Experimental study of coagulation-tubular microfiltration integrated with high-salt wastewater to remove hardness and silica

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Abstract. In the zero-discharge treatment processes of high-salt wastewater, calcium ions, magnesium ions and silica can lead to scaling problems in membrane equipment and pipelines. When fouling is difficult to remove completely, it eventually leads to deterioration in the performance of the wastewater treatment system. In order to ensure the long-term stable operation of the zero-discharge process for high-salt wastewater, hardness and silica must be effectively removed in the pre-treatment section of high-salt wastewater. In addition, the current zero-discharge pre-treatment process for high-salt wastewater has disadvantages, such as long processes, poor system stability, large floor space and high operating costs. In response to the above problems, this paper designs and processes an integrated dosing coagulation-tubular microfiltration process for hardness and silica removal based on dosing coagulation experiments with high-salt wastewater from a typical coal-chemical plant, and conducts the tests of wastewater hardness and silica removal. In the experiment, the removal rate of calcium ions, magnesium ions and total silicon were close to 90%, the turbidity of the effluent was less than 1NTU, all suspended solids (SS) were removed, and the recovery rate of wastewater was close to 100%.

1. Introduction

High-salt wastewater is generally defined as wastewater with a total salt mass fraction (in terms of NaCl) of 1% or more, mainly from coal and chemical plants, printing and dyeing plants, leather manufacturing plants, pesticide plants, antibiotic pharmaceutical plants and oil and gas gathering. Currently, high-salt wastewater is being generated on a larger scale, accounting for about a quarter of the total industrial wastewater volume. Untreated high-salt wastewater contains large amounts of inorganic salt ions such as sodium, potassium, calcium, magnesium, ammonium, chlorine, phosphate, nitrate and pollutants such as COD, silica and organic halogens [1-5]. If large quantities of high-salt wastewater are discharged directly, they will pollute surface water and seep down to contaminate groundwater, causing serious environmental pollution. In 2015, China introduced the " The Action Plan for Prevention and Treatment of Water Pollution", referred as "Ten-point Water plan". In order to systematically promote water pollution prevention and control, water ecology protection and water resources management, it is required that wastewater from high water-consuming enterprises be treated and reused in depth, and the high-salt wastewater is conducted zero-discharge treatment [6,7].

At present, the zero-discharge process for high-salt wastewater is basically mature, and that for wastewater in general industry is consisted of three parts: pretreatment, nanofiltration (NF)/reverse osmosis (RO) concentration, evaporation and crystallization [8-10]. The zero-discharge treatment of high-salt wastewater not only reduces wastewater pollution, but also plays an important role in water conservation and recycling of water resources. However, there are still many problems in the operation of zero-discharge wastewater process, among which the scaling problem of RO and evaporation crystallisation equipment is the most serious. The Scaling problem caused by hardness (Ca^{2+}, Mg^{2+}) in wastewater is currently considered a major problem in industry, with common scaling compounds including calcium carbonate, calcium sulphate and magnesium hydroxide [11]. Reducing alkalinity by acidifying the wastewater can prevent the formation of calcium and magnesium precipitates. But acidification treatment can lead to more serious silica scaling problems [12,13]. Silica scaling is difficult to remove completely from reverse osmosis membranes, and it ultimately leads to deterioration in wastewater treatment system performance, such as reducing reverse osmosis efficiency and system operating life. Although strong cleaning agents such as diammonium fluoride (NH_4HF_2) and hydrofluoric acid (HF) can be used to remove silica scale, but they can also lead to equipment damage and cause problems such as environmental contamination [14,15].

Therefore, to avoid the scaling problem of membrane equipment and pipelines, and to ensure long-term, stable operation of the zero-discharge process, calcium ions, magnesium ions and silica must be removed in the pre-treatment section of high-salt wastewater. Conventional

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zero-discharge pretreatment processes of wastewater mostly use the traditional chemical reaction + high density pool + multi-media filtration + ultrafiltration process flow, which has long processes, poor system stability, large occupies area and high operating costs [9,16,17]. In this paper, we take the high-salt wastewater of typical coal chemical industry as the subject, design and process an integrated dosing coagulation-tubular microfiltration process to remove hardness and silica by using chemicals screened from previous dosing coagulation experiments on high-salt wastewater, and conduct experimental studies to verify the effect of the integrated dosing coagulation-tubular microfiltration operation process to remove hardness and silica.

2. Experimental part

2.1. Experimental device and materials

Reagents: sodium hydroxide (AR), sodium bicarbonate (AR), hexamethylenetetramine (AR), catechol violet (AR), sodium carbonate (AR), magnesium chloride (AR), sodium meta-aluminate (AR), etc.

Experimental device: UV spectrophotometer T6-1650E (Beijing Puxi General Instrument Co., Ltd.), water quality analyzer XZ-041 (Shanghai Haiheng Electromechanical Instrument Co., Ltd.), etc.

2.2. Wastewater quality analysis

The high salt wastewater used in the experiment was taken from a coal chemical plant, and the determination of each water quality parameter was completed in strict accordance when the high salt wastewater was taken back within one week with the above determination method. The test results are shown in Table 1.

Table 1. Measurement results of water quality parameters for high salt wastewater

Serial number	Project	Unit	Result
1	pH	No dimension	8.31
2	Electrical conductivity	μS/cm	52312.25
3	Suspended solids	mg/L	20.24
4	Calcium ions	mg/L	440.88
5	Magnesium ions	mg/L	121.22
6	Turbidity	NTU	5.80
7	Silicon dioxide (calculated by total silicon)	mg/L	197.32

2.3. Process description and design

The traditional operation process of the removal of hardeness and silica for wastewater is a combination of dosing coagulation and gravity sedimentation. The clarification section is commonly used to set up a sedimentation tank, which separates the solids and liquids in the wastewater by gravity settling, and the supernatant of the sedimentation tank is pre-filtered by a multi-media filter. After passing through the security filtration equipment, hollow fiber ultrafiltration is used for further turbidity removal, and finally enters the membrane separation and other units for desalination and concentration, and the produced water returns to the main system. The whole treatment process is long, unreliable, with high investment, large floor space and high operating costs. In the traditional process, the solid-liquid separation stage requires the addition of flocculants, which indirectly brings greater negative impacts to subsequent equipment such as hollow fibre ultrafiltration and reverse osmosis, for example, fouling clogs which are difficult to recover from and broken filaments. The process flow is shown in Fig. 1.

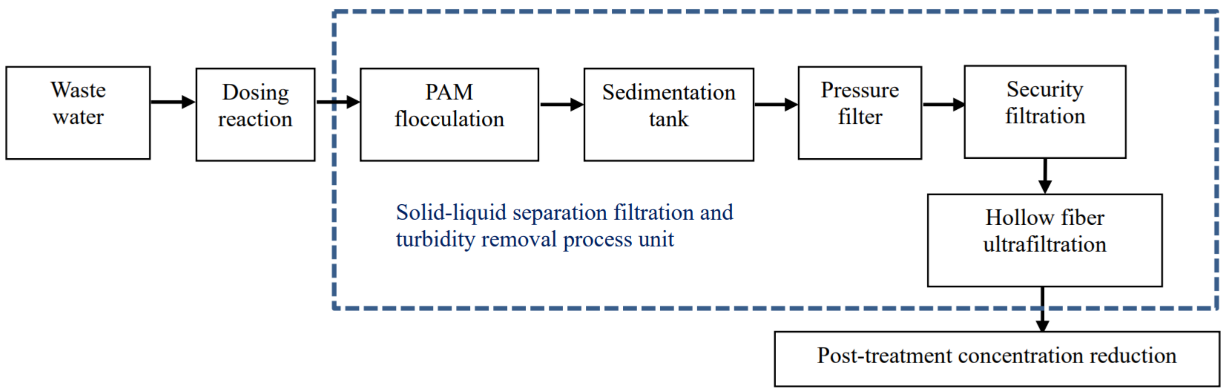

Figure 1. Flow chart of traditional dosing coagulation-free sedimentation

In order to shorten the traditional process of hardness and silica removal and ensure the stable operation of the subsequent wastewater treatment equipment, an integrated dosing coagulation-tubular microfiltration process for hardness and silica removal is designed and adopted. The process can be simply described as a two-step process of chemical dosing + TMF (tubular membrane filtration), shortening the traditional process flow. And the solid and liquid in the wastewater can be separated by filtration without adding flocculant after the hard and silicon removal by one-time dosing, effectively protecting the subsequent recovery reverse osmosis unit and improving its recovery rate and operational stability. The process flow is shown in Fig. 2.

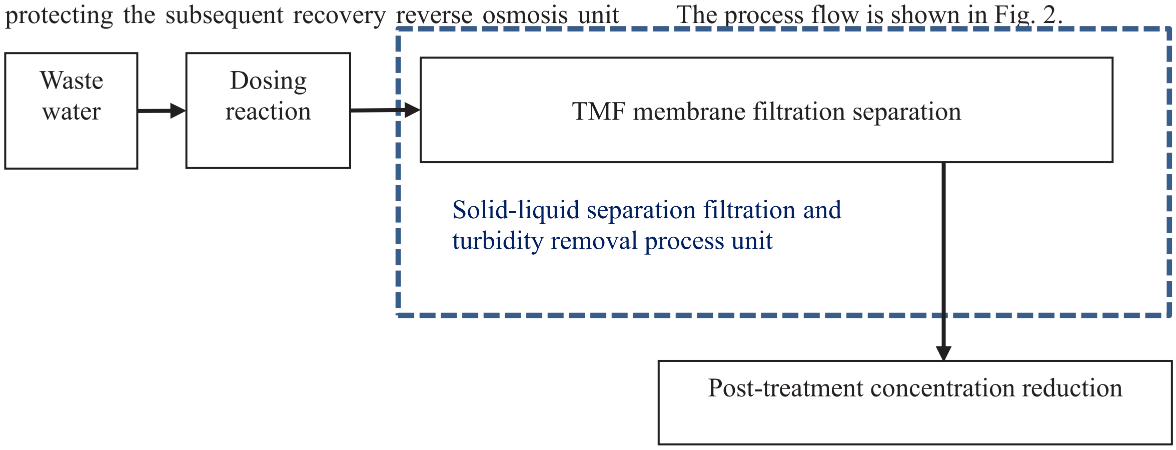

Figure 2. Flow chart of dosing coagulation-tubular microfiltration integration

The dosing coagulation-tube microfiltration process is equipped with two dosing reaction tanks, the first reaction tank is equipped with silicon removal agent, and the second reaction tank is equipped with hardness removal agent. A buffer sedimentation tank is set behind the dosing reaction tank to preliminarily settle the wastewater after dosing, and then the wastewater enters the tubular membrane system through the circulating water pump for solid-liquid separation. The wastewater filtered and treated by the tubular membrane system enters the subsequent reverse osmosis equipment, and the separated sediment enters the buffer sedimentation tank through the sludge discharge pipe. TMF (tubular membrane) used in dosing coagulation-tube microfiltration process is produced by Porex Company of the United States, and the membrane performance parameters are shown in Table 2.

Table 2. Main performance parameters of tubular membrane

Main project	Technical parameter
Membrane type	MME2005301VP
Effective filtration area	0.035m^2
Filter pore size	0.05μm
Number of membrane cores	1
Core size	1.27cm
Component length	91.4cm
Component diameter	DN32
Interface diameter at concentrated water side	DN32
Interface diameter at water production side	DN20
Maximum operating membrane permeability differential pressure	0.2MPa
Maximum inlet water pressure	0.4MPa
Maximum inlet water temperature	40°C
pH	0~14

2.4. Experimental method

2.4.1. Experimental method for the removal of hardness and silica by dosing coagulation

The dosing and coagulation experiment is carried out to remove hardness and silica from high-salt wastewater by using a double-alkali method and aluminium-based coagulants. The experimental procedure is as follows: take several copies of 250mL water samples of high salt wastewater in a beaker, adjust the temperature, add the hardness and silica removal agent step by step, stir at a constant speed of 150r/min for 20min. After standing at a constant temperature for 1h, remove an appropriate amount of water samples at 2cm below the liquid surface, filter the removed water samples through 0.45 μ m filter membrane and determine the residual amount of calcium ions, magnesium ions and total silica, and calculate the corresponding removal rate.

2.4.2. Test method for hardness and silicon removal by dosing coagulation-tubular microfiltration

A dosing coagulation-tubular microfiltration process is used to carry out the hardness and silica removal test. In the test, the optimum dosage of hardness and silicon removal agent is calculated according to on the treatment of water volume, and add the agent to the first and second reaction pools respectively. Using a circulation pump to pass the treated high-salt wastewater into the reaction pools in turn, with a residence time of 20min in each pool. The wastewater after dosing and coagulation is pumped into the tubular microfiltration membrane system through the circulating pump. The inlet flow is changed by adjusting the inlet pressure, and calculating the performance parameters of the tubular microfiltration membrane system, such as the stable operation time, outlet pressure, outlet flow, wastewater recovery rate, membrane flux.

3. Results and discussion

3.1. Test of dosing coagulation to hardness and silica removal

The water quality parameters of high-salt wastewater are measured after the addition of hardness and silica removal chemicals (NaOH 450mg/L, Na_2CO_3 1100mg/L, $NaAlO_2$ 600mg/L), and the results of test are shown in Table 3.

Table 3. The results of water quality parameters of high-salt wastewater after hardness and silicon removal

Number	Project	Unit	Result
1	pH	-	11.29
2	Conductivity	μS/cm	56215.61
3	Suspended solids (SS)	mg/L	2581.8
4	Calcium ions	mg/L	37.47
5	Magnesium ions	mg/L	11.97
6	Silicon dioxide (calculated by total silicon)	mg/L	19.53
7	Calcium ions removal rate (%)	-	91.5
8	Magnesium ions removal rate (%)	-	86
9	Silica removal rate (%)	-	90
10	Turbidity	NTU	952.5

Table 3 shows that calcium ions and magnesium ions and silica in the high-salt wastewater are removed efficiently after the addition of hardness and silica removal agents, with removal rates of 91.5%, 86% and 90% respectively. However, the content of suspended solids (SS) and turbidity in the wastewater rise rapidly after dosing. In order to ensure the normal operation of the subsequent equipment such as nanofiltration reverse osmosis, the precipitates need to be separated from the wastewater.

3.2. Test of dosing coagulation-tubular microfiltration integrated to hardness and silica removal

In the test of dosing coagulation-tubular microfiltration integrated hardness and silicon removal, the designed water volume for treating high-salt wastewater is 50L. After adding a quantitative hardness and silicon removal agent, the single-tube operating performance parameters of the tubular microfiltration membrane system are shown in Table 4.

Table 4. Performance parameters for single-tube operation of tubular microfiltration membrane systems

Main project	Inlet flow（L/h）			
	2500	3000	3500	4000
Inlet water pressure (kg/cm^2)	0.4	0.9	1.2	1.7
Output water pressure (kg/cm^2)	0.25	0.5	0.7	1
Flow rate of discharge water (L/h)	22.39	26.32	36.06	60
Running time (min)	40	34	25	15
Recovery rate (%)	97.2	97.2	96.8	96
Calcium ions removal rate (%)	90.2	90.4	90.8	89.11
Magnesium ions removal rate (%)	88.1	88.2	88.2	87.9
Silicon dioxide removal rate (%)	89.92	90.1	88.91	88.81
Turbidity of effluent（NTU）	0.51	0.4	0.71	0.55
SS（mg/L）	0	0	0	0
Membrane flux（L/m^2·h）	639.71	752	1030.29	1714.29

Table 4 shows that the removal rate of calcium ions and magnesium ions and silicon dioxide by the dosing coagulation-tube microfiltration process is basically the same as that of the previous hardness and silicon removal experiment. Under different influent flows, the turbidity of effluent is less than 1 NTU, and suspended solids (SS) is completely removed, with excellent solid-liquid separation effect. With the increase of influent flow, the running time of the system is significantly reduced, the membrane flux is greatly increased, and the wastewater recovery rate is close to 100%. In order to further shorten the running time of the system and improve the efficiency of high-salt wastewater treatment, the operation performance parameters of the tubular microfiltration membrane system are investigated by using the multi-pipe paralleling water inlet mode. The performance parameters of multi-tube tandem operation are shown in Table 5.

Table 5. Performance parameters for multi-tube tandem operation of tubular microfiltration membrane systems

Main Project	Inlet flow（L/h）			
	2500	3000	3500	4000
Inlet water pressure (kg/cm^2)	0.8	1	1.6	0.5~1.8
Output water pressure (kg/cm^2)	0.5	0.7	0.9	0.25~0.8
Flow rate of discharge water (L/h)	56.42	75	88.24	
Running time (min)	16	12	10	
Recovery rate (%)	94	92.8	92	
Calcium ions removal rate (%)	90.2	90.11	90.6	
Magnesium ions removal rate (%)	87.8	88.3	88.2	
Silicon dioxide removal rate (%)	88.71	89.22	90.1	
Turbidity of effluent（NTU）	0.68	0.65	0.7	
SS（mg/L）	0	0	0	
Membrane flux（$L/m^2 \cdot h$）	806	1071.43	1260.57	

It can be seen from Table 5 that when using a multi-tube tandem inlet mode, the removal effect of dosing coagulation-tube microfiltration process on calcium ions and magnesium ions, silica, turbidity and SS is basically the same as that of the single-pipe system, and the wastewater recovery rate is slightly decreased. At the same inlet flow rate, the running time of the system is significantly shorter than that of the single-pipe system. However, when the inlet flow rate is 4000L/h, the inlet and outlet water pressure fluctuates, and the circulating pump appears to be idling, resulting in the unstable operation of the system. Through comprehensive analysis, the multi-pipe tandem system can effectively improve the efficiency of wastewater treatment, but it also needs to control the inlet water flow in combination with the treatment water volume to maintain the stable operation of the system.

4. conclusion

- By using the dosing coagulation method and adding hardness and silica removal agents (NaOH 450mg/L, Na_2CO_3 1100mg/L, $NaAlO_2$ 600mg/L) to the high salt wastewater, calcium ions and magnesium ions and silica in the wastewater can be removed efficiently, with the removal rates of 91.5%, 86% and 90% respectively. However, after dosing treatment, the suspended solids (SS) and turbidity content in the wastewater rises rapidly. In order to ensure the normal operation of the equipment such as nanofiltration reverse osmosis in the subsequent process of zero-discharge wastewater, the precipitates need to be separated from the wastewater.
- The integrated coagulation-tubular microfiltration process can remove calcium ions and magnesium ions and silica from the wastewater with high efficiency, and the turbidity of the effluent is less than 1NTU at different influent flows, the suspended solids (SS) is removed completely and the wastewater recovery rate is close to 100%, with excellent solid-liquid separation. The process can provide reference for the development of wastewater hardness and silica removal and subsequent zero-discharge process.

References

1. Shi, J.X., Huang, W.P., Han, H.J., et al. Review on treatment technology of salt wastewater in coal chemical industry of China[J]. Desalination, 2020, 493:114640.
2. Chen, Z.C., He, Q., Cai, R., et al. Development and comprehensive application of mathematical simulation in wastewater treatment systems under the trend of carbon neutralization [J] China Environmental Science, 2022, 1-23.
3. Li, X., Gou, M.M., Liu, X.F., et al. Current Situation and Research Progress of High Salinity Wastewater Treatment [J] Water Treatment Technology, 2019, 45 (05): 6-10.
4. Wang, Q., Li, N., Bolto, B., et al. Desalination by pervaporation: A review[J]. Desalination, 2016, 38746-60.
5. Liu, Z., Li, N., Guo, R.Y., et al. "Zero Discharge" Case Analysis of High Salinity Wastewater [J] Chemical Engineering, 2020, 48 (11): 17-22.
6. Notice of the State Council on Printing and Distributing the Action Plan for Water Pollution Prevention and Control [J] Bulletin of the State Council of the People's Republic of China, 2015, (12): 26-37.
7. Lu, J.Y., Zhou, N.X., Zhou, Z.F., et al. The impact and mechanism of "Ten Water Strips" on industrial water pollution intensity [J] China Population, Resources, and Environment, 2021, 31 (02): 90-99.
8. Huang, K.D., Li, Q., Wang, Y., "Zero discharge" technology and engineering application status analysis of coal chemical wastewater [J] Industrial Water and Wastewater, 2012, 43 (05): 1-6.

9. Lassesson, H., Malovanyy, A., Andersson, A., Optimizing resource flow of industrial processes, with a case study of zero liquid discharge at a copper smelting plant[J]. Journal of Cleaner Production, 2020, 286125452.
10. Vishnu, G., Palanisamy, S., Joseph, K., Assessment of fieldscale zero liquid discharge treatment systems for recovery of water and salt from textile effluents[J]. Journal of Cleaner Production, 2008, 16(10): 1081-1089.
11. Shirazi, S., Lin, C.J., Dong, C., Inorganic Fouling of Pressure-Driven Membrane Processes - A Critical Review[J]. 2010, 250(1): 236-248.
12. Oren, Y., Korngold, E., Daltrophe, N., et al. Pilot studies on high recovery BWRO-EDR for near zero liquid discharge approach[J]. Desalination, 2010, 261(3): 321-330.
13. Alexander, G., Coronell, O., Fouling of nanofiltration membranes in full- and bench-scale systems treating groundwater containing silica[J]. Journal of Membrane Science, 2014, 468349-359.
14. Xu, J.L., Liang, L., Wang, J., Removal of silicon from oilfield heavy oil wastewater [J] Guangdong Chemical Industry, 2011, 38 (07): 85-96.
15. Sheikholeslaml, R., Koo, T., et al. Pretreatment and the Effect of Cations and Anions on Prevention of Silica Fouling[J]. Desalination, 2001, 139(1): 83-95.
16. Yu, J., Wang, S.Q., Economic Comparative Analysis of High Salinity Wastewater Pretreatment Process Routes in Thermal Power Plants [J] Cleaning the World, 2021, 37 (12): 1-3.
17. Tan, B., Li, J., Zhu, Z.M., et al. Research progress in physicochemical pretreatment methods of acrylic fiber wastewater in China [J] Chemical Environmental Protection, 2015, 35 (06): 599-602.