

Available online at www.sciencedirect.com

ScienceDirect

www.journals.elsevier.com/journal-of-environmental-sciences

Synergistic effect of ozonation and ionizing radiation for PVA decomposition

Weihua Sun¹, Lujun Chen^{2,3,*}, Yongming Zhang¹, Jianlong Wang⁴

1. College of Life and Environmental Sciences, Shanghai Normal University, Shanghai 200234, China. E-mail: swh@shnu.edu.cn

2. School of Environment, Tsinghua University, Beijing 100084, China

3. Zhejiang Provincial Key Laboratory of Water Science and Technology, Zhejiang Province, Jiaxing 314006, China

4. Laboratory of Environmental Technology, INET, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:

Received 18 October 2014

Revised 23 December 2014

Accepted 5 January 2015

Available online 14 May 2015

Keywords:

PVA

Ozonation

Ionizing radiation

Synergistic effect

Mineralization

ABSTRACT

Ozonation and ionizing radiation are both advanced oxidation processes (AOPs) without chemical addition and secondary pollution. Also, the two processes' efficiency is determined by different pH conditions, which creates more possibilities for their combination. Importantly, the combined process of ozonation and ionizing radiation could be suitable for treating wastewaters with extreme pH values, i.e., textile wastewater. To find synergistic effects, the combined process of ozonation and ionizing radiation mineralization was investigated for degradation of polyvinyl alcohol (PVA) at different pH levels. A synergistic effect was found at initial pH in the range 3.0–9.4. When the initial pH was 3.0, the combined process of ozonation and ionizing radiation gave a PVA mineralization degree of 17%. This was 2.7 times the sum achieved by the two individual processes, and factors of 2.1 and 1.7 were achieved at initial pH of 7.0 and 9.4, respectively. The combined process of ozonation and ionizing radiation was demonstrated to be a feasible strategy for treatment of PVA-containing wastewater.

© 2015 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

Published by Elsevier B.V.

Introduction

Textile wastewaters are known to have extreme pH values depending on the production processes, e.g., the desizing process generally uses sodium hydroxide or sulfuric acid as desizing agent. In addition, polyvinyl alcohol (PVA) has been widely used as a sizing agent in the textile industry. Therefore, the presence of PVA and extreme pH values (either acidic or alkaline) are typical characteristics of textile wastewater. PVA is non-biodegradable. However, a biological process is used as the core technology in most textile wastewater treatment plants (Choi et al., 2004; Liu et al., 2010), which has difficulty degrading PVA. Thus, effective methods for PVA removal need to be pursued. In the last decade, advanced oxidation processes (AOPs) have been proved to be effective

methods for PVA degradation (Jing et al., 2008; Jo et al., 2006; Oh et al., 2009; Sun et al., 2004, 2012; Wu et al., 2008; Zhang and Yu, 2004). Compared to other AOPs, the waters treated by ozonation are not harmful to most organisms because no foreign compounds are added. Importantly, the pH determines ozonation efficiency because it can alter the kinetics and pathways of O₃-initiated reactions. Under strongly acidic conditions, O₃ exclusively reacts with compounds with specific functional groups through selective reactions, i.e., nucleophilic, electrophilic or dipolar addition reactions. Under strong alkaline conditions, O₃ decomposes and yields hydroxyl radicals (OH). They react in a non-selective way with a wide range of organic and inorganic compounds in water. Thus, ozonation could be a suitable treatment method for PVA wastewaters with extreme pH values.

* Corresponding author. E-mail: chenlj@tsinghua.edu.cn (Lujun Chen).

Previously, a strong hydrogen-bonding complex formed between O_3 and PVA was discovered by Cataldo and Angelini (2006). Under acidic conditions, PVA addition to water could promote the solubilization and dispersion of O_3 into substrates by formation of a structured and persistent foam. This foaming ability permits O_3 to be trapped in the water system, which enhances the ozonation by prolonging O_3 persistence. The main viscosity drop of PVA could be achieved at the ratio of one ozone molecule to more than 20 PVA sub-units. Shin et al. (1999) reported that PVA could be removed completely in 20 min by ozonation. Moreover, PVA degradation was found to be more efficient under alkaline conditions compared to acidic conditions (Jing et al., 2008), which indicated that $\cdot OH$ radicals could accelerate PVA decomposition. Nowadays, O_3 -based AOPs, i.e., O_3 /ultrasound (Poyatos et al., 2010), O_3 /ultraviolet (Ratpukdi et al., 2010), O_3 /hydrogen peroxide (Xue and Jin, 2001) and O_3 /ionizing radiation (Hu et al., 2006; Pikaev et al., 1997) have proven to be effective methods for enhancing $\cdot OH$ radical yield.

Ionizing radiation (IR) is another AOP without chemical addition or secondary pollution (Chmielewski and Haji-Saeid, 2004). Also, its efficiency is determined by different pH conditions, which creates more combination possibilities with ozonation. Furthermore, IR such as gamma radiation and electron beam radiation is a special AOP (Wang and Wang, 2007). Similar to other AOPs, radiation technology employs very highly reactive species, primarily $\cdot OH$ radicals produced by water radiolysis, for the decomposition of toxic or refractory organic compounds. Interestingly, approximately equal amounts of reducing species, i.e. hydrated electrons (e_{aq}^-) and hydrogen atoms ($H\cdot$), are produced from water radiolysis under ionizing radiation. In this work, to accelerate PVA decomposition, the combined process of O_3 and IR for PVA wastewater treatment was studied at different pH conditions.

1. Materials and methods

1.1. Chemicals and analytical methods

PVA (polymerization degree 1700 ± 200 , analytically pure), O_2 (99.999%), and other chemicals were all purchased from commercial sources. The pH was measured by a pH meter (SevenEasy, Mettler Toledo, USA), and was adjusted by addition of sodium hydroxide or hydrochloric acid. Total organic carbon (TOC) was determined using a TOC analyzer (TOC-V_{CPH}, Shimadzu, Kyoto, Japan). All reagents and chemicals were used without further purification. All solutions were prepared in deionized water.

1.2. Ozonation and ionizing radiation

O_3 was produced from O_2 with a laboratory ozone generator (3S-A-T, Tonglin Technology, Beijing, China) with a gas flow rate of 12 L/hr. PVA aqueous solutions were prepared and ozonated in glass tubes ($\phi = 18$ mm). Ozonation runs were carried out continuously. The overall mass transfer mechanism of O_3 in aqueous solution could be described by the following steps: (i) diffusion of O_3 through the gas phase to the

interface between the gas and aqueous phases, (ii) transport across the interface to the aqueous phase boundary, and (iii) transfer into the bulk aqueous phase. Increasing the applied O_3 dosage enhanced mass transfer and caused an increased O_3 concentration in the liquid phase (Sevimli and Sarikaya, 2002).

Therefore, the relationship between applied O_3 dosage and O_3 concentration in aqueous solution was a linear relationship. In this study, the applied O_3 dosage (bubble time) represented the semi-quantitative concentration of O_3 , and the applied O_3 dosage was 6.46 mg/(min-tube), analyzed by the iodometric method.

Ionizing radiation was generated in a ^{60}Co source station (Tsinghua University, Beijing, China). The dose rate used in this study was 109 Gy/min. The radiation dosimetry was measured using a standard Fricke dosimeter. PVA aqueous solutions were prepared and irradiated in radiation-proof glass tubes ($\phi = 18$ mm). Samples were sealed by laboratory film (PM-996, Parafilm M, USA) before the irradiation.

For the O_3 -only process, the ozonated samples were sealed immediately, and then were analyzed after standing overnight. For the IR-only process, the irradiated samples were analyzed after standing overnight. For the combined O_3 /IR process, the ozonated samples were sealed and irradiated immediately, then analyzed after standing overnight. All operations were performed at ambient temperature.

1.3. Mineralization degree and synergistic effect assessment

The degree of mineralization was calculated from the decrease of TOC using Eq. (1), where TOC_0 (mg/L) is the TOC value of PVA solution before treatment, TOC_i is the TOC value after treatment.

$$\text{Mineralization}(\%) = ((TOC_0 - TOC_i) / TOC_0) \times 100\%. \quad (1)$$

In this study, a synergistic effect is defined as PVA mineralization degree achieved by the coupled O_3 and IR process more than the sum of the values of the O_3 process and IR process separately under the same conditions.

2. Results and discussion

2.1. Mineralization of PVA by O_3 -only process

For ozonation, normally, under acidic conditions ($pH < 4.0$) direct ozonation dominates, while under alkaline conditions ($pH > 9.0$) the indirect pathway of $\cdot OH$ radicals prevails, and in the range of pH 4.0–9.0 both are present (Pera-Titus et al., 2004). As shown in Fig. 1, TOC values of PVA aqueous solutions were decreased gradually by ozonation at initial pH 7.0 and 13.0, and PVA mineralization was 13% and 50% after 30 min ozonation, respectively. By contrast, PVA mineralization was not observable at initial pH 1.0. Thus, alkaline conditions ($pH = 13.0$) were more beneficial for PVA mineralization than acidic conditions ($pH = 1.0$), which indicated that $\cdot OH$ radical was more effective in PVA mineralization than O_3 molecules.

PVA mineralization could be described in terms of a pseudo-first order kinetic equation. The relationship between TOC_i and TOC_0 of PVA solutions can be described by Eq. (2), where

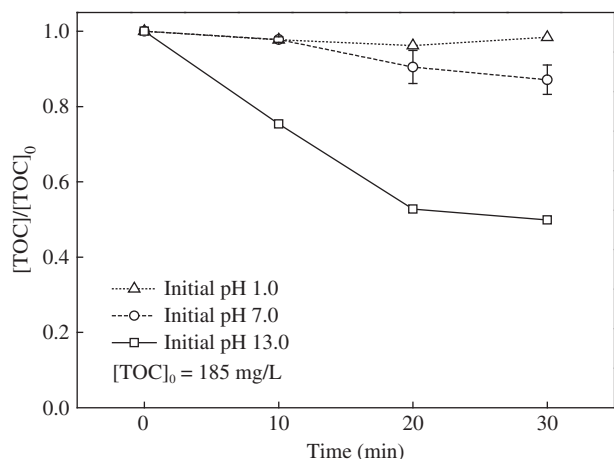


Fig. 1 – Variations of TOC with applied O_3 at different initial pH values. The applied O_3 dosage: 6.46 mg/(min·tube). TOC_0 : the TOC value of PVA solution before treatment; TOC_t : the TOC value after treatment.

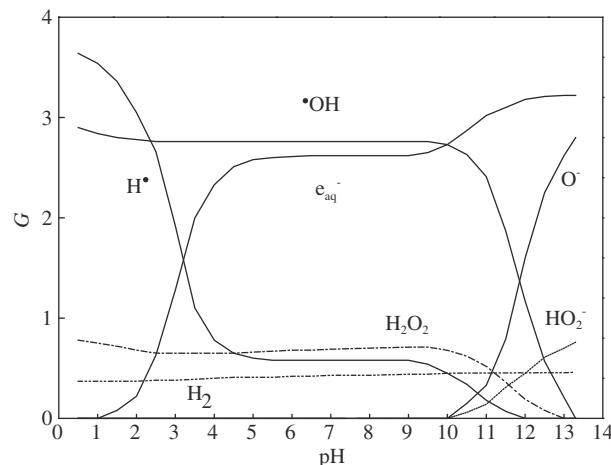


Fig. 2 – Variations of G values of the primary radicals with pH values (Getoff, 1996). G value: the number of decomposed or formed target molecules per 100 eV (1.60×10^{-17} J) absorbed energy.

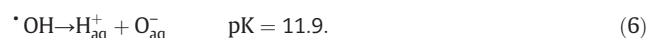
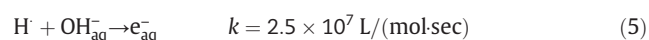
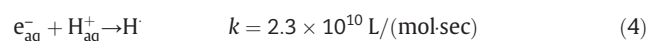
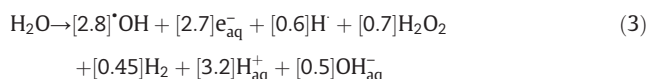
t (min) is ozonation time and k (min^{-1}) is the pseudo-first order rate constant.

$$-\ln(TOC_t/TOC_0) = k \times t. \quad (2)$$

When the PVA aqueous solution was strongly alkaline ($\text{pH} = 13.0$), k was 0.0261 min^{-1} , which was 5.8 times higher than the value of 0.0045 min^{-1} achieved under neutral conditions ($\text{pH} = 7$). If the mineralization rate of PVA aqueous solution is expected to be 90% at initial pH 13.0, the ozonation time predicted by Eq. (2) will be approximately 88 min.

2.2. Mineralization of PVA by IR-only process

The G value is defined as the number of decomposed or formed target molecules per 100 eV (1.60×10^{-17} J) absorbed energy. For the ionizing radiation process, the primary species were $\cdot\text{OH}$ radicals, hydrated electrons (e_{aq}^-) and hydrogen atoms ($\text{H}\cdot$). The G values of the primary products were also influenced by pH (Fig. 2). Around neutral conditions ($\text{pH} 4.0\text{--}9.0$), the G values of the radicals were constant (Eq. (3)). Below pH 4.0, e_{aq}^- could react with hydrated hydrogen ions (H_{aq}^+) to produce $\text{H}\cdot$, which broke the balance (Eq. (4)). By contrast, under alkaline conditions ($\text{pH} > 9.0$), $\text{H}\cdot$ could covert to e_{aq}^- by reacting with hydrated hydroxide ions (OH_{aq}^- , Eq. (5)). In addition, $\cdot\text{OH}$ was partially decomposed to H_{aq}^+ and hydrated oxygen ions (O_{aq}^- , Eq. (6)).



The variation of the TOC values with absorbed dose of ionizing radiation at different initial pH conditions is shown

in Fig. 3. The results indicated that acidic conditions were more beneficial for PVA removal than neutral and alkaline conditions. TOC was decreased gradually by radiation at initial pH 1.0 and pH 3.0, and PVA mineralization was 94% and 97% after 12 kGy, respectively. Interestingly, when the absorbed dose reached 9 kGy, sediments were found in the bottom of the radiation-proof glass tubes at pH 1.0 and pH 3.0. When the absorbed dose was 12 kGy, more sediments were accumulated, which caused a sharp decrease of TOC. As reported in our previous work (Sun et al., 2012, 2013), PVA degradation and PVA polymerization took place under ionizing radiation simultaneously. The PVA polymerization contributed to the TOC removal in the strongly acidic solutions. However, PVA mineralization was not reflected in the TOC values in neutral and alkaline solutions. As shown in Fig. 2, the ratio of $\cdot\text{OH}$, e_{aq}^- and $\text{H}\cdot$ was stable in the pH range of 4.0–10.0. When the pH decreased from 4.0 to 1.0, the content of $\text{H}\cdot$ increased sharply. Thus, $\text{H}\cdot$ played the key

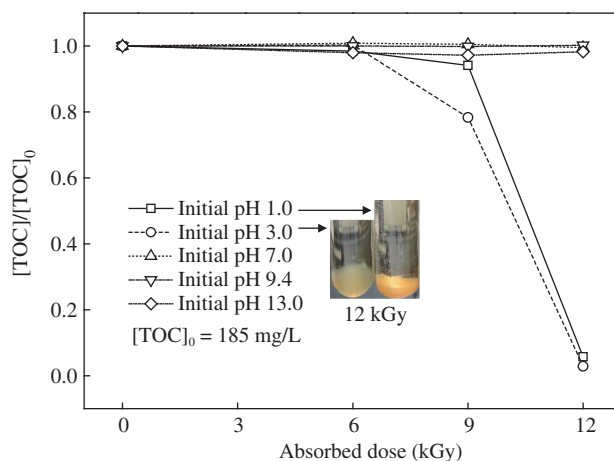


Fig. 3 – Variations of TOC with absorbed dose at different initial pH values. Dose rate: 109 Gy/min. TOC_0 : the TOC value of PVA solution before treatment.

role in PVA polymerization. In addition, pH 3.0 was found to be the best condition, which indicated that the ratio of $\cdot\text{OH}$, e_{aq}^- and H^+ played an important role in TOC removal.

2.3. Mineralization of PVA by combined O_3/IR process

A synergistic effect on PVA mineralization was found in the initial pH range of 3.0–9.4 using the combined O_3/IR process (Fig. 4). The PVA mineralization degree achieved by the combined O_3/IR process was more than the sum of the values for the O_3 -only and IR-only processes at initial pH 3.0–9.4. When the initial pH was 3.0, the PVA mineralization degree for the combined O_3/IR process was 17%, which was 2.7 times the sum of the two individual processes, and factors of 2.1 and 1.7 were achieved at initial pH 7.0 and 9.4, respectively. On one hand, it is well known that ozone decomposition usually has a high dependence on pH. Ozone decomposition into active species is catalyzed by OH^- ions, and primary radicals such as $\cdot\text{OH}$ are formed. However, OH^- was also reported to be a poor initiator of the aqueous phase radical chain reaction that accelerated the transformation of ozone. It is reported that OH^- exhibits an especially low reaction-rate constant ($k = 70 \pm 7 \text{ L}/(\text{mol}\cdot\text{sec})$) with ozone (Ma et al., 2005). On the other hand, water radiolysis is an easy way to generate $\cdot\text{OH}$, but the efficiency of the IR process is deteriorated by reducing species formed simultaneously. As Eqs. (7)–(11) show, O_3 addition can improve the efficiency by converting the reducing species and peroxide hydrogen into $\cdot\text{OH}$ and turning the IR process into a full AOP. Therefore, the combination of ozonation and ionizing radiation is a complementary strategy. This is the reason for the existence of the synergistic effect on PVA mineralization for the combined O_3/IR process.

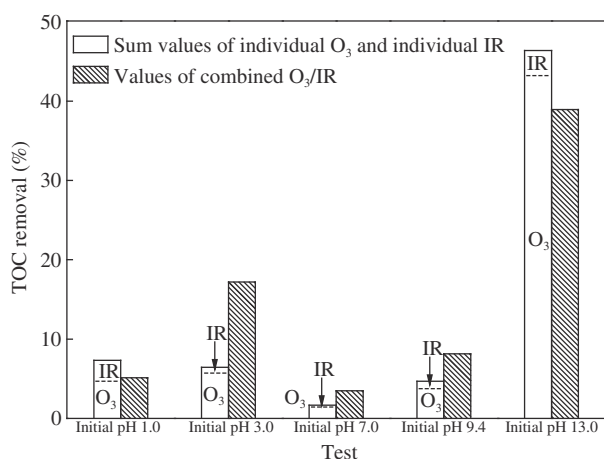
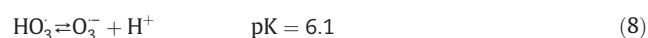


Fig. 4 – Comparison of IR, O_3 , and combined O_3/IR for TOC removal. Absorbed dose: 6 kGy; O_3 treatment for 20 min. IR: ionizing radiation only process; O_3 : ozonation only process.



Also, a synergistic effect was found in decomposition of 4-chlorophenol (Hu et al., 2006), trichloroethylene (Jung et al., 2003) and perchloroethylene (Jung et al., 2003) by combined IR/ O_3 treatment under neutral conditions (initial pH 6.4–7.4). Interestingly, the synergistic effect was not observed at initial pH 1.0 and 13.0 in this study. There were fewer types of radicals in these conditions than at pH 3.0–9.4 (Getoff, 1996). At initial pH 1.0, only O_3 , $\cdot\text{OH}$ and H^+ take part in PVA degradation; e_{aq}^- was absent. Moreover, the reaction rate of e_{aq}^- with O_3 was more rapid than that of H^+ . Due to the high OH^- concentration, most O_3 was decomposed to $\cdot\text{OH}$ at the ozonation stage at initial pH 13.0. Therefore, the synergistic effect was hard to observe during combined O_3/IR treatment under strongly acidic and strongly alkaline conditions.

3. Conclusions

A synergistic effect on the degree of PVA mineralization can be achieved by combining ozonation and ionizing radiation at initial pH 3.0–9.4. Reducing species generated by ionizing radiation were oxidized to $\cdot\text{OH}$ radicals by O_3 , which was confirmed to be the main reason for the synergistic effect. However, it was hard to find any synergistic effect under strongly acidic and strongly alkaline conditions. Under the strongly acidic condition, i.e., initial pH 1.0, hydrated electron was converted to hydrogen atom, which decreased the $\cdot\text{OH}$ production rate by ozonation. Under the strongly alkaline condition, i.e., initial pH 13.0, excess OH^- dominated the reaction process. Most O_3 was decomposed to $\cdot\text{OH}$, which decreased the possibility of a synergistic effect.

Acknowledgments

This work was supported by the National High Technology Research and Development Program (No. 2009AA063905), the General Research Program of Shanghai Normal University (No. SK201418), and the Young Teacher Training Scheme of Shanghai Universities (No. ZZshsf14008).

REFERENCES

- Cataldo, F., Angelini, G., 2006. Some aspects of the ozone degradation of poly(vinyl alcohol). *Polym. Degrad. Stab.* 91 (11), 2793–2800.
- Chmielewski, A.G., Haji-Saeid, M., 2004. Radiation technologies: past, present and future. *Radiat. Phys. Chem.* 71 (1–2), 17–21.
- Choi, K.K., Park, C.W., Kim, S.Y., Lyoo, W.S., Lee, S.H., Lee, J.W., 2004. Polyvinyl alcohol degradation by *Microbacterium barkeri* KCCM 10507 and *Paenibacillus amylolyticus* KCCM 10508 in dyeing wastewater. *J. Microbiol. Biotechnol.* 14 (5), 1009–1013.
- Getoff, N., 1996. Radiation-induced degradation of water pollutants—state of the art. *Radiat. Phys. Chem.* 47 (4), 581–593.
- Hu, J., Wang, J.L., Chen, R., 2006. Degradation of 4-chlorophenol in aqueous solution by gamma-radiation and ozone oxidation. *Sci. China B* 49 (2), 186–192.

- Jing, G.H., Zhou, Z.M., Li, Y., Dong, M.X., 2008. Degradation of polyvinyl alcohol with ozonation and other synergic oxidation. *Chin. J. Environ. Eng.* 2 (12), 1594–1598.
- Jo, H.J., Lee, S.M., Kim, H.J., Kim, J.G., Choi, J.S., Park, Y.K., et al., 2006. Improvement of biodegradability of industrial wastewaters by radiation treatment. *J. Radioanal. Nucl. Chem.* 268 (1), 145–150.
- Jung, J., Yoon, J.-H., Chung, H.-H., Lee, M.-J., 2003. Comparative study of H_2O_2 and O_3 effects on radiation treatment of TCE and PCE. *Chemosphere* 51 (9), 881–885.
- Liu, R.R., Tian, Q., Yang, B., Chen, J.H., 2010. Hybrid anaerobic baffled reactor for treatment of desizing wastewater. *Int. J. Environ. Sci. Technol.* 7 (1), 111–118.
- Ma, J., Sui, M.H., Zhang, T., Guan, C.Y., 2005. Effect of pH on MnOx/GAC catalyzed ozonation for degradation of nitrobenzene. *Water Res.* 39 (5), 779–786.
- Oh, S.Y., Kim, H.W., Park, J.M., Park, H.S., Yoon, C., 2009. Oxidation of polyvinyl alcohol by persulfate activated with heat, Fe^{2+} , and zero-valent iron. *J. Hazard. Mater.* 168 (1), 346–351.
- Pera-Titus, M., Garcia-Molina, V., Baños, M.A., Giménez, J., Esplugas, S., 2004. Degradation of chlorophenols by means of advanced oxidation processes: a general review. *Appl. Catal. B Environ.* 47 (4), 219–256.
- Pikaev, A.K., Podzorova, E.A., Bakhtin, O.M., 1997. Combined electron-beam and ozone treatment of wastewater in the aerosol flow. *Radiat. Phys. Chem.* 49 (1), 155–157.
- Poyatos, J.M., Munio, M.M., Almecija, M.C., Torres, J.C., Hontoria, E., Osorio, F., 2010. Advanced oxidation processes for wastewater treatment: state of the art. *Water Air Soil Pollut.* 205 (1–4), 187–204.
- Ratpukdi, T., Siripattanakul, S., Khan, E., 2010. Mineralization and biodegradability enhancement of natural organic matter by ozone-VUV in comparison with ozone, VUV, ozone-UV, and UV: effects of pH and ozone dose. *Water Res.* 44 (11), 3531–3543.
- Sevimli, M.F., Sarikaya, H.Z., 2002. Ozone treatment of textile effluents and dyes: effect of applied ozone dose, pH and dye concentration. *J. Chem. Technol. Biotechnol.* 77 (7), 842–850.
- Shin, H.S., Yoo, K.S., Kwon, J.C., Lee, C.Y., 1999. Degradation mechanism of PVA and HEC by ozonation. *Environ. Technol.* 20 (3), 325–330.
- Sun, Z.S., Yang, Y., Chen, Y.X., 2004. Photocatalytic degradation of polyvinyl alcohol in UV TiO_2 - H_2O_2 system. *Acta Energetica Solaris Sin.* 25 (6), 760–763.
- Sun, W.H., Tian, J.P., Chen, L.J., He, S.J., Wang, J.L., 2012. Improvement of biodegradability of PVA-containing wastewater by ionizing radiation pretreatment. *Environ. Sci. Pollut. Res.* 19 (8), 3178–3184.
- Sun, W.H., Chen, L.J., Tian, J.P., Wang, J.L., He, S.J., 2013. Radiation-induced decomposition and polymerization of polyvinyl alcohol in aqueous solutions. *Environ. Eng. Manag. J.* 12 (7), 1323–1328.
- Wang, J.L., Wang, J.Z., 2007. Application of radiation technology to sewage sludge processing: a review. *J. Hazard. Mater.* 143 (1–2), 2–7.
- Wu, Y., Lian, Y., Liu, J., Zhu, H., 2008. Sonochemical degradation of polyvinyl alcohol in aqueous solutions. *Technol. Water Treat.* 34 (2), 32–34 (59).
- Xue, X.D., Jin, Q.T., 2001. Advanced oxidation technology for water treatment. *Environ. Prot.* (6), 13–15.
- Zhang, S.J., Yu, H.Q., 2004. Radiation-induced degradation of polyvinyl alcohol in aqueous solutions. *Water Res.* 38 (2), 309–316.