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

Kuan-Chung Chen*, Yu-Hsiang Wang, Yu-Sum Tsai

*Department of Environmental Science and Engineering, Emerging Compounds Research Center (ECOREC), National Pingtung University of Science and Technology, No. 1, Shuehfu Rd., Neipu, Pingtung 91201, TAIWAN

Abstract

The catalytic activity of FeMn oxide and TiO_2/α-Al_2O_3 catalysts on ozonation of natural organic matter (NOM) and a model compound (pCBA) were investigated in a catalytic ozonation-FBR. Those analytic items in this study were including pCBA, DOC, UV254, simulated distribution system trihalomethanes (SDS-THMs), and nine simulated distribution system haloacetic acids (SDS HAA9). The catalyst of FeMn oxide was significantly improved the formation of hydroxyl radical in the catalytic ozonation process than using the TiO_2/α-Al_2O_3 catalyst. Nevertheless, the aqueous ozone concentration was increased with increased catalyst concentration when those catalysts were used catalytic ozonation process in pure water. The source water was polluted by domestic and agricultural wastewaters. In general, the catalytic ozonation showed better performance for removal efficiency of organic matter than adsorption in the study. Moreover, those removal efficiencies of UV254 value were significantly higher than DOC. The removal efficiency of DOC and UV254 were depending catalytic property. Thereamong, the catalyst of FeMn oxide have proved optimal character in experimental operating system. Then, that following used biofiltration column was significantly increased the removal efficiency of DPB precursor and decreased specific of DBPs yields.

Keywords
Catalytic ozonation, disinfection by-products, DOC, SUVA, pCBA, FeMn oxide, TiO_2/α-Al_2O_3

1. Introduction

Natural organic matter is widely exist surface water and groundwater, which is direct problem because it reacts with disinfectant as chlorine easily to form disinfection by products (DBPs) during water treatment, and that have been found to have carcinogenic properties [2, 14, 15].

Ozone is a recognized powerful oxidation and disinfectant that extensively used in water and wastewater treatment, which it has been affirmed to remove water contaminants effectively (discoloration, taste and odor control, elimination of micropollutants, etc.) [8, 19]. However, it has a few disadvantages, which limit its application in wastewater treatment technology. For example, relatively low solubility and stability in water, selectivity of ozone oxidation and incompletely oxidation of NOM.

Recently, the heterogeneous catalytic ozonation process (HCOP) has innovated as one of the advanced

oxidation processes (AOPs) technology in drinking water treatment. The HCOP was demonstrated that can increase formation of hydroxyl radicals (OH•) through ozone reacted with metal and/or metal oxide on catalyst surface than ozone alone [5, 11], and that promote the degradation of refractory organic compounds [3]. In addition, HCOP is equally effective under both highly acidic and highly alkaline conditions [4, 12], minimizes chlorine demand [18] and low cost. However, the previous studies has only a few using HCOP to control formation of DBPs in drinking water treatment, and that reaction mechanism of catalytic oxidation is not clearly understood.

In this study, we have investigated the catalytic effect of FeMn oxide and $TiO_2/\alpha-Al_2O_3$ on degradation of pCBA concentration (in pure water), water quality parameters (DOC and UV254) and formation of DBPs by using the experimental setup. Moreover, the biofiltration process has used to follow heterogeneous catalytic ozonation system, which uses biological treatment to remove those biodegradable organic compounds during the catalytic ozonation process, decrease microorganism regrowth in distribution system. Hence, the development of highly active catalysts removed DBPs precursor is the most important in heterogeneous catalytic ozonation system.

2. Materials and methods

2.1 Experimental operations and protocol

FeMn oxide and $TiO_2/\alpha Al_2O_3$ catalysts were choosing in this study, and using different treated model (adsorption and catalytic ozonation process) were observed removal efficiency of water quality parameters and DBPs formation reduction. Then, the treated water in the system was followed by biofiltration, which were analyzed water quality parameters (UV254 and DOC) and formation of DBPs concentration. The experimental operating conditions used in this study are given in Table 1.

Table 1. Operating conditions for the catalytic ozonation system.

Ozone gas flow rate (mL/min)	100
Ozonation concentration (mg O_3/L)	0, 2.5
Water temperature ℃	20
Catalyst types	FeMn oxide and $TiO_2/\alpha-Al_2O_3$
Catalyst dose (g) for raw water experiments	3.75
Catalyst dose (g) for pCBA experiments	0.5, 1.0, 1.5

Catalytic ozonation process

A catalytic ozonation-FBR in semi-continuous system and biofiltration system were used in this study. A schematic diagram of catalytic ozonation-FBR system is show in Fig. 1. The catalytic ozonation-FBR reactor was made of a clear acrylic column 6cm in diameter, 38cm in height, with a volume of 1.04L. The experimental temperature was maintained at 20℃. Ozone was generated using lab-scale ozone generator (Model OZ2PCS, Ozotech Inc., Yreka, CA), and that gas source was provided from pure oxygen gases cylinder. The air to be ozonized was precisely measured by UV/VIS

spectrophotometer (DR5000 HACH) at 254nm using a 1-cm path length quartz flow-through cell. An extinction coefficient of $3000M^{-1}cm^{-1}$ was used to convert absorbance reading into mg O_3/L. The ozone gas flow rate was defined 100 mL/min by using a mass flowmeter monitored, which ozonic gas was continual introduced to the FBR from the bottom of reactor. Excess in effluent gas was absorbed by 2% KI solution for the determination of ozone produce and consumption. The FBR reactor was stirred with a magnetic stirrer placed at its bottom to ensure good mixing of the three-phases contact (solid-water-vapor). The catalytic ozonation reaction time was controlled within 2 h, and followed the treated water immediate was using a high purity helium gas (99.999%) to quench residual dissolved ozone concentration before water quality analysis.
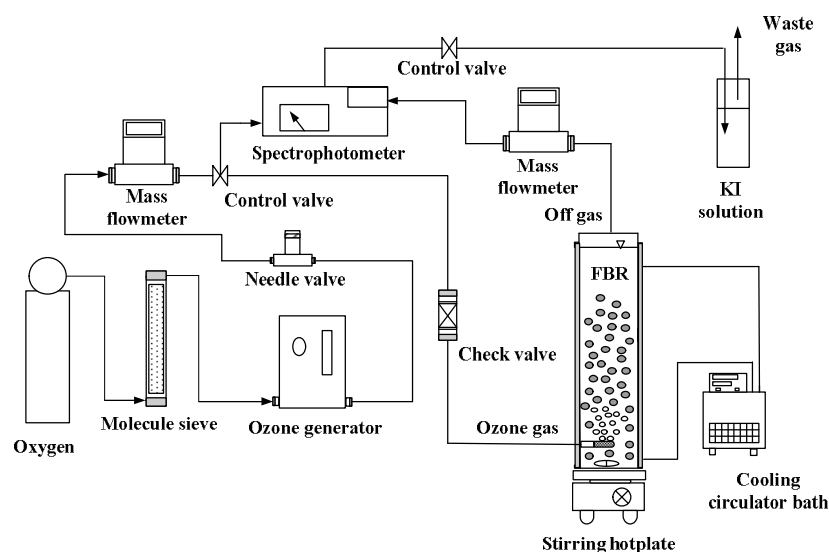

Fig. 1. Schematic representation of the catalytic ozonation system.

Adsorption experiments

In adsorption experiments, the catalyst dose was fixed 1.25mg/L, reaction time was 2 h, and experimental temperature was controlled at 20℃. Finally adsorption experiment the samples were filtered with a 0.45μm filters before analyzing water quality parameters.

Biofiltration system

The treated water from system was further treated in a biofiltration system that using recirculation mode for 3 days to discover removal efficiency of DBP precursors by the biofiltration process. The biofiltration system was accorded with previous study [3]. Untreated Wu-Lo River (WLR) water was used to seed the column, and the biomass reclamation was feeding by ozonated WLR water over period of 4 months, and make sure the biofiltration system treated efficiency became stable (as determined by analyzing the effluent quality periodically).

2.2 Preparation of catalyst

The FeMn oxide and $TiO_2/\alpha-Al_2O_3$ catalysts were prepared in our laboratory, which preparation methods was presented on the below. The catalysts characteristic were using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) on a Hitachi S-3000N system are

shown in Fig. 2. The BET surface area and pH of point of zero charge (pHpzc) are displayed in below Table 2.
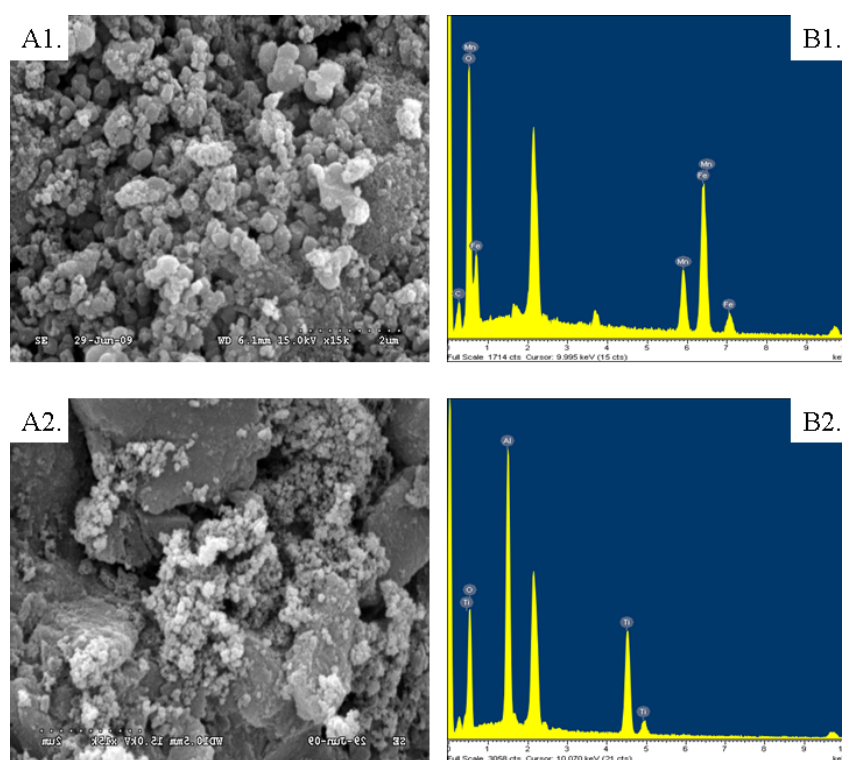

Fig. 2. SEM images of FeMn oxide (A1) and TiO_2/α-Al_2O_3 (A2); EDS surface analysis of FeMn oxide (B1) and TiO_2/α-Al_2O_3 (B2).

Table 2. Specific surface area and pHpzc of catalysts

Catalyst	BET surface area (m^2/g)	pHpzc
FeMn oxide	262.0	5.9 [20]
TiO_2/Al_2O_3	14.5	8.3 [24]

FeMn oxide

The FeMn oxide was using alkalic-deposition method according to Zhang et al. [21], which were prepared solutions of potassium permanganate ($KMnO_4$) and heptahydrate ($FeSO_4\cdot7H_2O$) that Fe/Mn mole ratio of 3:1. The $FeSO_4$ solution was slowly added into the $KMnO_4$ solution. Then, under vigorous magnetic-stirring, and 5M NaOH solution was simultaneously added to keep the solution pH in the range of 7 and 8. After addition, the formed suspension was continuously stirred for 1 h, followed to deposit at room temperature for 12 h, and then washed repeatedly with deionized water. The suspension was filtrated and dried at 105℃ for 4 h.

TiO_2/α-Al_2O_3

TiO_2 supported on alumina was prepared by adsorption in impregnation method [7]. Powdery α-Al_2O_3 (α-phase, Alderich) was immersed in a suspension consisting of TiO_2 anatase specimen (Degussa P25)

with constant shaking for 5 h for impregnation of TiO_2 in the support pores. The pH of the solution was 5.5 (H_2SO_4 0.1N). Then, the particles were washed by deionized water until the effluent was clear, and drying in the oven at 105℃ for 1 h, subsequently, put it in the oven to clacine at 500℃ for 24 h. Finally, the catalyst had been performed, which the catalyst contained about 10% impregnated TiO_2.

2.3 Water source

Water samples used in this study were collected from WLR, Pingtung, Taiwan, which is polluted by domestic and agricultural wastewaters. The characteristics of the raw water are summarized in Table 3. Water samples were collected in 25-L polyethylene tanks and stored in a refrigerator at 4°C for less than 7 days. Samples were warmed back to experimental operating temperature at 20℃ before being used, and through a 0.45 μm glass-fiber filter to remove coarse suspended and colloidal solids.

Table 3. Water characteristics of Wu-Lo River (Pingtung, Taiwan)

Parameters	Raw water
DOC (mg/L)	8.22–11.26
UV254 (cm^{-1})	0.150–0.219
NH_3-N (mg/L)	5.04–5.12
Alkalinity (mg/L as $CaCO_3$)	120–250
pH	8.15–8.57
SDS-THMs (μg/L)	216.1–265.9
SDS-HAAs (μg/L)	508.7–553.2

2.4 Analyses

pCBA and aqueous ozone

The detection of hydroxyl radical in solution was indirectly monitored by the p-chlorobenzoic acid (pCBA) as a hydroxyl radical (OH•) probe compound, and the initial pCBA was adjusted to 10μM concentration. The pCBA was analyzed by high performance liquid chromatography system (HPLC, D-7000, Merck-Hitachi) furnished a diode array detector (DAD, L-7544), an auto sampler, and a reverse-phased Mightysil RP-18 GP column (250×4.6mm). Then instrument operating parameter were 200μL injection volume, 65/35% of methanol/10mM H_3PO_4 acid eluent solution at speed of 1mL/min and UV-detection set at 240nm. The pCBA concentration detection limit was 0.03μM.

The concentration of ozone dissolve in the aqueous phase was determined using indigo method [1].

DOC, UV254 and SUVA

DOC were analyzed in accordance with Standard Method 5310B [1] that using a TOC analyzer (Model TOC-VCSH, Shimadzu, Tokyo, Japan) and determined by the combustion catalytic oxidation/NDIR method, which was the analytical variance of ±0.01mg • L^{-1} (n=3).

UV-254 was analyzed in accordance with Standard Method 5910B [1] that using a UV/VIS spectrometer (DR-5000, HACH) at 254 nm, which was the analytical variance of ±0.001 (n=3).

SUVA was calculated based on Chen et al. [3] as the UV-254 times 100 divided by the DOC concentration.

SDS-THMs and SDS-HAA9

Water samples were dosed with a chlorine concentration that allowed the free residual chlorine concentration to be in the range of 0.2 to 1.0mg/L after 48h incubation at room temperature according to the procedures delineated in Method 2350 and Method 5710 [1]. The SDS-THMs and SDS-HAA9 analyzed by a gas chromatography (Agilent HP 6890N) outfitted ^{63}Ni electron capture detector (ECD), an auto sample, Supelco Equity^{TM}-5 column (30 m × 0.25 mm I.D). The instrument operating condition was depended on our previous work [3]. At least three-replications of SDS-THMs and SDS-HAA9 measurements were performed.

Four SDS-THM compounds, chloroform ($CHCl_3$), bromodichloro methane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromo form ($CHBr_3$), were monitored in this study. SDS-THMs were extracted with hexane in accordance with Method 6232B [1].
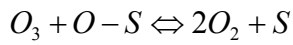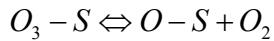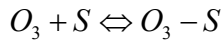
The SDS-HAA9 compounds were determined monochloroacetic acid (MCAA), mono bromoacetic acid (MBAA), dichloroacetic acid (DCAA), bromochlor oacetic acid (BCAA), trichloroacetic acid (TCAA), Bromodichloroacetic acid (BDCAA), dibromoaceti acid (DBAA). chlorodibromoacetic acid (CDBAA), Tribromoacetic acid　(TBAA), and which quantification was carried out according to USPEA method 552.2.
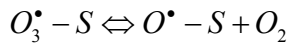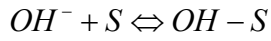
3. Results and discussion

3.1Decompostion of pCBA

The effect of decomposition of pCBA concentrations at various FeMn and TiO_2/α-Al_2O_3 concentrations are shown in Fig. 3A and 3B, respectively. This study was performed continuous-flow ozonation with pure water on the semi-batch unit, which water samples were spiked with 10μM of para-chlorobenzoic acid (pCBA) before ozonation and adjusted to the pH 8 by phosphate and sodium hydroxide. The pCBA was used for the OH•-probe; it has a very low reactivity with O_3 ($k_{O_3/pCBA} \leq 0.15$ $M^{-1}S^{-1}$), but reacts readily with OH• ($k_{OH•/pCBA} = 5 \times 10^9$ $M^{-1}S^{-1}$). The results show that removal rate of pCBA increased with increased both FeMn oxide and TiO_2/α-Al_2O_3 concentrations. Additionally, the results did not show any detectable adsorption of pCBA on the catalyst surface (data no shown). That means producing of hydroxyl radicals was accelerated by the catalytic reaction of ozone on the catalytic surface as follow as [9]:

$pH\,2-6:$

$$O_3 + S \Leftrightarrow O_3 - S$$

$$O_3 - S \Leftrightarrow O - S + O_2$$

$$O_3 + O - S \Leftrightarrow 2O_2 + S$$

$pH > 6$

$$OH^- + S \Leftrightarrow OH - S$$

$$O_3 + OH - S \Leftrightarrow O_3^\bullet - S + HO^\bullet$$

$$O_3^\bullet - S \Leftrightarrow O^\bullet - S + O_2$$

$$O_3 + O^\bullet - S \Leftrightarrow O_2^{\bullet-} + S + O_2$$

The aqueous ozone concentrations were monitored in pure water and those using the kind of catalysts are presented in Fig. 4. The results show that the aqueous ozone concentration increased with increased both catalyst concentrations. These results suggest that the catalysts of FeMn oxide and $TiO_2/\alpha\text{-}Al_2O_3$ could be able to increase solubility of ozone in water. Also, the maximum concentration of ozone in water was depending on the amount of catalytic surface area [9].
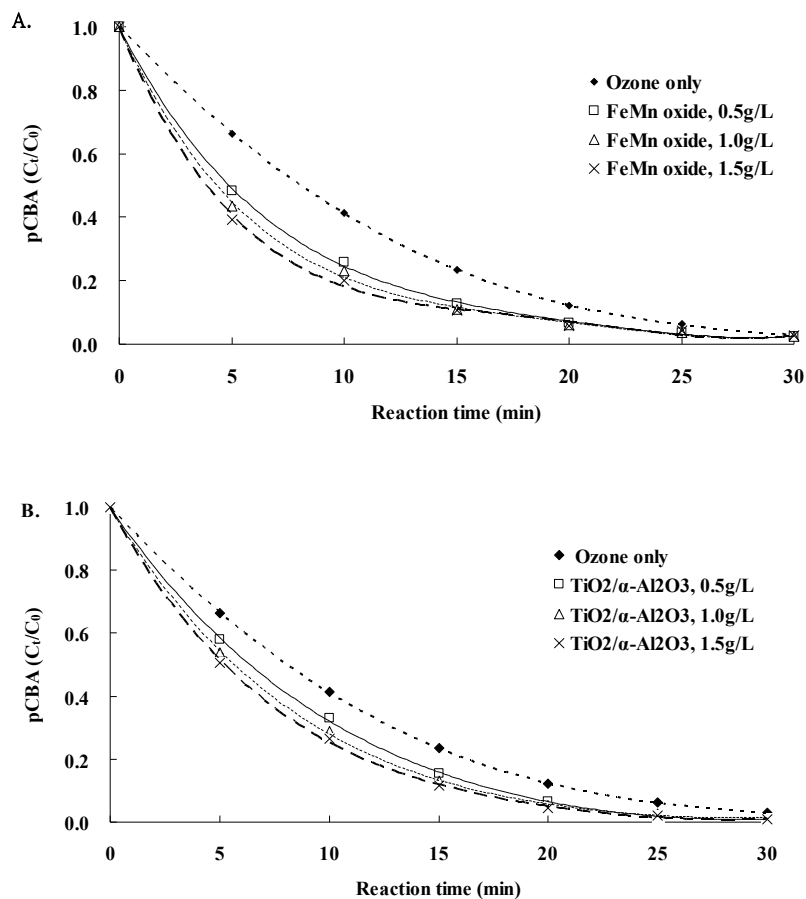

Fig. 3. Effect of initial catalysts concentration (A) FeMn oxide and (B) $TiO_2/\alpha\text{-}Al_2O_3$ on the decomposition of pCBA.
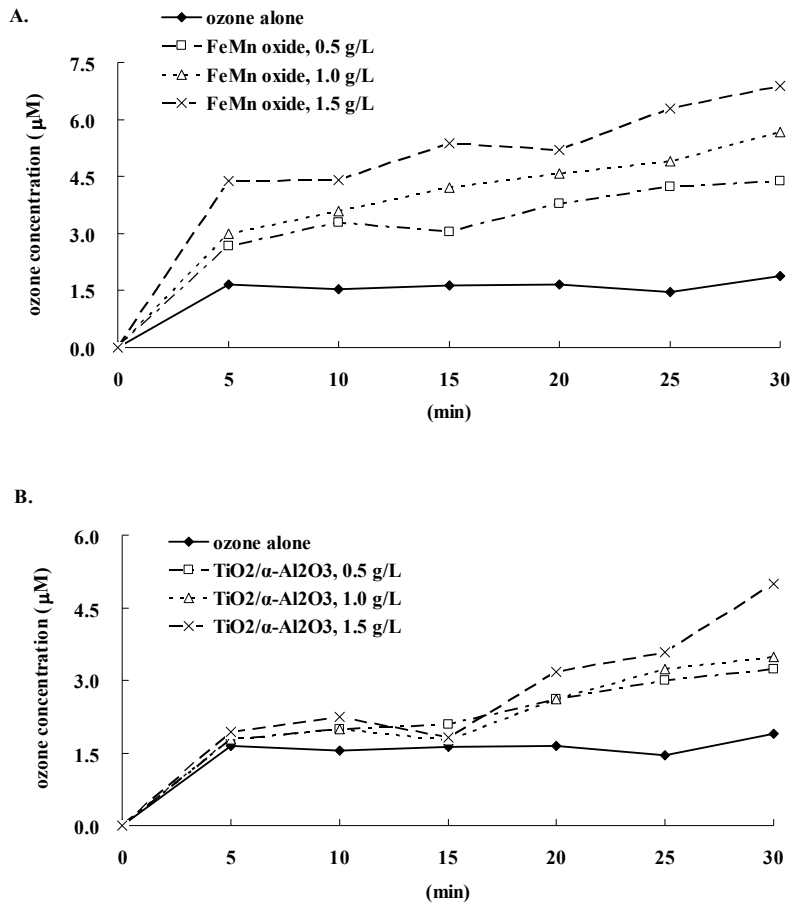
Fig. 4. Effect of initial catalysts concentration (A) FeMn oxide and (B) $TiO_2/\alpha\text{-}Al_2O_3$ on the ozone concentration.

3.2 Effect of water quality parameter on the catalysts

The effect of water quality parameters for adsorption and catalytic ozonation process treated raw water are shown in Fig. 5. Those catalysts were employed for the experimental operating conditions. Subsequently, that treated water followed by biofiltration system is shown in Fig. 6. Those UV254 and DOC in catalytic ozonation process were removed range from 74 to 83% and 12 to 38%, respective. The UV254 and DOC in adsorption were removed rang from 17 to 56% and 11 to 35%, respectively. For adsorption capability, it is depending on catalytic surface area and catalyst characteristic. Compared to the $TiO_2/\alpha\text{-}Al_2O_3$, the FeMn oxide has better removal efficiency for water quality parameters in the adsorption. Because the FeMn oxide has much larger surface areas than the other catalysts, for these could be able to absorb relatively large organic matter. On the other hand, the solution pH value is an important role of one for influenced catalytic surface property during adsorption. The catalytic surface will adsorb anions when the pH value was much below pHpzc. Whereas, the adsorption of the cations will takes place at a pH value higher than pHpzc [9]. These catalysts pHpzc were shown in Table 2. Comparison of adsorption and catalytic ozonation process, the results indicate that catalytic ozonation notably enhances the removal efficiency of UV254 and DOC than adsorption. This suggest that the

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adsorption effect is weakly due to the large extension of negatives charges on the catalytic surface excluded more organic species to be adsorbed. Hence, it might lead to adsorption capacity lower than catalytic ozonation process. This result is consisted with previous study [6, 16, 23]. Moreover, we found that the UV254 removed effective was higher than DOC removed. This implied that the loss of aromaticity and conjugation is easier to achieve than mineralization of the DOC. This result is mainly due to the catalytic surface specific functional group can increased reacting rate for decomposition of ozone and hydroxyl radical generation [9]. Besides, the results indicated that UV254 matter (i.e. aromatic structures, double bonds of DOC) was easily adsorbed on the catalytic surface (see Fig. 5), that will further increased reaction with ozone.

The treated water in the catalytic ozonation-FBR system had been followed biofiltration system and to observe the change of water quality parameters (see Fig. 6). The results show that the removal efficiency of water quality parameter was a sharp increased as system subsequent using biofiltration system. Furthermore, the biofiltration system before using catalytic ozonation process could attain good water quality parameters than adsorption. In the adsorption followed by biofiltration system experiment, the removal efficiency of UV254 and DOC was 60 to 73% and 71 to 73%, respectively. In addition, the removal efficiency of UV254 and DOC in biofiltration system before used catalytic ozonation process was 85 to 90% and 80 to 84%, respectively. This suggests that the catalytic ozonation process result in converting the DOC to more biodegradable compound and enhancing the removal efficiency. As expected, the oxidation processes which were followed with biofiltration decreased the DOC and UV254 levels in the treated water further and more effectively. Moreover, the results indicated that the removal efficiency of water quality parameters were no significantly differences from various catalysts if biofiltration system was treatment has finally treated process.
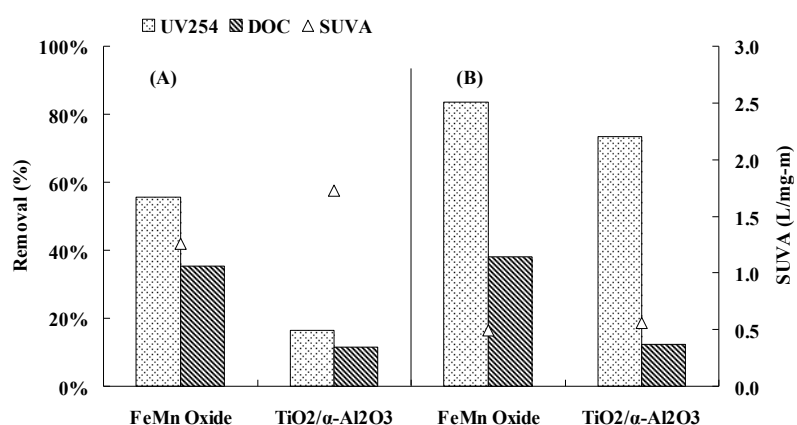

Fig. 5. Effect of different treatment processes (A) adsorption and (B) catalytic ozonation on the water quality parameters.
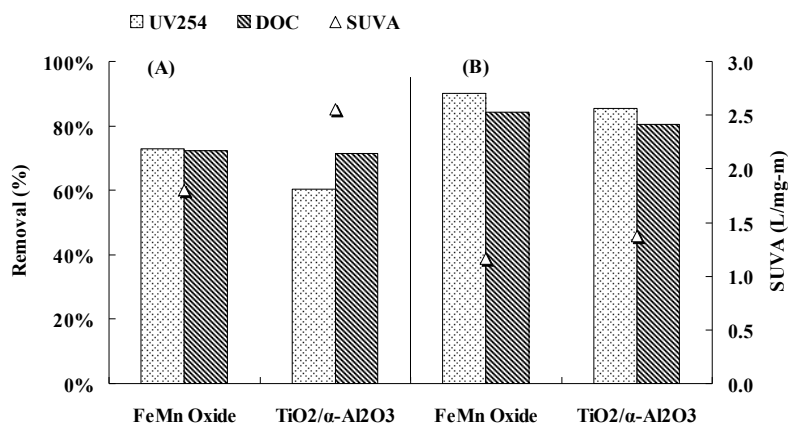
Fig. 6. Effect of different treatment processes (A) adsorption and (B) catalytic ozonation with Biofiltration on the water quality parameters.

3.3 Effect of disinfection by products on the catalysts

The effect of disinfection by products for adsorption and catalytic ozonation process are shown in Fig. 7. Furthermore, the catalysts were used in different treated process for adsorption and catalytic ozonation compared to specific of SDS-THMs and SDS-HAA9 yields (i.e. THMs/DOC or HAA9/DOC) are shown in Fig. 8. The removal efficiency of SDS-THMs and SDS-HAA9 precursors in the adsorption were 61% and 36% for FeMn oxide, 63% and 21% for $TiO_2/\alpha-Al_2O_3$, respectively. For the using catalytic ozonation process, the removal efficiency of SDS-THMs and SDS-HAA9 precursors were significant increased, which results were 71% and 52% for FeMn oxide, 75% and 55% $TiO_2/\alpha-Al_2O_3$, respectively. Comparison of adsorption, the results show that used catalytic ozonation could effective removed DBPs precursors, and that apparent decreased DBPs formation when the treated water was chlorinated (especially $TiO_2/\alpha-Al_2O_3$). This finding parallels the result of our previous study [3].
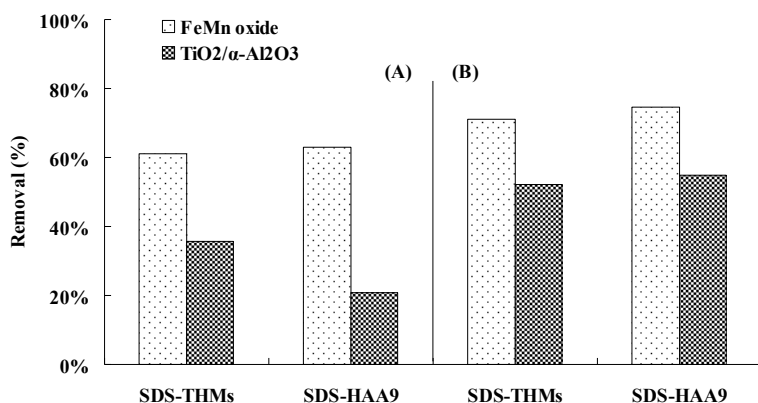

Fig. 7. Effect of different treatment processes (A) adsorption and (B) catalytic ozonation on the removal efficiency of DBPs

4. Conclusions

The degradation of pCBA and water quality parameters with adsorption and catalytic ozonation were compared and the effects of various factors were investigated. It was found that the catalysts of FeMn oxide and $TiO_2/\alpha-Al_2O_3$ were improved the formation of hydroxyl radical and increased aqueous ozone concentration in catalytic ozonation process. The maximum concentration of ozone in water was depending on the amount of catalytic surface area. The catalytic ozonation showed higher efficiency than adsorption for the water quality parameters. Thereamong, the removal efficiency of UV254 vale in treated water was higher than DOC in all treatment process. The used catalyst of FeMn oxide for catalytic ozonation system could be able to remove water quality parameters and decreased the formation of DBPs concentrations than using catalyst of $TiO_2/\alpha-Al_2O_3$. Furthermore, the catalytic ozonation system followed biofiltration column had further decreased the water quality parameters and DBPs concentrations. Additionally, the properties of catalytic surface were resulted in SUVA in the treated water, which was affected formation of SDS-THMs and SDS-HAA9 concentrations.

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