

The effect of two different catalysts on the formation of disinfection by-products in catalytic ozonation

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Summary

Two synthesized catalysts, which are Fe/Mn oxide and $\text{TiO}_2/\alpha\text{-Al}_2\text{O}_3$, were used in a catalytic ozonation system to investigate their effect on hydroxyl radical production and on the control of disinfection by-products (DBPs) formation. A fluidized bed reactor was used as the ozone contactor in order to maximize the contact surface between catalysts and dissolved ozone. A biofiltration column was used to evaluate its efficiency on treated water quality. It was found that the Fe/Mn oxide could effectively promote the formation of hydroxyl radicals more than the $\text{TiO}_2/\alpha\text{-Al}_2\text{O}_3$ did in the catalytic ozonation system. Using Fe/Mn oxide as the catalysts in the catalytic ozonation system also effectively decreased concentrations of dissolved organic carbon, levels of ultraviolet absorbance at 254 nm, and formation of DBPs in the treated water. Moreover, the treated water quality was further improved when the ozonation system was followed by a biofiltration process.

Keywords

Catalytic ozonation, disinfection by-products, DOC, SUVA, pCBA, Fe/Mn oxide, $\text{TiO}_2/\alpha\text{-Al}_2\text{O}_3$

Introduction

The heterogeneous catalytic ozonation process (HCOP) has been demonstrated that it can increase the formation of hydroxyl radicals ($\text{OH}\cdot$) through ozone reacts with catalysts such as metal and/or metal oxide in water (Pines and Reckhow, 2003), which promotes the degradation of refractory organic compounds (Chen et al., 2009). However, the HCOP is mostly applied in wastewater treatment and only few researches have studied its application on drinking water treatment for DBPs control. In this study, we used HCOP to treat polluted river water and compared the catalytic effect of two catalysts, Fe/Mn oxide and $\text{TiO}_2/\alpha\text{-Al}_2\text{O}_3$, in the catalytic ozonation process. First, the degradation of p-chlorobenzoic acid (pCBA), which was used as the probe to indirectly estimate the amount of hydroxyl radicals produced during catalytic ozonation, in model solution was determined. Then, river water samples taken from Wu-Lo River, Pingtung, Taiwan, were used to evaluate the treatment efficiency of HCOP. The effluent of HCOP was further treated by a biofiltration column to remove biodegradable organic compounds and improve treated water quality.

Materials and methods

A catalytic ozonation-fluidized bed reactor and a biofiltration column were used in this study. The Fe/Mn oxide and $\text{TiO}_2/\alpha\text{-Al}_2\text{O}_3$ catalysts were prepared in our laboratory according to the methods stated in Zhang et al. (2009) and Gracia et al. (2000), respectively. The pCBA was analyzed by high performance liquid chromatography system (HPLC, D-7000, Merck-Hitachi). DOC, UV254, and trihalomethanes (THMs) were analyzed in accordance with Standard Methods. The analysis of nine haloacetic acids (HAA9) was conducted according to USEPA Method 552.2. SUVA was calculated as the UV254 times 100 divided by the DOC concentration.

Results and discussion

The results show that both Fe/Mn oxide and $\text{TiO}_2/\alpha\text{-Al}_2\text{O}_3$ used in the catalytic ozonation process can promote the formation of hydroxyl radicals. Using Fe/Mn oxide as the catalysts resulted in more rapid decrease of pCBA concentrations than the $\text{TiO}_2/\alpha\text{-Al}_2\text{O}_3$ (Figure 1.1). The removal rate of pCBA also increased as the dosage of catalysts increased. This implied that more hydroxyl radicals were produced as the addition amount of catalysts increased.

Figure 1.2 shows the removal efficiency of DOC, UV254 and SUVA by adsorption of catalysts (A) and catalytic ozonation (B). The results show that the catalytic ozonation notably enhances the removal efficiency of UV254 and DOC than adsorption of catalysts. Besides, we found that the removal effectiveness of was higher than that of DOC. This implied that the loss of aromaticity and conjugation is easier to achieve than mineralization of the DOC. In the adsorption test, Fe/Mn oxide removed DOC and UV254 more effectively than TiO₂/α-Al₂O₃ did due to its high BET surface area. The SUVA values after catalytic ozonation treatment were lowered to about 0.5 L/mg-m indicated that a major fraction of hydrophobic substances of DOC was converted to hydrophilic ones. These water quality parameters were further reduced as the catalytic ozonation system was followed by biofiltration (data not shown). However, the effluent quality of the treated water was not affected by the type of catalysts as the biofiltration was installed after ozonation.

Figure 1.3 shows the reduction percentages of THMs and HAA9 formation by adsorption and catalytic ozonation. Using Fe/Mn oxide as the adsorbent and the catalysts in catalytic ozonation resulted in higher DBPs formation reduction than using TiO₂/α-Al₂O₃. The formation of THMs and HAA9 was reduced 87 and 88%, respectively, when Fe/Mn oxide was used in catalytic ozonation process. This implies that catalytic ozonation effectively removed DBPs precursors which apparently decreased DBPs formation when the treated water was chlorinated. This finding parallels the result of our previous study (Chen et al., 2009).

Conclusions

Fe/Mn oxide and TiO₂/α-Al₂O₃ used as catalysts in catalytic ozonation process produced more hydroxyl radicals than ozonation alone. The production of hydroxyl radicals increased as the dosage of catalysts increased. In the river water treatment, using Fe/Mn oxide in catalytic ozonation more effectively removed DOC and UV254, decreased SUVA, and reduced the formation of THMs and HAA9 than using TiO₂/α-Al₂O₃. Biofiltration followed the catalytic ozonation further improved the treated water quality, which was not affected by the type of catalyst used in the catalytic ozonation.

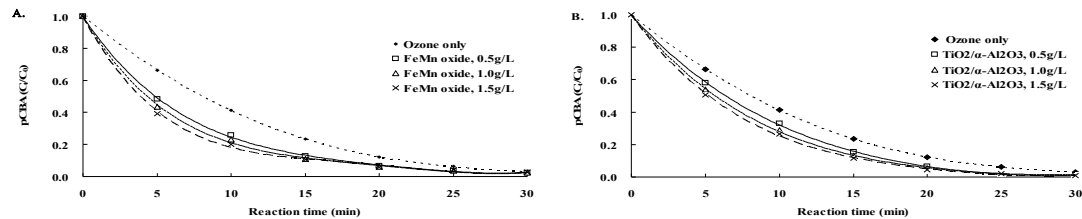


Figure 1.1 Effect of initial catalysts concentration (A) FeMn oxide and (B) TiO₂/α-Al₂O₃ on the decomposition of pCBA.

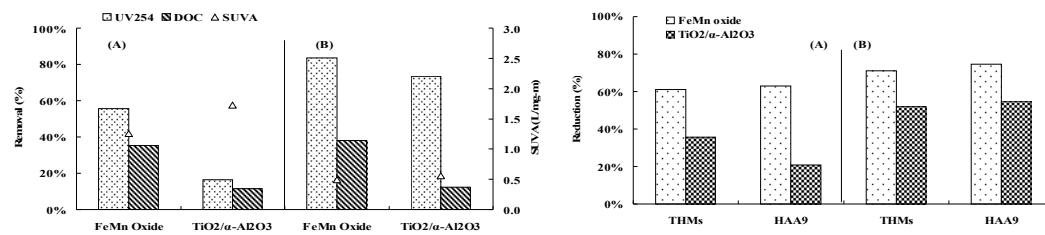


Figure 1.2 Removal efficiency of (A) adsorption and (B) catalytic ozonation on water parameters

Figure 1.3 Effect of (A) adsorption and (B) catalytic ozonation on DBPs formation reduction

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