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Catalytic Ozonation of Humic Acids with Fe/MgO

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Abstract−Humic acids were degraded by ozone at room temperature in a stirred tank reactor and a fixed bed reactor with Fe/MgO catalysts. Experimental results show that the ozonation with Fe/MgO induced a significant reduction in UV absorbance of humic acids as compared to ozone alone. Fe/MgO was the most efficient catalyst to degrade humic acids in the presence of ozone. GPC (gel permeation chromatography) showed that the humic acids with high molecular weight could be severely decomposed into organic compounds with low molecular weight on the Fe/MgO catalyst, indicating that humic acids could be catalytically decomposed. The continuous reaction experiments with the palletized catalysts supported that humic acids can be removed by catalysis as well as adsorption.

Key words: Fe/MgO, Catalytic Ozonation, Humic Acids, Ozone

INTRODUCTION

Ozonation has been used in advanced water treatment processes to minimize the formation of trihalomethanes during chlorination for sterilizing and to decompose NOM (natural organic matter) in all raw surface waters for drinking water [Rice, 1980; Amy et al., 1991; Shukairy and Summers, 1992; Kong et al., 2003]. Several processes have been attempted to enhance the oxidation performance of the ozonation. Ozone-H_2O_2 [Paode et al., 1995; Brodard, 1985] and ozone-UV [Schwammlein and Leizke, 1995; Glaze et al., 1987] systems led to the degradation of organic solvents such as alcohols, aliphatic acids and aldehydes that are refractory to the ozonation only. Catalytic ozonation has been attempted to decompose organics in the presence of transition metal. Fe(II), Mn(II), Ni(II), or Co(II) sulfate was reported to be effective for the TOC (Total Organic Carbon) removal during ozonation of waste waters as compared to ozonation only [Hewess and Davinson, 1972; Gracia et al., 1996; Andreozzi et al., 1992; Mok and Nam, 2004]. Zinc sulfate, silver nitrate and chromium trioxide were shown to catalyze the bleaching of dye effluents during ozonation, and it was reported that ozonation with transition metal ions required the pH control of wastewater and was effective in the highly acidic condition (pH<4.0) [Abdo et al., 1988]. MnO_2 was also suggested to be effective on a mineralization of benzene and 1,4-dioxane by the catalytic ozonation [Naydenov and Mehandjiev, 1992; Thompson et al., 1995], atrazine [Ma and Graham, 1997] and oxalic acid [Andreozzi et al., 1996] at acidic pH. The dissolved MnO_2 has been mostly used for the catalytic ozonation of pyruvic acids [Andreozzi et al., 1998], indicating that the dissolved MnO_2 has catalytic effects on catalytic ozonation in the presence of MnO_2. Goethite was attempted to oxidize chlorobenzene with ozone, which was more effective than ozonation alone [Bhat and Gurol, 1995]. It is interesting to note that that Fe ion in Fe-ZSM-5 could behave like homogeneous Fenton-type catalysts [Centi et al., 2000], but it required a high temperature above 100 °C and acidic condition below pH 5. It was observed that Fe in Fe/MgO catalysts was paramagnetic, indicating that it is in the ionic state [Jung et al., 2002]. In this study, the catalytic ozonation of humic acids was conducted to investigate the effect of the heterogenized Fe ion on the Fe/MgO catalysts.

EXPERIMENTAL

Fe/MgO, Fe/Al_2O_3, Fe/SiO_2 and Fe/ZrO_2 were prepared by impregnation method with aqueous iron nitrate solutions, followed by drying at 100 °C and subsequent calcination at 733 K in air for 5 h. After the calcinations, 6% Fe/MgO, 6% Fe/Al_2O_3 and 6% Fe/SiO_2, and Fe/ZrO_2 were obtained. MnO_2 sample (Alfa, Co) was also used for the catalytic ozonation for a comparison with Fe based catalysts.

A stirred tank reactor of 2.5 L volume (5 cm (Dia.)×40 cm (Height)) was used for the catalytic ozonation. Ozone was produced by an ozonizer (Pacific Ozone Technology, USA) supplied with oxygen (5 scfm). Humic acids (Acros-sodium salt tech Co.) are dissolved with ionized water and are filtered with a membrane filter (0.45 μm, Advantec MFS, Inc.) to remove solid phase un-dissolved in water. Catalyst (500 mg) was dispersed in the stirred reactor with ionized water of 2 L. Gases such as oxygen, nitrogen, and ozone were supplied in the stirred reactor filled with 2 L of ionized water through perforated diffuser, and 0.5 L of aqueous humic acid solution was introduced for the catalytic ozonation.

Extruded catalysts were prepared for continuous reaction. Fe/MgO catalyst (74 wt%) was mixed with SiO_2 (26 wt%). The physically mixed samples were ground and dried at 130 °C for 24 h and calcined at 600 °C for 2 h. The calcined powder was extruded into 0.3 cm (I.D.)×1 cm (Length) cylinder shape. The fixed bed reactor consisted of upper part filled with extruded catalysts (2.5 cm (I.D.)× 15 cm (Length)) and lower part for ozone alone (4 cm (I.D.)×20 cm (Length)). The extruded catalysts (32 g) were charged in the upper part of a fixed bed reactor for a continuous reaction. The reactor was charged with distilled water, which was saturated with ozone

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(7.5 mg O_3/L, 5 scfm). Glass beads instead of the palletized catalysts were used for the experiments with ozone alone. Aqueous humic acid solution (10 mL/min) was supplied into the reactor via diffuser with metering pump (Fluid Metering, Inc.) in the ozone stream. Humic acid concentration was dissolved to be 50 ppm in reactant solution for both a batch and a continuous reaction. Humic acid was not well dissolved at a concentration above 50 ppm. Ozone treated humic acid samples were analyzed by UV-vis spectroscopy, a TOC analyzer and a GPC. UV absorption measurements were performed at 254 nm (UV-vis spectrophotometer, Cary 100, Varian). Total organic carbon (TOC) was analyzed in NPOC (Non-purgeable organic carbon) mode with TOC-analyzer (Pharma TOC, Analytikjena). Molecular weight distributions were analyzed with Gel permeation chromatography (Spectra system P2000, Spectra-Physics Inc.) using Asahipak GF-510HQ column (Shodex). Molecular weights were calibrated with standard solution (Pullulan, Shodex). Fe valence state on Fe/MgO was confirmed by XPS (Phi 5800, Physical Electronics).

RESULTS AND DISCUSSION

Fig. 1 shows UV absorbance changes of aqueous humic acid solution in a stream of ozone with the reaction time. A slight decrease in UV absorbance at 254 nm is observed with the ozone introduction of 3.9 mg O_3/L. As the dosage of ozone increased with 7.5 mg O_3/L and 17.8 mg O_3/L, UV absorbance of product samples at 2.5 min reaction time decreased up to 91.7%, 82.7% and 60.7% of the initial value, respectively. The decreasing rate of UV absorbance is proportional to the first order of the ozone dosage in gas phase. The pH of the reaction solution during the reaction was 8.5 at 2.5 min and spontaneously approached to 9.1 and maintained at 9.1 afterwards. It has been known that ozonation of humic substances leads to a quick decolorization [Killops, 1986; Gilbert, 1988]. A decrease in UV absorbance was attributed to the loss of aromaticity [Anderson et al., 1986] which could be attributed to a depolymerization as observed in the case of natural waters containing high levels of humic substances [Rice, 1980]. It was shown that aromatic moieties or conjugated double bonds could be easily oxidized by ozone dosage [Xiong et al., 1992]. Fig. 2 shows the UV absorbance of products against reaction times in the catalytic ozonations on Fe/MgO, Fe/Al_2O_3, Fe/SiO_2, Fe/ZrO_2 and MnO with the ozone introduction of 7.5 mg O_3/h. Fe/MgO shows the lowest UV absorbance among the tested catalysts during the catalytic ozonation, indicating that Fe/MgO can be most effective for the catalytic ozonation of humic acids. MnO_2 has been known to be effective for the catalytic ozonation, but it has no catalytic activity in this reaction condition of higher pH than 7. It is interesting to observe that Fe/MgO catalyst shows high activity even at about pH 9. Fe/Al_2O_3 and Fe/ZrO_2 show lower UV absorbance than ozone alone, while Fe/SiO_2 shows the same UV absorbance as ozone alone. It has been reported that Fe/Al_2O_3 has been used in an attempt to enhance the ozonation of phenol [Hayek et al., 1989] and is also shown to be slightly effective for the ozonation of humic acids in this study. Fig. 3 shows UV absorbance of products in catalytic ozonation with Fe/MgO in a stream of N_2, O_2 and O_3. The aqueous humic acid solution with Fe/MgO was bubbled by 5 scfm of N_2 for examining the adsorption effect on the absorbance decrease. The absorbance of the products with Fe/MgO decreases up to 40% of the initial ones even by N_2. The absorbance decrease by N_2 bubbling can be ascribed to the physical adsorption of humic acids on Fe/MgO, although the N_2 bubbling cannot exclude the presence of oxygen. Catalytic oxidation with Fe/

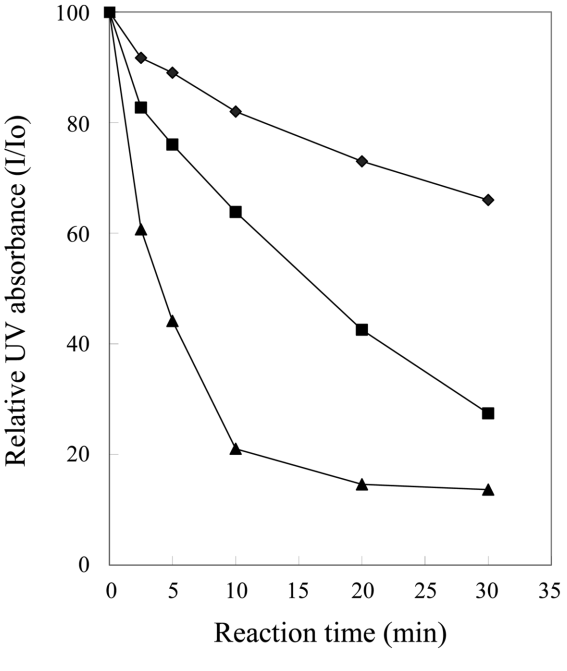

Fig. 1. Relative UV absorbance change at 254 nm of humic acid solution dosed with 3.9 mg O_3/L (◆), 7.5 mg O_3/L (■) and 17.8 mg O_3/L (▲); O_2 flow rate=5 scfm.

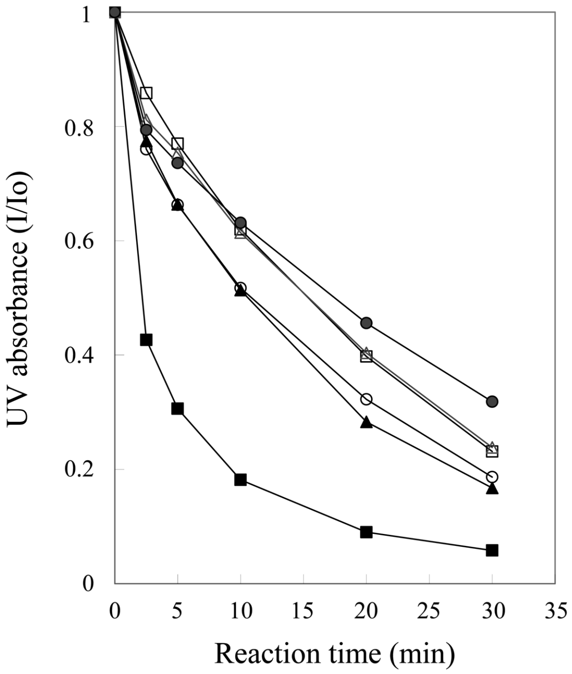

Fig. 2. Relative UV absorbance change at 254 nm of humic acid solution dosed with 7.5 O_3/L and catalysts: (△) ozone alone, (●) MnO_2+ozone, (□) Fe/SiO_2+ozone, (○) Fe/Al_2O_3+ozone, (▲) Fe/ZrO_2+ozone, (■) Fe/MgO+ozone.

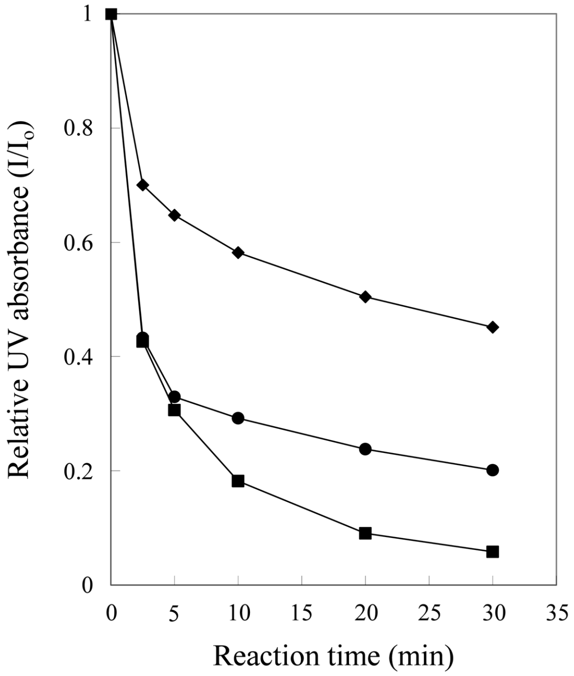

Fig. 3. Relative UV absorbance change at 254 nm of humic acid solution dosed with (◆) N_2+Fe/MgO, (●) O_2+Fe/MgO and (■) O_3+Fe/MgO; O_3 dosage=7.5 mg O_3/L; gas flow rate =5 scfm.

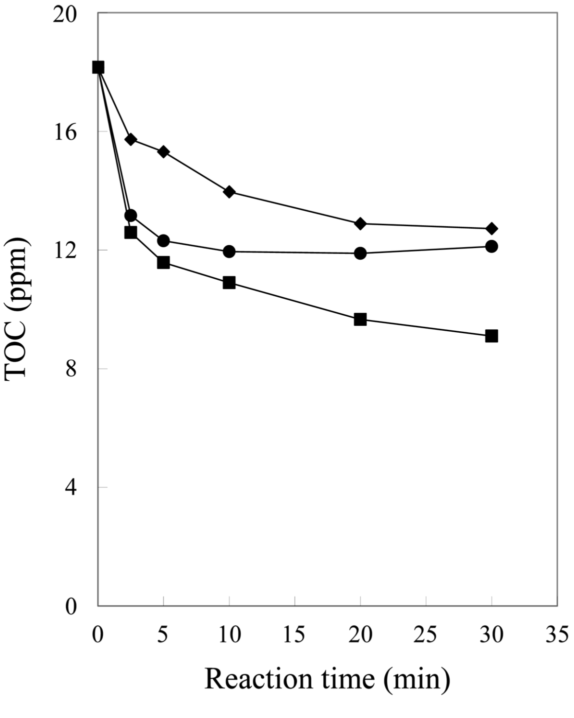

Fig. 4. TOC concentration against the reaction time dosed with (◆) O_3 alone, (●) N_2+Fe/MgO and (■) O_3+Fe/MgO; O_3 dosage=7.5 mg O_3/L; gas flow rate=5 scfm.

MgO in O_2 stream can reduce the absorbance more than N_2. The enhanced activity with O_2 indicates that humic acids can be catalytically oxidized even by O_2 with Fe/MgO, since the absorbance of humic acid was little changed in O_2 stream alone without Fe/MgO. As compared to the catalytic oxidation in O_2 stream and to the adsorption of humic acids with N_2 stream, the ozonation with Fe/MgO clearly shows high activity for the removal of aromatic compounds. At this moment, it cannot be ruled out that the high loss in UV absorbance with Fe/MgO in O_3 stream can be due to the sum of the adsorption and the ozonation by O_3 alone. The decrease in UV absorbance can be due to the loss of aromaticity of humic acids, but it does not mean that the humic acids can be decomposed to CO_2. For the confirmation of carbon content loss, TOC of aqueous humic acid solution was analyzed for the treated sample. Fig. 4 shows TOC reduction against the reaction time with O_3 alone and Fe/MgO in a stream of N_2 and O_3. TOC of initial aqueous humic acid solution was 18 ppm. The reduction of TOC in N_2 stream can be ascribed to the adsorption of humic acid on Fe/MgO. The reduction of TOC with Fe/MgO in N_2 stream is higher than that in O_3 alone, indicating that adsorption is more effective on the removal of TOC. It has been known that TOC reduction in O_3 alone is small (e.g. 10% at 1 mgO_3/mgC). In this case, 17.6 mgO_3/min in O_2 stream (O_3 concentration: 7.5 mg/L, gas flow rate: 2.35 L/min) was dosed and 45 mgC of humic acids (18 ppmC in 2.5 L) was charged. Therefore, 3.9% TOC reduction/min can be simply estimated. In 2.5 min reaction, 16.2 ppm of TOC can be predicted with this simple calculation. It is interesting to note that TOC reduction by a simple calculation is within 3% deviation of the experimental TOC reduction in O_3 stream. After 2.5 min, TOC reduction rate is retarded with the reaction time. One of important features of O_3 decomposition of humic acids was a slight decrease in the high apparent molecular weight fractions and a slight increase of small fractions. Fig. 5 shows GPC spectra of the samples after 5 min reaction. GPC shows

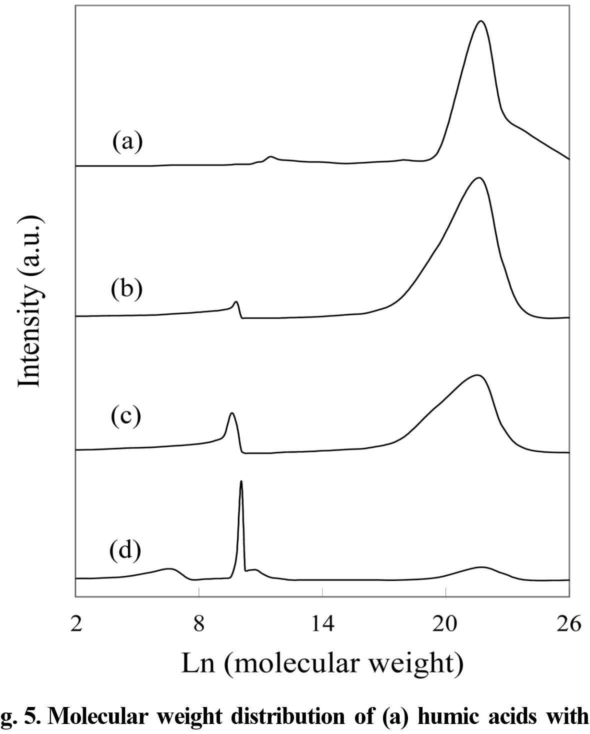

Fig. 5. Molecular weight distribution of (a) humic acids without treatment and humic acids treated for 5 min with (b) N_2+ Fe/MgO, (c) O_3 alone and (d) O_3+Fe/MgO; O_3 dosage=7.5 mg O_3/L; gas flow rate=5 scfm.

the molecular weights of humic acids are distributed from 5×10^9 g to 5×10^{11} g. The molecular weight distribution of humic acids is not much changed by the reaction with Fe/MgO in N_2 stream, indicating that most of the TOC reduction could be due to the adsorption of humic acids on Fe/MgO. The proportion of organics with about 16,000 g molecular weight increases with the reaction with O_3 alone, supporting that the humic acids with high molecular weight can be slightly decomposed into small molecules by O_3 treatment. The reaction of humic acids with Fe/MgO in O_3 stream shows that most of the humic acids can be decomposed into small molecules. From GPC analysis, not only can catalytic ozonation enhance the reduction of UV absorbance and TOC by a simple sum of the adsorption and the ozonation, but also by catalytic decomposition.

The continuous reactions were conducted with a fixed bed reactor. For comparison, the glass beads were charged in the fixed bed reactor instead of the catalyst pellets for the reaction in O_3 alone stream. Fig. 6 shows the change of UV absorbance at 254 nm and TOC of humic acids with O_3 alone and Fe/MgO in N_2 and O_3 stream. UV absorbance with Fe/MgO in N_2 stream steadily increases with the reaction time, while one with O_3 alone is not much changed after 7 h, indicating that steady state is obtained after 7 h. A steady state after 7 h reaction is also obtained with Fe/MgO in O_3 stream. The continuous experimental results suggest that the decrease of UV absorbance can be due to the catalytic reaction, supporting the result of GPC analysis. TOC measurements also support the result of UV absorbance measurements.

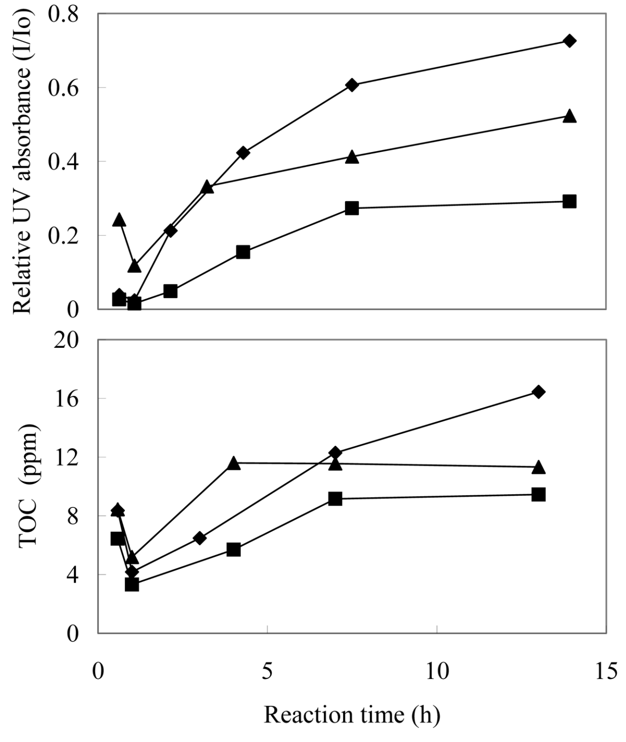

Fig. 6. Relative UV absorbance change at 254 nm and TOC changes of humic acids treated in a continuous reactor; (◆) N_2+Fe/MgO, (▲) O_3 alone and (■) O_3+Fe/MgO; O_3 dosage=7.5 mg O_3/L; gas flow rate=5 scfm; feeding rate of aqueous humic acid solution=10 mL/min.

Table 1. The physical properties of Fe/MgO, Fe/Al_2O_3, Fe/SiO_2 and Fe/ZrO_2

Catalysts	Fe/MgO	Fe/Al_2O_3	Fe/SiO_2	Fe/ZrO_2
BET surface areas (m^2/g)	49.3	168.2	247.6	12.4
Pore volume (cc/g)	0.14	0.22	0.37	0.04
Average dia. (nm)	11.5	5.2	6.0	13.8

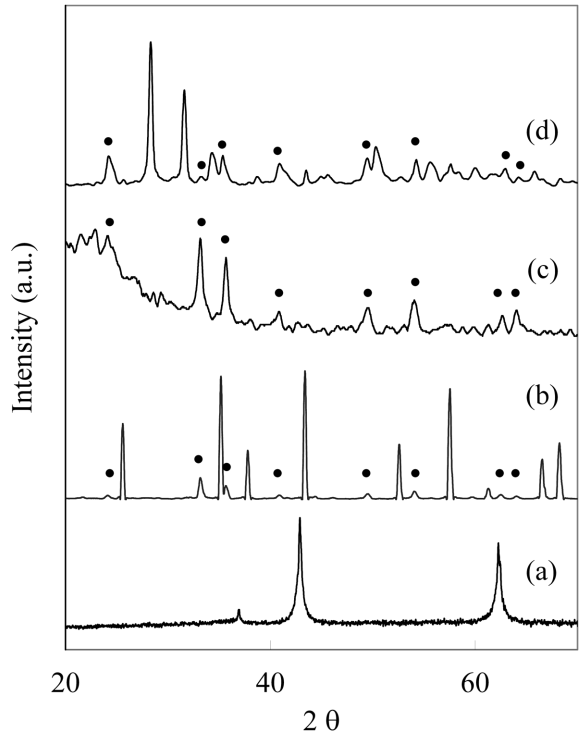

Fig. 7. XRD patterns of (a) Fe/MgO, (b) Fe/Al_2O_3, (c) Fe/SiO_2 and (d) Fe/ZrO_2: (●) Fe_2O_3

Table 1 shows the physical properties of Fe/MgO, Fe/SiO_2, Fe/Al_2O_3 and Fe/ZrO_2. Fe/SiO_2 has the highest surface area and pore volume and Fe/ZrO_2 has the highest average pore diameter among the prepared catalysts. It indicates that the surface areas are not closely related to the catalytic ozonation. Fig. 7 shows XRD patterns of Fe/MgO, Fe/SiO_2, Fe/Al_2O_3 and Fe/ZrO_2. The characteristic peaks of Fe_2O_3 (JCPDS-33-0664) are observed with Fe/SiO_2, Fe/Al_2O_3 and Fe/ZrO_2, but not with Fe/MgO. The absence of Fe characteristic peaks in XRD patterns means that Fe oxide is in amorphous phase or in smaller size than 5 nm. It was shown that Fe in Fe/MgO was in ionic state by a Mossbauer study [Jung et al., 2002]. The heterogenized Fe ions can facilitate both a redox reaction like catalytic wet oxidation of H_2S to sulfur on Fe/MgO [Jung et al., 2003] and the reaction by the radicals activated on Fe ions like fluorene oxidation with NHPI on Fe/MgO [Jung and Han, 2000]. However, Fe^{3+} valence state only was observed on the samples treated with an aqueous humic acid solution for 1 h by XPS, indicating that Fe ions on Fe/MgO could not be reduced with aqueous humic acids. It has been well known that ozone can produce a large amount of radicals. Therefore, it is proposed that the humic acid adsorbed on Fe/MgO can be decomposed by the radicals activated on Fe ions in Fe/MgO. A common objective of the advanced oxidation processes is to produce a large amount of radicals to oxidize the organic matters, but molecular ozone is less powerful than hydroxyl radicals [Legube and Leitner, 1999]. It was suggested that a heterogeneous catalyst could enhance the formation of free radicals or an increase of nucleophilic sites of adsorbed molecules [Al Hayek et al., 1989].

CONCLUSION

The degrading of humic acids by ozone was performed at room temperature in a batch reactor and a fixed bed reactor with heterogeneous catalysts. Experimental results showed that catalytic ozonation with Fe/MgO induced a significant reduction in UV absorbance and TOC of humic acids as compared to ozone alone. GPC showed that humic acids with high molecular weight could be severely decomposed into organic compounds with low molecular weight on the Fe/MgO catalyst, indicating that humic acids could be catalytically decomposed. The continuous reaction with catalyst pellets supported that humic acids could be removed by catalysis as well as adsorption. The characterizations of Fe/MgO suggest that the high activity of Fe/MgO can be attributed to the presence of Fe well-dispersed on Fe/MgO.

REFERENCES

Abdo, M. S. E., Shaban, H. and Bader, M. S. H., "Decolorization by Ozone of Direct Dyes in Presence of Some Catalysis," *J. Environ. Sci. Health*, **A23**, 697 (1988).

Al Hayek, N., Legube, B. and Dore, M., "Catalytic Ozonation of Phenol and its Ozonation Byproducts," *Environ. Technol. Letters*, **10**, 415 (1989).

Amy, G. L., Tan, L. and Davis, M. K., " The Effects of Ozonation and Activated Carbon Adsorption on Trihalomethane Speciation," *Wat. Res.*, **25**, 191 (1991).

Anderson, L. J., Johnson, J. D. and Christman, R. F., "Extent of Ozone's Reaction with Isolated Aquatic Fulvic Acid," *Environ. Sci. Technol.*, **20**, 739 (1986).

Andreozzi, R., Caprio, V., Insola, A., Marotta, R. and Tufano, V., "The Ozonation of Pyruvic Acid in Aqueous Solution Catalyzed by Suspended and Dissolved Manganese," *Wat. Res.*, **32**(5), 1492 (1998).

Andreozzi, R., Insolar, A., Caprio, V. and D'Amore, M. G., "The Kinetics of Mn(II)-Catalysed Ozonation of Oxalic Acid in Aqueous Solution," *Wat. Res.*, **26**, 917 (1992).

Andreozzi, R., Insola, A., Caprio, V., Marotta, R. and Tufano, V., "The Use of Manganese Dioxides as a Heterogeneous Catalyst for Oxalic Acid Ozonation in Aqueous Solution," *Appl. Catal. A: General*, **138**, 75 (1996).

Bhat, N. and Gurol, M. D., "Oxidation of Chlorobenzene by Ozone and Heterogeneous Catalytic Ozonation," 27th Industrial Waste Mid-Atlantic Conference, Bethlehem, PA, USA, 371 (1995).

Brodard, E., Duguet, J. P., Dusser, B. and Mallevialle, J., "Improvement in The Effectiveness of Ozonation of Drinking Water Through The Use of Hydrogen Peroxide," *Ozone Sci. Eng.*, **7**, 241 (1985).

Centi, G., Perathoner, S., Torre, T. and Verduna, M. G., "Catalytic Wet Oxidation with H_2O_2 of Carboxylic Acids on Homogeneous and Heterogeneous Fenton-type Catalysts," *Catal. Today*, **55**, 61 (2000).

Gilbert, E., "Biodegradability of Ozonation Products as a Function of COD and DOC Elimination by The Example of Humic Acids," *Wat. Res.*, **22**(1), 123 (1988).

Glaze, W. H., Kang, J. W. and Chapin, D. H., "The Chemistry of Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation," *Ozone Sci. Eng.*, **9**, 335 (1987).

Gracia, R., Aragues, S. and Ovelleiro, J. L., " Study of the Catalytic Ozonation of Humic Substances in Water and Their Ozonation Byproducts," *Ozone Sci. Eng.*, **18** (1996).

Hewes, C. G. and Davinson, R. R., "Renovation of Wastewater by Ozonation," *AIChE Symposium Seires*, **69**, 71 (1972).

Jung, K. D. and Han, S. H., "Room Temperature Catalytic Oxidation of Wastewater by Air (LOTECH)," *Achima 2000 Environ.*, 104 (2000).

Jung, K. D., Joo, O. S. and Kim, C. S., "Study on the Structure of Fe/MgO Catalysts for H_2S Wet Oxidation," *Catal. Lett.*, **84**(1-2), 53 (2002).

Jung, K. D., Joo, O. S., Cho, S. H. and Han, S. H., "Catalytic Wet Oxidation of H_2S to Sulfur on Fe/MgO Catalyst," *Appl. Catal. A.: General*, **240**, 235 (2003).

Killops, S. D., "Volatile Ozonization Products of Aqueous Humic Material," *Wat. Res.*, **20**(2), 153 (1986).

Kong, S. H., Kwon, C. L. and Kim, M. H., "Ozone Kinetics and Diesel Decomposition by Ozonation in Groundwater," *Korean J. Chem. Eng.*, **20**, 293 (2003).

Legube, B. and Leitner, N. K. V., "Catalytic Ozonation: A Promising Advanced Oxidation Technology for Water Treatment," *Catal. Today*, **53**, 61 (1999).

Ma, J. and Graham, N. J. D., "Preliminary Investigation of Manganese-Catalyzed Ozonation for the Destruction of Atrazine," *Ozone Sci. Eng.*, **19**, 227 (1997).

Mok, Y. S. and Nam, I. S., "Reduction of Nitrogen Oxides by Ozonation-Catalysis Hybrid Process," *Korena J. Chem. Eng.*, **21**, 976 (2004).

Naydenov, A. and Mehandjiev, D., "Complete Oxidation of Benzene on Manganese Dioxide by Ozone," *Appl. Catal. A: General*, **97**, 17 (1992).

Paode, R. D., Chandrakanath, M. S., Amy, G. L., Gramith, J. T. and Ferguson, D. W., "Theoretical Aspects of the Kinetics of Competitive Ozone Reaction in Water," *Ozone Sci. Eng.*, **17**, 25 (1995).

Rice, R. G., "The Use of Ozone to Control Trihalomethanes in Drinking Water Treatment," *Ozone Sci. Eng.*, **2**, 75 (1980).

Schwammlein, K. and Leitzke, O., In Proc. 12th Ozone World Congress, Lille, France, 1, 325 (1995).

Shukairy, H. M. and Summers, R. S., "The Impact of Preozonation and Biodegradation on Disinfection By-Product Formation," *Wat. Res.*, **26**, 1217 (1992).

Thompson, P. E., Sharaatt, P. N. and Hutchison, J., "Heterogeneous Catalytic Oxidation of Organic Pollutants in Aqueous Solutions," 1995 ICHEME research Event, 1st European Conference, 297 (1995).

Xiong, F., Croue, J.-P. and Legube, B., "Long-Term Ozone Consumption by Aquatic Fulvic Acids Acting as Precursors of Radical Chain Reactions," *Environ. Sci. Technol.*, **26**, 1059 (1992).