Ozone pre-oxidation to the degradation technology research of MC-LR

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Abstract. Ozone pre-oxidation can effectively degrade MC-LR, 2mg / L ozone for MC-LR removal efficiency of 65.28%. 2mg / L ozone for MC-LR removal efficiency reach to 65.28%. Ozone also has a better removal effect for turbidity and UV_{254} , 4mg / L ozone for UV_{254} and turbidity removal efficiency are 50% and 59.38%. But ozone removal efficiency of TOC and COD_{Mn} was poor, 3mg / L ozone for TOC and COD_{Mn} removal rate are only 15.06% and 14.29%.

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}.The experiment mainly to study the ozone removal of MC-LR.

Materials and Methods

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.

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 wavelength 238nm; column temperature was 25 ℃; 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℃, 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）	TOC（mg/L）	UV_{254}（cm^{-1}）	COD_{Mn}（mg/L）	MC-LR (ug/L)
3.2	7.57	0.16	5.6	5.3

Results and Analysis

The ozone pre-oxidation for MC - LR removal

Figure 1 shows that, ozone has good removal effect on MC – LR, with the increase of ozone dosing quantity, removal rate of MC - LR gradually strengthened. Ozone dosing 1 mg/L, MC - LR removal rate was 8.11%, at this point, the chroma of the water significantly reduce than raw water, analysis of the reasons may be due to ozone make the algal cells rupture and break down , resulting in decreased chroma. But the removal rate of MC - LR is low , possible reason is due to the bursting of the algal cells make intracellular toxin is released more [6, 7], lead to the removal rate of MC - LR is not obvious. Ozone dosing 2 mg/L, MC - LR removal rate reached 65.28%, removal rate significantly increased. 3 mg/L ozone for MC - LR removal rate reached 85.66%, relative to 2 mg/L ozone, removal rate increased by 20%, visible, ozone dosage exceeds 2mg / L, the removal efficiency of MC-LR showed a decreasing trend. Ozone can effectively remove the MC - LR is due MC - LR molecule contains plenty of unsaturated bond, ozone destroys the MC-LR unsaturated bonds, so as to be oxidized to become saturated small organic molecules.

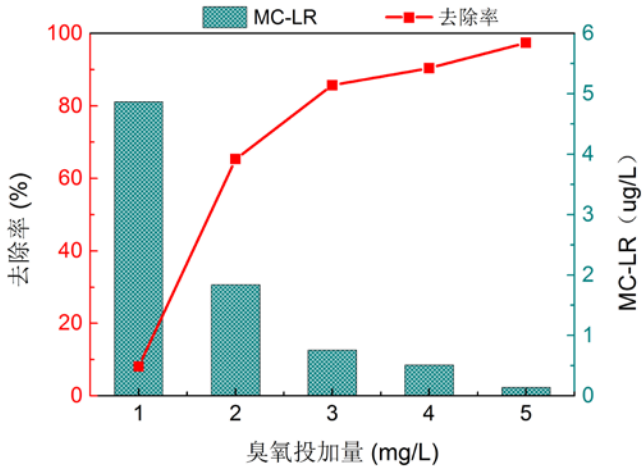

Fig. 1 Ozone pre-oxidation removal of MC-LR

The impact on other water quality characteristics of ozone pre – oxidation

The removal of turbidity and UV_{254}

The figure 2 shows, with the increase of ozone dosing quantity, ozone pre-oxidation for UV_{254} and turbidity removal rate gradually enhanced, dosing 4mg / L of ozone, turbidity and UV_{254} removal rate were 50% and 59.38%,continue adding ozone, the growth rate of removal rate is slow. Experiments show that ozone has a certain removal capability to turbidity and UV_{254} , but there are certain limits .

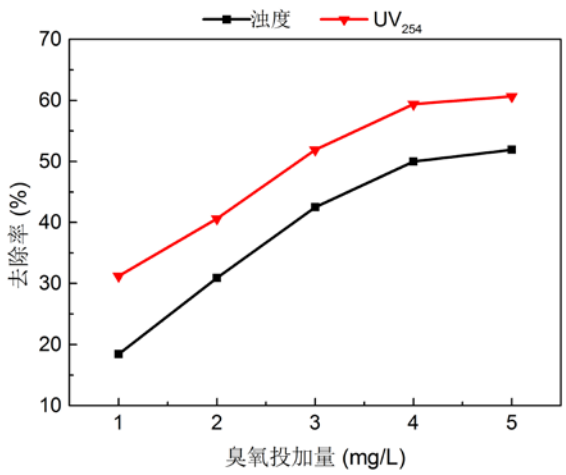

Fig.2 Ozone pre-oxidation to remove of turbidity and UV_{254}

The removal of TOC and CODMn

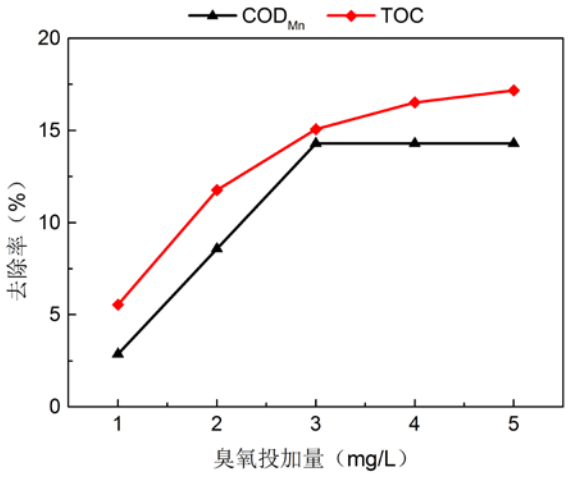

Fig. 3 Ozone pre-oxidation to removal of TOC and COD_{Mn}

The figure 3 shows, ozone pre - oxidation for TOC and COD_{Mn} removal capacity is limited, 3 mg/L ozone for TOC and COD_{Mn} removal rate was only 15.06% and 14.29%. Analysis of ozone can not effectively remove COD_{Mn} and TOC reason is due to ozone selective oxidation [8], ozone oxidation is mainly to change the structure and properties of organic matter, the macromolecular organic oxidation for small molecule organic matter,increase the organic matter composition with characteristics of saturated [9], and not the complete oxidation of organic matter.

Conclusion

Ozone can effectively degrade MC-LR, when ozone dosage of 2mg / L, MC-LR removal rate reached 65.28 percent, 3mg / L ozone for MC-LR removal rate was 85.66%, ozone can also effectively reduce turbidity and UV_{254}, 4mg / L ozone for UV_{254} and turbidity removal rates are 50% and 59.38%. But ozone removal efficiency of TOC and COD_{Mn} was poor, 3mg / L ozone for TOC and COD_{Mn} removal rate are only 15.06% and 14.29%.

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References

[1]Z.J.Zhou,Z.S. Xue and X.Z. Yu: 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] H.Y. Pei, W.R. Hu: Experimental study on ozone to kill algae characteristic [J]. Industrial Water Treatment, 2003,23 (9): 55-57.

[7] CHEN J J, YEH H H.The mechanisms of potassium permanganate on algae removal [J].Wat Res, 2005, 39(18) : 4420- 4428.

[8] P.K. Jin, X.C. Wang: Ozone oxidation characteristics of natural organic matter in water [J] . Environmental Chemistry, 2002, 21 (3): 259-263

[9] Owen D M, Amy D L, Chowdhury Z K et al., NOM Characterization and Treatability [J].J. AWWA.1995,87(1)B46)63