Photodegradation of Azithromycin in Aqueous System Under VIS/UV Irradiation

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ABSTRACT

Antibiotics, such as azithromycin, have become one major group of emerging contaminants in aquatic systems. It is urgent to explore efficient, safe, and economic methods to removal azithromycin in aquatic environment. This paper described the photolysis of azithromycin and its affecting factors (initial concentration of azithromycin, pH, nitrate and Fe (III)-oxalate complexes) under visible and UV light irradiation. The results indicated ultraviolet has stronger ability to degrade azithromycin than visible light. The photodegradation efficiencies of azithromycin decreased with the increase of its initial concentration under UV irradiation, as well as pH value. The maximum degradation rates occurred in the initial concentration of 10 mg·L^{-1} and pH value of 4, which was 53.1% and 82.6%, respectively. The addition of nitrate can promote the photodegradation of azithromycin but Fe (III)-oxalate complexes had the opposite effect. The achievements proved photodegradation is a promising technology to remove azithromycin from water environment.

Keywords: azithromycin; photodegradation; VIS/UV light; impact factors

INTRODUCTION

Since Alexander Fleming discovered penicillin in 1928, antibiotics have been widely used in clinical treatment, livestock breeding and aquaculture [1,2]. The incorporation of antibiotics in the effluent and sludge from domestic wastewater treatment plants (WWTPs), hospitals, and livestock farms results in their release to the recipient environments such as surface water and soil [1,3]. Various antibiotics have been detected in aquatic systems, including wastewater treatment plant effluents, surface waters, drinking water and groundwater [4, 5, 6]. The residual antibiotics in the water environment could lead to adverse effects on nontarget organisms [7, 8, 9], contamination of drinking water supplies [10, 11], and increased bacterial resistance [12, 13].

Macrolide antibiotics, such as erythromycin and the semi-synthetic azithromycin are broad spectrum antimicrobial agents for therapeutic treatment of infectious disease in humans and animals [14]. Due to their extensive utilization and the negligible human metabolism, these antibiotics and their derivatives are excreted predominantly unchanged into human fluids and can ultimately be detected in various water bodies [15, 16, 17]. However, conventional wastewater treatment is usually difficult to remove micro level pharmaceutical compounds, which results in antibiotics accumulation in the environment [18, 19].

Chemical treatment, physicochemical treatment and biological treatment are considered as the major strategies for future complementary methods to conventional wastewater treatments [20, 21, 22, 23]. The chemical treatment is to add oxidants to the wastewater under certain conditions to oxidize indecomposable organics into simple organics or inorganics, improving the biodegradability of the wastewater and facilitating subsequent treatment, mainly include catalytic wet oxidation, ozone oxidation, supercritical water oxidation, chlorine oxidation and photocatalytic oxidation.

Several studies have demonstrated that ultra-violet (UV) light is able to decompose pharmaceuticals by direct photolysis or indirect photolysis through an Advanced Oxidation Process (AOP) [24, 25, 26]. Among these AOPs, TiO2 photocatalysis showed great potentials due to its high stability, high efficiency, low toxicity, and low cost. However, it also associated with problems of wide band gap (3.2 eV), low specific surface area and charge separation efficiency, which greatly limited the application of non-modified TiO2 under visible light [27].

With the widespread use of antibiotics, azithromycin has become one major group of emerging contaminants in aquatic systems. In this paper, the degradation efficiency of azithromycin under visible and ultraviolet light and the effects of pH, nitrate, and ferric ion on it were investigated to explore efficient, safe, and economic approaches to removal azithromycin in aquatic environment.

MATERIALS AND METHODS

Materials and reagents

Azithromycin was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Sulfuric acid and hydrochloric acid were obtained from Sinopharm Chemical Regent Co., Ltd. (Shanghai, China). Sodium hydroxide, ferric chloride hexahydrate, and sodium oxalate were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China). Sodium nitrate was purchased form Chengdu Kelong Chemical Reagent Factory (Chendu, China). Pure water was obtained from Millipore Milli-Qwater system.

Photodegradation experiments

All photodegradation experiments were conducted in a photochemical reactor (HSX-UV300, Beijing NBET Technology Co., Ltd, China) equipped with a 300 W xenon lamp. Using the appropriate window glass filters, the transmission light was restricted in 200-400 nm and

400-780 nm to emit ultraviolet light (UV) and visible light, respectively. The azithromycin aqueous solution with a concentration of 20 mg·L^{-1} was prepared and irradiated with visible and UV light.

To determine the optimal concentration of azithromycin, solutions containing various amounts of this composition including 10, 20, 50 and 100 mg·L^{-1} were examined under UV irradiation.

To investigate the optimal pH, the experiments were performed using 0.1 mol·L^{-1} NaOH and HNO3 solutions at pH values of 4, 6 and 9, with azithromycin concentration of 20 mg·L^{-1} under UV irradiation.

To study the effect of nitrate, the 20 mg·L^{-1} azithromycin solutions mixed with different quantity of sodium nitrate (1, 5 and 10 mmol·L^{-1}) were made up and irradiated with UV.

To uncover the impact of Fe (III) -oxalate complex, the 20 mg·L^{-1} azithromycin solutions mixed with different concentration of ferric chloride (10, 50 and 100 μmol·L^{-1}) and sodium oxalate (120, 600 and 1200 μmol·L^{-1}) were prepared and irradiated with UV.

The azithromycin solutions were kept stirring by magnetic stirrer (Joanlab MS5S, Qun'an Experimental Instrument Co., Ltd. China) during the photodegradation process. All the samples were taken every 20 min and mixed with equal amount of sulfuric acid(v/v=75%), colored rendering for 30 min and determined the absorbance by visible spectrophotometer (V-1200, Shanghai Mapada Instrument Co., Ltd.) at 482nm.

The residual concentrations of azithromycin were obtained as following steps: (1) Azithromycin solutions with various concentration (0, 10,20, 40, 80 and 100 mg.L-1) were prepared; (2) 5 mL azithromycin solutionsof each concentration were taken and mixed with 5 mL sulfuric acid(v/v=75%), colored rendering for 30 min and detected the absorbance by visible spectrophotometer at 482nm; (3) The standard curve was drawn by taking the azithromycin concentration as the abscissa and the absorbance as the ordinate and linear equation of azithromycin concentration and absorbance was created in Microsoft Excel; (4) The azithromycin concentration of samples were obtained bythe interpolation method.

The photodegradation efficiency of azithromycin was calculated using equation (1):

$$R = \frac{c_0 - c_t}{c_0} \times 100\% \qquad (1)$$

where R is the azithromycin degradation rate (%), C0 is to the initial azithromycin concentration(mg/L), and Ct is the azithromycin concentration at time t (mg/L).

RESULTS AND DISCUSSION

Photodegradation efficiencies of azithromycin under visible and UV light irradiation
The photodegradation efficiencies of azithromycin irradiated with visible and UV light are shown in Figure 1. As it is obvious, azithromycin degraded under both visible and ultraviolet light irradiation, with degradation rates of 44.6% and 53.1% within 120 min, respectively. The photodegradation rate of azithromycin under UV is higher than that of visible light. It can be attributed to the stronger radiation energy of UV compared with that of visible light, which can accelerate the degradation of azithromycin.

In addition, after reaction for 60 min, the degradation rates of azithromycin under both visible and

UV light show a downward trend. This may be the result of the creation of intermediate product during the photodegradation process, causing increases in absorbance, generally leading to decreases in photodegradation rate. After 100 min, the intermediate products further degraded and the degradation rate went up again.
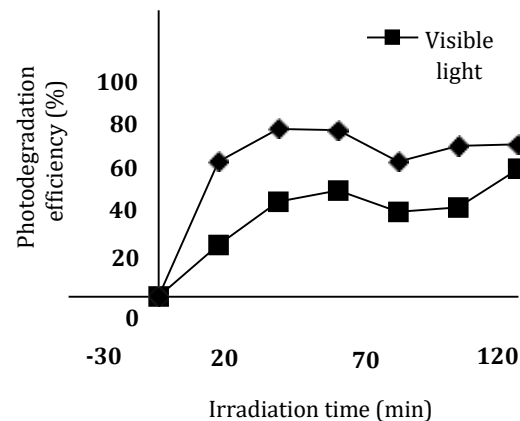

FIGURE 1: Photodegradation efficiency of azithromycin under visible and UV light

The effect of initial concentrations of azithromycin on its photodegradation efficiency
Figure 2 shows the effect of changes in the initial concentration of azithromycin on the photodegradation rate. As can be seen, the degradation percentage decreased with increasing azithromycin concentration, so that the maximum degradation rate (53.1%) occurred at the initial concentration of 10 mg·L^{-1}. At low concentrations of pollutants, the probability of photochemical reaction increase. By increasing the initial concentration of the pollutant, the photodegradation reaction decreases. This can be explained by the fact that the number of photons absorbed by the pollutant is reduced at high concentration, which results to the decreasing the optical degradation rate. In the later stages of the reaction, the degradation rate of azithromycin of all concentrations showed the trend similar to that in Figure 1, which maybe also related to the photodegradation intermediates.
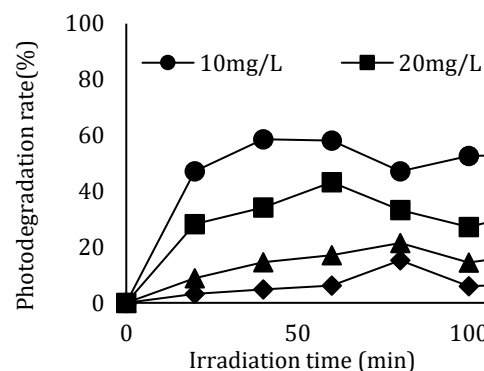

FIGURE 2: Efficacy of initial concentration of azithromycin on its photodegradation

The effect of pH on photodegradation of azithromycin
pH has a significant effect on the solubility and stability of antibiotics. Figure 3 showed the pH changes on the degradation rate of azithromycin under UV irradiation.

As can be seen, increasing the pH value from 4 to 9 decreases the degradation rate of this antibiotic. Thus, the maximum reduction in azithromycin was observed at pH of 4 with degradation percentage of 82.6%.

The reduction in azithromycin degradation rate at higher pH was due to the formation of insoluble compounds, which reduces the intensity of UV radiation [28]. In addition, the acidic conditions may promote the hydrolysis of azithromycin and thereby accelerate its degradation. Wilgaz-Gasman et al. had reported that pH is an effective factor in the destruction of organic pollutants and their reactivity, and most antibiotic degradation has occurred in acidic pH [29].
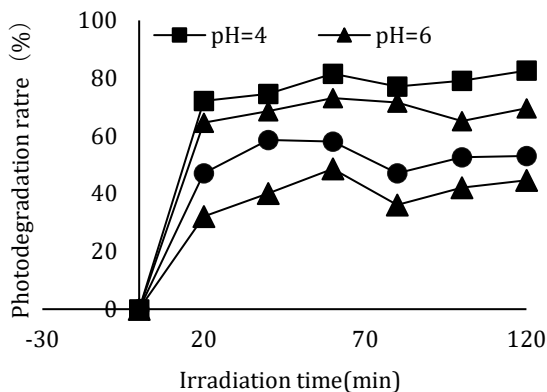

FIGURE 3: Efficacy of pH on azithromycin degradation by UV radiation

The effect of nitrate on photodegradation of azithromycin

Figure 4 presented the effect of nitrate concentration on the degradation rate of azithromycin. The results showed the addition of either 1 mmol·L-1 or 5 mmol·L-1 nitrate can promote the photodegradation of azithromycin compared to the control, with degradation percentage of 58.6% and 71.6%, respectively. This may be attributed to the fact that nitrate has a strong ability to absorb ultraviolet rays ($\varepsilon200=9,900$ M-1.cm-1) and generate hydroxyl radicals. The hydroxyl radicals can rapidly oxidize and decompose azithromycin, thus accelerating the degradation rate.

Different result was observed when the nitrate concentration was increased to 10 mmol·L-1. In the early stage of the reaction (0-40 min), the degradation rate is higher than that of control, indicating that the addition of nitrate promoted the photodegradation of azithromycin. In the later stage of the reaction (40-120 min), the photodegradation of azithromycin slowed down, and the degradation rate is only 37.6% within 120 min. This maybe cause by the consumption of hydroxyl radicals by nitrate. At high concentration of nitrate, the consumption rate of hydroxyl radicals exceeds the generation rate, leading to reduction in degradation rate of azithromycin.
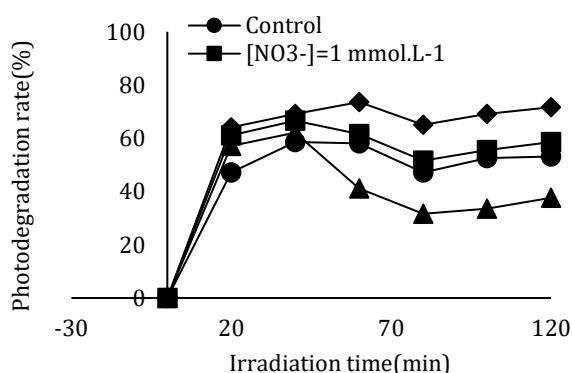

FIGURE 4: Efficacy of nitrate on azithromycin degradation by UV radiation

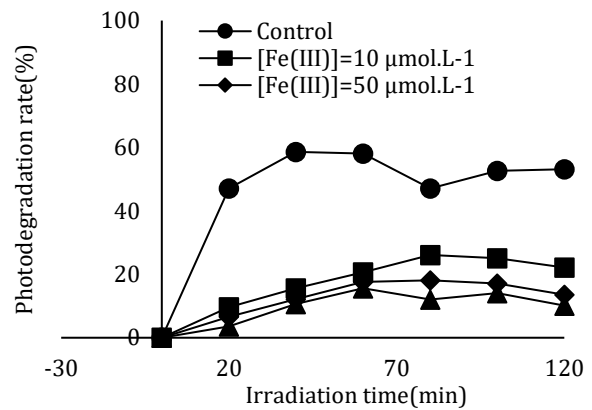**The effect of Fe (III)-oxalate complexes on photodegradation of azithromycin**

FIGURE 5: Efficacy of Fe (III)-oxalate complex on azithromycin degradation by UV radiation

The degradation efficiencies of azithromycin added with different concentration of Fe (III)-oxalate complexes under UV radiation were displayed in Figure 5. It is apparent that the addition of Fe (III)-oxalate complexes decreased the degradation rate compared to control. The minimum degradation rate (10.1%) of azithromycin was exhibited at the Fe (III)-oxalate complex concentration of 100 µmol. L-1 within 120 min. This can be ascribed to the neutral condition is not conducive to the production of the addition of Fe (III) -oxalate complex increased the chromaticity of azithromycin solution, leading to the increase of the absorbance of samples, which interfered with the determination of azithromycin concentration. As a result, the degradation rates of azithromycin decreased with the concentration of Fe (III)-oxalate complexes.

CONCLUSION

In this study, the degradation efficiencies of azithromycin in aqueous system irradiated with visible and UV light and its influencing factors were investigated. The outcomes showed the degradation rate of azithromycin under UV was greater than that under visible light. The increase in the initial concentration of azithromycin, as well as pH value, had a negative effect on its photodegradation. A certain amount of nitrate can promote the photodegradation of azithromycin. However, the addition of Fe (III)-oxalate complexes has the opposite effect.

REFERENCES

[1] Sarmah, A. K.; Meyer, M. T.; Boxall, A. B. A., A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment. Chemosphere, 2006, 65, (5), 725- 759.

[2] Zhou, L. J.; Ying, G. G.; Liu, S.; Zhang, R. Q.; Lai, H. J.; Chen, Z. F.; Pan, C. G., Excretion masses and environmental occurrence of antibiotics in typical swine and dairy cattle farms in China. Science of Total Environment, 2013, 444, 183-195.

[3] Zhou, L. J.; Ying, G. G.; Liu, S.; Zhao, J. L.; Yang, B.; Chen, Z. F.; Lai, H. J., Occurrence and fate of eleven classes of antibiotics in two typical wastewater treatment plants in South China. Science of Total Environment, 2013, 452, 365-376.

[4] Bhandari, A., Close, L.I., Kim, W., Hunter, R.P., Koch, D.E., Surampalli, R.Y., Occurrence of ciprofloxacin, sulfamethoxazole, and azithromycin in municipal wastewater treatment plants. Pract. Periodical Hazard. Toxic. Radioactive Waste Management, 2008, 12, 275–281.

[5] Grujic´, S., Vasiljevic´, T., Lauševic´, M., Determination of multiple pharmaceutical classes in surface and ground waters by liquid chromatography-ion trap-tandem mass spectrometry. J. Chromatogr. A, 2009,1216, 4989–5000.

[6] Loganathan, B., Phillips, M., Mowery, H., Jones-Lepp, T.L., Contamination profiles and mass loadings of macrolide antibiotics and illicit drugs from a small urban wastewater treatment plant. Chemosphere, 2009, 75, 70–77.

[7] Naslund, J.; Hedman, J. E.; Agestrand, C., Effects of the antibiotic ciprofloxacin on the bacterial community structure and degradation of pyrene in marine sediment. Aquatic Toxicology, 2008, 90, (3), 223-227.

[8] Underwood, J. C.; Harvey, R. W.; Metge, D. W.; Repert, D. A.; Baumgartner, L. K.; Smith, R. L.; Roane, T. M.; Barber, L. B., Effects of the Antimicrobial Sulfamethoxazole on Groundwater Bacterial Enrichment. Environmental Science & Technology, 2011, 45, (7), 3096-3101.

[9] Qian, H. F.; Li, J. J.; Pan, X. J.; Sun, Z. Q.; Ye, C. B.; Jin, G. Q.; Fu, Z. W., Effects of streptomycin on growth of algae Chlorella vulgaris and Microcystis aeruginosa. Environmental Toxicology, 2012, 27, (4), 229-237.

[10] Boonsaner, M.; Hawker, D. W., Evaluation of food chain transfer of the antibiotic oxytetracycline and human risk assessment. Chemosphere, 2013, 93, (6), 1009-1014.

[11] Westerhoff, P.; Yoon, Y.; Snyder, S.; Wert, E., Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. Environmental Science & Technology, 2005, 39, (17), 6649-6663.

[12] Luo, Y.; Mao, D. Q.; Rysz, M.; Zhou, D. X.; Zhang, H. J.; Xu, L.; Alvarez, P. J. J., Trends in antibiotic resistance genes occurrence in the Haihe River, China. Environmental Science & Technology, 2010, 44, (19), 7220-7225.

[13] Su, H. C.; Ying, G. G.; Tao, R.; Zhang, R. Q.; Zhao, J. L.; Liu, Y. S., Class 1 and 2 integrons, sul resistance genes and antibiotic resistance in Escherichia coli isolated from Dongjiang River, South China. Environmental Pollution, 2012, 169, 42-49.

[14] Bahal, N., Nahata, M.C., The new macrolide antibiotics: azithromycin, clar-ithromycin, dirithromycin, and roxithromycin. Ann. Pharmacother. 1992, 26, 46–55.

[15] Kü mmerer, K., Antibiotics in the aquatic environment—a review–part I. Chemosphere, 2009, 75, 417–434.

[16] Segura, P.A., Franc¸ ois, M., Gagnon, C., Sauvé, S.,Review of the occurrence ofantiinfectives in contaminated wastewaters and natural and drinking waters. Environmental Health Perspectives, 2009, 117, 675–684.

[17] Senta, I., Terzic, S., Ahel, M., Occurrence and fate of dissolved and particulateantimicrobials in municipal wastewater treatment. Water Research, 2013, 47, 705– 714.

[18] Jones, O.A., Lester, J.N., Voulvoulis, N., Pharmaceuticals: a threat to drinkingwater? Trends Biotechnology, 2005, 23, 163–167.

[19] Miao, X.-S., Bishay, F., Chen, M., Metcalfe, C.D., Occurrence of antimicrobialsin the final effluents of wastewater treatment plants in Canada. Environmental Science & Technology, 2004, 38, 3533–3541.

[20] Sannino, D., Vaiano, V., Ciambelli, P., Isupova, L.A., Structured catalysts forphoto-Fenton oxidation of acetic acid. Catal. Today, 2011, 161, 255–259.

[21] Murcia, J.J., Hidalgo, M.C., Navío, J.A., Vaiano, V., Sannino, D., Ciambelli, P., Cyclohexane photocatalytic oxidation on Pt/TiO2catalysts. Catal. Today, 2013, 209,164–169.

[22] Ochando-Pulido, J.M., Stoller, M., Bravi, M., Martinez-Ferez, A., Chianese, A., Batch membrane treatment of olive vegetation wastewater from two-phaseolive oil production process by threshold flux-based methods. Sep. Purrif. Tech-nol. 2012, 101, 34–41.

[23] Stoller, M., Bravi, M., Chianese, A., Threshold flux measurements of a nanofiltration membrane module by critical flux data conversion. Desalination, 2013, 315,142–148.

[24] Dimitrakopoulou, D., Rethemiotaki, I., Frontistis, Z., Xekoukoulotakis, N.P., Venieri,D., Mantzavinos, D., Degradation, mineralization and antibiotic inactiva-tion of amoxicillin by UV-A/TiO2photocatalysis. J. Environ. Manage. 2012, 98, 168–174.

[25] Prados-Joya, G., Sanchez-Polo, M., Rivera-Utrilla, J., Ferro-garcia, M., Pho-todegradation of the antibiotics nitroimidazoles in aqueous solution by ultraviolet radiation. Water Research, 45, 2011, 393–403.

[26] Xekoukoulotakis, N.P., Drosou, C., Brebou, C., Chatzisymeon, E., Hapeshi, E., Fatta-Kassinos, D., Mantzavinos, D., Kinetics of UV-A/TiO2 photocatalyticdegradation and mineralization of the antibiotic sulfamethoxazole in aqueousmatrices. Catal. Today, 2011, 161, 163–168.

[27] Szczepanik, B., Photocatalytic degradation of organic contaminants over clay-TiO2nanocomposites: a review. Appl. Clay Sci. 2017, 141, 227–239.

[28] Dehghani, M., Nasseri, S., Ahmadi, M., Samaei, M.R., Anushiravani, A., Removal of penicillin G from aqueous phase by Feþ 3-TiO 2/UV-A process. J. Environ. Health Sci. Eng. 2014, 12 (1), 56.

[29] Villegas-Guzman, P., Silva-Agredo, J., Giraldo-Aguirre, A.L., Flórez-Acosta, O., Petrier, C., Torres-Palma, R.A., Enhancement and inhibition effects of water matrices during the sonochemical degradation of the antibiotic dicloxacillin. Ultrason. Sonochem. 2015, 22 (2), 11-19.