Study on the Reverse Osmosis Rejected Water Treatment Process
Based on Vacuum Membrane Distillation

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Abstract
In this article, we utilize new high flux PVDF hollow fiber hydrophobic membrane to implement vacuum membrane distillation (VMD) treatment experiment to the rejected water produced in petrifaction enterprise after reverse osmosis (RO) treatment, and we study producing water flux, the change of producing water and rejected water quality with the concentration treatment process and the influence of chemical flocculation on the rejected water treatment effect in the process of VMD. The results indicated that under the conditions of 75°C and -0.096Mpa, the initial flux of VMD process would achieve 33L/m²h, and the process of VMD combined with chemical flocculation, and when RO rejected water was concentrated to 10 times, the process of VMD was kept above 16L/m²h, and the conductivity of producing water was stabilized in 4~7μS/cm, and the desalination rate was kept above 99.99%.

Keywords: Vacuum membrane distillation, Polyvinylidene fluoride, PVDF hollow fiber hydrophobic membrane, Reverse osmosis rejected water, Wastewater treatment

At present, RO technology has been applied in the wastewater treatment for sea water desalination, urban wastewater treatment, chemical industry, electric power, metallurgy and other industries. But the actual producing water rate in the RO process is only about 50%, so it still face serious discharge problem of rejected water (Zhao, 2005, p.58-59). It is very meaningful to develop high-effective rejected water treatment process to compensate the deficiencies of RO and realize water saving and wastewater reducing (Reddy, 2007, p.240-253 & Wang, 2003, p.49-52). VMD is a sort of new membrane separation process combining membrane technology with traditional distillation technology, and it has many advantages such as low operation temperature, simple equipment and large flux, and it is studied abroad in bitter and salt water desalination, water liquor concentration and volatile organic matter separation (Wu, 2003, p.67-79). The rejection rate of VMD process to inorganic salt, molecule and un-volatile matters could achieve 100%, and it could realize the treatment of high concentration liquor, so VMD technology may be the beneficial supplement or substitute technology for existing RO technology. However, most researches about VMD process centralize in sea water and bitter and salt water desalination, and researches using VMD technology to treat RO rejected water are few.

Aiming at the rejected salt water after RO treatment in petrifaction enterprise wastewater, we adopt hydrophobic polyvinylidene fluoride (PVDF) hollow fiber membrane to develop the experiment of VMD rejected water treatment. We study the influence of rejected water concentration multiple to the treatment effect of VMD in the process of VMD, and the changes of CODcr, conductivity and hardness for rejected water and producing water.

1. Experiment

1.1 Main experiment materials and instruments
PVDF hollow fiber hydrophobic micro-porous membrane, it is made by us, the interior diameter is 0.8mm, the depth of wall is 0.15mm, the average porous diameter is 0.160μm, and the porosity is 85%.

Hollow fiber membrane component, it is made by us, the effective length is 90mm and the effective membrane area is about 0.0226m².

RO rejected water of petrifaction enterprise wastewater, the conductivity value is about 6200μS/cm, CODcr is about 100mg/L, the hardness (CaO) is about 1000mg/L, and it is offered by Beijing Research Institute of Chemical Industry.

Electric balance, it is made by Tianjin Tianma Instruments Factory.
DDS-11A Conductivity Meter, it is made by Shanghai Rex Instrument Factory.

1.2 Experiment equipments and running

The experiment system flow of VMD is seen in Figure 1, and it is mainly composed by heat side loop, vacuum side loop and hydrophobic hollow fiber membrane component. The heat side loop mainly includes constant temperature water bathing, magnetic pump and thermometer. The vacuum side loop mainly includes condensation pipe, water cycle vacuum pump and producing water receiver. The RO rejected water on the heat side produces the transfer of heat and quality in the hollow fiber membrane porous, and the steams permeating the membrane porous condensate in the condensation system and are colleted by the producing water receiver.

2. Results and discussions

2.1 Influence of RO rejected water concentration multiple on the VMD treatment performance and the qualities of rejected water and producing water before chemical hardness ridding

From Figures, with the increase of concentration multiple, the membrane flux decreases very quickly, and CODcr, hardness and conductivity of rejected water obviously ascend, and the conductivity of producing water stabilizes in 4~7μS/cm, the CODcr of producing water is in 40mg/L~70mg/L, and the hardness of producing water is 0. The concentration multiple ascends from 1 to 2.5, and the membrane flux decreases from 33L/(m2·h) to 2.8L/(m2·h), and the CODcr of rejected water ascends from 104mg/L to 246mg/L, and the harness of rejected water ascends from 1011mg/L to 1305mg/L, and the conductivity of rejected water ascends from 6200μS/cm to 13000μS/cm. In addition, in the process of concentration, many scales occur in the material flume. The reasons that the flux of VMD decreases quickly with the concentration multiple of RO rejected water include two aspects. First, with the increase of concentration multiple, the concentration of RO rejected water gradually increases, which induces the steam pressure decreases. Second, according to the water quality composing of RO rejected water, we can judge that the separated matters include CaSO4, CaCO3, MgSO4 and difficulty soluble salts, which would easily induce the jam of membrane porous, but CaCO3 and MgSO4 have strong conglutination force, so CaCO3, MgSO4 and other separated matters and NaCl crystals may stick on the surface of heat side and form the surface folium to reduce the mass transfer and heat transfer coefficients on the heat side and further quickly reduce the membrane flux of VMD (Qu, 2007, p.14-17). The change of flux with the concentration multiple is the result that both parties function together.

2.2 Influence of total RO rejected water concentration multiple on the VMD treatment performance and the qualities of rejected water and producing water after chemical hardness ridding

Add chemical reagent in the rejected water with 2.5 times concentration, get rid of part of Calcium and Magnesium ions and other contaminations, and filter the deposits by the ultrafiltration membrane. Adjust the PH of ultrafiltration liquid to 9.5, and continue the experiment of VMD experiment, and the results are seen in Figure 6 to Figure 9.

From Figures, with the increase of total concentration multiple, the membrane flux decreases, but the decrease extent is small, and the CODcr, hardness and conductivity of rejected water obviously ascend, and the conductivity of producing water stabilizes in 4~7μS/cm, the CODcr of producing water is in 35mg/L~45mg/L, and the hardness of producing water is 0. The concentration multiple ascends from 2.5 to 10, and the membrane flux decreases from 22.2L/(m2·h) to 17.7L/(m2·h), and the CODcr of rejected water ascends from 247mg/L to 788mg/L, and the harness of rejected water ascends from 470mg/L to 1560mg/L, and the conductivity of rejected water ascends from 13000μS/cm to 46000μS/cm. In the process of concentration, there are no scale occur in the material flume.

After getting ride of hardness by the chemical flocculation method, the flux attenuation of VMD is obviously less than the attenuation before hardness ridding, and after 10 times concentration, when the conductivity of rejected water achieves 46000μS/cm, the flux of producing water keeps above 17L/(m2·h), and the conductivity, hardness, CODcr and other indexes of producing water all stabilized on the lower level, which primarily proves that the process of VMD is technically feasible for the concentration treatment of RO rejected water.

3. Conclusions

From above experiment results, we utilize homemade high flux PVDF hollow fiber hydrophobic micro-porous membrane and new VMD membrane component to disposal RO rejected water of petrifaction enterprise under the conditions that the vacuum degree is 0.096MPa, the temperature of original water is 75℃, and flow velocity of original water is 0.17m/s, and when the rejected water is concentrated to 10 times, the conductivity of producing water in VMD still keeps in 7μS/cm, and the desalination keeps above 99.99%, and the flux of producing water keeps in about 17L/(m2·h), and CODcr, hardness and conductivity of rejected water ascend obviously, which primarily indicates that the effect that the new VMD process utilizing PVDF hydrophobic micro-porous membrane and chemical flocculation and ultrafiltration process disposal RO rejected water of petrifaction enterprise is distinct.
References


Figure 1. Sketch Map of VMD Experiment Equipment (1. raw material flume in the water bathing of constant temperature, 2. hollow fiber membrane component, 3. condensation pipe, 4. cycle water vacuum pump, 5. producing water flume, 6. original water pump)

Figure 2. Influence of RO Rejected Water Concentration Multiple on the Treatment Performance of VMD Process
Figure 3. Influence of RO Rejected Water Concentration Multiple on CODcr of Rejected Water and Producing Water

Figure 4. Influence of RO Rejected Water Concentration Multiple on the Hardness of Rejected Water

Figure 5. Influence of RO Rejected Water Concentration Multiple on the Conductivity of Rejected Water
Figure 6. Influence of Total RO Rejected Water Concentration Multiple on the Treatment Performance of VMD Process

Figure 7. Influence of Total RO Rejected Water Concentration Multiple on CODcr of Rejected Water and Producing Water

Figure 8. Influence of Total RO Rejected Water Concentration Multiple on the Hardness of Rejected Water
Figure 9. Influence of Total RO Rejected Water Concentration Multiple on the Conductivity of Rejected Water