Research on Waste Leachate Treatment with Fenton Oxidation Technologies

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Abstract: Currently, the main method of disposal of municipal solid waste is sanitary landfill. However, a significant amount of leachate is produced during the landfilling process, which can lead to a series of environmental and economic problems. This paper reviews the research on Fenton and Fenton-like oxidation technologies in the treatment of waste leachate. The paper first introduces the characteristics of waste leachate and its hazards to humans and the ecological environment. Then, it will be followed by the technical principles and characteristics of the classic Fenton oxidation process. Starting from the limitations of classic Fenton in practical applications, the paper introduces combined oxidation technologies of ultrasound, microwave, light, and electricity with Fenton, and describes the different characteristics and optimal reaction conditions of various oxidation technologies. In practical applications, the most suitable oxidation technology can be selected based on the water quality characteristics of the leachate. Finally, introduce the development prospects and improvement methods of ultrasound-Fenton, microwave-Fenton, photo-Fenton, and electro-Fenton.

Keywords: waste leachate, Fenton, Fenton-like, improvement.

1. Introduction

As the mass of landfill production increases, so does the production of waste leachate. Waste leachate is characterized by significant variations in both quantity and quality of water; high concentrations of organic matter with a wide range of components, particularly high levels of ammonia nitrogen; high levels of heavy metals; an imbalance in nutrient factors, lacking in phosphorus; and the production of large amounts of foam during biochemical treatment [1]. Waste leachate also contains trace pollutants such as pesticides, hormones, and antibiotics, which harm human health.

For example, antibiotics are not completely absorbed by the maternal body after ingestion, so the remaining parts are excreted into the sewage system via urine or feces. After entering the wastewater treatment plants, most antibiotics cannot be completely removed either. Studies have shown that the removal efficiency for tetracyclines, sulfonamides, and fluoroquinolones is between 30% to 80%, and the rest of the organics will enter the environment with the effluent [2]. Antibiotics such as sulfamethazine and oxytetracycline have been found to have carcinogenic effects, and human exposure to tetracycline antibiotics (TCs) may lead to endocrine disruption, joint diseases, and adverse effects on the development of children’s teeth [2].

The traditional treatment method makes it difficult to meet the treatment requirements of waste leachate. Therefore, the general waste leachate is treated by the combination process of pretreatment + biological treatment + advanced treatment. Fenton Oxidation technology is an advanced oxidation method based on hydroxyl radical (·OH), which is generally used for pretreatment and advanced treatment. It can efficiently remove a variety of pollutants in the waste leachate, with mild reaction conditions, fast reaction rate, low equipment cost, and in the continuous improvement [3]. Because of its strong oxidation capacity, it has important application prospects in waste leachate treatment.

Based on the characteristics of waste leachate and the characteristics of Fenton oxidation technology, this paper summarizes its research and development prospects in the field of waste leachate, aiming to help readers fully understand the research dynamics in the current field.

2. Characteristics of the Landfill Leachate

As shown in Table 1, which presents the water quality characteristics of leachate from various sources, it is evident that different sources of leachate share some commonalities, such as high Chemical Oxygen Demand (COD), low Biochemical Oxygen Demand (BOD5)/COD ratio, poor biodegradability, and high total nitrogen levels. Leachate water quality is complex and variable, characterized by high concentrations of organic matter, total nitrogen, conductivity, and poor biodegradability. The leachate is rich in long-chain alkanes, humic substances, and other refractory biodegradable materials, and it also has a high concentration of salts and heavy metals. The biodegradability of old landfill leachate and wet waste sludge is not strong, and the water quality and quantity are subject to significant fluctuations due to external conditions, which also contributes to the increased difficulty in treating leachate [4].

Table 1. Water quality characteristics of waste leachate from different sources

target	Incineration plant	landfill site			freight station
		<5years (prime)	5-10 years (mid-term)	>10years (aging)	
pH	5-6	6-6.5	6.5-7.5	>7.5	<6.5
COD (mg/L)	>20000	>20000	4000-10000	<5000	5000-50000
BOD_5/COD	>0.3	>0.3	0.1-0.3	<0.3	>0.3
TN/(mg/L)	>2500	>2500	2000-3000	2500-4000	200-4000
specific conductance(s/m)	>1	>1	1-1.5	2-3	0.2-1

3. Fenton and Fenton-Like Oxidation Technologies of Waste Leachate

3.1. Tradition Fenton

The Fenton oxidation process is an advanced oxidation method that involves mixing Fe(II) with H2O2 under acidic conditions to produce ·OH radicals, which degrade organic pollutants. The Fenton process has advantages such as simple equipment and efficient reactions. Also, its product has high mineralization rates with no toxic side effects on the environment, making it a highly promising oxidation technology. However, the Fenton oxidation method also has several limitations.

Firstly, the concentration of the Fenton reagent significantly affects the generation of OH radicals. Treating complex wastewater requires a large amount of reagent, which makes cost control a barrier to practical application.

Secondly, the pH range for using the Fenton oxidation method is very narrow. It typically exhibits the strongest catalytic activity at pH=3. If the pH deviates from the optimal value, the treatment efficiency decreases significantly. When the pH is too high, Fe2+ will oxidize to form hydroxide precipitates, necessitating additional processes to remove iron sludge. When the pH is too low, it disrupts the balance between Fe2+ and Fe3+.

Lastly, the classic Fenton reagent cannot be regenerated. As the reaction progresses, H2O2 is consumed, and Fe2+ is oxidized to form iron oxide precipitates.

3.2. Ultrasound-Fenton

An ultrasonic wave is a kind of high-frequency sonic wave, which is a type of elastic mechanical wave. Ultrasonic technology is based on the transient cavitation bubbles bursting to produce free radicals, and causing localized high temperatures (about 5000K) and high pressures (about 500 bar). The effects of cavitation, high pressure, and high temperature can promote the rapid dissociation of H2O and O2 to generate more highly active free radicals, to provide a driving force for the degradation of pollutants.

Ultrasonic waves cause cavitation in wastewater, which brings both high temperatures and generates hydroxyl radicals. Pollutants are thermally decomposed by the high temperatures. On the other hand, they can also be oxidized by hydroxyl radicals. The ultrasonic Fenton technology combines the advantages of two methods, which improve the treatment effect on pollutants [5].

In Ren Baixiang's experiment, the experimental conditions were: ultrasonic frequency of 40 kHz, ultrasonic power of 200 W, water temperature of 20°C, and initial pH value of 6.20 [6]. The COD removal rate of beer wastewater gradually increases with the increase of ultrasonic time. The COD removal rate accelerates during the reaction from 5 minutes to 20 minutes, and after 20 minutes, the COD removal rate remains stable. This is because cavitation is produced under the effect of ultrasonic waves, and the cavitation effect generates a large number of hydroxyl radicals, causing degradation. As time goes by, hydroxyl radicals are continuously produced, therefore, the COD removal rate of the wastewater gradually increases [6]. However, at the same time, the cavitation also causes the temperature of the aqueous phase to rise. Although high temperatures are beneficial for improving the efficiency of hydroxyl radical degradation of organic pollutants, they are not conducive to the generation of ultrasonic cavitation bubbles. As time goes by, the number of hydroxyl radicals in the aqueous phase will not continue increasing, on the contrary, due to the high temperature affecting the ultrasonic cavitation effect, the concentration of hydroxyl radicals will decrease. Therefore, the ultrasonic degradation reaction process of wastewater shows that the COD removal rate gradually increases in the initial stage, but after 20 minutes, the reaction efficiency is not increased [6].

3.3. Microwave-Fenton

Microwave is a kind of electromagnetic wave with wavelengths ranging from 1 to 1,000 mm and frequencies from 300 MHz to 300 GHz. Due to their ability to selectively heat different pollutants and exhibit non-thermal effects, microwaves are characterized by rapid heating of materials, accelerating reaction rates, ease of control, and high energy efficiency. In recent years, they have been widely applied in the treatment of landfill leachate. The combination of microwaves with Fenton's reagent can increase reaction rates, reduce the amount of reagents used, and enhance the degradation rate of pollutants.

In the study by Li Guosheng et al., the effect of microwave treatment time on COD removal efficiency was examined under experimental conditions of pH=5, CFe2+=10 mmol/L, VH2O2=6 mL/L, P=700 W, and T=60 ℃ [7]. The experimental results indicated that extending the microwave treatment time did not increase the COD removal rate. Further tests revealed that a microwave treatment time of 2 minutes could achieve a satisfactory effect. Therefore, when using the Fenton oxidation method to treat waste leachate, the application of microwave radiation only serves to shorten the treatment time, but can not improve the COD removal rate [7].

In the study by Zhang Aiping et al., the treatment effect of microwave Fenton on reverse osmosis membrane concentrated waste leachate was examined [8]. The research indicates that the microwave-Fenton method has some advantages such as short reaction time, strong biodegradability, and good removal effect of organic matter. When the microwave power P is on 390 W, and the microwave Fenton reaction time is only 8 minutes, the removal rates of CODCr and UV254 are 75% and 83%, respectively, and the BOD5/CODCr ratio increases from 0.13 to 0.62 [8].

3.4. Photo-Fenton

Compared with classic Fenton, both photo-assisted and ultrasound-assisted Fenton can enhance the TOC degradation rate. Under UV irradiation, organic compounds undergo photolysis through electronic excitation or molecular homolysis to form intermediates. Photosensitive molecules present in dissolved organic matter (DOM) absorb light to form excited triplet states (3DOM*). The excited substances can react with O2 to generate O2 that can react with organic matter, and continue to react with organic compounds. Moreover, light drives the release of additional free radicals from the Fe3+-DOM complex and accelerates the regeneration of Fe2+. Those factors contribute to the better degradation effect of photo-Fenton [9].

Jacek Leszczyński et al. found that the addition of light during the Fenton reaction not only affected the efficiency of COD removal but also influenced the intensity of the process [10]. Studies have shown that the dosing method of hydrogen peroxide also affects the treatment efficiency. During the experimental process, the maximum COD removal effect (70.7%) was observed at a molar ratio of $H_2O_2/Fe = 9$ and a reaction time of 120 minutes. At the same time, by changing the dosing method of H_2O_2, the COD removal efficiency could be increased to 78% [10].

3.5. Electro-Fenton

As shown in Table 2, Table 2 is a summary of some research findings on the treatment of waste leachate by electro-Fenton oxidation technology in recent years. Different electrode materials, various operating conditions, and initial COD concentrations all affect the removal efficiency of COD, but there is no obvious pattern.

Table 2. Summary of research findings on the treatment of waste leachate by electro-Fenton oxidation technology in recent years.

Electrode material	operational condition	Initial COD/(mg·L-1)	COD removal rate/%
RuO2-Ir2O5/Ti positive pole active carbon fiber negative pole	Extra H_2O_2, Fe^{2+}	520.1	91.8
Iron electrode	Extra H_2O_2	2880.0	72.0
	Extra H_2O_2	48500.0	72.9
	Extra H_2O_2	3495.0	52.0
	Extra H_2O_2	2350.0	72
Aluminum electrode	Extra H_2O_2, Fe^{2+}	2950.0	94.0

Electric Fenton oxidation technology can be understood as a kind of enhanced Fenton oxidation technology. It can enhance the efficiency of oxidation reactions to remove pollutants and produce coagulation effect. On the other hand, it can reduce the amount of H_2O_2 and the consumption of Fe anode, save cost, and enhance the system stability. Electric Fenton oxidation technology and classic Fenton oxidation technology have the same problem which is the large production of iron mud [11].

4. Improvement

Whether traditional Fenton technology or combined Fenton technology, there are issues with technical imperfection and significant room for development. Investigation of the intermediates will be key to improving the Fenton technology. Fenton technology still has vast potential for development. In the future, it should focus on the innovative research and development of new materials, aiming to further enhance treatment effectiveness and economic benefits and to achieve larger-scale industrial development.

The microwave-Fenton method has a relatively small increase in the final removal rate for some wastewater, and the process conditions greatly affect the treatment efficiency, which limits its practical application [5]. Currently, most research on microwave-Fenton methods remains at the static testing stage, and further dynamic testing is key to large-scale industrial applications. The development of new high-efficiency and cost-effective microwave-absorbing materials has become a key to the advancement of microwave-Fenton technology [5].

For the moment, research on improved electrochemical treatment technologies such as three-dimensional electrochemical oxidation, electro-Fenton oxidation, coagulation-electrochemical oxidation, and photocatalytic oxidation is still incomplete and directly restricts the promotion and application of new technologies. Future research on electrochemical oxidation technology should focus on electrode materials, energy consumption costs, gas recovery and utilization, and the joint process development of electrochemical oxidation technology with other technologies [11].

5. Conclusion

Firstly, traditional Fenton processes have drawbacks such as a narrow pH range, unstable chemical reagents, the production of by-products during degradation, high dosages of reagents, and high costs. Secondly, Fenton-like research has broadened the application scope of the Fenton method, reduced the amount of reagents used, decreased the production of by-products, and improved treatment effectiveness. Lastly, photo/electro-Fenton reactions are clean and efficient, showing potential for sustainable development. Ultrasonic/microwave Fenton reactions are rapid and thorough, and the treatment method can be chosen based on the characteristics of the leachate.

Therefore, in the future, it is important to strengthen the optimization of combinations among advanced oxidation technologies to improve existing defects and to develop new and composite catalysts to reduce the costs of engineering applications.

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