at pH ranging from 3.0 to 11.0. As illustrated in Fig. 3(a), the highest K_{app} value of $0.0265\ \text{min}^{-1}$ was observed at pH 5.0, while the K_{app} values at pH 3.0 and 11.0 were only 0.0139 and $0.0172\ \text{min}^{-1}$, respectively. Apparently, neutral pH conditions were favorable for AO7 degradation in the fly ash-assisted US. The K_{app} contribution of hydroxyl radicals at pH 3.0, 5.0, 7.0, 9.0, and 11.0 are of 1.161×10^{-2}, 8.04×10^{-3}, 1.004×10^{-2}, 7.78×10^{-3}, and $7.90 \times 10^{-3}\ \text{min}^{-1}$, respectively. As a comparison, as illustrated in Fig. 3(b), the contribution percentage of hydroxyl radicals at pH 3.0, 5.0, 7.0, 9.0, and 11.0 are of 57.6, 38.2, 24.8, 36.7, and 46.0%, respectively. Apparently, the contribution of hydroxyl radicals was significant under all the pH conditions examined while it was more predominant at pH 3.0. Although both the highest contribution K_{app} and contribution percentage of hydroxyl radicals were observed at pH 3.0, the highest degradation efficiency of dye was found at pH 5.0.

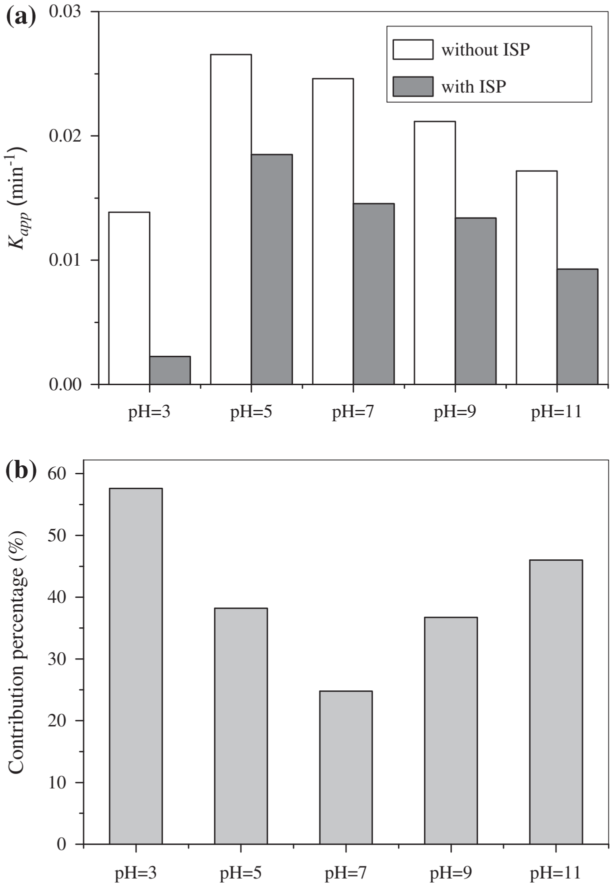

Fig. 3. Effect of solution pH on (a) K_{app} and (b) contribution of hydroxyl radicals for AO7 degradation in the combined process.

Some study found that at pH 10 $OH^{\bullet}$-induced reactions in the aqueous phase are entirely responsible for the ultrasonic degradation of phenol, whereas at pH 4 oxidative pyrolytic degradation is the predominating reaction [18]. The evidence is consistent with the aforementioned results as the oxidation mechanism by hydroxyl radicals were prevailing under alkaline condition. However, Jiang and co-workers found that the ultrasonic degradation rate for 4-nitrophenol decreased with increasing pH from 2.0 to 9.0, while the degradation rate for aniline increased with the increasing solution pH [19]. It seems that the degradation efficiency could vary with the organic pollutants involved, which might be partly attributed to the reactivity of these pollutants.

3.3. Effect of coexisting anions on the contribution of hydroxyl radicals

Coexisting anions such as chloride, sulfate, and nitrate ions might influence the decolorization process. The effect of coexisting sulfate, chloride, and nitrate anions on hydroxyl radicals contribution is presented in Fig. 4. Apparently, from Fig. 4(a), the coexistence of chloride, sulfate, and nitrate anions evidently inhibited AO7 decolorization, especially for nitrate ions. Some anions such as chloride, sulfate, and nitrate ions are considered as hydroxyl radicals scavengers as they can react with hydroxyl radicals to form weaker inorganic radical anions in photocatalytic oxidation process, as proposed in Eqs. (8)–(10) [20,21]:

$$Cl^{-} + OH^{\bullet} \rightarrow ClOH^{\bullet -} \tag{8}$$

$$NO_3^{-} + OH^{\bullet} \rightarrow NO_3^{\bullet} + OH^{-} \tag{9}$$

$$SO_4^{2-} + OH^{\bullet} \rightarrow SO_4^{\bullet -} + OH^{-} \tag{10}$$

It can be deduced that chloride, sulfate, and nitrate ions could quench hydroxyl radicals and consequently inhibit AO7 decolorization in the combined ultrasonic

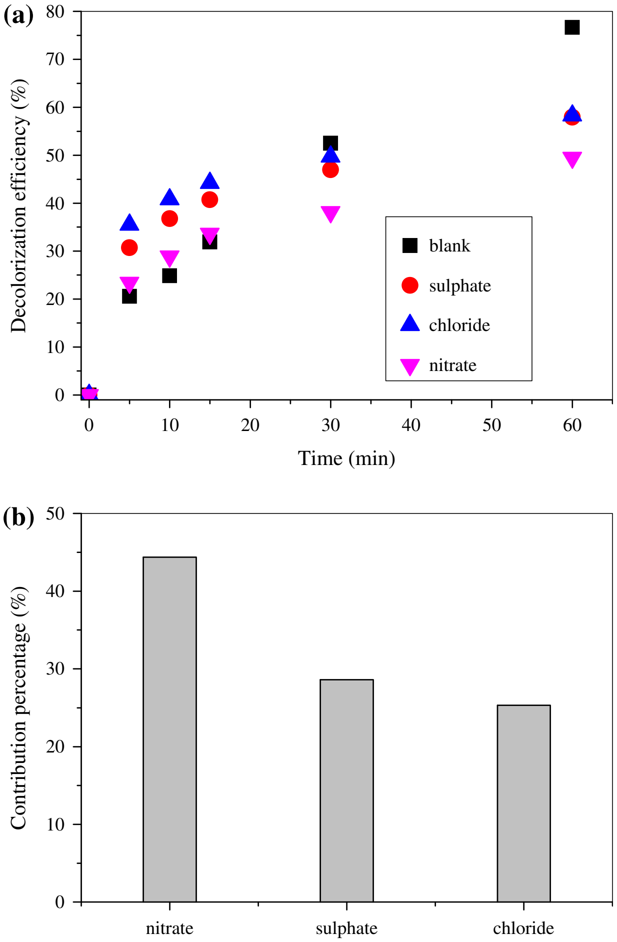

Fig. 4. Effect of coexisting sulfate, chloride, and nitrate ions on (a) K_{app} and (b) contribution percentages of hydroxyl radicals for AO7 degradation in the combined process. Coexisting anions concentration, 0.01 mol/L.

degradation process. In comparison with the K_{app} contribution of 0.0061 min^{-1} in the absence of coexisting anions, the K_{app} contribution in the presence of chloride, sulfate, and nitrate anions with a concentration of 0.01 mol/L were of 0.00622, 0.0074, and 0.01094 min^{-1}, respectively. As illustrated in Fig. 4(b), the contribution percentage of hydroxyl radicals in the presence of chloride, sulfate, and nitrate anions achieved 25.3, 28.6, and 44.4%, respectively. The above implies that the coexistence of chloride, sulfate, and nitrate ions could decline the concentration of hydroxyl radicals.

Some researchers found that the presence of NaCl (0.3419 and 1.3675 mol/L) increased ultrasonic degradation efficiency of phenol, which was attributed to the salting out effect. The increased phenol hydrophobicity resulted from the introduction of NaCl which forced phenol molecules move to the interfaces of the sonication cavities, and consequently improved the hydroxyl radicals attack on phenol molecules [22]. However, at low concentration of 0.01 mol/L, the presence of sulfate, chloride, and nitrate anions notably decreased the degradation rate. Similarly, KBr is known as a non-volatile scavenger which can be readily oxidized by free radicals, and a decrease in sodium dodecylbenzene sulfonate conversion was observed by for sonochemical degradation as well. These free radicals originate from the bulk liquid region and possibly from the interfacial region of the cavitation bubble [10,14]. Additionally, as mentioned above, the decrease in K_{app} value was evident by ISP quenching. Referring to the effect of 1-butanol, ISP could be used as a scavenger for the gaseous region and/or interfacial region of the collapsing bubble [14]. It can be concluded that AO7 degradation predominantly occurred on the interfacial region, though the degradation process also partly occurred in the bulk liquid region.

3.4. Effect of different minerals on the contribution of hydroxyl radicals

Natural minerals such as diatomite, tourmaline, and kaoline were used to investigate the effect of minerals on AO7 degradation in the combined process, as presented in Fig. 5. As presented in Fig. 5(a), the docolorization efficiencies at 60 min for fly ash, diatomite, tourmaline, and kaoline were of 76.7, 24.3, 22.8, and 2.3%, respectively. It is worthy to note that the adsorption removal by fly ash reached 41.5%, while the adsorption by the other three minerals was insignificant. On the other hand, the contribution K_{app} of hydroxyl radicals using fly ash, diatomite, tourmaline, and kaoline were of 1.004×10^{-2}, 1.94×10^{-3}, 4.37×10^{-3}, and 4.83×10^{-4} min^{-1}, respectively. As illustrated in Fig. 5(b), the contribution percentages of hydroxyl radicals using fly ash, diatomite, tourmaline, and kaoline were of 24.8, 86.0, 51.9, and 6.6%, respectively. The contribution percentage of diatomite and tourmaline were particularly higher than that of fly ash in the combined process. These results demonstrate that diatomite and tourmaline are capable of facilitating the generation of hydroxyl radicals, while kaoline actually failed to catalyze the generation of hydroxyl radicals in comparison to fly ash. Although fly ash outperforms other minerals in terms of AO7 degradation in the combined process, the effect of fly ash on the contribution of hydroxyl radicals was still not so predominant as these that of diatomite and tourmaline.

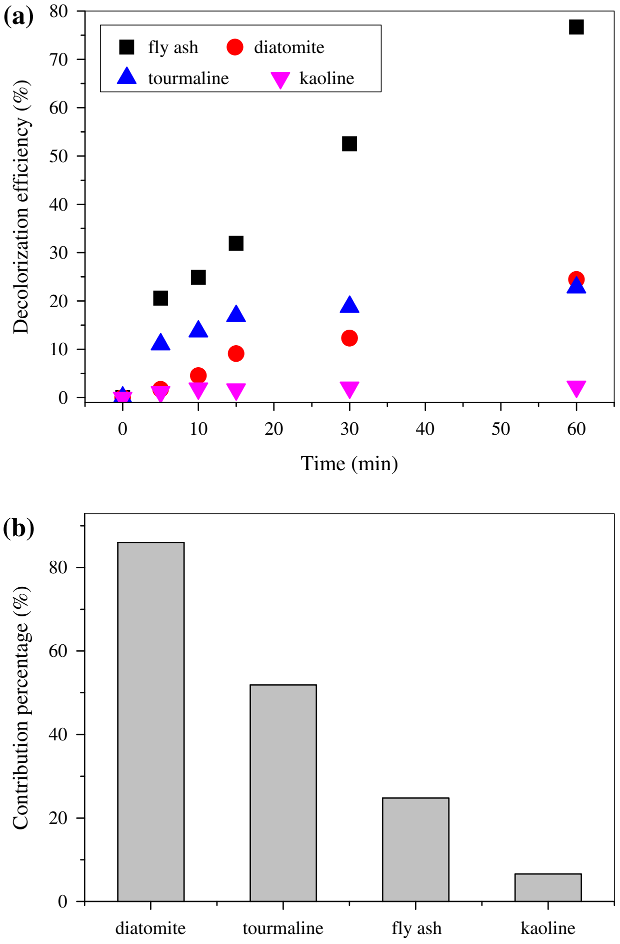

Fig. 5. Effect of different minerals on (a) K_{app} and (b) contribution percentages of hydroxyl radicals for AO7 degradation in the combined process.

4. Conclusions

During AO7 degradation by fly ash-assisted US, the contribution and contribution percentage of hydroxyl radicals were investigated by indirect ISP quenching method. The contribution of hydroxyl radicals in fly ash-assisted US was particularly higher than that in US alone, while the percentage of their contribution in the combined process was especially lower than that in US alone. Both the highest K_{app} contribution and contribution percentage of hydroxyl radicals were observed at pH 3.0, while the highest degradation efficiency was found at pH 5.0. The coexistence of chloride, sulfate, and nitrate ions inhibited the contribution of hydroxyl radicals. It proved that AO7 degradation predominantly occurred on the interfacial region. Considering the effect of fly ash, diatomite and tourmaline were capable of facilitating the generation of more hydroxyl radicals, while kaoline actually reduced the contribution percentage of hydroxyl radicals.

Acknowledgments

The authors would like to acknowledge the financial support by the Innovation Experimental Programs for college students of North China University of Water Resources and Electric Power (201319), and the foundation for university key youth teacher by Henan Province of China (2013GGJS-088).

References

[1] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, Catal. Today 53 (1999) 51–59.
[2] J. Peller, O. Wiest, P.V. Kamat, Hydroxyl radical's role in the remediation of a common herbicide, 2,4-dichlorophenoxyacetic acid (2,4-D), J. Phys. Chem. A 108 (2004) 10925–10933.
[3] L.H. Thompson, L.K. Doraiswamy, Sonochemistry: Science and engineering, Ind. Eng. Chem. Res. 38 (1999) 1215–1249.
[4] A. Henglein, Sonochemistry: Historical developments and modern aspects, Ultrasonics 25 (1987) 6–16.
[5] Y. Asakura, M. Maebayashi, S. Koda, Study on efficiency and characterization in a cylindrical sonochemical reactor, J. Chem. Eng. Japan 38 (2005) 1008–1014.
[6] J. Peller, O. Wiest, P.V. Kamat, Sonolysis of 2,4-dichlorophenoxyacetic acid in aqueous solutions. Evidence for ·OH-radical-mediated degradation, J. Phys. Chem. A 105 (2001) 3176–3181.
[7] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment I: Oxidation technologies at ambient conditions, Adv. Environ. Res. 8 (2004) 501–551.
[8] J.T. Ge, J.H. Qu, Degradation of azo dye acid red B on manganese dioxide in the absence and presence of ultrasonic irradiation, J. Hazard. Mater. 100 (2003) 197–207.
[9] S.B. Wang, Z.H. Zhu, Sonochemical treatment of fly ash for dye removal from wastewater, J. Hazard. Mater. 126 (2005) 91–95.
[10] E. Manousaki, E. Psillakis, N. Kalogerakis, D. Mantzavinos, Degradation of sodium dodecylbenzene sulfonate in water by ultrasonic irradiation, Water Res. 38 (2004) 3751–3759.
[11] G.T. Li, K.H. Wong, X.W. Zhang, C. Hu, J.C. Yu, R.C.Y. Chan, P.K. Wong, Degradation of Acid Orange 7 using magnetic AgBr under visible light: The roles of oxidizing species, Chemosphere 76 (2009) 1185–1191.
[12] Y. Sun, J.J. Pignatello, Evidence for a surface dual hole-radical mechanism in the titanium dioxide photocatalytic oxidation of 2,4-D, Environ. Sci. Technol. 29 (1995) 2065–2072.
[13] X.W. Zhang, D.D. Sun, G.T. Li, Y.Z. Wang, Investigation of the roles of active oxygen species in photodegradation of azo dye AO7 in TiO_2 photocatalysis illuminated by microwave electrodeless lamp, J. Photochem. Photobiol. A: Chem. 199 (2008) 311–315.
[14] D.G. Wayment, D.J. Casadonte, Frequency effect on the sonochemical remediation of alachlor, Ultrason. Sonochem. 9 (2002) 251–257.
[15] G.T. Li, M.Y. Zhu, J. Chen, Y.X. Li, X.W. Zhang, Production and contribution of hydroxyl radicals between

the DSA anode and water interface, J. Environ. Sci. 23 (2011) 744–748.

[16] Y. Nagata, K. Hirai, H. Bandow, Y. Maeda, Decomposition of hydroxybenzoic and humic acids in water by ultrasonic irradiation, Environ. Sci. Technol. 30 (1996) 1133–1138.

[17] H. Nakui, K. Okitsu, Y. Maeda, R. Nishimura, Effect of coal ash on sonochemical degradation of phenol in water, Ultrason. Sonochem. 14 (2007) 191–196.

[18] R. Kidak, N.H. Ince, Ultrasonic destruction of phenol and substituted phenols: A review of current research, Ultrason. Sonochem. 13 (2006) 195–199.

[19] Y. Jiang, C. Pétrier, T.D. Waite, Effect of pH on the ultrasonic degradation of ionic aromatic compounds in aqueous solution, Ultrason. Sonochem. 9 (2002) 163–168.

[20] M. Abdullah, G.K.C. Low, R.W. Matthews, Effects of common inorganic anions on rates of photocatalytic oxidation of organic carbon over illuminated titanium dioxide, J. Phys. Chem. 94 (1990) 6820–6825.

[21] S. Gazi, A. Rajakumar, N.D. Pradeep Singh, Photodegradation of organic dyes in the presence of [Fe(III)-salen]Cl complex and H_2O_2 under visible light irradiation, J. Hazard. Mater. 183 (2010) 894–901.

[22] N.N. Mahamuni, A.B. Pandit, Effect of additives on ultrasonic degradation of phenol, Ultrason. Sonochem. 13 (2006) 165–174.