water

Review

Current Status of Zero Liquid Discharge Technology for Desulfurization Wastewater

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Abstract: Desulfurization wastewater is industrial wastewater with a high salt content, high metal ions, and high hardness produced by flue gas desulfurization of the limestone-gypsum method in coal-fired power plants. This paper summarizes the source of desulfurization wastewater, water quality characteristics, water quality impacts, and other factors, combined with the current status of research worldwide to introduce the advantages and shortcomings of the existing desulfurization wastewater treatment technology. In addition, zero liquid discharge technology as a novel method to treat desulfurization wastewater is also summarized. It mainly includes evaporation and crystallization, flue gas evaporation, membrane distillation removal, etc. Finally, this manuscript looks forward to the future development direction of desulfurization wastewater based on its existing technology and emission standards.

Keywords: coal-fired power plant; desulfurization wastewater; zero liquid discharge

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1. Introduction

Coal is one of the most important sources of energy in industry and is widely used in thermal power generation, mechanical drives, flue gas boilers, and other industrial production. Although coal is a relatively cheap source of energy, the components of coal contain small amounts of nitrogen, sulfur, and other elements in addition to the main components of carbon, hydrogen, and oxygen. Therefore, coal combustion will emit a large amount of carbon dioxide and harmful gases, of which sulfide (SO_2) is very easy to cause atmospheric pollution, resulting in haze, acid rain, and other serious environmental problems [1]. Generally, coal-fired exhaust gas must be desulfurized to reduce pollutant emissions. Flue gas desulfurization is mainly divided into wet desulfurization (ammonia method, limestone/lime-gypsum method [2], magnesium oxide method) and dry desulfurization. Due to the high investment and operating costs of dry desulphurization equipment, wet desulphurization technology is usually used to treat coal-fired waste gas [3].

In recent years, the concept of zero liquid discharge has been strongly advocated in industrial wastewater treatment. As shown in Figure 1, this technology reduces the pollutant content of wastewater through certain technical treatments, so that it constantly tends to be a means of zero wastewater treatment. With this treatment method, not only can the resources in the wastewater be recycled, but it also effectively reduces the pollution of wastewater discharge to the environment. However, the desulfurization process will produce a large amount of desulfurization wastewater, the composition of which is quite complex, which mainly includes water, sulfuric acid, sulfate, suspended solids, and other components [4,5]. Sulfides (SO_2) are converted into sulfuric acid and sulfates during this transformation process. Although this process effectively reduces the emission of pollutants into the air, it introduces these chemicals into the wastewater. The concentration and types of sulfuric acid and sulfates are significantly influenced by the desulfurization techniques and types of raw materials used [6]. For example, the use of different desulfurizing agents or the adoption of different operating conditions during the desulfurization process can lead to variations in the concentrations of sulfuric acid and sulfates in the wastewater [7]. In addition to sulfuric acid and sulfates, desulfurization wastewater also contains a large amount of suspended solids, which primarily include unreacted desulfurizing agents, ash, and other solid particles [8]. The coal type and its combustion mode, boiler load, denitrification catalyst, desulfurization agent, and many other factors jointly affect the composition of desulfurization wastewater, which results in a continual change in the water quality of desulfurization wastewater in the process of desulfurization. The main characteristics of desulfurization wastewater include the following: (a) it is weakly acidic, and its pH value is 4~6; (b) it contains a high concentration of sulfide ions; (c) the wastewater contains a large number of suspended solid particles, heavy metal ions, COD (chemical oxygen demand), selenate, and many other pollutants [9]. Dyes and toxic elements [10] that cause environmental pollution are mixed into drinking water and thus threaten human health. The direct discharge of untreated desulfurization wastewater will seriously damage the water quality structure, erosion of soil, and corrosion of large industrial equipment pipelines, etc., which will cause serious harm to the human body and the environment [11]; therefore, how to effectively deal with the desulfurization wastewater has become the focus of many scientific research units and enterprises to study the problem. As shown in Figure 2, this paper introduces the characteristics of traditional desulfurization wastewater treatment technology and summarizes the main zero-discharge desulfurization wastewater treatment technology.

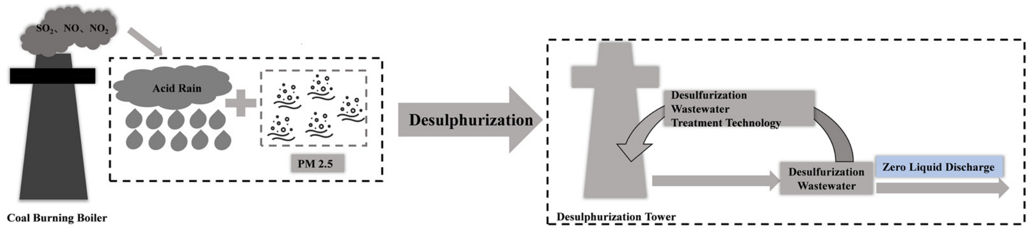

Figure 1. Desulphurization wastewater from power plants.

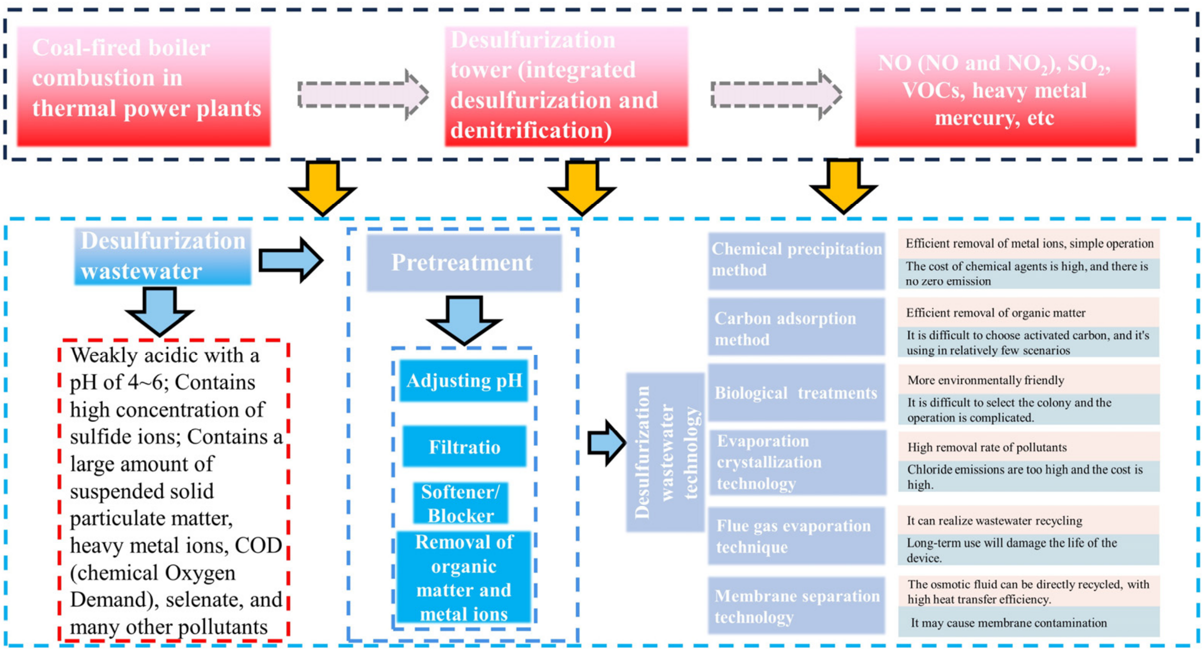

Figure 2. Formation of desulfurization wastewater and treatment technology.

2. Conventional Treatment Technologies for Desulfurization Wastewater

In order to solve the environmental hazards of desulfurization wastewater and realize zero discharge and resource recycling at an early date, many research units and enterprises have carried out research on desulfurization wastewater treatment technology. At present, desulfurization wastewater is mainly represented by traditional treatment technology and zero discharge technology, and traditional desulfurization wastewater treatment technology is based on chemical precipitation, biological treatment, and activated carbon adsorption.

2.1. Chemical Precipitation

The process flow of the chemical precipitation method is shown in Figure 3. The chemical precipitation method mainly removes pollutants such as heavy metals and suspended solids from desulfurization wastewater through neutralization, precipitation, flocculation, and other processes [12]. The chemical precipitation method is an effective method of treating desulfurization wastewater by introducing specific chemical agents to induce the precipitation of pollutants in the wastewater to form solid particles, thus realizing the purification of the wastewater. This method involves the collection of samples of desulfurization wastewater from the desulfurization system to understand the composition and nature of the wastewater, and via testing and sample analysis, the main types and concentrations of pollutants in the wastewater are determined. Next, the pH of the wastewater is adjusted, usually by adding a neutralizing agent $Ca(OH)_2$, and proper pH adjustment contributes to the mildness of the treatment environment and promotes subsequent chemical reactions and precipitation formation [13]. In general, precipitants for pH adjustment include $Ca(OH)_2$, NaOH, $FeCl_3$, and $AlCl_3$ [14]. These chemicals react with sulfides, suspended matter, etc. in the wastewater to form insoluble precipitates. At the same time, the formation and dispersion of the precipitates are induced by stirring or mixing to ensure an adequate reaction. Subsequently, the precipitate is separated from the treatment tank by filtration. Finally, the chemically precipitated water is treated to ensure that the water quality meets discharge standards.

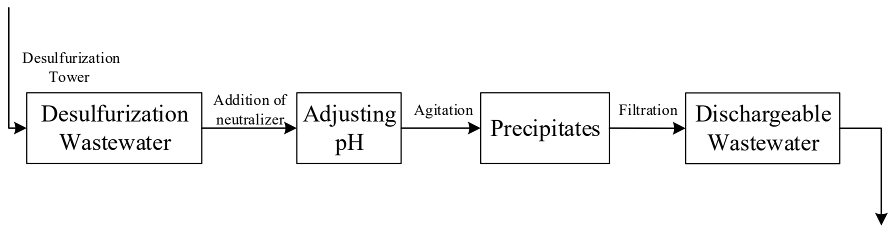

Figure 3. Chemical precipitation process for desulfurization wastewater treatment.

The chemical precipitation method is simple to operate and does not have high operating costs. However, the precipitation method cannot completely eliminate the harmful metal ions (selenium, mercury) in the desulfurization wastewater, which often leads to the COD content exceeding the emission standard and causing harm to the environment. As early as 1990, Enoch et al. [15] used hydroxide with sulfide synergistic precipitation to remove the harmful inorganic substances in desulfurization wastewater. The use of staggered flow microfiltration to remove sediments can effectively solve the problem of repeated chemical rinsing and membrane fouling after cleaning, but it cannot completely remove harmful metals such as Se, Hg, and so on. To address this problem, Huang et al. [16] proposed the use of hybrid zero-valent iron (HZVI) technology to treat Se, Hg, nitrate, and other substances that are difficult to remove completely from desulfurization wastewater. It was found that the proposed HZVI technology can produce a self-sustaining, highly reactive mixture that can be used in near-neutral pH environments. The technology is capable of rapid reduction, transformation, immobilization, and mineralization of each heavy metal, oxygen ions, and other impurities in wastewater. The experimental results showed that the HZVI technology could effectively remove heavy metals from desulfurization wastewater and meet the most stringent environmental requirements for selenium and mercury, i.e., selenium < 10 ppb and mercury < 10 ppb, with a removal rate of 99%. In addition, Yi et al. [17] proposed a two-stage desalination process in which the effects of dosage, reaction time, sulfate concentration, and other factors on Friedel's salt precipitation were investigated through batch tests. In the first stage, the addition of CaO effectively removed Mg^{2+} and part of $SO_4{}^{2-}$, and in the second stage, the remaining $SO_4{}^{2-}$ and 48.1% Cl^- were precipitated as calomel and Friedel's salt. The process flow is shown in Figure 4. The water treated by the two-stage method is alkaline with low turbidity, showing a strong desulfurization capacity. The results of the techno-economic evaluation show that the two-stage process is technically feasible, economically viable and environmentally friendly for treating flue gas desulfurization wastewater.

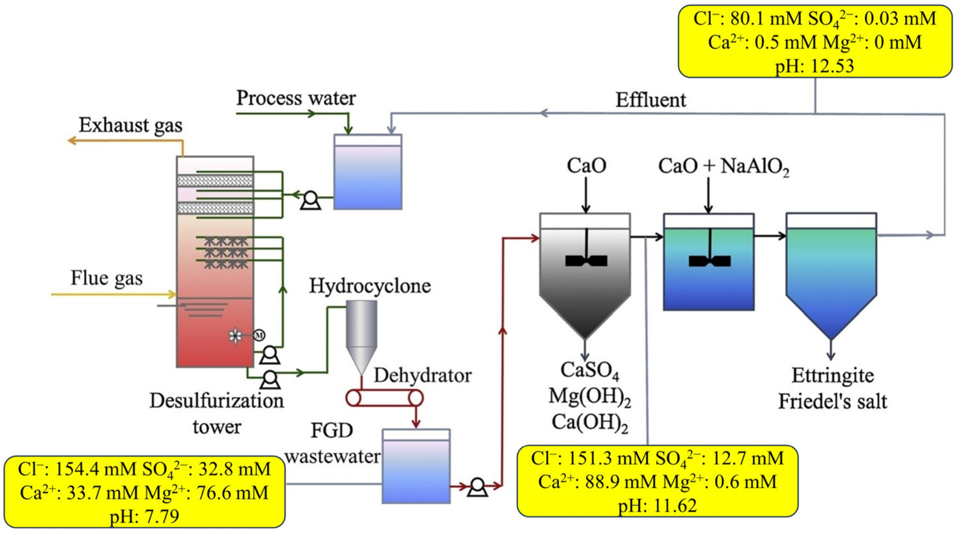

Figure 4. Two-stage desalination process [17].

The chemical precipitation method is simple to operate; it is easy to form the precipitation of calcium, magnesium, and other metal ions; the removal effect is good; and it can effectively reduce the concentration of suspended solids in the wastewater to improve the clarity of the treated water. However, the desulfurization wastewater has a complex composition, which makes it more difficult to select a suitable precipitant, and this technology cannot completely remove the heavy metal ions in the wastewater.

2.2. Activated Carbon Adsorption

Activated carbon adsorption is an effective technology for treating desulfurization wastewater, which utilizes the excellent adsorption properties of activated carbon to remove organic substances and other pollutants from wastewater. The principle is that activated carbon has a large number of micropores and pores on its surface, which provide a large surface area that enables it to adsorb organic molecules. Adsorption is realized based on mechanisms such as van der Waals forces, electrostatic forces, and chemical bonding on the surface of the adsorbent [18].

Hsu et al. [19] used sulfurized activated carbon (SAC) to remove Hg^{2+} from desulfurization wastewater with good results. This method can adsorb organic substances in desulfurization wastewater with high efficiency, but the adsorption effect on inorganic substances is poor, and the activated carbon needs to be replaced or regenerated periodically. Furthermore, in the actual industrial application, it is necessary to select suitable adsorption materials and operating conditions according to the characteristics of the wastewater and treatment requirements. The selection and specific operation of activated carbon has certain difficulties, so it is not widely used in industrial applications.

2.3. Biological Treatment

Biological treatment is a wastewater treatment method that converts various types of pollutants in wastewater into relatively stable and harmless products by utilizing the metabolic activities of microorganisms (bacteria, fungi, etc.). For desulfurization wastewater, biological treatment usually involves the conversion of sulfides in the wastewater to more stable forms through chemical changes in microbial metabolism. Some researchers have utilized biological treatments in coal-fired power plants to treat desulfurization wastewater to meet wastewater discharge standards, considering that biological treatments are more environmentally friendly compared to some physicochemical methods. Blázquez et al. [20] investigated the simultaneous reduction of sulfate to sulfide on a biocathode from the perspective of sulfur recovery, sulfate treatment with partial sulfide oxidation, and recovery of monomolecular sulfur, with a sulfur recovery of 64%. Appropriate biological treatment requires appropriate microbial communities, suitable environmental conditions, and stable operation, but it requires long treatment time and complex operation, and it is not suitable for desulfurization wastewater treatment in coal-fired power plants.

3. Zero Liquid Discharge Technologies for Desulfurization Wastewater

In order to solve the drawbacks of the traditional treatment technology of desulfurization wastewater, the solidification treatment technology of desulfurization wastewater was introduced, which aims to achieve ultra-low emission of desulfurization wastewater. The so-called "zero liquid discharge" technology [21] is an ideal closed water system, where the working system does not discharge water to the outside, and the internal recirculation system reprocesses and utilizes the wastewater, which saves water resources and protects the environment. However, in the existing state of the art, the zero liquid discharge technology of desulfurization wastewater is only the near-zero discharge of wastewater, and it is difficult to achieve zero discharge in the true sense. Generally, the zero discharge of desulfurization wastewater technologies mainly include evaporation and crystallization, flue gas evaporation, and membrane distillation.

3.1. Evaporation Crystallization Technology

Evaporation crystallization technology, as an important means of zero-discharge treatment of desulfurization wastewater, realizes the separation and recovery of hazardous substances in wastewater based on the characteristics of crystallization produced when the concentration of solution exceeds the saturation degree. According to the principle that the solubility of a substance in a solution varies with temperature, when the concentration of a solute in a solution exceeds its saturated solubility, the excess solute will undergo the phenomenon of crystallization, forming solid particles that will ultimately be disposed of in landfills, as shown in Figure 5.

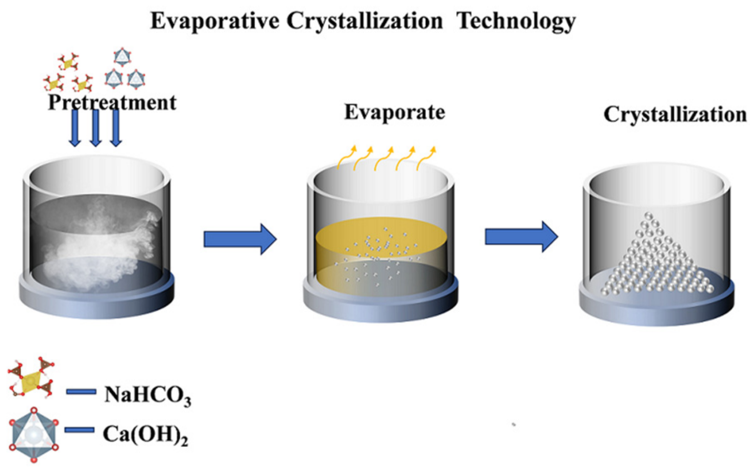

Figure 5. Evaporative crystallization technology.

This process can be realized by heating evaporation and cooling crystallization to remove hazardous substances from the desulfurization wastewater. According to the U.S. Environmental Protection Agency, two new gas-fired power plants in Texas used GE's zero liquid discharge system to treat circulating cooling water, mainly using brine concentration and crystallization treatment processes, with a reuse rate of more than 98% [22]. Li et al. [23] took the desulfurization wastewater of a coal-fired power plant as the actual research object, designed the system process flow, and carried out an experimental study combining wastewater pretreatment with evaporation and crystallization. In the pretreatment stage, sodium sulfate was added to the water, and then the effluent was pumped into the evaporation crystallization device to prepare high-purity sodium chloride based on the method of gypsum crystallization. The experimental results show that the zero-discharge system treatment technology of desulfurization wastewater from this power plant is feasible and can realize the crystalline salt resource utilization. The purified sodium chloride salt crystals have a purity of more than 99.10%, which meets the standard for industrial use. The results provide an idea of resource recycling for the treatment of desulfurization wastewater using evaporative crystallization technology. In addition, a similar technology is also reported by Lu et al. [24], as shown in Figure 6.

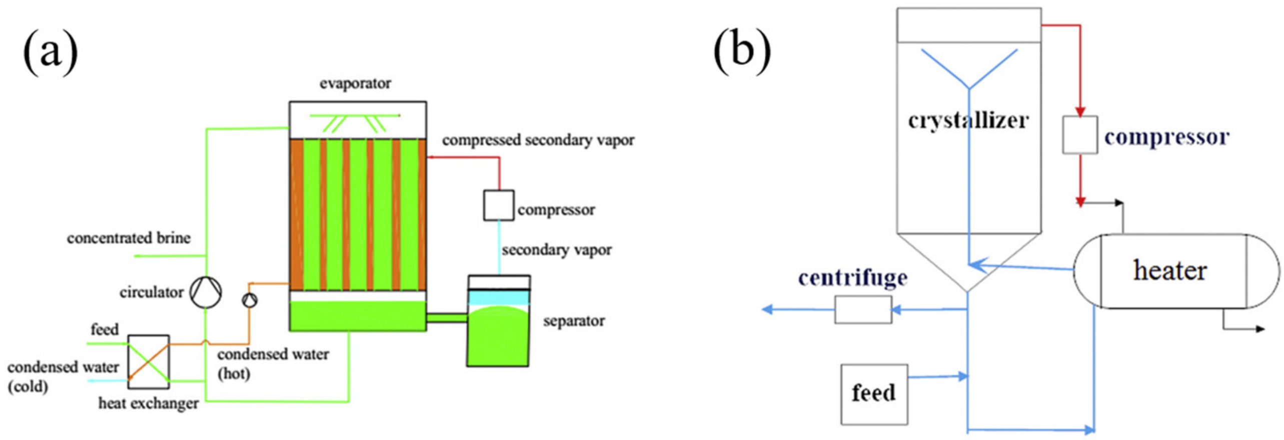

Figure 6. (**a**) Mechanical vapor recompression crystallization experimental system, (**b**) MVRC system for desalination of ammonium sulfate wastewater [24].

With respect to the evaporative crystallization properties, Liang et al. [25] studied the coal-fired power plant desulfurization wastewater droplet evaporation crystallization characteristics and the relationship between operating conditions. In the range of 15–45 °C/min, the higher the rate of temperature rise, the faster the rate of evaporation and crystallization. During the crystallization process, the higher the concentration of SO_4^{2-}, the higher the evaporation rate, and the lower the crystallization rate compared to Cl^-, mainly because the higher the concentration of SO_4^{2-}, the higher the vapor pressure and the lower the super solubility. Mg^{2+} has little effect on the evaporation rate due to the similarity of the vapor pressure as compared to Na^+. The higher the concentration of Mg^{2+}, the faster the rate of crystallization. The experimental results of Zheng et al. [26] confirmed this conclusion. It is to be noted that, in Ca^{2+}, Mg^{2+}, and Na^+ measurements, evaporation time and crystallization time were almost the same due to low solute concentration. When different ions were added, the crystallization rate was in the order of $Mg^{2+} > Ca^{2+} > Na^+$ [27]. In general, the traditional evaporation process has a high investment and energy consumption, and the contact efficiency between flue gas and liquid droplets is low, which cannot control costs. In order to meet the requirements of a low investment and low energy consumption, an energy efficient wastewater evaporation and crystallization technology is needed. Liu et al. [28] proposed a new type of drying tower that introduced a Wurster fluidized bed into the drying of desulfurization wastewater to achieve a high gas–liquid heat transfer and applied it to a 380 mW coal-fired power plant. It is reported that a power plant in

Nanjing [29] used a 660 mW, tangential combustion boiler equipped with air pollution control devices such as SCR, ESP, WFGD, etc. to meet the ultra-low emission requirements. After treatment with gypsum cyclone, a rotary atomizer atomizes the wastewater into liquid droplets. The high-temperature flue gas is extracted and introduced into the drying tower as an evaporation drive. Under the strong heat and mass transfer, the wastewater solidified into evaporation products. The migration characteristics of Cl were also investigated, and the results showed that less than 3% of Cl was released into gaseous HCl, and the concentrations of other typical pollutants such as NO_x and SO_2 remained unchanged after treatment. However, due to the special nature of desulfurization wastewater, its composition is complex, with calcium, magnesium, and other scaling ions making the evaporation process prone to scaling; the economic cost is high; it cannot be recycled; and it can only be disposed of in landfills. Therefore, determining how to reduce the economic cost and how to realize the separation, purification, and resource recycling of mixed salt are the research hotspots and difficulties of this technology.

3.2. Flue Gas Evaporation Technology

Flue gas evaporation technology requires desulfurization wastewater to be sprayed or showered into the flue gas; the water will evaporate rapidly and diffuse into the atmosphere, so that the water in the wastewater will be evaporated, and the harmful substances will be separated. The zero liquid discharge technology involves spraying desulfurization wastewater mixed with compressed air in the form of liquid droplets into the flue between the air preheater (AH) and the electrostatic precipitator (ESP) under high-temperature and high-humidity ambient conditions. The technology utilizes exhaust heat to evaporate the desulfurization wastewater, and the evaporated solidified material is captured with the dust in the ESP, resulting in "zero discharge" of desulfurization wastewater. The schematic diagram of this technology is shown in Figure 7.

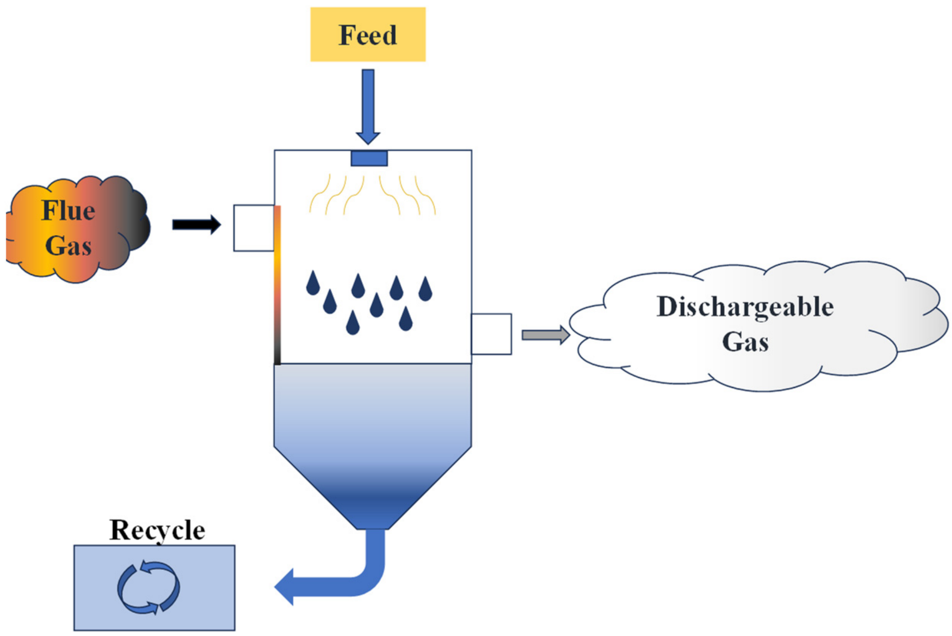

Figure 7. Schematic diagram of flue gas evaporation technology.

Flue gas evaporation technology has reasonable operating costs, requires no additional energy input, and can realize zero discharge performance. Therefore, it has been widely applied in chemical, metallurgical, and electric power industries. In order to further optimize the zero liquid discharge technology of desulfurization wastewater, Fu et al. [30] compared experimental and simulation results in a 330 mW coal-fired power plant and obtained key operating parameters such as boiler loading conditions, the ratio of the number of droplets captured by the flue wall to the total number of droplets, the optimization of the arrangement of atomization nozzles, the diameter of atomized droplets, the enthalpy of flue gases, the exact calculated value of flue gas changes, and the characteristics of the fly ash after injection of the desulfurization wastewater. It was found that under different boiler loading conditions, the higher the temperature and the faster the flue gas velocity, the shorter the time required for the complete evaporation of wastewater droplets. Different amounts of desulfurization wastewater can be completely dried with little change in fly ash properties and no negative impact on downstream processes. This wastewater evaporation treatment method is characterized by short process, low investment, low operating cost, and low maintenance. In addition, Ma et al. [31] proposed an independent bypass evaporation tower technology on the basis of flue gas evaporation technology and made a detailed study on its efficiency in removing hazardous substances in desulfurization wastewater. The process of desulfurization wastewater treatment and experimental setup are displayed in Figure 8.

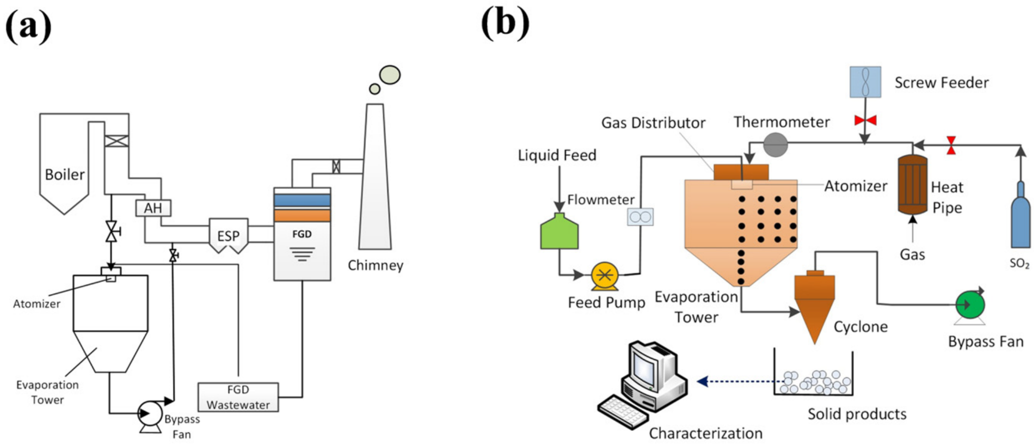

Figure 8. Schematic diagram of the process: (**a**) Desulfurization wastewater treatment by independent bypass evaporation tower, (**b**) experimental system for desulfurization wastewater removal by independent bypass evaporation tower [31].

The experimental results show that after the desulfurization wastewater is evaporated, Na^+, Mg^{2+}, and Ca^{2+} are removed, except for a small increase in Cl^-. However, the release of chlorides during evaporation hinders further application of the technology. Ma et al. [32] proposed that the use of $Ca(OH)_2$ to adjust the pH of desulfurization wastewater to 9.0–10.0 can effectively inhibit the volatilization of HCl in flue gas. Chen et al. [33] used the single droplet drying method to study the chloride release characteristics during evaporation and proposed three periods of chloride release based on the rate of chloride release and the characteristics of wastewater droplets (mass, temperature, and diameter) for the first time. During the free water evaporation period, almost no released chloride can be detected. During the unstable shell phase, 19.8% of the chloride is released, mainly due to the increase in droplet temperature. During the shell pyrolysis phase, nearly 10% of the chloride is released, which is directly related to the hydrolysis of chloride salt hydrates in the evaporating particles. Therefore, it is important to find a balance between chloride release and evaporation efficiency in engineering practice. In addition, they found that the evaporation products of single-drop drying and spray drying were similar in composition, with the main components being $MgCl_2$, $CaCl_2$, NaCl, and $CaSO_4$, and the mass fraction of chloride in the final product was less than 0.06% [34].

Xu et al. [35] conducted a study including experiments and simulations to investigate the release characteristics of HCl during the evaporation process, and the results showed that when the inlet temperature was increased from 200 °C to 350 °C, the gas-phase HCl concentration increased significantly from 5.02 ppm to 70.96 ppm, and the HCl release rate increased from 1.57% to 17.32%. In the evaporation process, it is suggested that the inlet temperature of the flue gas should not be too high. And when the wastewater contains only $CaCl_2$, the release of HCl is effectively suppressed. The results of Ma et al. [32] and Xu et al. [35] indicate that the problem of chloride volatilization caused by flue gas evaporation technology for treating desulfurization wastewater can be solved by the formation of salt products from chloride and calcium ions. This finding provides key data for the application of high-temperature flue gas evaporation technology, and the research results have important theoretical and practical value for the engineering practice of this technology. Moreover, Sun et al. [36] also proposed a new desulfurization wastewater treatment technology using spray evaporation and turbulent agglomeration, and experimentally investigated the effect of spraying of desulfurization wastewater on the agglomeration and removal of fine particles. The results showed that the spray-turbulence agglomeration system could effectively promote the agglomeration and removal of fine particles through capillary forces and the adhesion of precipitated crystals from the desulfurization wastewater droplets. After ESP treatment, the fine particle agglomeration efficiency was increased to 39.3%, which was 10.9% higher than the single turbulent agglomeration efficiency, and the number and mass concentration of fine particles were reduced by 46.5% and 38.9%, respectively. Zhang et al. [37] conducted a similar study to evaluate the performance of a 660 MW coal-fired unit with zero liquid discharge technology of desulfurized wastewater. In the project, the desulfurization wastewater with total dissolved solids of about 48,768.9 mg/L and Cl content of about 12,507.2 mg/L can realize zero liquid discharge treatment of desulfurization wastewater through the flue gas evaporation process. The hot smoke content introduced into the drying tower was about 52,351.0 m^3/h, and the moisture content of the dried product was only 0.15%. The HCl content in the flue gas of the import and export of the drying tower is 53 mg/L and 165 mg/L, respectively; the mass fraction of Cl removal and volatility in the desulfurization wastewater is 93.10% and 6.90%, respectively; and the average content of chlorine in the fly ash is about 0.225%, which meets the requirements of the relevant standards. However, flue gas evaporation technology is limited in its application to the removal of fine particulate matter from desulfurization wastewater due to the slow evaporation rate and agglomeration efficiency of fine particles. In order to address this topical issue and to improve the removal efficiency of flue gas evaporation techniques, Lu et al. [38] proposed a droplet evaporation technique for charged desulfurization wastewater and studied the effects of induction electrode voltage, atomization pressure, Cl^- concentration, and other factors on the agglomeration of fine particles and the charge transfer characteristics between droplets and particles.

In particular, Guodian Jiujiang Generating Co., Ltd. (Jiujiang, China) utilized "flash concentration and high temperature flue gas bypass flue evaporation technology" to achieve zero liquid discharge of desulfurization wastewater [39]. As shown in Figure 9, the methods of exhaust gas heating and flash evaporation are combined to heat the desulfurization wastewater, which not only achieves the utilization of exhaust heat, but also reduces the temperature of the flue gas entering the desulfurization system. Therefore, water consumption of the desulfurization system is reduced. It is reported that after the desulfurization wastewater evaporation treatment, the wastewater recovery rate can reach 97% at maximum. The water quality of desulfurization wastewater after evaporation and condensation is good enough to be used for boiler make-up water, realizing the reuse of desulfurization wastewater after treatment.

This method is relatively simple, equipment investment costs are low, it uses flue gas waste heat, it has low energy consumption, the system recovers wastewater of good quality, and ancillary products can be selected according to the actual situation of the power plant treatment. However, the multi-effect evaporator and thickener equipment for long-term operation of corrosion and masonry plugging problems needs to be tested over time; there are thick liquid processing difficulties; and if the subsequent evaporation uses the flue spray process, the dust collector and the flue brought about by the corrosion of the potential problems and the impact on the quality of fly ash need to be tested over time.

Figure 9. Zero liquid discharge project implemented in Guodian Jiujiang Generating Co., Ltd. [39].

Overall, the flue evaporation technology still has some problems. If the desulfurization wastewater is not fully evaporated, or if the evaporated solidified material is not fully captured by the ESP, highly corrosive chlorine-containing substances can corrode the flue and subsequent facilities. In addition, the composition of desulfurization wastewater is complex and contains pollutants such as heavy metals, which may have an impact on the comprehensive utilization of fly ash. Lastly, the theoretical studies on the mechanism of product migration and transformation of the evaporation process, numerical simulation of the heat transfer process between the flue gas and wastewater, and high-fit kinetic modeling are lacking to guide the practical engineering applications.

3.3. Membrane Distillation Removal Technology

In addition to the zero liquid discharge desulfurization wastewater technology mentioned above, the potential of membrane separation technologies such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), forward osmosis (FO), and reverse osmosis (RO) for treating desulfurization wastewater has been investigated in recent years, as shown in Figure 10. The attractiveness of membrane separation technologies lies in their ability to remove almost all contaminants by reducing the addition of chemicals (only the amount required for membrane pretreatment and cleaning).

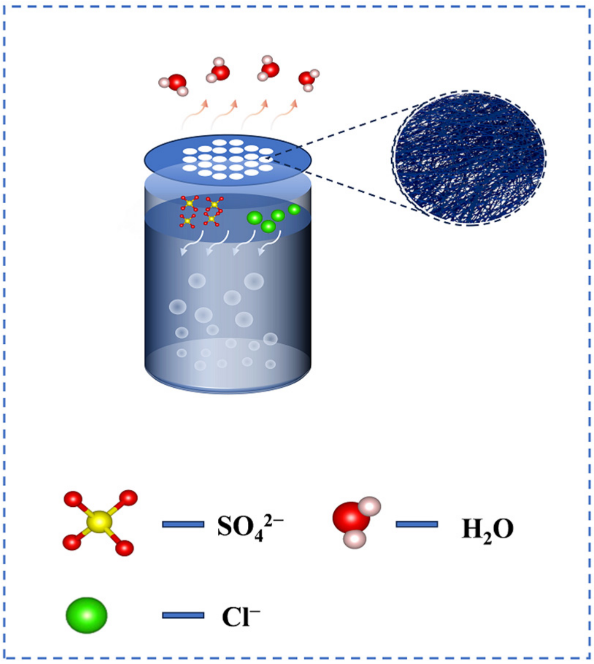

Figure 10. Desulfurization wastewater treatment by membrane distillation.

Yin et al. [40] proposed an integrated membrane process consisting of ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) for wastewater treatment in order to recover usable substances in the wastewater, such as suspended sulfur (SS) and ammonium salts such as $(NH_4)_2S_2O_3$ and NH_4SCN, and to avoid serious environmental problems caused by improper disposal. In the UF process, a ceramic membrane was used to remove SS with a removal efficiency of 99.9%. In the NF step, $(NH_4)_2S_2O_3$ was separated from NH_4SCN with 95.0% retention, and 83.0% of $(NH_4)_2S_2O_3$ was ultimately recovered in the retention solution. In the RO process, NH_4SCN can be recovered through a four-pass filtration process with a recovery efficiency of up to 99.0%. Lee et al. [41] developed a forward osmosis (FO) hybridized with membrane distillation (MD) (FO-MD) technology to treat desulfurization wastewater with high fouling conditions, which provides a good solution for the problem of membrane distillation technology to treat desulfurization wastewater. Later, Conidi et al. [42] also treated the desulfurization wastewater using an integrated membrane process technology–reverse osmosis/membrane distillation (RO/MD) technology, as shown in Figure 11. The process achieved a total recovery rate of about 94% with a conductivity of 80 μS/cm for the MD permeate stream. Therefore, it was experimentally verified that the integrated membrane distillation technology is more suitable for reuse in power plants.

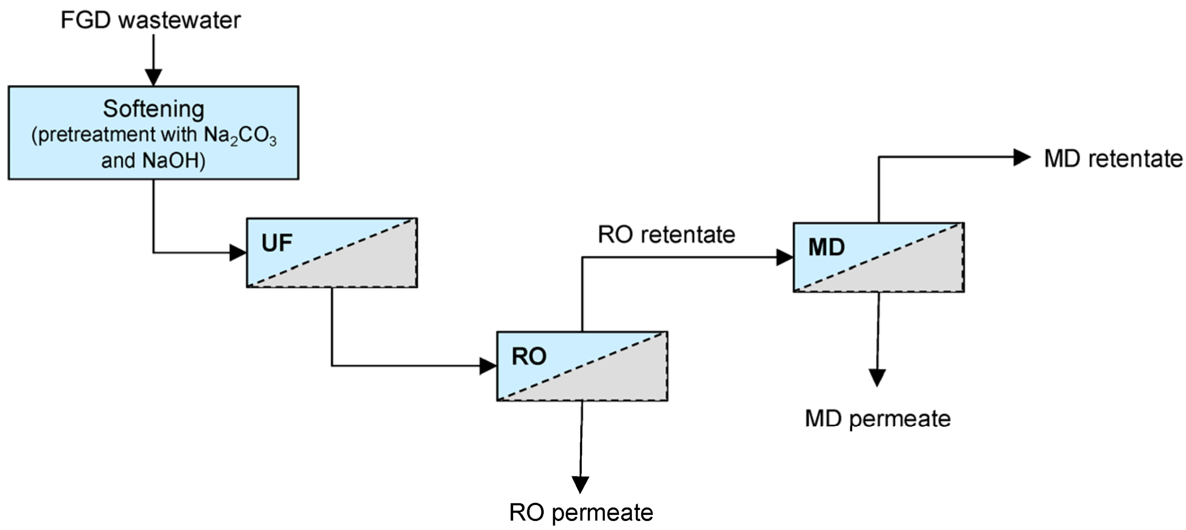

Figure 11. Integrated RO/MD desulfurization wastewater treatment process [42].

Jia et al. [43] conducted a near-zero liquid discharge treatment process study using integrated nanofiltration–membrane distillation (NF–MD) technology, and the system achieved a desalination rate of more than 99.99% and a water recovery rate of more than 92%. Meanwhile, the low salinity of MD permeate ($Cl^- \leq 3$ mg/L, $SO_4^{2-} \leq 1$ mg/L) can be directly recycled into thermal power plants, high purity (≥97%) brine (10% NaCl) can be produced after MD concentration, and chemical softening and NF pretreatment were found to significantly reduce MD membrane fouling. Namaghi et al. [44] synthesized polyamide/titanium dioxide (PA/TiO_2) thin-film nanocomposite (TFN) membranes for removing sulfur compounds from sulfur recovery unit (SRU) wastewater. Anderson et al. [45] used a permeation–membrane distillation (FO/MD) system to investigate the effectiveness of this system on desulfurization wastewater in terms of water recovery, waste salt removal, and heat demand. The FO/MD wastewater treatment process and heat exchange are shown in Figure 12.

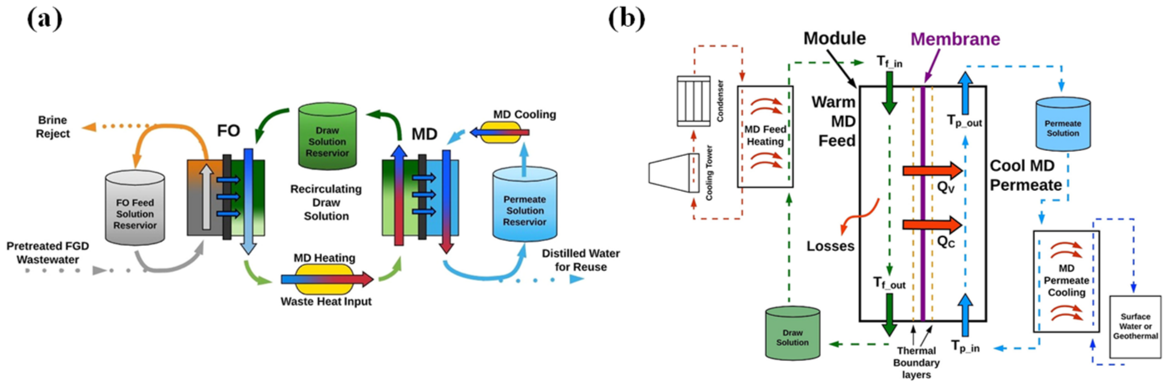

Figure 12. Schematic diagram of the process: (**a**) FO/MD desulfurization wastewater treatment system, (**b**) FO/MD heat exchange system [45].

The results show that water recovery through the FO/MD process is effective, with recovery rates as high as 89%, and that the FO/MD system effectively removes 99.7% of the analyzed ions, yielding a distilled permeate with a low conductivity that can be used on-site or discharged. By utilizing on-site waste heat, the FO/MD process may be an economically sustainable option for desulfurization wastewater treatment. In addition to integrate membrane distillation, bipolar membrane electrodialysis has also been used in desulfurization wastewater treatment scenarios. This is an electrochemical separation technique typically used to separate ions or molecules, and the separation process involves the use of bipolar membranes that selectively allow ions to pass through them [46]. Zhang et al. [47] proposed a hybrid technology of sustainable ion exchange and bipolar membrane electrodialysis, but membrane contamination may reduce the flux and membrane performance. Therefore, there is a need to investigate scaling and fouling management techniques for the sustainable operation of FOs and MDs. Li et al. [48] used direct contact membrane distillation technology and softening pretreatment technology to treat desulfurization wastewater, thus realizing the recovery of desulfurization wastewater for recycling. It was found that membrane contamination caused by $CaSO_4$, Mg-Si complexes, Al colloids, and organic matter crystallization in the desulfurization wastewater reduced the flux of produced water. It was also reported that pretreatment using $NaCO_3$, NaOH, and polyacrylamide, combined with coagulation and chemical precipitation processes, removed almost 100% of Ca^{2+} and Mg^{2+} and prevented membrane contamination. Cheng et al. [49] also proposed calcium hydroxide precipitation–air volatilization integrated process pretreatment of flue gas desulfurization wastewater technology to reduce membrane pollution. The removal efficiency can reach more than 99%, and the operating cost is low, and the technical operation is easy to realize. The above technology shows that the addition of alkaline substances in the use of membrane distillation technology to treat desulfurization wastewater can effectively improve the problem of membrane fouling and membrane contamination. In addition, Chen et al. [50] proposed the use of tannic acid-reduced graphene oxide membranes to improve the removal of Hg^{2+} from desulfurization wastewater. The results showed that the separation performance was related to the reduction degree of the membrane, and the optimum Hg^{2+} interception was 91.61% with a flux of 56.5 $L{\cdot}m^{-2}{\cdot}h^{-1}$, which had a significant effect on the removal of heavy metal ions from the desulfurization wastewater.

In summary, membrane separation technology for desulfurization wastewater treatment has a high heat transfer efficiency, can remove sulfide efficiently, covers a small area, is easy to operate, produces less waste residue, and the permeate can be recycled. However, this technology has a high cost, high water quality requirements, and the membrane maintenance also requires certain technology and may cause membrane contamination, so it is necessary to comprehensively consider the economy and technical feasibility in the selection of the treatment technology.

4. Conclusions and Outlook

Current desulphurization wastewater treatment technologies have achieved significant success in reducing sulphide emissions and improving atmospheric and water quality. Some of the common technologies include wet desulfurization, biological desulfurization, and redox methods, which are widely used in different industrial sectors. The main advantages of these technologies include environmental friendliness, regulatory compliance, and resource recovery. Wet desulfurization, which absorbs sulfide from wastewater and converts it to sulfate by means of an absorbent, is a well-established and effective method and can provide ideas for resource recycling. Biological desulfurization is the employment of a microorganism that converts sulfide into soluble sulfate, which is environmentally friendly. In order to further improve the removal efficiency and application scope of desulfurization wastewater treatment technology and realize resource recycling, zero liquid discharge technology has become the environmental hotspot of coal-fired power plants. Technologies such as evaporation and crystallization, flue gas evaporation, and membrane separation and removal have made considerable breakthroughs. The future development of desulfurization wastewater treatment technology will focus on improving technical efficiency, reducing costs, reducing energy consumption, and further reducing the negative impact on the environment.

Future desulfurization wastewater treatment technology may carry out research and innovation from the following aspects: (a) high-efficiency and low-cost technology: researchers should be committed to developing more efficient and low-cost desulfurization wastewater treatment technology in order to prompt more enterprises to adopt environmental protection measures; (b) energy-saving technology: future technology should pay more attention to reducing energy consumption and improving the overall energy efficiency through innovative process and equipment design; (c) comprehensive utilization of resources: in order to better realize the recycling of resources, future technologies should pay more attention to recovering valuable substances from wastewater and reducing waste; (d) intelligent and automated: intelligent and automated technologies and desulfurization wastewater synergistic effects should be introduced to improve operational efficiency, reduce human error, and reduce operating costs. Future research can be interdisciplinary, integrating chemistry, biology, engineering, environmental science, and other fields of technical knowledge in order to find a more comprehensive solution. Through continuous innovation and research, desulfurization wastewater treatment technology is expected to develop more advanced and sustainable solutions in the future, providing cleaner and more environmentally friendly options for industrial production.

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