Research Progress on High Salinity and High COD Industrial Wastewater Treatment Technology

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Abstract: In the production process of chemical products such as ethylene and epichlorohydrin, a large amount of industrial wastewater is generated, which has high salt content (over 3.5%), high COD value (over 10000mg·L-1), and characteristics such as biological inhibition and toxicity. At present, it is difficult for sewage treatment plants to effectively treat this type of wastewater. Therefore, the treatment of this type of industrial wastewater has become one of the main obstacles to the green development of the chemical industry. This article reviews the research progress on the generation and treatment technology of high salinity and high COD industrial wastewater, including physicochemical, biological, and physicochemical biological coupling methods. The next steps in the treatment of such industrial wastewater are proposed.

Keywords: High Salt Content; High COD value; Industrial Wastewater; Wastewater Treatment; Green Development

1. Introduction

Ethylene is one of the important raw materials in the chemical industry, and its derivatives are widely used in plastic parts, automotive tires, textile products, paint dyes, and pharmaceutical synthesis. Epoxy propane is an important intermediate in the petrochemical industry, with a large number of downstream products and increasingly diverse applications, involving fields such as furniture, automobiles, construction, and industrial insulation [1-3]. Although the production and application of chemical products such as ethylene and epichlorohydrin not only promote the development of the chemical industry, but also bring many conveniences to our lives, a large amount of industrial wastewater is generated in their production process. This wastewater has high salt content, high COD value, biological inhibition and toxicity, and complex components (such as sulfur, benzene rings, various aldehydes, small molecule organic acids, and peroxides).

In theory, existing wastewater treatment technologies can basically achieve the standard discharge of industrial wastewater mentioned above, but there are also the following main problems: (1) Due to the high salt content and the presence of organic compounds such as benzene rings in wastewater, it is easy to cause bacterial inactivation or inhibition of their activity during biochemical treatment, leading to excessive discharge; (2) The impact of aldehyde polymerization and small molecule acid corrosion in wastewater on the long-term operation of equipment and facilities in factories; (3) In some cases, although wastewater is treated and discharged to meet standards, the total amount of salt remains unchanged. A large amount of salt is discharged into the receiving water body, which can easily cause ecological problems such as land salinization.

Therefore, it is currently difficult for sewage treatment plants to effectively treat industrial wastewater with high salt content and high COD value. Developing treatment and comprehensive utilization technologies for this type of industrial wastewater as soon as possible plays a crucial role in the green development of the chemical industry.

2. The Generation of High Salinity and High COD Wastewater

There are many technologies for preparing ethylene in industry, mainly related to the selected raw material resources. In the ethylene production process, the alkaline washing method is commonly used to remove acidic gases such as CO_2 and H_2S from the cracking gas. The alkaline washing process produces a large amount of waste alkali solution containing Na_2S and Na_2CO_3.

At the same time, the condensation of heavy components in the cracking gas and the polymerization of dienes and aldehydes during the alkaline washing process result in a certain amount of organic matter in the waste alkali solution. The water volume of ethylene waste alkali solution is usually 3-20 tons/hour. The typical composition of ethylene waste alkali solution wastewater is shown in Table 1.

Table 1. Typical Composition of Ethylene Waste Alkali Liquid Wastewater

Composition	Range
Sodium hydroxide (mass fraction),%	1.0~3.0
Sodium sulfide (mass fraction),%	0.5~5.0
Sodium carbonate (mass fraction),%	1.0~9.0
Dissolved hydrocarbons (mass fraction),%	0.1~0.3
Chemical Oxygen Demand/($mg \cdot L^{-1}$)	20000~50000

The main technologies for preparing epichlorohydrin in industry include: chlorohydrin method, co oxidation method (PO/SM, PO/MTBE, CHP method), and direct oxidation method (HPPO method). Among them, in the CHP method epichlorohydrin process, high salt wastewater, aldehyde wastewater, and oily wastewater are generated, with a waste liquid volume usually between 20-35 tons/hour. The typical composition of epichlorohydrin (CHP method) wastewater is shown in Table 2.

Table 2. Typical Composition of Epoxide Propane (CHP Method) Wastewater

Composition	Range
Sodium salt content (mass fraction),%	4.5~5.2
Aldehydes content (mass fraction),%	0.1~0.2
Chemical Oxygen Demand/($mg \cdot L^{-1}$)	30000~50000

3. Current Status of High Salinity and High COD Wastewater Treatment Technology

With the increasingly strict environmental protection policies and the booming development of the chemical industry, the attention to high salinity and high COD industrial wastewater treatment technology is increasing, and the corresponding research directions are also becoming wider, mainly including: physicochemical method, biological method, and physicochemical biological coupling method. Among them, physicochemical method includes incineration method, membrane separation method, advanced oxidation method (AOP), etc. [4].

3.1 Physical and Chemical Methods

3.1.1 Incineration method

Incineration method is a high-temperature heat treatment technology. Under the conditions of 800 ℃~1000 ℃, the organic matter in the wastewater undergoes a violent chemical reaction with oxygen in the incinerator, completely burning into CO_2, H_2O, and inorganic ash. The incineration method is generally suitable for high COD value (COD>100000mg · L^{-1} or above) and high calorific value (calorific value>10467 kJ/kg) wastewater [5]. For the incineration of low COD and low calorific value wastewater, auxiliary fuels may need to be added. Otherwise, methods such as evaporation need to be used to concentrate the wastewater, increase the calorific value, and then proceed with incineration [6]. Yin Yanxing et al. [7] used a circulating fluidized bed boiler to incinerate and treat methanol containing wax wastewater. The furnace temperature was controlled between 800 ℃ and 950 ℃, which can meet the requirement of zero discharge of industrial wastewater. Chen Huichao [8] used circulating fluidized bed incineration to treat saline organic waste liquid. By adding an appropriate amount of limestone to suppress bed coking, the temperature of the furnace incineration area was controlled between 850 ℃ and 900 ℃ to achieve complete combustion, and the pollutant emission concentration was low. But when the salt content of wastewater is high, it can cause corrosion and coking of the incinerator, and incineration may produce toxic and harmful exhaust gases that need to be treated before discharge.

3.1.2 Membrane separation method

Membrane separation method is a technique that uses special thin films to selectively separate certain components in the liquid phase [9]. It can be divided into micro-filtration, ultra-filtration, nanofiltration, and reverse osmosis based on the size of the membrane pore size. The membrane separation method has advantages such as mild conditions, no phase changes, good selection, good adaptability, and low energy consumption. However, its disadvantages include high equipment and operating costs, and easy membrane blockage[10]. Lu Yanyue et al. [11] used reverse osmosis to treat high salinity wastewater from a chemical plant. After using reverse osmosis technology to achieve desalination, the mass concentration of Cl - can be reduced to 4000mg·L-1. Jiao Tao [12] used a combination process of ultra-filtration and nanofiltration to treat high salt printing and dyeing wastewater. By adding H_2SO_4 to adjust the pH, a dyeing tank wastewater with sulfate as the main auxiliary was formed. After the combination process treatment, the COD removal rate of the wastewater reached 77.2%, and the salt content of the wastewater decreased from 9500mg·L-1 to 563mg·L^{-1}.

3.1.3 Advanced oxidation technology

As shown in Figure 1, Advanced Oxidation

Process (AOP) utilizes various physical and chemical processes such as light, sound, magnetism, and electricity to generate a large number of highly active and oxidizing free radicals (such as· OH), which cause organic matter in wastewater to undergo oxidation reactions with free radicals, converting them into CO_2 and H_2O [13]. Advanced oxidation technology can play two roles in treating industrial wastewater with high salt content and high COD value: (1) improving the biodegradability of industrial wastewater; (2) Realize the removal of recalcitrant organic compounds from industrial wastewater. Advanced oxidation technologies include Fen-ton method, photo-catalytic oxidation method, electrochemical oxidation method, and wet oxidation method [14].

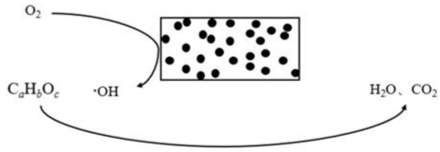

Figure 1. Schematic Diagram of the Basic Principle of Advanced Oxidation Technology

(1) Fen-ton method

The Fen-ton method refers to the degradation and mineralization of organic compounds in wastewater by adding H_2O_2 and Fe^{2+}within the pH range of 2-4, and catalyzing the production of hydroxyl radicals (·OH) by Fe2+in H2O2. He Qingsheng et al. [15] studied the degradation effect of pollutants by coupling methods such as Fen-ton oxidation and ultraviolet photo-catalysis (UV) on alcohol ether wastewater from HPPO plant. The results showed that Fen-ton method can effectively reduce the chemical oxygen demand (COD) of wastewater, but the sludge production is relatively large. The efficiency of UV Fen-ton method in degrading alcohol ether wastewater is higher than that of traditional Fen-ton method, and the sludge production is significantly reduced.

(2) Photo-catalytic oxidation method

The photo-catalytic oxidation method uses semiconductor materials as catalysts at room temperature and pressure to produce hydroxyl radicals under sunlight or ultraviolet light irradiation to degrade organic compounds in wastewater. Liang Xizhen [16] used TiO_2 as a catalyst to perform photo-catalytic degradation of organic phosphorus pesticide wastewater containing dimethoate. Under the conditions of initial concentration of $20mg \cdot L^{-1}$, TiO2 dosage of $0.4\ g \cdot L^{-1}$, and aeration rate of 23 L/h, the removal rate of dimethoate reached 80.5%.

(3) Electrochemical oxidation method

The electrolysis method for treating wastewater mainly involves generating a series of chemical reactions under an external DC power source to remove organic compounds from the wastewater. When wastewater contains a certain electrolyte, electrolysis produces certain active substances (such as hypochlorous acid, ozone, etc.) that have strong oxidizing properties, thereby oxidizing and removing organic matter from wastewater [17-18]. Cao Min et al. [19] investigated that when the anode was Ti/Ta2O5 IrO2, the COD removal efficiency was 62.0%, the energy consumption was 16.7 W·h/mg, and the wastewater treatment effect was good.

(4) Wet catalytic oxidation method

Wet oxidation method refers to a wastewater treatment process that utilizes the oxidizing properties of air or oxygen to remove organic pollutants in the liquid phase at a certain temperature (125~350 ℃) and pressure (0.15~20MPaG)[20]. Li Yanhui investigated the optimal experimental conditions: under the conditions of temperature 280 ℃, residence time 60 minutes, and catalyst Fe^{2+}content 100mg·L-1, the TOC removal rate of high salinity wastewater reached 97.9%. And the wet oxidation effluent was subjected to evaporative crystallization treatment, and the Na Cl mass fraction in the crude salt reached 93%, which is higher than the second level industrial salt standard in the national standard 《GBT5462-2003 Industrial Salt》[21] . At the same time, the B/C of the evaporative condensate is about 0.62, with good biochemical properties. Through conventional biochemical treatment measures, it can be ensured that the final effluent meets the first level national sewage comprehensive discharge standard 《GB8978-2002》.

3.2 Biological Method

Biological methods mainly remove organic matter from wastewater through the metabolism of microorganisms themselves. At present, the cultivation and domestication of salt tolerant microbial strains, as well as the development of different biological treatment processes, are the main research directions of biological methods in the treatment of high salt content and high COD industrial wastewater. Yang Bo et al. [22] screened three strains of halophilic sewage purification microorganisms from the eutrophic water area of Tianjin Port. When the highly efficient halophilic sewage purification bacteria were tested in a composite experiment in high salinity wastewater, their COD removal rate reached 81.5% after 48 hours. When adding composite halophilic microorganisms to artificial high salinity wastewater, they grow well within the temperature range of 25 ℃~40 ℃, pH value of 6.0~9.0, and salt content of 6%~12%. The COD removal rate of high salinity wastewater remains around 70%. Wang Jicheng et al. [23] used a method of gradually increasing salinity load to acclimate activated sludge to salt tolerance. The results showed that after long-term acclimation, the microorganisms in activated sludge were able to adapt well to high salt environments. Under high salinity conditions, the average COD removal rate of domesticated activated sludge for mixed high salinity wastewater is 85.7%, which is 10% higher than that of conventional activated sludge method.

3.3 Physicochemical Biological Coupling Method

In order to better improve the removal efficiency and economic benefits of industrial wastewater with high salt content and high COD value, and to achieve segmented, modular, and distinctive wastewater treatment technologies, people's attention and related research on physicochemical biological coupling methods are also increasing. For example, the combination of incineration and biological methods in physical and chemical methods concentrates high salinity and high COD industrial wastewater and sends it to the incinerator. After concentration, the discharged wastewater is mixed with easily degradable wastewater and sent to the sewage treatment plant for biological treatment before reaching the standard for discharge.Wang Yu et al. [24] used a combination process of electrodialysis and activated sludge to treat high salinity wastewater. By using an electrodialysis device and a low salt content extraction solution, the salt in high salt wastewater is removed, and the desalinated wastewater is treated using an activated sludge process for biochemical treatment. After 5 changes in the extraction solution and 160 minutes of electrodialysis treatment, the salt content in the wastewater decreased from 22000mg·L-1 to 1630mg·$L^{-1.}$ The desalination wastewater was treated with activated sludge method, and the COD removal rate of the wastewater remained around 85% within 24 hours of reaction. Qiu Zhi et al. [25] used iron carbon micro electrolysis Fen-ton oxidation as a pretreatment process, and the COD removal rate of wastewater reached 75%. The B/C ratio of wastewater was increased from 0.21 to 0.43, significantly improving the biodegradability of wastewater.

4. Summary and Outlook

Although the physicochemical method is effective in treating industrial wastewater with high salt content and high COD value, it also has shortcomings such as high investment, operating costs, and possible secondary pollution; The equipment and facilities of biological methods are relatively simple, requiring a relatively stable biological environment and a certain domestication cycle. At the same time, the application of biological methods in high salt and bio-toxic wastewater still needs further industrial practice verification; Due to the limitations of single physicochemical or biological methods, the physicochemical biological coupling method has emerged. This method can achieve segmented, modular, and distinctive wastewater treatment technology, which has good guiding significance for the development of different wastewater treatment processes and the treatment of high salinity and high COD industrial wastewater under the increasingly strict environmental policies.

Industrial wastewater with high salt content and high COD value has the characteristics of high salt content and high COD value, biological inhibition and toxicity, and complex components (such as sulfur, benzene rings, various aldehydes, small molecule organic acids, and peroxides). At present, it is difficult for sewage treatment plants to effectively treat this type of wastewater. Developing effective treatment and comprehensive utilization technologies for this type of industrial wastewater, while achieving standard discharge and recycling of resources in wastewater, plays a crucial role in the green development of the chemical industry.

Reference

[1] Cong Di. Research on Energy Efficiency Analysis and Optimization Methods for Ethylene Production Process [D] Beijing: Beijing University of Chemical Technology, 2022.

[2] Pang Jiao Technical comparison between PO/SM method and CHPPO method for producing epichlorohydrin [J] Yunnan Chemical Industry, 2024, 51 (05): 123-126.

[3] Dan Jie, Wang Qi, etc Process route and technical transformation analysis of epoxy propane [J] Tianjin Chemical, 2023, 37 (01): 90-94.

[4] Wu Zhenglei, Yuan Wenbing, Du Qingqing The application and prospects of zero emission technology in the treatment of high salt organic wastewater [J] Water Treatment Technology, 2016295 (08): 1-5+10.

[5] Zhong Jing, Han Guanglu, Chen Qun New progress in research on high salt organic wastewater treatment technology [J]

Chemical Progress, 2012, 31 (4): 920-926.

[6] Venkateswaran P， Palanivelu K. Solvent extraction of hexavalent chromium with tetrabutyl ammonium bromide from aqueous solution[J]. Separation & Purification Technology，2004，40(3)：279-284.

[7] Yin Yanxing, Ma Jianfei, Duan Yuhua, etc Incineration treatment of methanol distillation wastewater in a circulating fluidized bed boiler [J] Henan Chemical Industry, 2011000 (015): 61-62.

[8] Chen Huichao Experimental Study on Circulating Fluidized Bed Incineration of Salty Organic Waste Liquid [D] Fuzhou: Southeast University, 2006.

[9] Zhang Zhenchuang, Han Xiuli, Fang Shuqi, etc Research on membrane separation method for treating ethanol fermentation wastewater [J] Water Treatment Technology, 2018044 (008): 57-60.

[10] Wang Hua, Liu Yanfei, Peng Dongming, etc Research progress and application prospects of membrane separation technology [J] Applied Chemistry, 2013, 42 (003): 532-534.

[11] Lu Yanyue, Hu Yangdong, Xu Dongmei, etc Optimization design of reverse osmosis seawater desalination system [J] Water Treatment Technology, 2005, 31 (3): 9-14.

[12] Jiao Tao The application and desalination effect analysis of ultrafiltration+nanofiltration process in the treatment of high salt printing and dyeing wastewater [J] Environmental Technology, 2010, 23 (006): 4-7.

[13] Li Fengjuan, etc Research progress on the application of advanced oxidation technology in the treatment of refractory industrial wastewater [J] Environmental Technology, 2017 (2).

[14] Wu Qing, Liu Jinquan, Wang Kai, etc Research progress of advanced oxidation technology in refractory industrial wastewater [J] Water Treatment Technology, 2015041 (011): 25-29.

[15] He Qingsheng, Tian Xiaofeng, Fan Jingfu, etc Comparative study on advanced oxidation treatment of alcohol ether wastewater in HPPO plant [J] Refining Technology and Engineering, 2021, 51 (05): 25-29.

[16] Li Jingbo The application of advanced oxidation technology in industrial wastewater treatment [J] Global Market, 2017 (003): 208-208.

[17] A.V.L.N.S.H. Hariharan，Sudhakar C ，Rao B V. Solvent extraction of Iron (III) with Tetra butyl ammonium Iodide from aqueous acid solutions[J]. Frontiers in Plant Science，2013，4(2)：199-199.

[18] Vlnsh A，HARIHARAN，CH，et al. Studies on the Solvent Extraction of Iron (III) with Tri-iso-octylamine from Aqueous Mineral Acid Solutions[J]. Oriental Journal of Chemistry：An International Research Journal of Pure & Applied Chemistry，2012，28(4)：1785-1790.

[19] Cao Min, Cao Di, Li Nuo, etc Electrocatalytic oxidation treatment of high salinity wastewater [J] China Nonferrous Metallurgy, 2021, v.50 (02): 68-71.

[20] Kwak H W ， Lee K H. Polyethylenimine-functionalized silk sericin beads for high-performance remediation of hexavalent chromium from aqueous solution[J]. Chemosphere，2018， 207(SEP.)：507-516.

[21] Li Yanhui, Wang Shuzhong, Sun Panpan, etc Experimental study and economic analysis on wet oxidation degradation of high chlorine chemical wastewater [J] Chemical Progress, 2017, v.36; No.308 (05): 1906-1913.

[22] Yang Bo, Hao Jian'an, Zhang Xiaoqing, etc Research on the treatment of high salinity wastewater by composite halophilic microorganisms [J] Salt and Chemical Industry, 2015, v.44; No.242 (11): 33-39.

[23] Hu Changshun, Du Yi Research on the renovation plan of the wastewater treatment system of Heihua Group [J] Heilongjiang Environmental Bulletin, 2008033 (002): 74-75.

[24] Wang Yu, Jie Lixin, Li Hui, etc The combination process of electrodialysis and activated sludge treatment for high salinity wastewater [J] Industrial Water Treatment, 2014, v.34; No.277 (03): 61-64.

[25] [25]Chou Zhi Iron carbon micro-electrolysis/Fen-ton oxidation combined with bio enhanced technology for treating high salt wastewater from epoxy resin [D]. Hefei University of Technology, 2020.

