Ozone pre-oxidation to the degradation technology research of MC-LR under the condition of different pH

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Abstract. Ozone pre-oxidation removal of MC-LR better, under the condition of pH4,ozone for MC-LR removal of 76.22%,than the original water removal increased by about 11%.With the increasing value of pH, ozone for MC-LR removal decreased, but higher pH beneficial ozone removal of turbidity, UV_{254}, TOC and COD_{Mn}. In the pH10,ozone dosage of 2mg / L case, turbidity, UV_{254}, TOC and COD_{Mn} removal rates were 33.75%, 41.88%, 12.68% and 11.43%, the removal has been enhanced than the original water.

1 Introduction

Algal toxins is a cyclic heptapeptide substance, there is a strong heat resistance[1] and can withstand extreme pH, natural degradation speed is very slow[2,3]. Microcystin isomers are about more than 60 kinds, which the widely distributed and the representative of microcystin (Microcystin, namely MC). Especially MC-LR, the widely distributed, and the strongest toxicity .World Health Organization (WHO)[4] recommended the algal toxins in drinking water standard for MC-LR should be less than 1. 0μg/L. Our country provides MC-LR limit of 1 μg/L in drinking Water Standards 2012. The study found that ozone on algal toxin has good removal effect Hengfeng Miao [4] and other analysts believe, in the O_3: MC is 6, MC - LR removal efficiency can reach 92%,the study found that Kejia Zhang[5], etc, the degradation of ozone in MC - LR pseudo-first-order reaction kinetics, the ozone dosing quantity increased from 0.31 mg/L to 0.31 mg/L,MC - LR degradation rate increased by 0.0103 min^{-1} to 0.0407 min^{-1}, and the acidic conditions more conducive to MC-LR removal. The experiment mainly to study the ozone removal of MC-LR, and analyze the different pH conditions, the influence of ozone on MC - LR.

2 Materials and Methods

2.1 Experimental Materials

Experiments with water taken from a water source of raw water of the north, through the cultivation of algae.MC-LR standard solution (20ug / L) was purchased from scientific testing by the Environmental Protection Department of Agriculture. Trifluoroacetic acid (purity > 99%) was purchased from Scharlau Company, methanol and other agents were of analytical grade.

2.2 Experimental apparatus and method

Using high performance liquid chromatography (HPLC) of Agilent 1200C for MC-LR was measured, measurement parameters: the injection volume was 20uL; UV-visible detector waveleng-

th 238nm; column temperature was 25 C; mobile phase 0.05% TFA aqueous solution/Methanol is 45/55; the flow rate was 1.0ml / min.Application of ozone generator (3S-A3), through iodometric method to measure the concentration of ozone, Control the ozone dosing quantity is 1 mg/L, 2 mg/L, 3 mg/L, 4 mg/L, 5 mg/L, the reaction time was 30min, the reaction temperature using room temperature is 25 C, and observe the response to the phenomenon.Determination of MC - LR containing algae water quality concentration is 5.3 ug/L.The TOC - VCPN total organic carbon analyzer of island ferry company to measure the TOC, measurement of turbidity using HACH 2100N turbidity analyzers,UV_{254} measured using CV-1700 UV-visible spectrophotometer. Water containing algae water quality characteristics are shown in table 1.

Table 1 raw water quality characteristics

turbidity(NTU)	pH	TOC(mg/L)	$UV_{254}(cm^{-1})$	COD_{Mn} (mg/L)	MC-LR (ug/L)
3.2	9.0	7.57	0.16	5.6	5.3

3 Results and Analysis

3.1 The effects of different pH values by ozone pre-oxidation

Ozone reflected at different pH values are distinct, under acidic conditions, a direct reflection of ozone with organic compounds, which are selective oxidation to produce carboxylic acids and some other simple organic matter or direct oxidation processes produce carbon dioxide and water. And under basic conditions, ozone and organic matter belongs indirectly reflects， the ozone production of hydroxyl radicals (·OH) under basic conditions, (·OH) and organic reflecting the rapid and strong oxidized, which are not selective oxidation, direct the organics were oxidized to carbon dioxide and water or an inorganic matter process[6].

3.1.1 Impact of ozone pre-oxidation on MC-LR under different pH conditions

Separately with sulfuric acid and sodium hydroxide adjust the pH of raw water to 4, 5.5, 7, 8.5 and 10,ozone dosage of 2mg/L, reaction time was 30min , the temperature reacting the using room temperature 25C, and observe the reaction phenomena, and retain the remaining water samples to other water quality characteristics were measured.

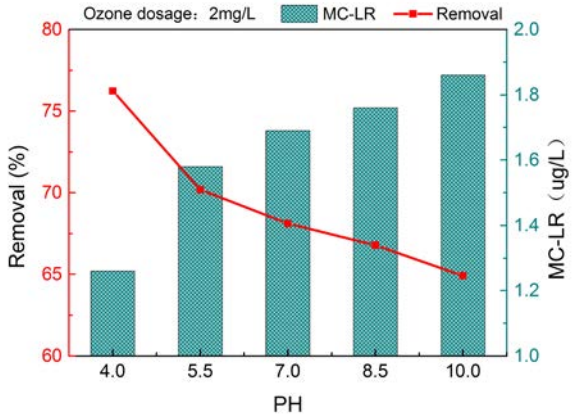

Fig. 1 Ozone pre-oxidation removal of MC-LR under different pH conditions

Figure 1 shows that the ozone removal efficiency of MC-LR decreases with the increase of pH, pH at 4, the ozone removal rate of MC-LR was 76.22%, the reason may be due to the acidic conditions, ozone mainly reflected a direct reaction, due to MC-LR molecules containing large amounts of unsaturated bond, under acidic conditions, the selective oxidation of ozone destroyed unsaturated bond of MC-LR, causing damage to the MC-LR, make it inactivated. And under alkaline conditions, ozone reflects indirectly reaction that (·OH) with organic matter in water reflects, (·OH) does not have a selective oxidation, other organic and algal toxins in the water to form the oxidation of competition, so that MC-LR can not be effectively removed.

3.1.2 The impact of ozone pre-oxidation on the water quality characteristics under different pH conditions

3.1.2.1 The removal of turbidity and UV_{254}

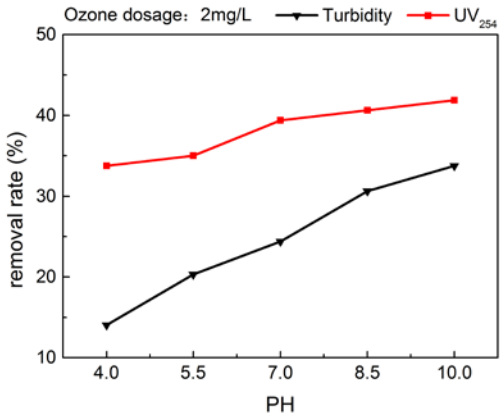

Fig. 2 Ozone pre-oxidation remove of turbidity and UV_{254} at different pH conditions

Seen from Figure 2,with the increase of pH value, ozone and water turbidity and UV_{254} removal rate is also increasing , pH 10, under the conditions, ozone oxidation of UV_{254} and turbidity removal rate was 33.75% and 41.88%, likely due to ozone produced under alkaline conditions more conducive (· OH) removal of turbidity and $UV_{254.}$

3.1.2.2 The impact of the TOC and COD_{Mn}

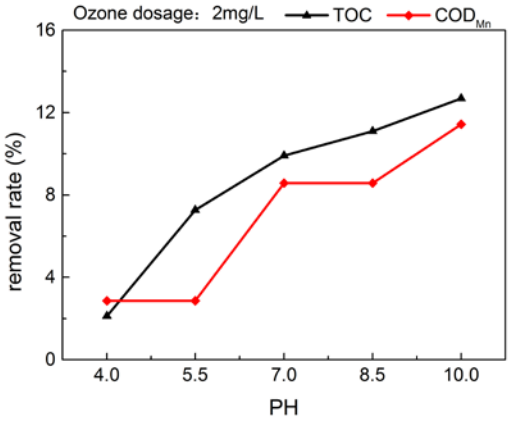

Fig.3 Ozone pre-oxidation remove of TOC and COD_{Mn} at different pH conditions

Seen from Figure 3, ozone removal rate of TOC and COD_{Mn} with the increase of pH value, under the condition of pH for 10, the ozone removal of TOC and COD_{Mn} were 12.68% and 11.43%, compared with the raw water the removal rate has enhanced. Analysis of the reasons may be due to ozone produced(·OH) under alkaline conditions,(·OH) will organics in water completely oxidized to carbon dioxide and water, thus removal of organic matter.

4 Conclusion

Ozone can effectively degrade MC-LR,under the condition of acid can improve the effect of ozone on algal toxin removal, under the condition of pH4, 2 mg/L ozone to MC - LR removal rate reached 76.22%,than the original water removal increased by about 11%.With the increase of pH,ozone to gradually reduce the removal rate of MC - LR, however, turbidity, UV_{254}, TOC, COD_{Mn} removal has been enhanced,in the pH of 10,ozone dosage case 2mg / L of ozone on water turbidity, UV_{254}, TOC, COD_{Mn} removal rate were 33.75%, 41.88%, 12.68%, 11.43%,the removal has been enhanced than the original water.

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References

[1] Z.J. Zhou, X.T. Zheng and Y.S. Zhang: Algae Toxins and Cancer. Carcinogenesis Distortion Mutation, Vol 9 (1997) No.6, p.335

[2] Hong-Xing S., Jiu-Hui Q., Ai-Min W., et al.: Degradation of Microcystins in Aqueous Solution with in Situ Electrogenerated Active Chlorine. Chemosphere, Vol (2005) No.60, p.326.

[3] Rivasseau C., Martins S., HennionM. C: Determination of some Physicochemical Parameters of Microcystins (Cyanobacterial Toxins) and Trace Level Analysis in Environmental Samples Using Liquid Chromatography. Journal of Chromatography A, Vol (1-2) (1998) No. 799, p.155.

[4] H.F. Miao, X. Lu, Q. Yan, L.J. Xie and W.Q. Ruan: Ozone Degradation Research of Microcystin Algae Toxin- LR [J].Environmental Science, Vol 30 (2009) No.11, p 3288.

[5] K.J. Zhang, N.Y. Gao, D.D. Yin and M.H. Sui: Dynamics Research of Ozone Oxidation Degra-dation of Algal Ttoxins - LR [J].Journal of Tongji University (Natural Science Edition), Vol 37 (2009) No.7, p.919.

[6] Y.B. Wu, R.Q. Li, Y.L. Tian, M. and J.N. Li: The Reaction Mechanism and Influence Factors of Ozone Degradation of Organic Pollutants (POPS) [J]. China Environmental Protection Industry, Vol (2010) No .03, p.44.