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Reverse Osmosis Concentrated Water Treatment Technology Research

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Abstract

With the national "double carbon" goal, energy saving and consumption reduction strategic plan to promote, more and more enterprises will be "zero discharge" of wastewater as the ultimate goal of industrial wastewater. Reverse osmosis (RO) process is the most common way of water treatment process, in the treatment of water treatment and pure water preparation at the same time, will be accompanied by a variety of inorganic and organic pollutants contained in the by-products of concentrated water, these difficult to deal with high salt, complex composition of the reverse osmosis concentration of water, not directly discharged without treatment, not only to make a lot of water in the concentration of water to be a waste of water resources, will be a large extent on the ocean, soil and other natural environments to cause irreversible damage. Reversible damage to the ocean, soil and other natural environments. Therefore, it is of great significance to protect the environment by finding an economical and efficient treatment method for RO concentrated water. For the regeneration of fresh water resources of RO concentrated water, there have been many international reports on the development of zero liquid discharge (ZLD) or near-zero liquid discharge technology, through the membrane technology to reverse osmosis concentrated water concentration, water recycling, reduce the volume of concentrated water, and then based on the thermal technology of concentrated water desalination, evaporation and crystallization process leads to the recovery of water, and at the same time, the process of solid by-products after dehydration, purification, can also produce a considerable amount of water. At the same time, the solid by-products produced in the process can be dehydrated and purified, which can also produce considerable economic value of commodities. Concentrated water concentration process around how to achieve low-cost RO concentrated water concentration process, in the disc tube reverse osmosis (DTRO), electrodialysis (ED), membrane distillation (MD) and forward osmosis (FO) and other new membrane concentration technology field carried out a wide range of research on the concentration of further concentrated water to provide more prospects for application. Solidification crystallization through reasonable crystallization control and solid-liquid separation technology, can achieve effective separation and purification of solutes, for various industries to provide solid products in line with the quality requirements, commonly used evaporation crystallization, cooling crystallization, solvent crystallization, ion exchange methods and other ways. Through the study of reverse osmosis concentrated water concentration treatment, crystallization and solidification of the two important links of the production process plan, summarize the practicality of various technologies and advantages and disadvantages, integration of existing technologies, research suitable for reverse osmosis concentrated water resources utilization of economic technology solutions, optimize the treatment process, and ultimately realize the application of engineering examples, is the direction of the efforts of researchers in recent years.

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Keywords

Reverse Osmosis Concentrate; Processing Technology; Sewage Treatment.

1. Principles of Reverse Osmosis

The realization of reverse osmosis technology, mainly relying on a semi-permeable membrane that only allows the passage of solvents, when two different solutions through the semi-permeable membrane, the solvent (generally water) spontaneously diffuse from the low concentration to the side of the concentration of the high side, resulting in the high concentration of the side of the water level rises, rises to a certain height, the two sides to reach the pressure to reach equilibrium, this is the osmosis process, the formation of the difference in pressure is known as the osmotic pressure (Fig. 1). When the applied pressure is greater than the natural osmotic pressure, the solvent flows from the concentrated solution side to the dilute solution side, at this time, the concentration of concentrated solubility is getting bigger and bigger, and the concentration of dilute concentration is getting smaller and smaller, contrary to the free diffusion, which is called the reverse osmosis effect. Through the semipermeable membrane selective permeability flow to the low-pressure area of the solution is called leachate, the loss of solvent in the high-pressure area of the solution is called concentrate.

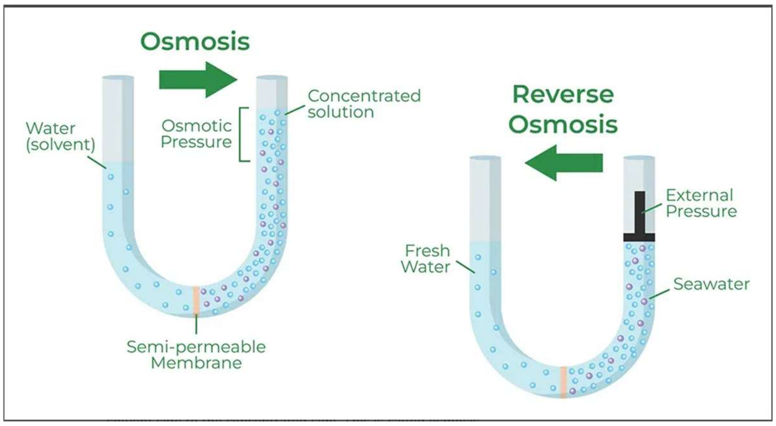

Fig. 1 Principles of Reverse Osmosis

Reverse osmosis membrane technology originated in 1960, scholars Sourirajan and Loeb first prepared asymmetric cellulose acetate reverse osmosis membrane, since then, reverse osmosis membrane technology began to develop rapidly At present, the preparation of reverse osmosis membrane materials are mainly divided into two categories, one is cellulose acetate, such as general-purpose cellulose acetate and modified cellulose acetate materials by mixing cellulose acetate with other polymers or nano-species to improve its mechanical strength, heat resistance, or chemical stability, and to extend its range of applications at high temperatures or in harsh chemical environments. These materials are good heat and water resistance, low production cost, biodegradable, but less stable at high temperatures and high strengths, and cellulose acetate membranes are more susceptible to contamination. The other category is aromatic polyamides, which are usually made from aromatic dicarboxylic acids and aromatic diamines by polycondensation reaction, have amide groups (-CO-NH-), exhibit good hydrophilicity, as well as excellent mechanical, thermal and hydrolytic stability. These materials have excellent heat resistance, chemical resistance, and high strength resistance, but poor chlorine resistance and water flux, so as to cause the loss of membrane or element function, which makes the membrane less suitable for chlorination disinfection after the environment, with the improvement of production technology, aromatic polyamide reverse osmosis

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membranes have been gradually replaced by cellulose acetate membranes to become the mainstream of the market. A research team from Nanjing University of Science and Technology developed a new polyester reverse osmosis membrane, which overcomes a number of native defects of mainstream commercial polyamide reverse osmosis membranes, such as insufficient chlorine resistance, and significantly outperforms traditional polyamide membranes in terms of index performance. Through the co-solvent interfacial polymerization (CAIP) technology, surface modification can be carried out on the matrix and active layer of the membrane to control and improve the performance of polyamide thin film composites membrane, and to improve the performance of the membrane in terms of permeability and desalination .

2. Reverse Osmosis Concentrated Water Characteristics

Reverse osmosis technology separates solvents and solutes in a solution for the purpose of purification or concentration. It is widely used in wastewater reuse because of its high reliability and economy. However, along with high quality reclaimed water, RO technology also produces concentrated RO water with contaminant concentrations that are several times higher than the influent water, typically 25% to 50% of the influent water depending on the recovery rate of the RO process, Table 1 lists some of the ROC related parameters reported in the literature. The main hazards of concentrated RO water are the total dissolved solids (TDS) and dissolved organic matter (DOM) contained in it.DOM contains fluoride, organophosphorus, phenol, benzene, and other organics, as well as emerging pollutants such as endocrine disruptors and environmental priority control pollutants, which can have a huge impact on plant and animal growth and development, and on human health.TDS refers to soluble inorganic salts, mainly composed of Ca Inorganic salts, mainly by Ca^{2+}, Na^{+}, SO_4^{2-}, CO_3^{2-}, HCO_3^{-}, NO_3^{-} ions, etc., the higher the ion concentration, the greater the conductivity, the more impurity components in the water. In recent years, the state has increased the requirements for the reuse rate of water, and solving the mROC problem has become a top priority.

Table 1. The quality index of ROC

COD/ ($mg{\cdot}L^{-1}$)	DOC/ ($mg{\cdot}L^{-1}$)	TOC/ ($mg{\cdot}L^{-1}$)	c(NH_4^+-N)/ ($mg{\cdot}L^{-1}$)	conductivity /($mS{\cdot}cm^{-1}$)	pH	TN/ ($mg{\cdot}L^{-1}$)	c(Cl-)/ ($mg{\cdot}L^{-1}$)
	17.0~30.1		36.0~300.6	3.5~5.1	7.5~8.1		442~815
	21.3				7.8		762.7
105	27.4				7.8		1743.6
168(±12)	37				7.7		1263
	62(±5)		5.6(±0.1)	13(±1)	8.1	13(±1)	
31.44~41.86	36	9.28~10.69	4.6		7.7		
60(±5)		18(±2)			6.9(0.2)		256(±16)
16			4.99(±0.91)		7.99(±0.53)		648(±36.9)
120(±19)	36(±4)		4.3(±0.8)	21.4(±4.5)	7.4(±0.4)	21.4(±4.5)	

3. Reverse Osmosis Concentrated Water Treatment Technology

Reverse osmosis concentrated water is not treated directly discharged will cause serious secondary pollution, so in order to make the reverse osmosis concentrated water quality to meet the discharge standards or reduce the amount of concentrated water as much as possible, there are a lot of research on the treatment of reverse osmosis concentrated water, usually using advanced oxidation (AOPs), membrane separation method, thermal process to reduce the concentration of reverse osmosis water for treatment or part of the reuse.

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3.1. Advanced Oxidation

Advanced oxidation processes (AOPs) are a class of non-traditional chemical treatment technologies that break down difficult-to-degrade organic contaminants by generating strong oxidizing agents (e.g., ozone, peroxides, hydroxyl radicals, etc.). When combined with existing reverse osmosis (RO) systems, these processes can significantly improve the treatment efficiency and recovery potential of concentrated water. Commonly used processes include ozone oxidation, Fenton oxidation, photocatalysis, and electrochemical oxidation. Zhang Xiaojuan [1] et al. found that the COD removal rate could reach 58.7% at an O3 concentration of 5.5 mg/L and a reaction time of 2h by ozone/activated carbon advanced oxidation of petrochemical reverse osmosis (RO) concentrated water. Li Xinxin [2] developed a fixed-bed ozone catalytic oxidation reaction device with reflux for coal chemical reverse osmosis concentrated water, which improved the removal rate of ozone catalytic oxidation technology by about 18.61%, and the removal rate of total COD reached 74.33%. Wang Xiao [3] for 420m3/d refinery reverse osmosis concentrated water treatment, reverse osmosis concentrated water COD from 100mg/L to 50mg/L, the removal rate of 50%. Zhang Cong [4] et al. By using the traditional electrode (Ti/SnO_2-Sb_2O_3/α,β-PbO_2) and a new type of electrode preparation (Ti/TiO_2-NTs/SnO_2-Sb) on the reverse osmosis concentrated water treatment effect of the study, the experimental results show that the two electrodes on the concentrated water of the difficult to degrade the organic matter have a better ability to remove. And some of the chloride ions present in the concentrated water will produce active chlorine substances through the electrode reaction, so that the ability of the electrode to remove COD is effectively improved. Gong Xiaozhi [5] et al. through the use of catalytic ozone oxidation method for petrochemical reverse osmosis concentrated water treatment, experiments to determine the optimal catalyst, and add 15-30mg/L ozone to the system, the reaction after 30min, the concentrated water COD<60mg/L.

3.2. Thermal Method

Thermal processes, as a more mature process, are widely used in the water treatment industry, and common thermal processes include evaporation ponds, flue evaporation, multi-stage flash (MSF), multi-effect distillation (MED), and mechanical compression and reevaporation (MVR) [6]. Evaporation ponds are used to reduce water in wastewater by natural evaporation, which concentrates and precipitates salts and other impurities. The process has essentially zero cost for the process equipment, but has a wider total footprint, is very dependent on natural geographic location and weather conditions, and has a longer treatment time. Secondly, the design and construction are very demanding, taking into account a number of aspects, such as the location and dimensions of the evaporation ponds, land survey and environmental assessment, the basic structure and equipment design of the evaporation ponds, as well as quality and safety management during construction. The flue evaporation process is carried out by atomizing and spraying concentrated water in the flue, contacting with low-temperature flue gas (110~125℃), and heat exchange occurs to evaporate the water into water vapor, and the precipitated salt crystals are captured with the flue gas dust in the electrostatic precipitator, thus realizing zero wastewater discharge, but the precipitated salt crystals are easy to be deposited in the flue, resulting in siltation. Compared to the previous two processes, MVR and MED can quickly reduce the volume of reverse osmosis concentrate water, and the high purity crystals obtained can be reused or sold. Although heat treatment can effectively remove the salts and water from the concentrated water, the initial investment cost is high and the energy consumption is large [7], and the high inorganic salt content in the concentrated water is easy to scale on the heat exchanger wall, which reduces the evaporation efficiency of the system, leading to a reduction in the heat transfer effect and a reduction in the evaporation volume. Therefore, it is necessary to increase the softening process or membrane method to further

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concentrate the concentrated water before heat treatment, to reduce the amount of treated water, and to reduce the operating cost of subsequent heat treatment.

3.3. Membrane Concentration Method

Common membrane separation methods include membrane distillation (MD), forward osmosis (FO), reverse osmosis (RO), electrodialysis (ED) and so on. Membrane distillation is a combination of membrane separation technology and traditional distillation technology, the use of hydrophobic microporous membrane on both sides of the vapor pressure difference as a solute drive driving force, to achieve the process of mass and heat transfer of concentrated brine, when the concentration of the solution is too high, the membrane on both sides of the osmotic pressure will be extremely high, the conventional reverse osmosis technology will be ineffective, the membrane distillation technology will not be affected, the ability to concentrate the aqueous solution to the saturated state to achieve the concentration of concentrated water. Chan Mya Tun [8] and others studied the MD flux and water recovery, and the results showed that in the process of further concentration of reverse osmosis brine, the flux reached 3-5 $L \cdot m^2 \cdot h^{-1}$, and when the concentration of MD feed solution increased to near saturation, the flux decreased, and the final water recovery reached 90%. Therefore, the integrated RO+MDC system can achieve up to 95% overall water recovery, while the remaining MD concentrate/retention is discharged by only 5%, opening a new window for a zero-discharge process. Zhu Liang [9] and others, in the direction of treating membrane concentrate of waste leachate, developed a new ultrasound-enhanced direct-contact membrane distillation device, which improves the membrane permeate flux and reduces the content of Ca ions in the contaminated layer from 25.7% to 15%, which further slows down the contamination of the membrane surface. Chen Li [10] found that the hollow fiber membrane in the feed temperature of 50℃, the feed flux as well as the membrane flux will increase, the retention rate of the class reached more than 99.99%, the study proved the ability of membrane distillation technology to effectively concentrate reverse osmosis concentrated brine. Due to the membrane distillation technology, the water flux is small, and the operating conditions are more stringent they are not yet put into actual production [11].

Positive osmosis is a spontaneous process, water from the side of the osmotic pressure is high through the selective permeable membrane to the higher side of the osmosis, to achieve the purpose of concentration of concentrated water, the requirement of positive osmosis phenomenon drive water osmotic pressure of the driving fluid is higher than the treatment of concentrated brine, so that the concentrated water in the water spontaneously flow into the driving fluid, to achieve the concentration of reverse osmosis concentrated water. Zhang Jun [12] to reverse osmosis seawater concentrated water after concentrated brine as raw liquid, analyze the impact of the driving solution concentration, tangential flow rate, membrane active layer orientation, etc., the study shows that, in the same concentration of the driving solution, the use of positive osmosis concentration of higher concentration of brine, the active layer towards the original solution than the active layer towards the driving solution to get a high flux of water. Guo Shiyi [13] used positive osmosis technology to concentrate desulfurization wastewater, the influent TDS of 12000mg/L or so power plant desulfurization wastewater concentration 8 to 10 times to 100000~120,000mg/L or so, the concentration multiplier is larger, to meet the needs of the concentration of the reduction.

Electrodialysis is a process of selective migration of ions from electrolytes in water using an ion exchange membrane and a DC electric field as a means to desalinate, concentrate, refine or purify a solution. Compared with reverse osmosis technology, electrodialysis has less environmental pollution, higher water utilization and higher desalination rate. Xu Shuwei [14] through the electrodialysis technology for primary reverse osmosis concentrated water and secondary reverse osmosis concentrated water treatment and reuse, the water production rate

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have reached more than 70%, significantly reducing the amount of reverse osmosis concentrated water production, improve the utilization of water resources. But for the feed water quality requirements are high, energy consumption, so it is not suitable for processing high salt, high organic matter reverse osmosis concentrated water. Huang Haibo adopts electrodialysis technology to concentrate reverse osmosis concentrated water of chemical enterprises, the concentration multiplier of TDS is generally 7-8 times, while the concentration multiplier of organic matter is lower, and the concentrated water can directly enter the evaporation crystallization section after concentration.

In summary, the treatment technology for reverse osmosis concentrated water is mainly to remove the inorganic and organic components contained in the concentrated water, concentrate the concentrated water, thereby reducing the volume of concentrated water and saving operating costs.Maya Khellaf [15] and others used the “adsorption+evaporation crystallization+ recrystallization” process to treat acidic high-salt wastewater to prepare pure MaSO Turek [16] and others optimized a single evaporation and concentration process and crystallization process, using ED +evaporation and crystallization technology, the same amount of treatment under the reduction of power consumption is nearly double, the effect is significant. The system gives priority to softening the raw water to reduce the silicon content and some hardness in the water, which is conducive to the better work of the ED membrane. Wang Haitang [17] for high magnesium desulfurization wastewater, under the action of $Ca(OH)_2$-$NaSO_4$ combined softening method, the use of “high salt reverse osmosis membrane (HSRO) + MVR evaporation”, to obtain high-purity sodium chloride crystalline salt, to achieve zero discharge of desulfurization wastewater.Boya Qiu et al. Boya Qiu et al. used membrane distillation and evaporative crystallization technology to recover water and salt in the preparation of fresh water with low conductivity, while recovering the salt enriched in the membrane through the stirring crystallization process, which saves about 61% of the cost of their business. Therefore for the regeneration of resources in concentrated water is very important to choose the appropriate concentration and reduction + solidification and crystallization of the joint process means.

4. Conclusion

Reverse osmosis concentrated water contains more harm to human health and the ecological environment of the difficult biodegradable organic substances, so that we have to pay attention to its concentrated water can be recycled, take recycling and reuse, not only can reduce the industrial production of sewage treatment costs, but also reduce the cost of industrial water use to improve the overall competitiveness of the enterprise; for the difficult to recycle concentrated water, in the conditions of the treatment costs allow, it is necessary to treat it to Remove the pollutants to prevent secondary pollution. At present, the commonly used reverse osmosis concentrated water treatment process in the treatment effect and operating costs and other aspects of the existence of certain defects, and with the continuous development of reverse osmosis water treatment technology and people's awareness of environmental protection continues to improve, relying solely on the traditional treatment process is difficult to meet the water quality discharge standards, so the study of the use of efficient and economical new concentrated water treatment technology is imperative.

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