Wet Oxidation Technology Based on Organic Wastewater Treatment

Yongxun Zhang
Logistics Department, Guangzhou College of Technology and Business, Guangzhou, China
670511263@qq.com

Abstract. Wet oxidation technology is a kind of advanced oxidation technology, which is suitable for the treatment of high concentration, toxic, harmful and biodegradable organic wastewater. WAO technology has been effectively applied in the following wastewater treatment: cyanide wastewater, sulfur wastewater, paper black liquor, municipal sludge, pesticide wastewater, coal gasification wastewater and activated carbon regeneration. (2) chemical reaction between dissolved oxygen and matrix. The front part of WAO reaction is controlled by oxygen mass transfer and the back part is controlled by reaction kinetics. It is generally believed that the WAO reaction mainly belongs to the free radical reaction, which goes through four stages of induction, proliferation, degradation and termination. The reaction temperature is the main factor affecting the wet oxidation reaction.

1. Introduction
With the rapid development of petroleum, chemical and pharmaceutical industries, the amount and types of chemical synthetic substances entering the water have increased sharply, resulting in many high concentration, toxic and harmful industrial wastewater. At present, by combining the traditional process, the part of the composition is simple and has good biodegradability, low concentration wastewater can be processed, and high concentration, hard biochemical waste water degradation efficiency is very low, sometimes even unable to run, and there is also a great difficulty in economy [1], so the development of new water treatment technology is very necessary and practical. Wet oxidation is an effective new water treatment technology for this problem.

Wet Air Oxidation (WAO) is an advanced Oxidation technology developed in the 1950s, which is suitable for the treatment of high concentration, toxic, harmful and refractory wastewater. It is a chemical process in which organic pollutants are oxidized and decomposed into inorganic matter such as CO₂ and H₂O or small molecule organic matter in liquid phase with oxygen or air as oxidant under high temperature (125-320 ℃) and high pressure (0.5-20 MPa) [2]. WAO technology was first proposed by F. J. Zimmermann of shalwar chemical company in 1944, so it is also known as Zimmerman method [3]. In 1958, the first WAO pilot plant was built in the Chicago area of the United States to treat sewage sludge. In the same year, a WAO plant was built in Norway, which was used to treat the black liquor of papermaking. Under high temperature (150-350 ℃) and high pressure (5-20 MPa), the organic matter in the black liquor of papermaking was oxidized, and the removal rate of COD₅₅ of waste water reached more than 90%. Before 1970s, the wet oxidation process was mainly
used for the disposal of municipal sludge, the recovery of lye in the black liquor of papermaking and the regeneration of activated carbon. After entering the 70s, wet oxidation process has been developed rapidly, further expansion of application range from recycling useful chemicals and energy to the handling of hazardous wastes, especially in the treatment of phenol, poisonous and harmful material such as phosphorus, cyanide has a large number of literatures, the research content is from the initial optimum process conditions of applicability and grope for deep into the reaction mechanism and kinetics, and device number and size also is increased. In foreign countries, WAO technology has been industrialized, mainly used for the treatment of cyanide wastewater [4-5], sulfur wastewater [6-7], paper black liquor [8-9], municipal sludge [10-11], pesticide wastewater [12-13], coal gasification wastewater [14-15] and activated carbon regeneration [16-17]. WAO technology has been studied in China since the 1980s, and experimental studies have been carried out on papermaking black liquor [18-19], sulfur-containing wastewater [20-21], phenol-containing wastewater [22-23], pesticide wastewater [24-25], dye wastewater [26-27], petrochemical alkali residue wastewater [28-29], etc. At present, WAO technology is still in the experimental stage in China. There are three reasons why WAO technology has not been industrialized in China. (2) reaction equipment one-time investment; Domestic environmental protection requirements relative to foreign is not strict.

2. Mechanism of wet oxidation reaction
The wet oxidation process is relatively complex, and it is generally believed that there are two main steps: (1) the mass transfer process of oxygen from the gas phase to the liquid phase; (2) chemical reaction between dissolved oxygen and matrix. This shows that the first part of WAO reaction is controlled by oxygen mass transfer, while the second part is controlled by reaction kinetics. If the mass transfer process affects the overall reaction rate, it can be eliminated by strengthening stirring.

The current research results generally believe that WAO reaction mainly belongs to free radical reaction [30-31], which goes through four stages: induction stage, proliferation stage, degradation stage and end stage. During the induction and proliferation periods, molecular oxygen is involved in the formation of various free radicals $HO \cdot$, $RO \cdot$, $ROO \cdot$, and the generated free radicals attack organic RH, triggering a series of chain reactions to generate other low molecular organic acids, carbon dioxide and water. The whole reaction process is shown in Equation (1) - (9):

Induction period: \[ RH + O_2 \rightarrow R \cdot + HOO \cdot \] (1)

\[ 2RH + O_2 \rightarrow 2R \cdot + H_2O_2 \] (2)

Proliferation period: \[ R \cdot + O_2 \rightarrow ROO \cdot \] (3)

\[ ROO \cdot + RH \rightarrow ROOH + R \cdot \] (4)

Degradation period: \[ ROOH \rightarrow RO \cdot + HO \cdot \] (5)

\[ ROOH \rightarrow R \cdot + RO \cdot + H_2O \] (6)

Ending period: \[ R \cdot + R \cdot \rightarrow R - R \] (7)

\[ ROO \cdot + R \cdot \rightarrow ROOR \] (8)

\[ ROO \cdot + ROO \cdot \rightarrow ROH + R_1COR_2 + O_2 \] (9)
RH is a kind of organics in Equation (1). The formation of H₂O₂ in Equation (2) indicates that the wet oxidation reaction belongs to the free radical reaction mechanism. Shibaeva et al. [32] detected the formation of H₂O₂ in WAO studies of phenol containing wastewater, confirming that the wet oxidation reaction of phenol is a free radical reaction.

It should be noted that the formation of free radicals is not only by the above Equation (1) - Equation (9), there are many different explanations. Li and Tufano et al. [33] believe that the wet oxidation reaction of organic matter can also be carried out by the generation of the following free radicals:

\[
\begin{align*}
\text{O}_{2} & \rightarrow \text{O} \cdot + \text{O} \cdot \\
\text{O} \cdot + \text{H}_2 \text{O} & \rightarrow \text{HO} \cdot + \text{HO} \
\text{RH} + \text{HO} \cdot & \rightarrow \text{R} \cdot + \text{H}_2 \text{O} \\
\text{R} \cdot + \text{O}_2 & \rightarrow \text{ROO} \cdot \\
\text{ROO} \cdot + \text{RH} & \rightarrow \text{R} \cdot + \text{ROOH}
\end{align*}
\]

From Equation (10) to Equation (14), it can be seen that free radical \( \text{HO} \cdot \) is first formed, and then the free radical \( \text{HO} \cdot \) react with organic RH to form low level organic acid ROOH, which is further oxidized to form CO₂ and H₂O.

Through the analysis of the wet oxidation reaction mechanism, it is believed that the attack of free radicals on organic matter will produce low organic acid, and other reaction mechanisms such as REDOX also indicate that the break of - C- C- bond will produce low molecular organic matter. All these mechanisms indicate that the oxidation of organics follows the following modular model, as shown in Figure 1.

![Figure 1. Sketch map of WAO reaction process.](image)

In the figure: A=[initial and unstable intermediate organic compound]-[acetic acid], B=[acetic acid], C=[oxidation final product, CO₂, H₂O]. The typical stable intermediates are acetic acid, methanol and ethanol.

For different wastewater, a large number of empirical formulas for wet oxidation have been reported in recent years [34-35], most of which are fitted by Formula (15):

\[
-\frac{dC}{dt} = K_0 e^{-\frac{E_a}{RT}} [C]^m [O]^n
\]

In the formula: \( K_0 \)- reaction rate constant, \( E_a \)- the activation energy of reaction, \( R \)- the gas constant (8.314J/mol*K), \( T \)- the thermodynamic temperature of K, \([C]\)- concentration of organic matter (mol/L), \([O]\)- concentration of oxidant (mol/L),
T- reaction time of S, M,n- reaction series.

In fact, the wet oxidation reaction process is mainly a synthesis of various reactions, and the process is complex. Moreover, the different composition of wastewater and the change of reaction conditions will affect the empirical formula of wet oxidation kinetics. Therefore, it is not possible to derive accurate reaction rate equations based on primitive reactions. It is customary to use measurable comprehensive water quality indicators such as CODcr, to represent organic content, and to assume that the process is a first order reaction, which is feasible for most wastewater.

3. Main influencing factors of wet oxidation reaction

The influencing factors of WAO reaction include reaction temperature, reaction pressure, reaction time, stirring intensity, inlet pH value, inlet concentration, salt effect and inlet property. The reaction temperature is the main factor affecting the wet oxidation reaction.

Temperature is a crucial factor in the WAO reaction process. The chemical reaction rate increases with the increase of temperature, and the relation between most chemical reaction rate constant $k$ and temperature obeys Arrhenius formula, see Formula (16) [36]:

$$k = Ae^{-Ea/RT}$$

In the formula: $k$- reaction rate constant, 
A- the prefactor, 
Ea- the activation energy of reaction, 
R- molar gas constant (8.314 J/mol•K), 
T- the thermodynamic temperature of K.

When the temperature range is not large, such as about 100 °C, A and Ea do not change with the temperature and can be regarded as A constant. As for the influence of Ea and T on k, the following conclusions can be drawn: (1) for the same reaction, when Ea is constant, the higher the temperature is, the larger the value of k will be. In general, for every 10 degree increase in temperature, the value of k will increase by 2 to 10 degree. (2) for the same reaction, when the temperature increases in the high temperature region, the multiple of k value increases is small; When the temperature is increased in the low temperature region, the multiple of k value is large.

Changes in temperature can cause changes in the physical properties of water and oxygen. Some physical properties of water and oxygen at different temperatures are given in Table 1 below [37].

| Nature of the species | Temperature (°C) |
|-----------------------|-----------------|
|                        | 25* 100 150 200 250 300 320 335 |
| Water vapor pressure (MPa) | 0.003 0.103 0.485 1.586 4.056 8.762 11.511 14.005 |
| Hydrodynamic viscosity (10^-3 Pa•s) | 0.922 0.281 0.181 0.137 0.116 0.106 0.104 0.103 |
| Water density (10^3 kg•m^-3) | 0.944 0.991 0.955 0.934 0.908 0.870 0.848 0.828 |
| Oxygen diffusion coefficient K (10^5 cm^2•s^-1) | 2.24 9.18 16.2 23.9 31.1 37.3 39.3 40.1 |
| Henry's constant of oxygen H (10^3 MPa•mol^-1) | 4.38 7.04 5.85 3.94 2.38 1.36 1.08 0.90 |
| Oxygen solubility (mg•L^-1) | 190 145 195 320 565 1040 1325 1585 |

Indication*: at 25 °C, P_{O_2}=0.5 MPa.

As can be seen from Table 1 above, when the temperature is lower than 100 °C, the solubility of oxygen in wastewater decreases with the increase of temperature. When the temperature is higher than 100 °C, with the increase of temperature, the saturated vapor pressure of water increases, so the solubility of oxygen increases. The mass transfer coefficient of oxygen in water increases with the increase of temperature. A rise in temperature can also reduce the viscosity of water. Therefore, as a
common result of multiple actions, increasing the temperature can increase the concentration of oxygen in the liquid phase and the mass transfer rate. In addition, raising the temperature can increase the percentage of active molecules and speed up chemical reactions by increasing the number of effective collisions between molecules.

4. Conclusion
Wet oxidation is an appropriate treatment technique for high concentration, toxic, harmful and biodegradable organic wastewater. WAO treatment of cyanide wastewater, sulfur wastewater, paper making black liquor, municipal sludge, pesticide wastewater, coal gasification wastewater and activated carbon has achieved good results. It is generally believed that the WAO process consists of two main steps :(1) the mass transfer process of oxygen from the gas phase to the liquid phase; (2) chemical reaction between dissolved oxygen and matrix. WAO reaction mainly belongs to free radical reaction, which goes through four stages: induction, proliferation, degradation and termination. The main factor affecting wet oxidation reaction is the reaction temperature

Acknowledgments
This work was supported by 2019 Lateral Project from Guangzhou College of Technology and Business.

References
[1] Lei lecheng, Wang dahui. Advanced oxidation technology for water treatment [M]. Beijing: chemical industry press, 2001, 2-53.
[2] Dietrich, M.J.. Wet air oxidation of hazardous organics in wastewater [J]. Environ. Prog., 1985, 4 (3): 171-172.
[3] F.J. Zimmermann. New Waste Disposal Process [J]. Chem. Eng. 1958, 65 (8): 117-121.
[4] Graham D.. The Separate Effects of Pore Size and Surface Acidity upon the Adsorbent Capacity of Activated Carbon [J]. Phys. Chem., 1955, 59: 896-900.
[5] Mundale V.D., Joglekar H.S., Kalam A., et al. Regeneration of Spent Activated Carbon by Wet Air Oxidation [J]. Chem. Eng., 1991, 69: 1149-1159.
[6] Chowdhury A.K., Copa W.C., Wet Air Oxidation of Toxic and Hazardous Organics in Industrial Waste Waters [J]. Ind. Chem. Eng., 1986, 28: 3-10.
[7] Wilhelmi A.R., Knopp P.V.. Wet Air Oxidation an Alternative to Incineration [J]. Chem. Eng. Prog., 1989, 75 (8): 46-52.
[8] Kwang-Deog J., Oh-Shim J., Seong-Hoon C., et al. Catalytic wet oxidation of H$_2$S to sulfur on Fe/MgO catalyst [J]. Applied Catalysis, 2003, 24 (1): 235-241.
[9] Stein, Ariel F., Dennis L.. The sensitivity of sulfur wet deposition to atmospheric oxidants [J]. Atmospheric Environment, 2000, 34 (11): 1681-1690.
[10] Verenich, S., Laari, A., Kallas J.. Wet oxidation of concentrated wastewaters of paper mills for water cycle closing [J]. Waste Management, 2000, 20 (4): 287-293.
[11] Besson, Michele, Gallezot, et al.. Deactivation of metal catalysts in liquid phase organic reactions [J]. Catalysis Today, 2003, 81 (4): 547-559.
[12] Khan, Y., Anderson, G.K., Elliott, D.J.. Wet oxidation of activated sludge [J]. Water Research, 1999, 33 (7): 1681-1687.
[13] Dinsdale, Richard M., Hawkes, Freda R., Hawkes, Dennis L.. Anaerobic digestion of short chain organic acids in an expanded granular sludge bed reactor [J]. Water Research, 2000, 34 (9): 2433-2438.
[14] Mantzavinos D., Sahibzada M., Livingston A.. Wastewater treatment: wet air oxidation as a precursor to biological treatment [J]. Catalysis Today, 1999, 53 (1): 93-106.
[15] Ishii W.. Catalyst for Treating Organic Waste Water by Wet Oxidation [J]. Applied Catalysis B: Environmental Volume, 1991, 19 (5): 880-884.
[16] Gurvich, B.. Air pollution control and heat recovery system [J]. Fuel and Energy Abstracts,
1997, 38 (2): 113-115.

[17] Gurvich B., Palkes M., Wesnor J. Air pollution control and heat recovery system and process for coal fired power plant [J]. Applied Thermal Engineering, 1997, 17 (4): 8-10.

[18] Sun S, Hao Y K, Yang Y, et al. Study on catalytic wet oxidation technology for treatment of high concentration industrial wastewater [J]. Environmental pollution and prevention, 2004, 26 (3): 114-117. (In Chinese)

[19] Wang Ren, Qi Yunshi. Treatment of black liquor of papermaking straw by wet air catalytic oxidation [J]. Journal of east China university of chemical technology, 1982, 10 (3): 285-295.

[20] Xin S C. Study on treatment of high-concentration sulfur-containing wastewater by wet air oxidation [J]. Environmental protection of chemical industry, 1990, 10 (6): 326-329. (In Chinese)

[21] Xu J W. Wet oxidation treatment of concentrated waste liquid [J]. Environmental pollution and prevention, 1990, 12 (2): 17-20. (In Chinese)

[22] Yan X H, Xu D Q, Xu Z Y. Wet oxidation degradation of p-aminophenol wastewater using Fe/activated carbon as catalyst [J]. Dyestuff industry, 2002, 39 (3): 42-44. (In Chinese)

[23] Bu L L, Chen S, Quan S. Study on microwave-assisted wet oxidation of p-nitrophenol solution [J]. Science in China series E (engineering science, materials science), 2005, 35 (3): 324-336. (In Chinese with English abstract)

[24] ZhaoB X, Han Y Y, Zhang X L. Catalytic wet oxidation catalyst for high concentration imidacloprid pesticide wastewater [J]. Journal of northwestern university (natural science edition), 2005, 35 (5): 111-114. (In Chinese with English abstract)

[25] Dong J M, Zeng G G, Yang X H. Study on catalytic wet oxidation pesticide wastewater and catalyst [J]. Environmental pollution control technology and equipment, 2005, 6 (8): 114-118. (In Chinese)

[26] Wang Y Y, Yang Z H, Jiang Z P. Wet air oxidation of waste mother liquor [J], environmental science, 1996, 17 (1): 119-122. (In Chinese)

[27] Zeng X P, Tang W W, Zhao J F, et al. Wet oxidation of highly dispersed blue dye wastewater [J]. Environmental pollution and prevention, 2005, 27 (2): 88-90. (In Chinese with English abstract)

[28] Xiang Meili. Treatment of spent alkali liquor by wet oxidation [J]. Industrial water treatment, 2004, 24 (12): 62-63.

[29] Cheng J m. treatment of gasoline alkali residue and liquid hydrocarbon alkali residue by wet oxidation method [J]. Industrial safety and environmental protection, 2006, 32 (3): 44-45. (In Chinese)

[30] A.A. Thhomsen. Degradation of Quinoline by Wet Air Oxidation-Kinetic Aspects and Reaction Mechanisms [J]. Wat. Res. 1997, 32 (1): 136-146.

[31] L.Li, P. Chen, E.F. Gloyna. Generalized Kinetic Model FOR Wet Oxidation of Oragnic Compounds [J], AICHE, 1991, 37 (11): 1678-1697.

[32] L.V. Shibaeva. Oxidation of Phenol with Molecular Oxygen on Aqueous Solution [J]. Kinetics and Catalysis. 1969, 10 (5): 401-403.

[33] Li X.L., Tufano. Generalized kinetic model for wet oxidation of organic compounds [J]. JAICHE, 1991, 37 (11): 1687-1697.

[34] Hocevar, Stanko; Batista, Jurka; Levec, Janez. Wet Oxidation of Phenol on Ce1-xCuxO2-δ Catalyst [J]. Journal of Catalysis, 1999, 184 (1): 39-48.

[35] Eftaxias A., Font J., Fortuny A. et al. Kinetic modelling of catalytic wet air oxidation of phenol by simulated annealing [J]. Applied Catalysis B: Environmental Volume, 2001, 33 (2): 175-190.

[36] Inorganic chemistry (Volume 1, Third edition) [M]. Beijing: higher education press, 1990. (In Chinese)

[37] Tang S Y, DaiY Z. Hydrothermal oxidation technology for wastewater treatment [M]. Beijing: chemical industry press, 2002. (In Chinese)