Pilot Study on Catalyzed Oxidation-Ceramic Membrane-High Pressure Reverse Osmosis for Desulfurization Wastewater Recovery

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Abstract. With the increasing pressure of environmental protection, the zero-discharge project construction of power industry was speeding up. However, the unstable operation of equipment was often occurred. With regard to this, the process of catalytic ozonation-ceramic membrane-high pressure reverse osmosis for desulfurization wastewater reuse was established in Huaneng Yunhe Power Plant. The amount of catalyst was firstly evaluated and the COD could be reduced from 264 ppm to 107 ppm. Even after the ozone catalytic oxidation process continuously operated for more than 20 days, the catalytic efficiency of the catalyst was still maintained at the original level. The operating pressure of the ceramic membrane was maintained at 0.17 MPa, and the wastewater recovery rate was more than 90%. Moreover, the membrane flux of the ceramic membrane after backwashing could be recovered well. The desulfurization wastewater treated by catalytic ozonation process and ceramic membrane process was reused in the high pressure reverse osmosis unit. The operating pressure was maintained at 1.21 MPa and the water recovery could reach about 55%. The overall water recovery rate of ozonation ceramic membrane reverse osmosis process was 50%. The operation efficiency of each treatment unit was high and stable, and the performance recovery effect was excellent after the decline of membrane flux, which improved the operation stability of the whole treatment process.

Keywords: Desulfurization wastewater; Ozone catalytic oxidation; Ceramic membrane; High pressure reverse osmosis

1. Introduction

As wastewater zero emissions policy is promoted into the electric power industry, wastewater zero discharge engineering was largely covered in power generation companies [1, 2]. However, the cost of construction and operating are much higher. Especially, the highly polluted and corrosive waste water is greatly affected by some obstacles thus shorting cycle shorten and elevating operating cost [3, 4]. Therefore, operation stability is one of the most important index and cost factor for the zero-discharge project. Due to the high pollution indicators and high salinity of desulfurization wastewater, the key to the desulfurization wastewater zero discharge engineering is mainly the desulfurization wastewater reduction, thus construction of the stain resistance and steady operation of concentrated reduction unit is the key factor, which exerts the direct affection on the plant wastewater zero discharge [5, 6].
Ceramic membrane is an inorganic ultrafiltration membrane with stable properties, strong anti-pollution property and easy performance recovery [7], which is widely applied in the range from acid to alkali. It is usually used in the treatment of highly polluted wastewater resulting in membrane fouling and plugging. The primary particulate matter in desulfurization wastewater is calcium sulfate, which has a strong pollution effect on organic ultrafiltration membrane. Moreover, the performance of organic membrane is difficult to recover after fouling, thus the organic ultrafiltration membrane usually faced with the possible scrap. At the same time, the current recycling of desulfurization wastewater lacks efficient process for organic matter removal from the desulfurization wastewater, resulting in high COD index of desulfurization wastewater after pretreatment, which affects the stability of subsequent membrane system operation and recovery performance.

This study established the catalytic ozonation-ceramic-high pressure reverse osmosis membrane process based on Huaneng Yunhe Power Plant for the pilot scale and adopted joint box as treatment object, in which the enrichment recycling for desulfurization wastewater of high concentration rate was processed. Compared with traditional membrane recycling process, the established process not only improves the stability of the desulfurization wastewater, also resolves low enrichment efficiency operation stability. This process could be used in industrial application with high popularization value.

2. Experimental and Materials

2.1. Materials
Titanium dioxide (TiO$_2$), silicon dioxide (SiO$_2$), magnesium oxide (MgO), calcium oxide (CaO), and Fe(iron powde) are analytical grade, which are directly used without further treatment.

2.2. Catalyst Preparation
Catalyst preparation: firstly, TiO$_2$, SiO$_2$, MgO, CaO and iron powder were mixed with the mass ratio of 2:10:6:6:1, and then milled by ball mill. After fully mixture, the powder was pressed into pieces by tablet press. Finally, the pieces were heated by muffle furnace. The temperature was raised from 5℃/min to 550℃ and remained 2h. Then the temperature was raised from to 950℃ with heating rate of 2℃/min and kept for 1h. Afterwards, the obtained catalyst was soaked in 3% hydrochloric acid for 6 h and washed with clean water, the sintered pieces were used as ozone catalyst.

2.3. Ozonation Reaction System
The volume of Ozonation reactor is 3m$^3$, which was made of HDPE plastic, the desulfurization wastewater entered the ozonation reactor from the bottom and overflowed from the top to the next wastewater treatment unit. The gas-liquid distributor was arranged at the bottom, the gas outlet was set on the top of the ozone reaction tank, and an ozone destruction device was connected with the gas outlet. The ozonation reactor was showed in figure 1. The ceramic membrane equipment was obtained from Nanjing Jiuwu Hitech Equipment Co., Ltd, the filtration accuracy is 100 nm, the maximum inflow is 2m$^3$/h, and the maximum operating pressure is 0.3 MPa. The high pressure reverse osmosis equipment was obtained from GE Company, the maximum inflow is 2m$^3$/h, and the maximum operating pressure is 1.8 MPa.
The desulfurization wastewater produced from Huaneng Yunhe Power Plant Phase 3 unit was tested on site. The water inflow of catalytic ozonation unit adjusted according to the bypass valve at the outlet of the triple header, the water quality analysis of desulfurization wastewater produced by Huaneng Yunhe Power Plant Phase 3 unit was shown in table 1. The water quality of wastewater was tested every 10 days, and the detection value was the average value of three measurements within 0-20 days.

**Table 1.** Quality of desulfurization wastewater at outlet of triple header.

| Test items       | Value | Test items | Value | Test items | Value | Test items | Value |
|------------------|-------|------------|-------|------------|-------|------------|-------|
| Suspended matter | 5270 ppm | K         | 155.4 ppm | Sn         | 0.016 ppm | Fe         | 0.41 ppm |
| COD              | 264 ppm | Mg        | 2249.5 ppm | Sr         | 0.38 ppm | Co         | 0.21 ppm |
| Al               | 0.81 ppm | Na        | 1625 ppm | pH         | 6.6     | Cr         | 0.017 ppm |
| Ca               | 611.3 ppm | Ni       | 0.044 ppm | SO\textsubscript{4}\textsuperscript{2-} | 1746 ppm | Hg         | 0.013 ppm |
| Cl\textsuperscript{-} | 3297 ppm | Pb       | 0.044 ppm | Cu         | 0.016 ppm |

2.4. Desulfurization Wastewater Treatment Process

The desulfurization wastewater treatment capacity of 1.5 m\textsuperscript{3}/h through control the bypass valve of the triple header. The desulfurization wastewater was treated by catalytic ozonation, and then the desulfurization wastewater was transferred into the ceramic membrane treatment unit. The operating pressure of the ceramic membrane treatment unit was controlled at about 0.22 Mpa, the water recovery rate was controlled at more than 90 %, and the concentrated water was discharged back to the triple header. The desulfurization wastewater treated through ceramic membrane was reused by high-pressure reverse osmosis. The operating pressure was controlled at about 1.6 Mpa, the water recovery rate was controlled at about 55%, and the concentrated water was discharged back to the
triple header to ensure that the effluent of reverse osmosis production water could reach 0.75 m³/h, and the overall process water recovery rate could be controlled at about 50%.

2.5. COD Analysis of Desulfurization Wastewater
2.0 mL waste water was taken into the COD analysis tube and the tube was heated by COD digester. The heating temperature was 150 °C and the heating time was 2 h. The desalted water was regarded as the reference. The COD of the desulfurization wastewater was directly read from the COD analyzer after cooling.

3. Results and Discussion

3.1. Catalytic Ozonation

![Figure 2](image)

**Figure 2.** Effect of mass ratio of catalyst on COD.

Catalyst plays critical role in the catalytic ozonation process. As ozone converted into hydroxyl radicals, the ozone solubility and the utilization efficiency could be improved, on the other hand, the oxidation ability of ozone could be improved. Catalyst is the main medium to catalyze the conversion of ozone into hydroxyl radicals. At the same time, catalyst could provide the necessary gas-liquid contact area and the contact opportunity between gas and liquid, which increase the utilization efficiency of ozone [8, 9]. The effect of catalyst addition on the final COD of desulfurization wastewater was shown in figure 2. The bulk density of catalyst was 1.0 g/cm³ and the mass ratio of catalyst addition to wastewater treatment capacity per unit time was 1:10-5:10. While no catalyst added in the reactor, the COD of desulfurization wastewater was only reduced from 264 ppm to about 245 ppm, this proved the ozonation capacity was limited without catalyst addition, which showed significant effect on the reduction of COD of desulfurization wastewater. When the amount of catalyst and wastewater treatment capacity per unit time reached 4:10, the COD of desulfurization wastewater was reduced to 107 ppm, as the amount of catalyst continued to increase, the COD of desulfurization wastewater was only decreased to 100 ppm, thus it indicated proved that ozone catalytic oxidation was hardly affected by excessive catalyst. At the same time, excessive catalyst would increase the operation cost and construction cost of the treatment process. Therefore, the catalyst amount was set as 40% of the wastewater treatment capacity per unit time.
The stability of catalyst is another important characteristic of catalyst. The catalyst with excellent stability could keep high catalytic efficiency for a long time without deactivation, so the formation of new solid waste could be avoided due to catalyst deactivation [10]. The desulfurization wastewater COD index change with the reaction time after the treated by catalytic ozonation process was shown in figure 3. After 20 days of continuous operation of catalytic ozonation process, the COD of the desulfurization wastewater could still be reduced to around 110ppm, which proved that the catalyst has no property change during the treatment of desulfurization wastewater and could maintain its own activity. This could be due to that the catalyst was prepared through high temperature calcination, which could give stable chemical properties to catalyst and would not easy to be inactivated in the polluted desulfurization wastewater. At the same time, the surface properties of the catalyst were stable and not easy to be covered by pollutants. Under the scouring effect of water flow and explosion gas, the pollutants on the surface of the catalyst could be quickly washed away, which ensured the contact between ozone and the catalyst and the stable source of hydroxyl free radical formation, so the stability and the service life of the catalyst could be improved [11].

3.2. Operation Process of Ceramic Membrane

Ceramic membrane is an inorganic ultrafiltration membrane, which is an asymmetric membrane made of inorganic ceramic materials by special process. Therefore, ceramic membrane has the characteristics of stable chemical properties, easy to maintain surface pore morphology, wide application range, etc., which gave the advantages of large and stable effluent flux, good performance recovery, high water recovery rate to ceramic membrane [12]. The desulfurization wastewater treated...
by ozone catalytic oxidation was treated by ceramic membrane subsequently. The water recovery rate and operating pressure were shown in figure 4. When the desulfurization wastewater was treated by ceramic membrane, the water recovery rate could reach more than 90%, and the operating pressure rose steadily and slowly. Under normal operation, it could be maintained at 0.17-0.2 MPa. When the pressure reaches 0.25 MPa, the ceramic membrane would backwash automatically. The ceramic membrane had a long backwashing cycle, and the flux recovery is ideal after backwashing, which proved that the ceramic membrane suitable for the treatment of desulfurization wastewater, as the desulfurization wastewater showed highly corrosive, highly polluting and contains some viscous particles. As the ceramic membrane surface chemical properties are more stable than organic ultrafiltration membrane. Thus, when the pollutants were absorbed on the membrane surface, the pollutants were washed away more easily after water washing or backwashing, so the recovery effect of ceramic membrane flux was excellent. At the same time, ceramic membrane obtained excellent mechanical strength, compared with organic ultrafiltration membrane, ceramic membrane could maintain its own shape and pore structure under higher pressure, which could ensure operating condition of ceramic membrane was more stable [13].

3.3. High Pressure Reverse Osmosis Operation Process

![Figure 5. Operation pressure(a) and water recovery(b) of the high pressure reverse osmosis.](image)

The operating efficiency of high pressure reverse osmosis, especially the change of water recovery rate and operating pressure, is the key factor affecting the reuse efficiency of desulfurization wastewater [14]. As shown in figure 5, high-pressure reverse osmosis could reuse about 55 % of desulfurization wastewater after catalytic ozonation and ceramic membrane treatment, and the operating pressure could basically be stabilized at about 1.21-1.3 MPa. When the operating pressure raised to 1.4 MPa, the high-pressure reverse osmosis was cleaned by chemical cleaning, and the original chemical cleaning agent (dilution ratio is 1: 20) was used to clean the reverse osmosis, meanwhile, the water recovery rate could still maintain at about 55 %. The operating pressure of the reverse osmosis system could still be recovered to about 1.24 MPa, which proved that the reverse osmosis performance could recover well, and the heterogeneous oxidation process could fully separate the components, colloids, small suspended solids, viscous substances, etc. of the desulfurization wastewater without regulating water quality, thus the operation stability of the reverse osmosis system could be ensured.

The desulfurization wastewater come out from the triple header could be concentrated and reused through catalytic ozonation-ceramic membrane-high pressure reverse osmosis process. The catalytic ozonation and ceramic membrane could fully separate the components, colloids, small particle suspended solids and viscous substances in the desulfurization wastewater, especially could significantly adjust the COD of desulfurization wastewater without adjusting the initial water quality, which was not available in the traditional softening-clarification-filtration process, but also the necessary technical requirement for the reuse of desulfurization wastewater by traditional membrane
technology [15]. Therefore, for the desulfurization wastewater of Huaneng Yunhe Power Plant Phase 3 unit, this process could stably obtain a recovery rate of about 50%, and the equipment operation was stable and the regeneration was good.

4. Conclusions
In view of the unstable operation of the whole process equipment and the gradual decline of operation stability during the construction of zero emission project of desulfurization wastewater in Yunhe Power Plant, the process of catalytic ozonation-ceramic membrane-high pressure reverse osmosis for wastewater concentrated and reused was established on the site of Yunhe Power Plant. By optimizing each process, COD could be reduced from 264 ppm to 107 ppm when the amount of catalyst added and the amount of wastewater treated per unit time were 4: 10. At the same time, after operation of catalytic ozonation process continued for more than 20 days, the COD of desulfurization wastewater was still decreased to 110 ppm. The operating pressure of desulfurization wastewater after catalytic ozonation maintained at 0.17 MPa, the recovery rate of wastewater could reach more than 90%. Moreover, the flux of ceramic membrane after backwashing could be recovered well, so that it would not be difficult to recover after membrane fouling. Ozone catalytic oxidation process and ceramic membrane process could remove most of pollutants in desulfurization wastewater, so high pressure reverse osmosis could obtain water recovery rate of about 55% under the pressure of 1.21 MPa. The overall process of catalytic ozonation-ceramic membrane-reverse osmosis could obtain about 50% of desulfurization wastewater. At the same time, the ozone catalytic oxidation process ran efficiently and stably, the ceramic membrane and high-pressure reverse osmosis ran smoothly, and the performance recovery effect was good after the membrane flux drops, which could maintain the stable and efficient operation of the overall desulfurization wastewater concentration and reuse process.

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