

Review on the End Distilled Water Treatment from MVR+VP landfill leachate process by Fenton method

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Keywords: Landfill leachate; Mechanical Vapor Recompression; Fenton oxidation

Abstract. Landfill leachate has the characteristics of high concentrations of toxic and hazardous substances and complex and varied characteristics. After the Mechanical Vapor Recompression (MVR) + Vapor Processing (VP), the distilled water at the end of the treatment still contains a large amount of dissolved organic matter (DOM). Further oxidation reprocessing can meet China's discharge standards for landfill leachate. Among many oxidation methods, the Fenton method is characterized by extremely high oxidability. When the terminal distilled water is oxidized and retreated by the Fenton method, the refractory organic components are reduced, and the biodegradability can be improved. By analyzing the reaction mechanism, main influencing factors and research status of the Fenton method, the technical status, key issues and development prospects of the "MVR+VP" process end distilled water treatment by Fenton method are comprehensively analyzed and forecasted.

Introduction

With the acceleration of the process of production development and industrialization in China, the amount of garbage generated during production and living has increased year by year, and landfill is a major method for handling waste in China for a long period of time. Landfill leachate produced during landfill process has very high values of COD and BOD₅, and contains a lot of organic matter, nitrogen, phosphorus and heavy metals. If landfill leachate is directly discharged into rivers, lakes and seas without treatment, it will have a serious impact on the environment around the river basin and the health of residents. Due to the variety and complexity of wastes, landfill leachate has the characteristics of high concentrations of toxic and hazardous substances and is complex and varied, making the treatment of landfill leachate much more difficult than conventional wastewater. With the increasingly stringent environmental protection requirements in <Standard for pollution control of domestic waste landfill> (GB16889-2008) proposes discharge standards for landfill leachate from the aspects of COD, total nitrogen, heavy metals, and transport operations. With more stringent requirements, effective and effective measures must be taken to effectively treat landfill leachate to minimize environmental pollution.

Conventional landfill leachate treatment technologies include physical chemistry and biological methods. The physical and chemical methods mainly include activated carbon adsorption, chemical precipitation, ion exchange, membrane dialysis, etc. The biological methods mainly include biofilm method and activated sludge method. However, the materialization method has a high processing cost and is not suitable for the treatment of large-scale landfill leachate. Although the biofilm method and the activated sludge method have mature operation and management experience, the construction of a dedicated leachate treatment plant requires a large investment and high operation and management costs. And with the closure of the landfill, the water treatment facilities will eventually be scrapped.

Based on the above, advanced technologies that meet new standards such as UASB+MBR+RO (Up-flow Anaerobic Sludge Bed + Membrane Bio-Reactor + Reverse Osmosis), MBR+NF (Nanofiltration) + RO, Mechanical Vapor Recompression (MVR) + Vapor Processing (VP) etc.,

gradually entered the people's attention. The "MVR+VP" can effectively recycle the secondary steam, and it can maintain the steam temperature without or with a small amount of raw steam after start-up. The structure is simple, the operation is simple, the operation is stable and the cost is low, and the ammonia nitrogen and refractory degradation of the leachate are solved. With the high concentration of materials, it can meet the requirements of energy-saving and high-efficiency. However, with the emphasis on environmental protection and the increasing demand for water standards, the Fenton method is required to oxidize the distilled water at the end of "MVR+VP" to achieve higher standards.

MVR+VP Landfill Leachate Evaporation Treatment Process

MVR+VP Technology Principles and Features. "MVR+VP" belongs to the evaporation process. It uses mechanical methods to recompress the secondary steam to a higher pressure, so that its internal energy can be increased, and the original evaporator replaces the fresh steam as a heat source to realize the continuous cycle of this energy. That is, as long as the evaporation initiates the production of secondary steam, no additional heat source is needed during the operation to allow continuous evaporation [1]. This evaporation system is abbreviated as MVR (Mechanical Vapor Recompression).

MVR+VP are physical separation methods that separate the landfill leachate into two liquids: the big stock solution is the terminal distilled water, and the small stock solution is the concentrate. Most of the leachate contained in the leachate is concentrated in the turbid liquid. The terminal distilled water contains some volatile organic pollutants and a small amount of ammonia nitrogen. The technology and products have the advantages of high resource recovery rate, no need to add medicaments, stable operation, small footprint, clean and environmental protection, and a wide range of applications.

MVR+VP Evaporation Process Temperature and pH. Studies have shown that the pH value of leachate affects the concentration of ammonia nitrogen and COD in the secondary steam condensate. When the pH value is 4 to 5 and the temperature is 98°C, the ammonia concentration in the condensate is low and the COD is high. When the pH value is 6, the condensate has high ammonia nitrogen and low COD. Garbage incineration plant storage pit leachate (stock solution pH = 5.23, NH₄-N = 917 mg/L) was evaporated at 0.016 MPa and 55°C, and the resulting condensate (85.6%) was pH = 3.46, NH₄-N = 0, 21.58% of organic matter volatilizes into the vapor condensate; the analysis shows that the volatiles consist essentially of organic acids with less than 7 carbon atoms. This means that with evaporation at pH=5 and temperature of 60°C, only water and a small amount of low-molecular-weight fatty acids boil off during the evaporation process, and the ammonia contained in the concentrate stays in the concentrate. The ammonia concentration of the condensate can be as low as 0; The COD of the condensate is higher than the evaporation at alkaline conditions, but it is easily biochemically treated. The antiseptic problem of evaporation under acidic conditions is not large, and the pH can be adjusted with sulfuric acid. 316 stainless steel can tolerate H₂SO₄ with a concentration as high as 15%. According to the requirement of material corrosion, when Cl⁻=500~2000mg/L at 50~80°C, 254 stainless steel can be used; at 60°C, Cl⁻≤300mg/L, 316 stainless steel can be used. In this way, the reasonable process conditions should use vacuum evaporation with pH=5 and temperature 60°C. The final material selection is determined by the level of insitu leachate Cl⁻. The condensate produced by vaporization of the produced meta-acids has a high COD (estimated 1000 mg/L) and good biochemical properties.

MVR+VP End Distilled Water Treated by Fenton Process

Fenton Principle. In 1894, H.J. Fenton discovered for the first time that a mixture of H₂O₂ and Fe²⁺ could rapidly oxidize malic acid, and this mixture was called standard Fenton reagent [2]. Studies have shown that the ·OH radical generated by the decomposition of hydrogen peroxide catalyzed by Fe²⁺ in Fenton's reagent is the main oxidizing agent. ·OH radicals are highly oxidizing and can oxidize organic substances [3].

Main Factors Influencing the Treatment of MVR+VP Distilled Water by Fenton Method.

Since the form of Fe^{2+} is affected by the pH value in the solution, Fe^{2+} cannot catalyze H_2O_2 to $\cdot\text{OH}$ in a neutral or alkaline environment, so the reaction can only be performed under acidic conditions. With the decrease of pH, humic acid is negatively charged and most of Fe^{2+} is less hydrolyzed. The removal of humus is mainly due to complexation and neutralization [4]. The effect of micro-flocculation is not obvious and organic contaminants are suspended. The catalytic performance of Fe^{2+} is weakened [5]; however, when the pH is too low, Fe^{3+} is difficult to be reduced to Fe^{2+} , and the supply of Fe^{2+} is insufficient, which is also unfavorable to the generation of $\cdot\text{OH}$. When the pH is higher, on the one hand, the self-decomposition rate of H_2O_2 is accelerated, and the production of $\cdot\text{OH}$ is inhibited. On the other hand, iron ions form hydroxides to precipitate and lose the ability to catalyze flocculation and affect the utilization rate [6]. Scientific research shows that the optimal pH of the Fenton reaction is around 3 [7].

Fe^{2+} dosage. In the process of treating wastewater, with the increase of Fe^{2+} , the removal rate of wastewater COD increases first and then decreases. The main reason is that Fe^{2+} is a necessary condition for catalyzing the decomposition of H_2O_2 to generate $\cdot\text{OH}$ radicals. When the amount of Fe^{2+} added is too small, the concentration of Fe^{2+} is too low, and the rate of $\cdot\text{OH}$ radicals generated by the reaction is extremely slow. The amount of production and production rate are very small, so that the degradation process is inhibited; and when the Fe^{2+} addition amount is too large, so that the concentration of Fe^{2+} is too high, it reacts with $\cdot\text{OH}$ radicals to generate Fe^{3+} , thereby consuming $\cdot\text{OH}$ radicals, so that The removal rate is reduced.

H_2O_2 dosage. In the treatment of wastewater, when the H_2O_2 concentration is too low, the amount of $\cdot\text{OH}$ radicals produced is small, although the $\cdot\text{OH}$ radicals increase as the H_2O_2 concentration increases, but when the H_2O_2 concentration increases to a certain degree, it increases again. H_2O_2 concentration will not only increase the removal rate but will decrease. The main reason is that when the concentration of H_2O_2 is too high, Fe^{2+} is rapidly oxidized to Fe^{3+} at the beginning of the reaction, so that the oxidation process proceeds under the catalysis of Fe^{3+} , which consumes both H_2O_2 and $\cdot\text{OH}$. Produced, the $\cdot\text{OH}$ produced at the same time also produces the compound, the reaction produces H_2O_2 . In addition, the excessive H_2O_2 , its reducibility still increases the COD value in the effluent to a large extent, which in turn leads to a decrease in the COD removal rate.

Different $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ Dosing Ratios. With the increase of the ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ addition, the removal rate of COD increases continuously; if the ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ addition is continued to increase, the removal rate of COD will decrease and tend to be stable.

The Advantages of the Distilled Water Technology at the End of the MVR+VP Process by the Fenton Process

Fenton's application in terminal distilled water treatment Compared to other traditional water treatment methods, Fenton oxidation technology has the following advantages:

High oxidizing power. Fenton reagent can generate a large number of very active $\cdot\text{OH}$ radicals with an oxidation-reduction potential of 2.8 V, second only to fluorine (2.87 V). As an intermediate reactive species, Fenton reagent has high oxidation activity.

High cleanliness. The resulting $\cdot\text{OH}$ radicals react directly with the organic contaminants in the terminal distilled water without selectivity, degrade them into non-toxic, easily biodegradable small molecular substances, and even mineralize them into CO_2 , water and inorganic salts, No secondary pollution will occur.

Economic security. Fenton method uses H_2O_2 reagent as an oxidant, and H_2O_2 is safe and easy to obtain. Its reaction has green characteristics and can be popularized and used. Fenton oxidation technology can be used as a stand-alone treatment technology, can also be combined with other processes to reduce processing costs.

Wide range of applications. The Fenton oxidation process can oxidize and decompose organic substances with substituents such as benzene ring, hydroxyl group, $-\text{CO}_2\text{H}$ and $-\text{SO}_3\text{H}$, $-\text{NO}_2$, etc., to improve the biodegradability of landfill leachate and reduce its toxicity.

Conclusions and Prospects

Landfill leachate is a complex and highly toxic and hazardous waste water, and its water quality is affected by the type of waste, water, landfill time, climatic conditions and other factors. With the enhancement of the environmental protection awareness of the whole society and the increasingly stringent environmental protection policies, the leachate emission standards will further increase.

Because the ammonia leachate concentration and organic matter concentration of the landfill leachate are very high, the terminal distillate after the "MVR+VP" evaporation process needs to be further oxidized by the Fenton method, thereby making it COD, BOD_5 , ammonia nitrogen, total nitrogen, total Phosphorus and other indicators were further optimized. Through a large number of experiments in the past, it is shown that the treatment effect is most significant when the Fenton oxidation reaction conditions are about $\text{pH}=3$ and the ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ is 3:1.

The Fenton process is a mature Advanced Oxidation Process (AOPs) process. Based on the actual conditions of the landfill site, various types of reaction factors are integrated and the Fenton oxidation technology is reasonably improved in practical applications. According to the "MVR+VP" terminal distilled water the specific water quality conditions optimize various reaction conditions.

Based on the current research progress of the Fenton method, the focus of future research work will be to reduce the processing cost, simplify the equipment structure, and increase the efficiency of converting oxidants into free radicals. At present, the combination of Fenton technology and other technologies is also a focus of related researchers. With the deepening of research, Fenton's reagent oxidation method will have a broader application prospect as a potential wastewater treatment technology.

Acknowledgements

The research was financed by the Fundamental Research Funds for Innovation and entrepreneurship training program for College Students (201812026059) and the Fundamental Research Funds for the Central Universities in China.

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