

# Degradation COD in sewage by active oxygen species

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**Abstract:** In conventional depth sewage treatment processes, COD concentration can only be decreased from 1064 mg/L ~ 1280 mg/L to 100 mg/L ~ 150 mg/L, which can not meet the requirement of COD concentration ( $\leq 50$  mg/L) in the sewage reuse criterion. Therefore, the paper describes that active oxygen species ( $O_2^+$ ,  $O_3$ ) produced by strong ionization dielectric barrier discharge were injected into the sewage to quickly and non-selectively degrade COD into  $CO_2$  and  $H_2O$ . The COD concentration after conventional depth sewage treatment can be degraded from 132 mg/L to 28.2 mg/L using active oxygen species within 3 min plasma reaction time. The COD concentration of 28.2 mg/L can meet the sewage reuse criterion. Compared with conventional sewage treatment methods, the present method has lower initial investment, operating costs, and simple processes.

**Keywords:** Degradation COD; Strong ionization discharge; Active oxygen species;  $\cdot OH$  radicals; COD concentration

## 1. Introduction

A conventional sewage treatment process is constituted of a primary and depth sewage treatment method. The primary sewage treatment method with a coagulation-sedimentation-filtration has been commonly used for the removal of suspended solids in sewage. The depth sewage treatment method can further remove colloidal and dissolved organic pollutants (COD) in sewage, including Fenton (Chamarro et al., 2001), Fenton-like technology (Yang et al., 2009), ozone (Andreozzi et al., 2005; Hostachy et al., 1997) supercritical water oxidation (Zou et al., 2014; Nugroho et al., 2014), photocatalytic (Grzechulska et al., 2000; Bessa et al., 2001), membrane separation (Baheri et al., 2015; Zhou et al., 2013), biochemical methods (Barak et al., 2015), electro-catalytic oxidation (Comninellis et al., 1994; Li et al., 2003) and the combined process (Tony et al., 2009; De et al., 1994; Shu et al., 1995). The COD concentration after the primary and depth sewage treatment can be decreased from 1064 mg/L ~ 1280 mg/L to 100 mg/L ~ 150 mg/L, which still does not meet the requirement of COD concentration ( $\leq 50$  mg/L) in sewage reuse criterion. How to continue to degrade COD concentration has become a research focus.

The paper described that active oxygen species ( $O_2^+$  and  $O_3$ ) produced by strong ionization dielectric barrier

discharge were injected into the sewage to rapidly and non-selectively oxidize COD from the sewage to form  $CO_2$  and  $H_2O$  based on hydroxyl radicals ( $\cdot OH$  radicals) solution with the reaction rate of  $2.2 \times 10^6$  L/mol·s and oxidization potential of 2.80 V (Poyatos et al., 2010; Mental et al., 2010). The sewage purified by active oxygen species could meet the criterion for sewage reuse. The plasma chemistry reaction for degradation COD by the active oxygen species is introduced. The effects of the molar ratios between the active oxygen species ( $O_2^+$ ,  $O_3$ ) and COD in the sewage, energy consumption and plasma reaction time on COD removal are investigated.

## 2. Experimental section

An experimental setup for degradation COD by active oxygen species is shown in Fig. 1. The active oxygen species ( $O_2^+$ ,  $O_3$ ) generated in a active oxygen species generator were transferred into the bottom of the plasma reaction tower (3.2 cm diameter  $\times$  1.4 m height) through the pipe. In the plasma reaction tower, a large number of active oxygen species bubbles were formed by active oxygen species through nozzle into the sewage, and oxidized COD to  $CO_2$  and  $H_2O$ . In whole experiment process, the sewage treated by conventional primary and depth sewage treatment compose of 8.16 pH, 132 mg/L COD, 31.4 mg/L BOD, 411.1 mg/L  $HCO_3^-$ , 95.3 mg/L  $Ca^{2+}$ , 29.8 mg/L  $Mg^{2+}$ , 254.9 mg/L  $Cl^-$  and 478.9 mg/L  $SO_4^{2-}$ . The temperature of the sewage were 22  $^\circ C$ . The quantity of active oxygen species was adjusted by a valve and a flow meter. The concentrations of  $O_2^+$  and  $O_3$  were detected by a ball probe ( $\varnothing 6$  mm) Bai et al., 2009; Sun et al., 2006) and ozone concentration detector (BMT964, BMT Messtechnik GmbH, Stahnsdorf, Germany), respectively. The concentration of COD in the sewage was analyzed by a dichromate titration method.

Active oxygen species generator (Bai et al., 2008) is an important equipment for degradation COD by active oxygen species. The rectangular active oxygen species generator (L $\times$ W $\times$ H, 280 $\times$ 50 $\times$ 220) contained discharge electrodes, grounding electrodes, spacers, and dielectric layers, with a discharge gas spacing of 0.1 mm between the discharge and grounding electrodes, as shown in Fig. 2. A high-voltage, high-frequency discharge output from the high-voltage, high-frequency power supply was applied to

the discharge electrodes, and the peak voltage (6 kV), current (100 mA) and waveform (11.5 kHz) were measured by an oscilloscope (TDS3032, Tektronix, Beaverton, OR), as shown in Fig. 3. The effective reduced electric field strength  $E/n$  (Eliasson et al., 1986) in Townsend ( $1 \text{ Td}=10^{-17} \text{ V}\cdot\text{cm}^2$ ,  $E$ =electric field intensity,  $n$ =concentration of neutral particles) was increased from original 150 Td to existing 350 Td, according the mean electron energy was increased to 8.6 eV in the discharge gaps of 0.1 mm (Penetrante et al., 1997). Therefore, the dielectric barrier discharge (DBD) in active oxygen species generator is strong ionization discharge (SID) based on Xu *et al* (Xu et al., 1996). whose report stated SID formation at mean dielectric energy above 8.6 eV. The strong ionization discharge could create substantial high energy electron ( $\geq 8.4 \text{ eV}$ ) which can dissociate or ionize  $\text{O}_2$  into active oxygen species ( $\text{O}_2^+$ ,  $\text{O}_3$ ).

### 3. Results and discussions

#### 3.1 Effect of molar ratio between active oxygen species and COD on COD concentration

The substantial high energy electrons in discharge gap of the active oxygen species generator can dissociate or ionize  $\text{O}_2$  into oxygen plasma such as  $\text{O}_2^+$ ,  $\text{O}_3$ ,  $\text{O}$ ,  $\text{O}^+$ ,  $\text{O}^-$ ,  $\text{O}_2^-$ ,  $\text{O}(^1\text{D})$  and  $\text{O}_2(\text{a}^1\Delta\text{g})$  (equation of 1-10). The lifetimes of  $\text{O}$ ,  $\text{O}^+$ ,  $\text{O}^-$ ,  $\text{O}(^1\text{D})$  and  $\text{O}_2(\text{a}^1\Delta\text{g})$  are approximately 10 ns, they pass through a series of plasma reactions to form long-lived active oxygen species ( $\text{O}_2^+$ ,  $\text{O}_3$ ) (equation of 11-16). The plasma chemistry reactions and their rate coefficients are presented (Lowke et al., 1995).

$\text{O}_2^+$  reacts with  $\text{H}_2\text{O}$  (g) to form water cluster ions,  $\text{O}_2^+\cdot\text{H}_2\text{O}$ , and then these dissociated to form  $\cdot\text{OH}$  radicals (Person et al., 1988).  $\text{O}_3$  is decomposed to the  $\cdot\text{OH}$  radical solution in the water under the action of  $\text{H}_2\text{O}$ ·initiator produced by  $\cdot\text{OH}$  radical reacting with  $\text{O}_3$  (Staelin et al., 1985; Tomiyasu et al., 1985).

In order to verify the plasma chemistry mechanism for degradation COD by the active oxygen species, the effect of molar ratios between the active oxygen species and COD from the sewage on COD concentration was researched. The experimental result is shown in Fig.4. When the molar ratio increased from 0 to 4.5, the concentration of COD rapidly decreased from 132 mg/L to 27.3 mg/L. The molar ratio further increased to 6.0, COD concentration slowly decreased to 22.6 mg/L, which is only 4.7 mg/L higher than molar ratio of 4.5. The molar ratio finally increased to 7.5, COD concentration was almost no charge. The optimal molar ration was selected at the rang of 4.5 ~ 6.0 in degradation COD by active oxygen species.

In addition, the effect of energy consumption rate on COD removal efficiency was researched, and the result is shown in Fig.5. The energy consumption rate is defined where 1 L sewage treated by active oxygen species consumes electric energy Wh of active oxygen species generator. The energy consumption rate were 6.9 Wh/L, 10.5 Wh/L,

12.5 Wh/L, 13.2 Wh/L and 15.6 Wh/L, the COD removal efficiency were 46.1%, 68.6%, 78.3%, 82.9% and 83.8%, respectively. When the energy consumption rate increased from 0 to 12.5 Wh/L, COD removal efficiency quickly increased from 0 to 78.3% in a liner manner. The energy consumption rate continues to increase to 13.2 Wh/L, COD removal efficiency slowly increased to 82.9%. The consumption rate finally increased to 15.6 Wh/L, COD removal efficiency was almost unchanged. The optimal energy consumption rate was selected at the range of 12.5 Wh/L ~ 13.2 Wh/L in degradation COD by active oxygen species.

#### 3.2 Effect of Plasma reaction time on COD concentration

The effects of plasma reaction time of active oxygen species reacting with COD in the plasma reaction tower (in Fig. 1) on COD concentration were researched. The results are shown in Fig. 6. When the plasma reaction time increased from 0 to 3 min, the COD concentration quickly decreased from 132.0 mg/L to 28.2 mg/L. When the plasma reaction time increased from 3 min to 5 min, the COD concentration was almost no charge. Experimental results was clearly observed that COD concentration decreased from 132.0 mg/L to 28.2 mg/L within plasma reaction time of 3 min, and according COD concentration decreases rapidly by 34.6 mg/L per minute.

However, long reaction time is required in the conventional depth sewage treatment, such as Fenton reaction time of 6.5h (2.9 mg/L·min), biochemical reaction time of 16.8 h (1.1 mg/L·min), electrocatalytic reaction time of 2.5 h (7.7 mg/L·min), acidification-microelectrolysi-fenton combined processes reaction time of 5.5 h (3.5 mg/L·min). The degradation rate of COD per minute by active oxygen species is 5 more times faster than the present conventional method. This is mainly because the active oxygen species ( $\text{O}_2^+$ ,  $\text{O}_3$ ) produced by strong ionization dielectric barrier discharge was injected into the sewage to form  $\cdot\text{OH}$  radicals solution radicals. Therefore, the reaction rate coefficient and oxidization potential of  $\cdot\text{OH}$  radicals were about  $2.2 \times 10^6 \text{ L/mol}\cdot\text{s}$  and 2.80 V, respectively, the  $\cdot\text{OH}$  radicals solution could rapidly and non-selectively oxidize COD to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

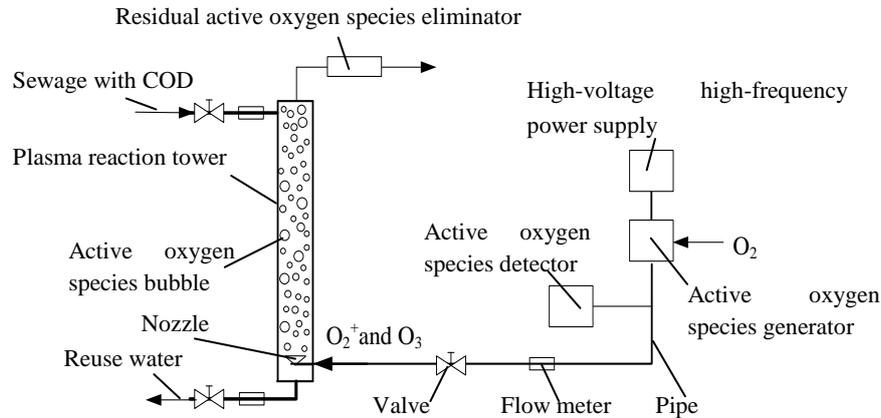
### 4. Conclusion

High concentration  $\cdot\text{OH}$  radical solution generated by active oxygen species ( $\text{O}_2^+$ ,  $\text{O}_3$ ) of strong ionization discharge can quickly and non-selectively oxidize COD to the harmless substance of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The result shows that the COD concentration after conventional depth sewage treatment, can be decreased from 132 mg/L to 28.2 mg/L and removal efficiency is 78.6%. The purified sewage by active oxygen species can meet the sewage reuse criterion. This paper can provide an economical, efficient, and simple process for realization sewage reuse.

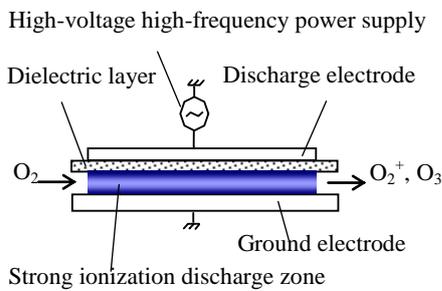
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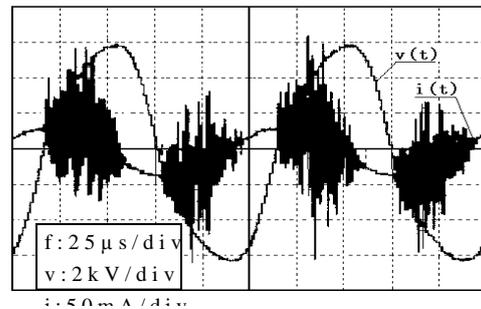
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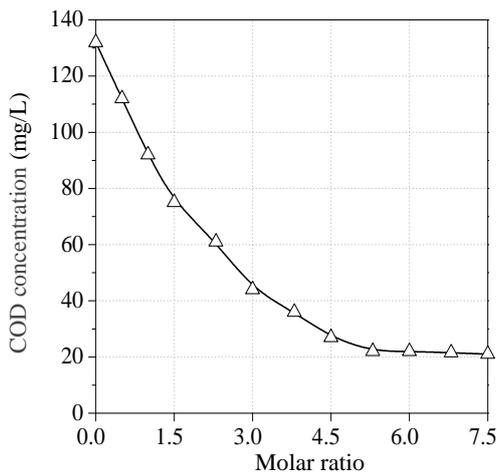
**Figure 1.** Experimental setup for degradation COD by active oxygen species



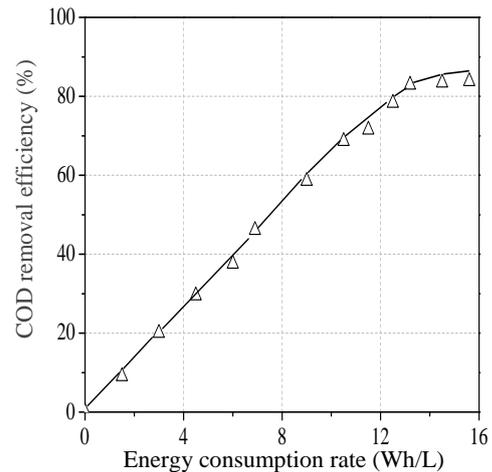
**Figure 2.** Structure diagram of active oxygen species generator



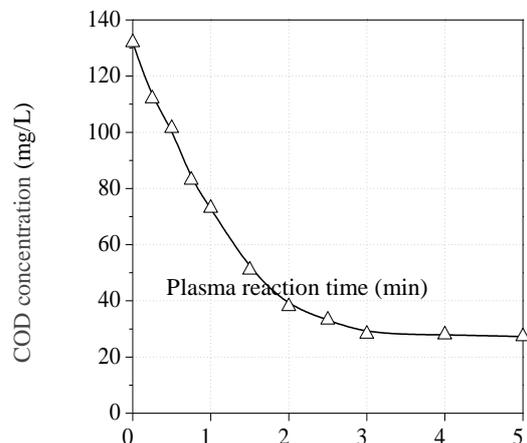
**Figure 3.** Voltage, current and waveform output from high-voltage high-frequency power supply



**Figure 4.** Effect of the molar ratio between active oxygen species and COD on COD concentration



**Figure 5.** Effect of energy consumption rate on COD removal efficiency



**Figure 6.** Effect of the plasma reaction time of degradation COD by active oxygen molecules on COD

## References

- Andreozzi R., Canterino M., Marotta R. and Paxeus N. (2005), Antibiotic removal from wastewaters: The ozonation of amoxicillin, *J Hazardous Materials*, **122**, 243-250.
- Bessa E., Santanna G. L. and Dezotti M. (2001), Photocatalytic/H<sub>2</sub>O<sub>2</sub> treatment of oil field produced waters, *Applied Catalysis B: Environmental*, **29**, 125-134.
- Baheri B., Shahverdi M., Rezakazemi M. and Motae E, and Mohammadi T. (2015), Performance of PVA/NaA Mixed Matrix Membrane for Removal of Water from Ethylene Glycol Solutions by Pervaporation, *Chemical engineering communications*, **202**, 316-321.
- Bai M.D., Yang B., Xue X.H., Liu D. and Sun J. (2009), Studies on the Measuring Method of Number Density of Ions in the High Speed Flow Field, *IEEE Transactions on Plasma Science*, **37**, 2257-2260.
- Bai M.D., Qiu X.M., Liu D., Yang B., Zhou J.G., Xue X.H. and Gu J.L. (2008), The minimization of non-equilibrium plasma source at high pressure, *Chinese Science Bulletin*, **53**, 3425-3428.
- Barak S., Mudqil D. and Khatkar B.S. (2015), Biochemical and Functional Properties of Wheat Gliadins: A Review, *Critical reviews in food science and nutrition*, **55**, 357-368.
- Cominellis C. (1994), Electrocatalysis in the electrochemical conversion/combustion of organic pollutants wastewater treatment, *Electrochimica Acta*, **39**, 1857-1862.
- Chamarro E., Marco A. and Esplugas S. (2001), Use of Fenton reagent to improve organic chemical biodegradability. *Water Research*, **35**, 1047-1051.
- De Laat J., Tace E., Dore M. (1994), Degradation of chloroethanes in dilute aqueous solution by H<sub>2</sub>O<sub>2</sub>/UV. *Water Research*, **28**, 2507-2519.
- Eliasson B. and Kogelschatz U. (1986), Electron impact dissociation in oxygen, *Journal of Physics B*, **19**, 1241-1247.
- Grzechulska J., Hamerski M. and Morawski A.W. (2000), Photocatalytic decomposition of oil in water, *Water Research*, **34**, 1638-1644.
- Hostachy J.C., Lenon G., Pisciocchio J.L., Coste C. and Legay C. (1997), Reduction of pulp and paper mill pollution by ozone treatment, *Water Science Technology*, **35**, 261-268.
- Lowke J.J. and Morrow R. (1995), Theoretical analysis of removal of oxides of sulphur and nitrogen in pulsed operation of electrostatic precipitators, *IEEE Transactions on Plasma Science*, **23**, 661-671.
- Li Y.J., Wang F., Zhou G.D. and Ni Y.M. (2003), Aniline degradation by electrocatalytic oxidation, *Chemosphere*, **53**, 1229-1234.
- Mandal T., Maity S., Dasgupta D. and Datta S. (2010), Advanced oxidation process and biotreatment. Their roles in combined industrial wastewater treatment, *Desalination*, **250**, 87-94.
- Nugroho A. and Kim J. (2014), Effect of KOH on the continuous synthesis of cobalt oxide and manganese oxide nanoparticles in supercritical water, *Journal of industrial and engineering chemistry*, **20**, 4443-4446.
- Person J.C. and Ham D.O. (1988), Removal of SO<sub>2</sub> and NO<sub>x</sub> from stack gases by electron beam irradiation, *Radiation Physics and chemistry*, **3**, 1-8.
- Poyatos J.M., Muño M.M., Almecija M.C., Torres J.C., Hontoria E. and Osorio F. (2010), Advanced Oxidation Processes for Wastewater Treatment, *State of the Art Water Air Soil Pollution*, **205**, 187-204.
- Penetrante B.M., Bardsley J.N. and Hsiao M.C. (1997), Kinetic analysis of non-thermal plasmas used for pollution control, *Japanese of Journal Applied Physics*, **36**, 5007-5017.
- Staelin J. and Hoigne J. (1985), Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions, *Environmental Science & Technology*, **19**, 1206-1213.
- Sun J., Bai M.D., Zhou J.G. and Gu J.L. (2006), Effect of energy density and gas velocity on transport rate of ions, *Plasma Science Technology*, **28**, 554-557.
- Shu H.Y. and Huang C.R. (1995), Degradation of commercial azo dyes in water using ozonation and UV enhanced ozonation process, *Chemosphere*, **31**, 3813-3825.

- Tony M.A., Purcell P.J., Zhao Y.Q. and Tayeb A.M. and El-Sherbiny M.F. (2009), Photo-catalytic degradation of an oil-water emulsion using the photo-fenton treatment process: Effects and statistical optimization, *Journal of Environmental Science and health part a-toxic*, **44**, 179-187.
- Tomiyasu H., Fukutomi H. and Gordon G. (1985), Kinetics and mechanisms of ozone decomposition in basic aqueous solutions, *Inorganic Chemistry*, **24**, 2962-2966.
- Xu X.J. and Zhu D.C. (1996), Gas discharge physics. Shanghai: Fudan University Press.
- Yang Y., Wang P., Shi S.J. and Liu Y. (2009), Microwave enhanced Fenton-like process for the treatment of high concentration pharmaceutical wastewater, *Journal of Hazardous Material*, **168**, 238-245.
- Zou D.A., Chi Y., Dong J., Fu C. and Ni M.J. (2014), Supercritical Water Oxidation of MSW Leachate: Factor Analysis and Behavior of Heavy Metals, *Environmental Progress and Sustainable energy*, **33**, 1117-1124.
- Zhou J.B., Ye W., Gao L.P., Zhao Z.Y. and Li H.T. (2013), Study of Anion Membrane Electrolysis Technique for Desalination of Mother Liquor in the process of Baking Soda, *International Journal of Electrochemical Science*, **8**, 10578-10585..