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Applications of Advanced Oxidation Technologies for Sludge Treatment

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Abstract. Treatment of sludge is an important issue in water treatment. At present, the traditional sludge treatment process still faces problems such as high sludge production and low solid content, and it is impossible to achieve environmental and economic benefits. Advanced oxidation technology can not only reduce sludge dry base production, but also improve sludge dewatering performance, which has attracted much attention in the field of sludge treatment. On the basis of a brief description of Fenton reagent oxidation, ozone oxidation, wet air oxidation and supercritical water oxidation mechanism, the effects of several advanced oxidation techniques on sludge dry yield and dewatering performance are discussed, and various oxidation methods are introduced. Finally, the advantages and disadvantages of various advanced oxidation technologies are discussed, and the main research directions of advanced sludge oxidation are pointed out.

1. Introduction

With the acceleration of China's urbanization process and the continuous growth of the national economy, the discharge of sewage has increased sharply, and the sewage treatment industry has also developed. According to statistics, as of 2017, about 40 % of the sludge in urban and rural areas in China has not been properly disposed of. The sludge has the characteristics of high water content, large volume and high treatment cost. Relevant personnel are usually used to temporary treatment during the sludge disposal process, and 15% of the sludge has environmental hazards during disposal. The large amount of organic pollutants, heavy metals and pathogenic microorganisms contained in the sludge can easily cause secondary pollution to the environment, endangering people's health and ecological environment. The sludge contains not only a large amount of pollutants from natural water sources, such as suspended solids, colloidal substances, algae and coloring organic matter, but also a large amount of water treatment agents [1]. Compounds such as $CaCO_3$, SiO_2, Fe_2O_3, and Al_2O_3 are the main components of feed water sludge [2]. In many countries (especially in developing countries such as China and India), most of the sludge is directly discharged to the drainage system without any treatment. Or, after dehydration treatment, it is transported to the landfill for disposal [3]. At present, the main treatment methods of sludge are: direct discharge into water bodies, discharge into sewers by urban sewage treatment plants, landfilling of sludge, sanitary landfill of sludge, ocean dumping of sludge, and land use of sludge [4]. The advanced oxidation technology developed in the 1980s can produce a large number of strong oxidizing intermediates ·OH, which can accelerate the recessive growth of microbial cells and degrade organic matter into carbon dioxide, water and intermediates through oxidation [5-6]. An efficient sludge reduction treatment technology has the characteristics of strong oxidizing ability and less secondary pollution, and has become a research hotspot in the field of sludge treatment. The advanced oxidation treatment technology of sludge mainly includes Fenton reagent oxidation [7], O_3 oxidation [8], wet air oxidation [9] and supercritical water oxidation [10]. This study focuses on the application of several oxidation processes in sludge treatment.

2. Application of Fenton for sludge treatment

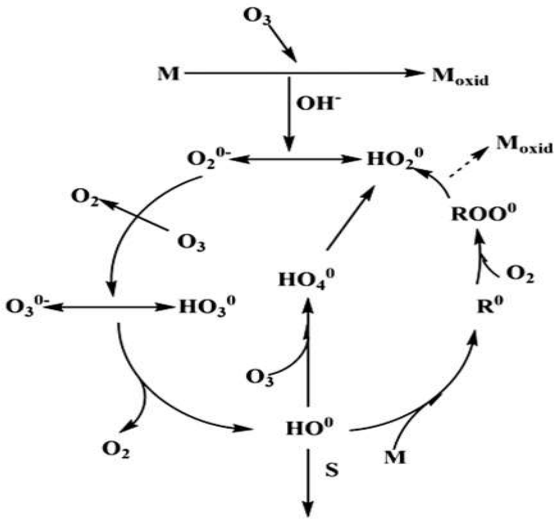

Figure 1. Ozone oxidation mechanism diagram.

The Fenton system refers to a mixed system composed of Fe^{2+} and H_2O_2. Under acidic conditions (pH≈3), Fe^{2+} acts as a catalyst to promote the decomposition of H_2O_2 into a highly reactive ·OH. The strong oxidizing OH can oxidize and degrade various organic substances. Fenton oxidation has the advantages of rapid, economic and environmental friendliness, but the incompleteness of organic mineralization limits its wide application. Currently, Fenton reagents have been used for sludge conditioning [11]. Yu [12] summarized the steps of Fenton reagent in sludge conditioning: Fenton oxidation and Fe^{3+} flocculation, the main mechanism is as follows: 1) Extracellular polymer EPS is oxidatively degraded to soluble organic matter by Fenton; 2) EPS degraded to bind water The release is converted into free water; 3) The sludge particles are broken into small particles by oxidation; 4) Fe^{3+} produced by Fenton reaction is used as a flocculant to polymerize small sludge particles into large-sized sludge particles with high density and low water binding. 5) The cement cake has a large pore size (>10nm) and is a porous structure with good permeability.

3. Application of ozone oxidation for sludge reduction

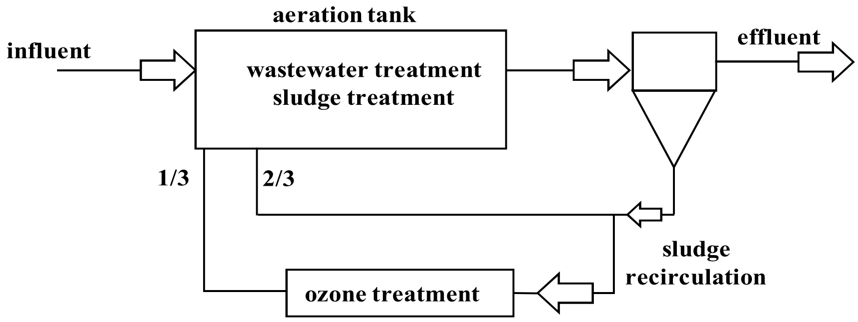

Figure 2. Sludge production reduction system.

The mechanism of action of O_3 is shown in Figure 1 The direct reaction includes: 1) a cycloaddition reaction, that is, O_3 can undergo a cycloaddition reaction with an unsaturated bond of an organic compound to form a lower O_3, which is oxidized in an aqueous solution to a carbonyl compound such as an aldehyde or a ketone and a part of a zwitterion, and the zwitterion rapidly Oxidation to a carbonyl-peroxy state, eventually forming a carbonyl compound and hydrogen peroxide; 2) Electrophilic reaction, ie, a position where the electron cloud density is high, is prone to electrophilic reaction, with electron-donating groups (eg, -OH, $-NH_2$). The aromatic substitutions have high electron cloud density at the ortho and para-carbon atoms, and react faster with ozone, while aromatic substitutions with electron-withdrawing groups (such as -COOH, $-NO_2$) react slowly with ozone. 3) The nucleophilic reaction generally occurs in the electron deficient position, especially on the carbonyl site with an electron withdrawing group, or by the transfer of O. Indirect reactions include: 1) Electron transfer reaction, ie, OH captures electrons on organic matter and is reduced to OH-; 2) Hydrogen extraction reaction, ie, OH, extracts H from different substituents of organic matter, and generates organic radicals and water; 3) The OH addition reaction, that is, the addition reaction of ·OH with a double bond on an olefin or an aromatic compound, forms OH-. The three destinations after O_3 oxidation of sludge include: direct oxidation to CO_2, H_2O; conversion to soluble intermediates; conversion to inert sludge. And O_3 has an effect on the degree of mineralization of the sludge, biodegradability, sedimentation performance, filtration performance, protein, polysaccharide, TOC and EPS in the sludge. At the same time, the sludge after O_3 cracking can be used for anaerobic digestion, sludge stealth growth, carbon source for nitrogen and phosphorus removal. The reduced sludge system treated with ozone is shown in Figure 2 [13]. The higher the soluble chemical oxygen demand (SCOD) caused the better the subsequent aerobic/anaerobic digestion of the sludge. Srinivasan [14] used thermal-chemical techniques to treat sludge and found that SCOD increased significantly during O_3 treatment. Erden [15] also found that when the O_3 dose was 0.1 g/g (DS), the SCOD increased from 240 to 960mg/L.

4. Application of air oxidation for sludge reduction

Wet air oxidation (WAO) is a high-temperature and high-pressure oxidation treatment technology for organic or inorganic substances using oxygen as an oxidant in a solution [16]. Figure 3 shows the sludge wet oxidation test process [17]. Organic or inorganic substances can be converted into carbon dioxide, water and biodegradable short-chain organic acids, including acetic acid, the most important short-chain organic acid. The influencing factors mainly include reaction temperature, reaction pressure, pH value of the solution, reaction time, nature of the treatment object and the dosage of the catalyst.

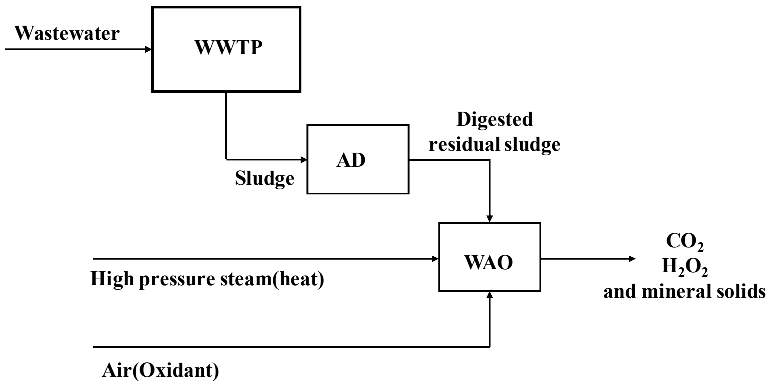

Figure 3. Wet air oxidation in a sludge treatment line.

Heavy metals such as Cu and Ni can be used as a catalyst for humid air oxidation, that is, catalytic wet air oxidation (CWAO). CWAO is developed on the basis of WAO, with fast response rate and low operating cost. However, BENHAMED [18] proposed that WAO has high energy consumption and high equipment input shortcomings, and CWAO faces difficulties in catalyst separation and recovery and by-product poisoning. A large number of studies have shown that: Wet air oxidation can be directly used for municipal sludge treatment, which will affect sludge sedimentation/dewatering performance, TSS and VSS content, TOC distribution and volatile fatty acids (VFAs) production. Bernardi [19-20] found that in the process of humid air oxidation, insoluble organic matter is first converted into simple soluble organic matter by dissolution, and then continues to be oxidized to carbon dioxide, water and biodegradable intermediates.

5. Application of supercritical water oxidation for sludge reduction

Supercritical water (SCW) is a special state in which the temperature and pressure of water are higher than the inherent critical temperature and critical pressure, respectively. In this state, the liquid has the same gas [22] (the ratio of the actual oxidant to the theoretical value), which can be divided into supercritical water gasification (SCWG, n=0), supercritical water partial oxidation (SCWPO, 0<n<1), and supercritical water oxidation (SCWO, n>1). Among them, the main goal of SCWG and SCWPO is to produce hydrogen-rich gas, and SCWO is an effective method to completely degrade organic matter, sometimes accompanied by the generation of flame. The experiments were carried out in the experimental apparatus of the University of Valladolid by using a new SCWO reactor design which was developed by the personnel of the High Pressure Process Group of the University of Valladolid working under hydrothermal flame regime. The apparatus operated continuously and was designed to operate at pressures up to 30MPa and temperatures between 400_C and 700_C with a treatment capacity of 24L/h of feed (waste in aqueous solution). The flow diagram of the facility is shown in Fig. 4. Cabeza [23] is a nitrogen-containing compound that is difficult to degrade sludge, and isopropyl alcohol is injected into the SCWO system as an auxiliary fuel to promote flame generation. It is found that 99.99% of TOC and 99.90% of ammonia are converted, TOC The concentration of total nitrogen in the sludge effluent is lower than 10, 20mg/L. The traditional SCWO is formed at < 600°C, and is not accompanied by flame generation, but the organic matter removal rate is still high. Miller [24] explained: The dissolved organic matter forms a homogeneous environment in supercritical water, which greatly reduces the mass transfer resistance between phases, so supercritical water is an ideal reaction medium. The organic matter is gasified in an oxygen-free or oxygen-poor state, and the organic matter is rapidly converted into CO_2 and H_2O in an oxygen-rich state. Xu [25] studied China's first pilot-scale sludge SCWO treatment plant. Zou [26] studied the effects of temperature, oxidant coefficient and residence time on the degradation rate of COD. The results show that the degradation rate of COD increases with increasing temperature. In particular, the reaction rate above the critical point is significantly higher than subcritical and near. At the same time, as the oxidant dose and reaction time increase, the COD degradation efficiency also increases.

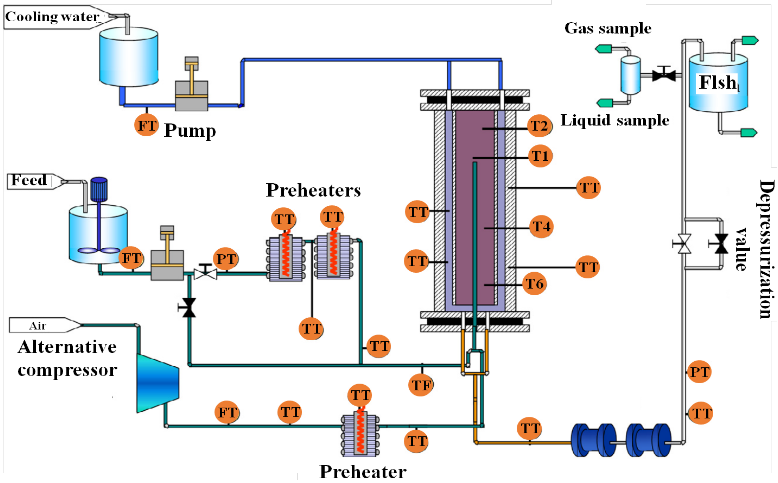

Figure 4. Diagram of the apparatus used in SCWO.

6. Conclusion & Outlook

In summary, O_3 oxidation mainly reduces sludge dry basis production, while Fenton reagent oxidation can enhance dewatering performance and reduce sludge moisture content. Both WAO and SCWO are carried out in the presence of high temperature, high pressure and oxidant, and the organic matter in the sludge is directly oxidized into carbon dioxide, water and intermediate products. Therefore, the combination of advanced oxidation technology and complementary advantages can maximize the advantages of advanced oxidation technology in sludge reduction applications.

Acknowledgements

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