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Application status and progress of ion exchange membrane

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Abstract

Traditional methods for removing pollutants in aqueous solutions are relatively inefficient and complex, and have low recovery rates. Ion exchange membrane technology has gradually been widely used due to its high efficiency, low energy consumption and simple operation. Ion exchange membrane is a solid phase membrane with selective permeability. In recent years, it has been mainly used for solution separation, purification, concentration and the removal of some pollutants. Through a large number of literature research, this article summarizes the preparation, classification, working principle and application of ion exchange membranes, and membrane pollution and cleaning processes, in order to enrich and deepen the understanding of ion exchange membranes, and further expand the scope of its application, providing reference for the selection of advanced treatment technology of water, sewage and industrial wastewater.

Keywords

Electrodialysis; diffusion dialysis; Donnan dialysis; membrane pollution.

1. Development and classification of ion exchange membranes

As early as 1890, it was discovered that animal bladder membranes have selective permeability to ions; in 1911, Donnan proposed the Donnan equilibrium model of electrolyte solution and membrane phase concentration [1]; in 1940, Meyer and Strauss first discovered the electrodialysis process [2]; in 1950, Juda used a binder to make ion exchange resin into an ion exchange membrane with selective permeability [3]. Due to the uneven distribution of the ion exchange resin at this time, it is called a heterogeneous ion exchange membrane. The research on ion exchange membrane also started from this time [4].

The ion exchange membrane is composed of three parts: skeleton, fixed group and mobile ion on the fixed group. Common cation exchange groups include sulfonic acid group, phosphonic acid group, carboxylic acid group and phenol group; anion exchange group include quaternary ammonium groups, tertiary amine groups, secondary amine groups, primary amine groups and mixed amine groups, etc [5]. The preparation technology of ion exchange membranes has gone through three stages. One is the heterogeneous ion exchange membrane prepared by the connection of functional groups-non chemical bonds-main skeleton. The second is the homogeneous ion exchange membrane prepared by connection of functional groups-chemical bonds- main skeleton. The third is membrane developed from single selective permeability to special selective permeability ion exchange membrane [6], which has the advantages of low energy and environmental protection, good separation effect, etc. Now it has been gradually used in chemical, pharmaceutical, environmental protection, wastewater treatment, waste liquid recycling, and other industries [7].

According to the combination of the fixed group and the skeleton, it can be divided into homogeneous, heterogeneous and semi-homogeneous membranes; and according to the different types of charge groups, it can be divided into anion membrane and cation membrane. The negative membrane is a membrane containing positively charged basic groups, which do not allow cations to permeate but selectively permeate anions; on the contrary, the positive membrane contains negatively charged acidic groups and does not allow anions to permeate. In addition, the basic performance parameters of ion exchange membranes include exchange capacity, water content, swelling degree, thickness, mechanical strength, pore size, membrane conductivity, membrane potential, actual migration number, selective permeability coefficient, etc. In actual application, the ion exchange membranes should has better selective permeability, higher exchange capacity and good conductivity [8].

2. Principle and application of ion exchange membrane

Electrodialysis technology originated in the early 20th century. It refers to the directional migration of charged ions in a solution through ion exchange membranes under the action of a direct current electric field to achieve the purpose of separating, concentrating and purifying the solution [9]. Generally, the cost of desalination is similar to the original one. The salt content in the water is proportional to the 0.6th power, and the optimal concentration range for desalination is several hundred to several thousand mg/L.

At present, electrodialysis technology is widely used in industrial production such as seawater desalination, sewage treatment, amino acid separation and purification [10]. For example, when the pH of the amino acid solution is higher than the isoelectric point, the amino acid is negatively charged and passes through the anion exchange membrane under the action of an electric field; when the pH is lower than the isoelectric point, the amino acid is positively charged and passes through the cation exchange membrane under the action of the electric field, which can be used for amino acids separation. When the pH of the treatment solution is 4.0 and the current is 11A, Na^+ can be reduced to 42.88mg/L after 2 h, and the salt rejection rate reaches 99% [11].

But at the same time, electrodialysis technology can only remove charged ions in the solution, organic matter and uncharged substances cannot be removed, and when the resistance of the ion exchange membrane is large, it will consume a lot of electricity. Various researchers have used surface modification and doping modification, hollow fiber structure modification and modification to increase the porosity of the membrane matrix to solve such problems. Ion exchange membrane is the core of electrodialysis technology. The research on ion exchange membranes with high selectivity, high pollution resistance and reduced energy consumption of electrodialysis has been and will continue to be the focus of future research on this technology.

Diffusion dialysis technology is mainly based on the concentration difference between the two sides of the ion exchange membrane to allow the solute to diffuse and selectively separate. This process does not require a DC electric field. Anion membrane is often used to separate cations to achieve acid recovery, or cation membranes to separate anions to achieve alkali recovery. In general, the water content of ion exchange membranes in diffusion dialysis is relatively high, and the dialysis rate of acid and alkali can be increased under the impetus of the difference in solution concentration on both sides [12].

Iron and steel production, metal smelting and other industries often produce a large amount of waste acid containing heavy metal ions which must be treated. Chang Wei et al. [13] found that when the sulfuric acid concentration in the waste acid is 61.7 g/L, iron 11.2 g/L and vanadium

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4.6 g/L, and the flux is 0.19×10^{-3} $m^3/(m^2\bullet h)$, The recovery rate of sulfuric acid can reach more than 80%. In addition, diffusion dialysis can recover about 80% of alkali, and this method is gradually used to treat a large amount of alkali waste liquid produced in industries such as papermaking, printing, printing and dyeing. Yang Ji et al. [14] showed that when ion exchange membranes were used, the initial pH of the alkaline waste liquid has a greater impact on the recovery of sodium hydroxide by diffusion dialysis. Due to the small processing volume of diffusion dialysis, the recovery volume is susceptible to the influence of equilibrium concentration, and is currently not as widely used as reverse osmosis, nanofiltration and other technologies. Researchers have improved the recovery efficiency of acid and alkali by preparing ion exchange membranes with good separation, acid and alkali resistance and high flux, and preparing efficient diffusion dialysis devices.

Donnan dialysis is using the selective permeability of the counter ions in the solution to achieve the separation of the counter ions by mutual diffusion on both sides of the ion exchange membrane without the direct current electric field. Because of its advantages of energy saving, no need for regeneration and continuous operation, it is used to separate and remove fluoride, perchlorate, heavy metal ions in polluted water, and it also can be used to detect and analyze the concentration of trace heavy metals in water [15]. Xie [16] based on the principle of Donnan dialysis and used homogeneous cation exchange membranes to separate and remove heavy metal ions such as Cu^{2+}, Mn^{2+} and Zn^{2+} in wastewater. The results showed that when the concentration of heavy metal ions is 0.0787mmol/L, the removal rate of Cu^{2+}, Mn^{2+} and Zn^{2+} can reach to 85%, 79% and 75%, respectively.

3. Pollution and cleaning of ion exchange membrane

The pollution mechanism and degree of ion exchange membranes are affected by their affinity/hydrophobicity, charged nature, etc. Generally, cation membranes are not easily polluted due to negatively charged functional groups [17], while negative membranes are easily affected by negatively charged colloids in water and organic pollution. Some organic substances such as humic acid, surfactants and proteins may enter the membrane voids to restrict other ions from penetrating the membrane. At the same time, the increase in membrane resistance leads to a decrease in current efficiency and desalination efficiency. The research of Chen showed that after adding 50mg/L of humic acid to the raw water, a large amount of black humic acid was attached to the surface of the cation exchange membrane at the end of the test operation, which had an adverse effect on the removal of Cu^{2+} from the membrane [18]. Cationic surfactants can enter the membrane and contaminate the membrane, thereby affecting the membrane's removal efficiency of heavy metal ions. If the fermentation cells are not pre-treated when the fermentation method is used to prepare organic acids, microorganisms may also deposit on the membrane surface and cause membrane fouling.

In addition, ionized calcium and carbonate plasma can react with the active groups on the membrane after entering the electrodialyzer, and become irreversible pollution when fixed on the membrane, causing membrane "poisoning". As the test operation cycle increases, the contamination degree of the membrane will also increase, which would affect the removal effect of the membrane, but generally after alternate cleaning with acid (hydrochloric acid) or alkali (potassium hydroxide), the ion exchange function of the membrane can basically be restored. Therefore, the pollution of ion exchange membrane should be paid more attention in time

4. Conclusion and tendency

Nowadays, ion exchange membrane technology has been applied more widely in water treatment. Electrodialysis technology can realize solution separation, concentration and purification under a DC electric field; diffusion dialysis and Donnan dialysis can respectively

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realize acid-base recovery, ion separation and removal, and detection and analysis of trace heavy metals without DC electric field. In the future, for different heavy metal ion wastewater and specific industrial polluted water, we can gradually move from laboratory research to applied research to study the optimal technical conditions, pretreatment and advanced treatment technologies which are suitable for engineering practice; and develop special ion exchange membranes to improve the removal efficiency. In addition, develop some ion exchange membranes with high pollution resistance, and membrane cleaning and reuse technology, improve the efficiency of membrane use, to realize low-carbon environmental protection and high efficiency.

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