The Oxidation phenomenon and anti-pollution ability of ultrafiltration membrane in water treatment: A review

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Abstract

In recent years, with ultrafiltration become the core of water treatment technology has achieved rapid development around the world. However, in the process, people are paying more attention to the influence mechanism of external process conditions on the physico-chemical propertys of membrane materials and the anti-pollution ability. In the oxidation process of chemical cleaning, there is an internal relationship among the physico-chemical propertys of membrane surface, pollutant deposition order and membrane pollution。It shows the influence of ultrafiltration membrane oxidation on its anti-pollution performance. This review summarizes the research progress of ultrafiltration membrane oxidation and anti-fouling performance in membrane water treatment in recent years。It is expected to lay a theoretical foundation for further optimizing membrane filtration process and perfecting membrane fouling theory.

Keywords

Ultrafiltration membrane; Oxidization; Anti-pollution;Water treatment.

1. Introduction

With the development of social economy, the pollution of drinking water sources has attracted more and more attention.It has become an important issue affecting the quality of life of residents and the sustainable development of society. The conventional "coagulation-sedimentation-filtration-disinfection" process is difficult to meet the more stringent national standards for drinking water in the face of the current complex water source conditions. In the face of the new requirements of drinking water treatment technology in the new era, the water purification technology with membrane separation technology as the core shows a unique advantage [1]. Compared with the traditional water treatment process, Ultrafiltration (UF) technology can greatly improve the removal of organic pollutants and pathogenic microorganisms in water, so it is called the "third generation urban drinking water purification process" by many scholars. [2]. In recent years, membrane method has made many breakthroughs in China, and has gradually become a viable process for drinking water safety. However, in the large-scale application process, especially when the ultrafiltration technology is coupled with other synergistic processes, the stability of the membrane material and the change of anti-pollution performance have become important factors that restrict its further promotion.

2. Membrane Method Water Treatment

The membrane separation process belongs to single-stage transient filtration. Although the process is short and easy to control automatically, it also puts forward higher requirements on the integrity and stability of membrane materials [3]. At the same time, in order to ensure membrane separation efficiency and control membrane fouling development in actual production, it is usually necessary to cooperate with pre-coagulation treatment and chemical cleaning measures. Membrane materials frequently contact with chemicals further aggravates the stability risk of membrane materials: on the one hand, The oxidation and corrosion of chemical agents can cause irreversible changes to the structure and properties of the membrane material, which in turn affects the separation accuracy and filtration resistance of the UF membrane [4], resulting in a decrease in the efficiency of the water treatment system; on the other hand, oxidation of the membrane material It is also a key factor affecting its service life. Inappropriate process strategies will accelerate the performance degradation of membrane materials, leading to premature aging or failure of UF membranes, greatly increasing the operating and maintenance costs of the system. Therefore, how to combine the technical characteristics of water treatment technology with the structural characteristics of membrane materials, to study the formation mechanism and influencing factors of UF membrane oxidation phenomenon, has important practical significance for clarifying the reliability of UF technology and ensuring the stable operation of the system.

Although membrane separation technology has shown many advantages in the field of water treatment, the membrane separation efficiency caused by membrane fouling is reduced, and the system energy consumption is also unavoidable. In the membrane water treatment process, membrane fouling depends not only on the external factors such as the composition of the influent pollutants, operating conditions, etc. The surface characteristics of the membrane material and its interaction with the pollutants are also the key factors affecting membrane fouling behavior. At the same time, the surface properties of the membrane material in the actual water treatment process are not static, especially in the chemical cleaning process, the oxidation of the reagent can significantly affect the inherent characteristics of the surface hydrophobicity, charge characteristics, roughness, etc. of the membrane material, thereby enhancing membrane fouling control and The complexity of the study. However, the change of surface characteristics caused by oxidation of ultrafiltration membrane and its influence on membrane fouling behavior have not attracted attention. The change of inherent properties of membrane materials is often attributed to the increase of external pollution, which not only disturbs the formulation and implementation of filtration technology. It also led to the inability to confirm the development of membrane fouling in actual production. Therefore, how to use the oxidation phenomenon of UF membrane as a breakthrough to study the relationship between the surface properties of membrane materials and membrane fouling behavior.Not only helps to optimize the existing process, but also has important theoretical significance for elucidating the mechanism of membrane fouling formation.

3. The Oxidation Phenomenon of UF Membrane

In the practical application of membrane water treatment, in order to control the development of membrane fouling and ensure the safety of effluent, regular chemical cleaning of membrane units is the main means. Common chemical cleaning reagents include oxidizing cleaning agents, acid cleaning agents, alkaline cleaning agents, and surfactants. Among them, sodium hypochlorite (NaClO) is widely used because of its oxidation and broad-spectrum sterilization. The study of oxidation phenomena is also concentrated in this [4, 5].

Arkhangelsky et al. [6] found in the oxidation study of polyethersulfone (PES) ultrafiltration membrane that NaClO can cause the CS bond cleavage in PES, and the increase of sulfur in the polymer after oxidation indicates that the terminal group is converted from sulfone to sulfonic acid. At the same time, Ross et al. [7] found in the oxidation study of polyvinylidene fluoride (PVDF) ultrafiltration membrane that the oxidation and pH conditions of NaClO are the key factors affecting the structure of PVDF molecular segments, and the PVDF membrane is alkaline. Dehydrofluorination occurs in the environment, and the deprotonation process of -CH_2 eventually leads to an increase in the C=C double bond on the membrane surface [8].

On the other hand, the change in the functional group properties during the oxidation of the polymer can further change the physicochemical properties of the membrane surface, thereby affecting the filtration behavior of the ultrafiltration membrane. Hajibabania et al. [9] believed that the oxidation of NaClO could cause the surface of the PVDF membrane to be hydrophobized, thereby increasing the hydrophobic interaction between the membrane material and the contaminant, and ultimately leading to an increase in membrane fouling rate. However, many studies have found that the hydrophilicity of the PVDF membrane surface is improved after the chemical cleaning of NaClO. Therefore, it is considered that the increase of the initial flux of the membrane material is the root cause of the membrane fouling rate change. It can be seen that the existing ultrafiltration membrane oxidation studies focus on the hydrophobicity of the membrane surface while neglecting other characteristics, which leads to the evolution of the membrane surface characteristics and its influence on the membrane properties. Therefore, how to incorporate membrane surface functional group properties, charge intensity, roughness and other factors into the ultrafiltration membrane oxidation research process will be the key to solving the above controversy, and it is also the main direction of scholars' future research.

In addition, the “coagulation-membrane filtration” combination process has shown unique advantages in improving water purification effect, shortening process flow, and mitigating membrane fouling, so it has been widely used [10, 11]. However, most of the existing researches focus on floc morphology control [12], coagulation kinetics regulation [13], etc., often overlooking the potential impact of coagulating reagents on membrane materials. In the actual application process, due to the excessive addition of coagulant [14], insufficient coagulation [15], incomplete floc precipitation [16], etc., resulting in residual coagulant in the coagulation supernatant And the incompletely precipitated flocs can enter the membrane unit, thereby forming membrane fouling by deposition or adsorption. At the same time, existing studies have confirmed that aluminum ions, iron ions and their hydrolyzed products, when contacted with oxidizing NaClO, trigger a chain catalyzed reaction, which in turn produces strong oxidizing hydroxyl radicals (•OH).

Behin et al. [17] achieved rapid degradation of aromatic organic compounds in wastewater in Fe^{2+}/NaClO system. The results show that hydroxyl radicals in this system can be produced under a wide range of pH conditions, and the yield and Fenton reaction process Close. At the same time, the catalytic effect of Fe^{3+} on ClO- has also been mentioned. The results of electron spin resonance (EPR) indicate that high-valent iron will be re-reduced to form Fe^{2+} in the related catalytic process, which will promote the catalytic reaction and continue to generate hydroxyl radicals [18]. On the other hand, in the "coagulation-oxidation" combination process, the catalytic effect between the aluminum salt, the iron salt hydrolyzate and the oxidizing agent has been widely concerned. In the above system, in addition to the hydroxyl radical chain reaction initiated by hydroxide in water, the coagulant can also generate a large amount of hydroxyl functional groups on the surface of the floc by hydration, thereby further converting into hydroxyl radicals under specific circumstances [19]. However, in the existing research, the above catalytic reaction and the influence of hydroxyl radicals on the membrane material have not attracted attention, posing a potential threat to the integrity and stability of the membrane material. Therefore, how to comprehensively analyze the synergistic oxidation effect existing in process coupling is the key to reveal the formation mechanism of ultrafiltration membrane oxidation phenomenon.

4. The Anti-pollution Ability of UF Membrane

Membrane fouling refers to the reduction of the effective volume of membrane pores and the decay of membrane flux due to the deposition and adsorption of particles, colloids or dissolved substances during the separation process [20]. Natural organic Matters (NOM) are widely recognized as major contaminants in ultrafiltration membrane fouling during membrane water treatment. As a mixture widely existed in water, NOM has a complex chemical composition and various forms. It can carry various functional groups such as hydroxyl, carboxyl, carboxylic acid, phenol and aldehyde at the same time, resulting in a complicated process of membrane fouling.[21]. In addition, due to the obvious interface characteristics of membrane fouling, the surface properties of membrane materials and the behavior of pollutants are also the key factors affecting membrane fouling.

In order to investigate the effect of surface properties of membrane materials on membrane fouling behavior, Nilson et al. [22] used DAX-8 resin to classify NOM and found that hydrophobic humus and its hydrophobic interaction with the membrane surface Hydrophobic interaction. It is a key factor in causing membrane fouling. This result is also supported by Schafer et al. [23], pointing out that the adsorption of hydrophobic humic acid on the surface of the hydrophobic membrane is the most important factor causing irreversible pollution, while reversible pollution is mainly derived from fulvic acid and other hydrophilicity. Small molecule. At the same time, organic substances with high affinity to the membrane surface and easy to form adsorption pollution usually have heterogeneity in molecular composition, resulting in complex interface interaction between pollutants and membrane surface, and different membrane surfaces and different pollutants. There are also significant differences in the interactions. Therefore, the hydrophilicity of membrane materials is generally considered to be a key factor affecting its anti-pollution ability. How to improve the hydrophilicity of membrane surface is also the focus of UF membrane modification research [24].

On the other hand, the surface charge of the membrane material also has an important influence on its anti-contamination properties. First, the preferential adsorption of charged functional groups on the surface of the membrane or specific ions in the water is the main cause of its charging [25]. Many studies have shown that the action of pollutants on the surface of the membrane also follows the principle of “same-charge repulsive, heterogeneous charge attraction” [26]. Miao et al. [27] found in the separation process of BSA that when the pollutants were negatively or electrically neutral, the irreversible pollution resistance of the UF membrane decreased significantly, indicating that the increase of electrostatic repulsion helps to inhibit the pollutants. The tendency of deposition and adsorption on the surface of the membrane. However, some studies have also questioned the utility of electrostatic repulsion.Chan et al. [28] found in the study of PEG-based self-assembled coatings that many negative-charged coatings on the surface do not have electrostatic repulsion. Therefore, it is speculated that the key reason for achieving anti-contaminant adhesion is polymer chains in different forms.

In addition, the surface morphology of ultrafiltration membranes, especially roughness, is also considered to be a key factor affecting membrane fouling resistance. First, Elimelech et al. [29] believed that the interaction between colloidal particles and the membrane surface will increase with the increase of surface roughness. Therefore, it is proposed to reduce the surface roughness of the membrane to reduce the occurrence of membrane fouling. However, in recent years many studies based on Young's equation [30] have suggested that solid surface roughness has an effect on the properties of liquid wetting. Jiang et al. [31] found in the study that appropriate increase of membrane surface roughness can effectively improve its surface energy, improve the hydrophilicity of the membrane surface, and thus achieve the construction of anti-pollution surface. At the same time, we also found in the previous research that the use of hydrophilic micelles to construct the micro-nano structure on the surface of the membrane can greatly enhance the binding ability of the membrane surface to water, strengthen the membrane hydration boundary layer, and then pass the hydration repulsion [27] inhibit protein adhesion and enhance anti-pollution ability.

5. Conclusion

It can be seen that the surface hydrophobicity, charge characteristics, morphology and other factors of the membrane material are the key factors affecting its anti-pollution performance, but there are still many controversies in related theories:

i) Most of the existing research focuses on a specific factor and The relationship between membrane fouling behavior, but the synergistic mechanism and strength relationship between different factors in membrane fouling process is still unclear;

ii) Existing research usually ignores the dynamic process of surface characteristics of ultrafiltration membrane, resulting in inability to accurately grasp membrane fouling The development of behavior and resistance.

The reason for the above problems is that the surface functional group properties, zeta potential, average roughness and other factors of the ultrafiltration membrane are related to each other and the complex effects are affected. Therefore, it is difficult to clarify the synergistic principle and the primary and secondary relationship of various factors in the membrane fouling process. , exacerbating the complexity of research. However, we noticed in the previous research that due to the significant differences in chemical stability and oxidation reaction mechanism of different polymers, the rate of change of hydrophilicity, charge intensity and roughness of ultrafiltration membranes under different oxidation intensities also appeared in time series. Sexual differences.

Therefore, based on the scientific analysis of the oxidation process of membrane materials and its corresponding pollution behavior, it is expected to resolve the multi-factor complex effects of the surface characteristics of ultrafiltration membranes, thus clarifying the anti-pollution principle of ultrafiltration membrane surface, and providing a new scientific path for perfecting membrane fouling theory.

In summary, in the research of membrane water treatment technology, there are many common problems between the oxidation mechanism of membrane materials and the principle of anti-pollution: the correlation mechanism between the surface characteristics of ultrafiltration membrane and membrane fouling behavior. Although some researches have been made on the oxidation of membrane materials and the theory of membrane fouling at home and abroad, the combination of the two is still a blank.

Therefore, in view of the characteristics of membrane water treatment technology and the structure characteristics of ultrafiltration membrane, this topic innovatively proposes the ultrafiltration membrane oxidation phenomenon as the entry point, by accurately analyzing the surface hydrophobicity, charge characteristics, physical shape of the ultrafiltration membrane during oxidation. The synergistic relationship between appearance and membrane fouling behavior, thus solving the interaction principle and strength relationship of hydrophobic interaction, electrostatic repulsion and hydration repulsion in membrane fouling process, and finally optimizing the current membrane filtration process and improving water treatment the membrane fouling theory of the process provides scientific support.

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