Study on Influencing Factors of Wet Oxidation Technology

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Abstract. For refractory organic wastewater treatment, this water treatment industry is difficult, wet oxidation technology can effectively play a role. The effect of chemical reaction is closely related to the process conditions of operation (that is, the influencing factors). The influencing factors of wet oxidation technology include nine aspects: reaction temperature, reaction pressure, reaction time, stirring strength, influent pH value, influent concentration, salt effect of influent, nature of influent, reaction heat of wastewater and amount of air needed. Among these factors, the reaction temperature is an important influence factor, and the relationship between the chemical reaction velocity constant and temperature follows the arenius formula.

1. Introduction
The comprehensive treatment of high concentration organic wastewater has not been fundamentally solved in China, especially the treatment of high concentration organic wastewater which is difficult to biodegrade. The COD concentration of such wastewater is high, and it contains a variety of biological toxic substances, and its BODs/COD value is very low, which is far less than the industry recognized more difficult biochemical value 0.3 and difficult biochemical value 0.25 [1]. The biochemical treatment of wastewater cannot meet its needs, and the efficient treatment of high concentration organic wastewater has become one of the difficult problems to be solved in domestic sewage treatment industry. Wet oxidation method (WAO) [2] is an advanced oxidation technology developed from the 1950s. This method is suitable for the treatment of refractory organic wastewater with high concentration, toxic and harmful, and difficult to degrade by biochemical method. It is to oxidize dissolved or suspended organic matter or reduced inorganic matter in water under high temperature (125-320°C), high pressure (0.5-20 MPa) operating conditions, using oxygen or air as catalyst in liquid phase, to form inorganic and small molecular organic matter such as CO₂ and water, without secondary pollution. The wet oxidation belongs to the free radical reaction and needs to go through three stages: chain initiation, chain development and transmission, and chain termination. WAO method has been used effectively in sulfur-containing wastewater [3-4], municipal sludge [5-6], paper black liquor [7-8], cyanide-containing wastewater [9-10], activated carbon regeneration [11-12], pesticide wastewater [13-14] and coal gasification wastewater [15-16].

The effect of chemical reaction is closely related to the process conditions of operation (that is, the influencing factors) [3], and the process conditions of operation directly determine the reaction results.
The influence factors of wet oxidation technology are many, so it is necessary to analyze these factors one by one to improve the effect of wet oxidation reaction.

2. Factors affecting wet oxidation technology

The factors influencing wet oxidation are summarized in Table 1.

| No. | Influencing factor                      | Relationship between influencing factors and reaction effects                                                                 | Cases       |
|-----|-----------------------------------------|-----------------------------------------------------------------------------------------------------------------------------|-------------|
| 1   | Reaction temperature                    | The main influencing factor of the reaction, the chemical reaction velocity increases with the increase of temperature, and the relationship between most chemical reaction velocity constants and temperature follows the Arrhenius formula. | [18, [19]  |
| 2   | Reaction pressure                       | The total pressure of the system has no significant effect on the wet oxidation reaction, but the partial pressure of oxygen has a direct effect on the oxidation rate in a certain range, and the pressure and temperature are a pair of coupling factors. | [20], [21] |
| 3   | Reaction pressure                       | Reaction time is determined by the required removal rate of organic matter and operating conditions, which directly determines the volume of the reactor in WAO plant. | [23]        |
| 4   | Stirring intensity                      | Industrial reactors are generally equipped with a stirring device, within a certain range, the greater the stirring intensity, the better the mass transfer effect of oxygen. | [24], [25] |
| 5   | Feedwater pH value                      | There are three cases for different wastewater: the lower the pH value, the better the oxidation effect; the higher the pH value, the better the oxidation effect; the effect of the pH value on the COD removal rate has extreme points. | [26]-[28]  |
| 6   | Concentration of influent               | When the actual oxygen supply is less than the amount of oxygen needed in the water sample, the smaller the influent concentration, the faster the degradation rate of organic matter; when the actual oxygen supply is greater than the amount of oxygen needed in the water sample, the higher the influent concentration, the faster the degradation rate of organic matter. | [30]        |
| 7   | Salt effect of influent                 | Salt effect has a negative effect on wet oxidation, and high salt content (especially Cl) has serious corrosion on equipment. | [31], [20] |
| 8   | Nature of influent                      | Different influent properties (organic structure), the degree of difficulty of wet oxidation will also be different. | [32]        |
| 9   | Reactive heat and air requirements of wastewater | The wet oxidation process releases heat to maintain the reaction temperature. Oxygen demand for the wet oxidation process is calculated from the COD value of wastewater degradation. | [33]        |
| 10  | Reaction product                        | Large molecular organic matter is oxidized to small molecular oxygen-containing organic matter such as acetic acid after wet oxidation treatment. But the accumulation of reaction products will affect the subsequent reaction. | [34]        |

2.1. Reaction temperature

For the WAO process, the reaction temperature is a very important factor. The rate of chemical reaction increases with increasing temperature. Most of the relationship between the rate constant of chemical reaction and temperature follows the Arrhenius formula, see formula (1) [18]:

\[ k = A e^{-\frac{E_a}{RT}} \]  

(1)
In the formula: $k$ - reaction velocity constant;
$A$ - refers to the former factor;
$E_a$ - reaction activation energy (J/mol), molar gas constant ($8.314 \text{ J/(mol·K)}$);
$T$ - Thermodynamic temperature (K).

Of course, it can not only increase the reaction temperature, because the higher the temperature, the higher the pressure of the reaction, the greater the power consumption of the inlet and inlet water, and the higher the temperature and pressure resistance required by the resulting high pressure to the reactor. For exothermic and reversible reactions, elevated temperature reactions will move in an unfavorable direction. Also under medium pressure, excessive temperature will lead to a large amount of evaporation of water in the oxidation solution, COD too concentrated, or even coking phenomenon, so that the oxidation reaction cannot continue. Gao Feng et al. [19] found that when the temperature exceeded 260°C, steam drying appeared in the reactor.

2.2. Reaction pressure
The effect of the total pressure of the system on the wet oxidation reaction is not significant, and the effect of the pressure is mainly to keep the reaction in the liquid phase [20]. Oxygen partial pressure has a direct effect on the oxidation rate in a certain range. It provides the oxygen needed for the reaction and promotes the mass transfer of oxygen to the liquid phase. If the oxygen partial pressure is insufficient, the mass transfer of oxygen becomes the control step of the reaction. Hook source [21] pointed out that the effect of oxygen partial pressure on the reaction rate of wet oxidation depends on the temperature of the system, and the higher the temperature, the less significant the effect.

The total pressure and temperature are a pair of coupling factors. Increasing the reaction temperature, the reaction pressure must be increased accordingly. At a certain temperature, the low limit of the total pressure is the saturated vapor pressure in the water at that temperature. If the total pressure is too low, a large amount of reaction heat will be consumed on the vaporization of water, so that not only the reaction temperature cannot be guaranteed, but also the reactor will be evaporated when the air intake is less than the vaporization. Therefore, under the condition that the total amount of organic matter is certain, the air intake has a suitable duty.

The relationship between reaction temperature and reaction pressure is determined by the amount of evaporation and the heat balance of the system. The general relationship can be referred to Table 2 [22]. At a certain total pressure, the reaction temperature is determined by the influent concentration, the influent flow rate.

| Reaction temperature (℃) | Saturated vapor pressure(MPa) | Reaction pressure (MPa) |
|--------------------------|-------------------------------|------------------------|
| 150                      | 0.47                          | 1.5~2.5                |
| 200                      | 1.56                          | 3.5~5.0                |
| 230                      | 2.79                          | 4.5~6.0                |
| 250                      | 3.97                          | 7.0~8.5                |
| 280                      | 6.41                          | 10.5~12.0              |
| 300                      | 8.58                          | 14.0~16.0              |
| 320                      | 11.27                         | 20.0~21.0              |

2.3. Reaction time
Reaction time is determined by the required removal rate of organic matter and operating conditions, which directly determines the volume of the reactor in WAO plant. Achieving the same removal rate, the higher the temperature, the shorter the reaction time required and the smaller the reactor volume. When the reaction temperature is below a certain limit, even if the reaction time is prolonged, the oxidation efficiency will not be significantly improved. This temperature limit is different for different
organic matter. Foussard et al. [23] summarized the relationship among temperature, oxygen partial pressure, time and removal rate, and pointed out that: (1) increasing the reaction temperature can shorten the oxidation reaction time; (2) the higher the removal rate, the higher the required reaction temperature or residence time; (3) the higher the oxygen partial pressure, the lower the required reaction temperature or the shorter residence time.

Many studies have shown that the reaction temperature is the determining factor in the WAO treatment device, while the reaction time is the less important factor. The optimum reaction time can be determined according to the difficulty of oxidation and the requirement of treatment effect.

2.4. Stirring intensity

The reaction rate of wet oxidation carried out in the reactor is directly controlled by the oxygen mass transfer rate between water and gas. Different reactors are used with different reaction rates, and industrial reactors are generally equipped with stirring devices. In a certain range, the greater the stirring intensity, the better the mass transfer effect of oxygen. In supercritical water oxidation, the mass transfer resistance of oxygen is very small due to gas-liquid phase mixing, and the effect of stirring intensity on the treatment effect is very small at this time.

When the reaction is carried out in an autoclave, the mass transfer of oxygen from the gas phase to the liquid phase is related to the stirring strength [24]. The stirring intensity increases in a certain range and the mass transfer rate of oxygen in the liquid phase increases; however, the excessive stirring intensity causes the fluid to roll violently, the bubble becomes larger, the gas holdup decreases [25], and the mass transfer rate decreases instead.

2.5. Feedwater pH value

The influent pH value can affect the WAO degradation efficiency, but the effect is different for different kinds of wastewater, mainly divided into the following three cases:

(1) For some wastewater, the lower the pH value, the better the oxidation effect. Wang Yongyi, Tsinghua University, et al. [26] found that the oxidation degree of H acid from high to low in order of pH value was: 2.5, 7, 13 in wet oxidation treatment.

(2) For some wastewater, the higher the pH value, the better the oxidation effect. The COD removal rate of olive oil and distillery wastewater oil and distillery wastewater increased with the increase of influent pH.

Therefore, regulating the wastewater to the appropriate pH value is beneficial to accelerate the reaction rate and the degradation of organic matter.

2.6. Concentration of influent

When the actual oxygen supply is less than the oxygen required for the complete degradation of organic matter in water samples, the oxygen supply and mass transfer become the control step of the reaction. At this time, it is obvious that the smaller the influent concentration, the faster the degradation rate of organic matter; when the actual oxygen supply is greater than the oxygen required for the complete degradation of organic matter in water samples, the faster the degradation rate of organic matter with influent concentration. Norwegian chemists C.M.Guldberg and P.Waage summarized the relationship between reactant concentration and reaction rate based on more than 300 experimental data [29], and proposed the law of mass action: at constant temperature, reaction rate and each reactant. The product of the concentration is proportional.

Of course, the influent concentration of wastewater is not unlimited. When Cai Mingchu [30] expounded "wet oxidation and its application in petrochemical wastewater treatment ", taking the operating pressure of the reactor 10.55 MPa, the reaction temperature 289℃ as an example, it was pointed out that in order to ensure the presence of water phase in the reactor, the influent COD value should be lower than 104g/ L. Otherwise, the reaction could not be carried out if all steam state, and the reaction could not be carried out.
2.7. Salt effect of influent

Many literatures show that salt effect has a negative effect on wet oxidation. Dihara Yifang [31] found that sodium salt had an adverse effect on wet air oxidation of polyethylene glycol, and thought that the solubility of oxygen decreased in salt-containing water, and the oxygen diffusion rate decreased. Tan yajun et al. [20] investigated the influence of Na$_2$SO$_4$ on the wet oxidation of H acid. For H acid with a concentration of 10 g/L, the reaction was set as 200 ℃, the partial pressure of oxygen was 3 MPa, and the pH value of water inlet was 7.

Another high salt content (especially Cl I) is also more serious corrosion to the equipment, so it is better to remove salt before wet oxidation, which can not only improve the effect of wet oxidation, but also reduce the corrosion of the equipment.

2.8. Influent properties

Different influent properties (organic structure), the degree of difficulty of wet oxidation will also be different. The oxidation of organic matter has a great relationship with its charge characteristics and spatial structure, and different wastewater have different reaction processes and reaction activation energy, so the difficulty of wet oxidation is different: the electron-absorbing groups, such as chlorine and nitro, have stable effect on the aromatic ring, which makes it difficult to carry out wet oxidation treatment, while the electron-supplying groups, such as hydroxyl, amino amino group and methyl group, increase the electron cloud density on the aromatic ring and make it easy to wet oxidation treatment. Randall[32] found that aliphatic and halogenated aliphatic compounds, Hydrides, aromatics (e.g. toluene), aromatic groups and aromatic compounds containing nonhalogenated hydrocarbons are easily oxidized; halogenated aromatic compounds (e.g. chlorobenzene and polychlorinated biphenyls) without other groups are difficult to be oxidized.

Although the organic matter in wastewater varies widely, they must be oxidized to small molecules first before they can be completely oxidized. In general, the wet oxidation process is divided into two processes: rapid reaction period of large molecule oxidation to small molecule and slow reaction period of continuous oxidation of small molecule intermediate product. A large number of studies have found that the intermediate products benzoic acid and acetic acid inhibit the continuation of wet oxidation. The reason is that acetic acid has a high oxidation value and is difficult to be oxidized, so it is a common intermediate product accumulated during wet oxidation. The degree of oxidation of treated wastewater depends on the degree of oxidation of intermediate products such as acetic acid.

2.9. Reactive heat and air requirements of wastewater

Wet oxidation, also known as wet combustion, in this system relies on the oxidation heat released by the oxidation of organic matter to maintain the reaction temperature. The calorific value produced by the oxidized substance per unit mass during oxidation is the combustion value. Air consumption is also required during wet oxidation, and the amount of air required can be obtained from the COD value of wastewater degradation [33]. The actual oxygen demand is higher than the theoretical value due to the influence of oxygen utilization ratio. Although the combustion values and air requirements of various substances and components are different, the heat they consume per kilogram of air is roughly the same, generally about 3000-3200 kJ.

2.10. Reaction product

Under general conditions, after wet oxidation treatment of macromolecular organic matter, the macromolecule breaks and is then further oxidized to small molecular oxygen-containing organic matter. Acetic acid is a common intermediate product, which is often accumulated because of its difficulty in further oxidation. The intermediate products such as acetic acid can be oxidized to the final product CO$_2$ and H$_2$O. If the reaction temperature is further increased selecting suitable catalysts and optimizing process operating conditions can degrade the intermediate products, which is beneficial to the complete oxidation of organic matter [34].
3. Conclusion
The treatment of refractory organic wastewater has always been a difficult problem in the water treatment industry, and wet oxidation technology can effectively treat such wastewater. Effect and influencing factors of wastewater treatment are closely related. The influencing factors of wet oxidation technology include nine aspects: reaction temperature, reaction pressure, reaction time, stirring intensity, influent pH value, influent concentration, salt effect of influent, nature of influent, reaction heat of wastewater and required air quantity. As the relationship between the velocity constant and temperature of the chemical reaction follows the Arrhenius formula, the reaction temperature is an important factor of WAO technology.

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