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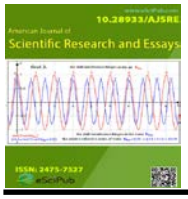

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Research Status of Purification Process of Eutrophicated Water

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ABSTRACT

There are widespread eutrophication problems in lakes and rivers in China. Eutrophication means that the water body receives too much nutrients such as nitrogen and phosphorus, and the organic matter is excessive. When the algae dies, it rots, causing the water quality to deteriorate, thereby causing damage and destruction of the ecological functions of the water, bringing huge use of water resources. loss. While a considerable number of countries or regions use lakes, rivers, etc. as drinking water sources, the problems caused by eutrophication cannot be ignored, and it is urgent to find a reliable and effective method to provide safe water supply. The combination process with ultrafiltration as the core removes algae and has good effects, low energy consumption, simple process and easy control, and has broad application prospects in the future water treatment industry. However, the problem of membrane fouling is still seriously hindering the further development of membrane technology in the water treatment industry.

Keywords: Eutrophication Ultrafiltration technology Algae removal Ultrafiltration combined process

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Introduction

In the 2017 United Nations World Water Development Report, it is pointed out that the contradiction between supply and demand of fresh water is deteriorating in the next few years. Two-thirds of the world's population lives in water-deficient areas, and water resources are extremely precious. In recent years, Li Na et al. [1] surveyed 22 lakes across the country and found that 59% of the surveyed lakes are in eutrophication. The side also verifies the widespread eutrophication problems in lakes and rivers in China. Eutrophication means that the water body receives too much nutrients such as nitrogen and phosphorus. The organic matter is too much, so that the algae and other aquatic microorganisms in the water are overproduced. The transparency of the water body is reduced, the dissolved oxygen is lowered, and sometimes floating on the surface of the water. "Shuihua" or "red tide", and the decay of algae will cause the water to smell and cause the water quality to deteriorate, thus causing damage and destruction of the ecological function of the water, causing huge losses to the utilization of water resources [2]. In summer and autumn, the disturbance of water bodies in lakes and reservoirs is enhanced. The sediments in the sediments float up to the water, providing enough N, P and other nutrients for the growth of algae. In addition, photosynthesis forms a large number of algae breeding, leading to water pollution. China's lake-pool water source, which accounts for 30% of the total number of water sources, provides more than 20% of water supply and is an indispensable component of urban water supply [3]. Moreover, the average temperature in the southern part of China is high, most of the water source comes from natural surface water, and there are widespread eutrophication problems in lakes and rivers.

The danger of eutrophicated source water

Algal cell characteristics and effects

The algae cell density is small, close to water, and the individual size is only 20~200 μm, which is difficult to handle. It also increases the turbidity of the source water. Studies have found that algae is one of the important precursors of disinfection by-products in drinking water. It is a factor affecting the biological stability of drinking water treatment, especially the breeding and breeding of toxic cyanobacteria, and the resulting algal toxins have caused widespread wildness. Animals, birds, poultry poisoning and even death. Even human poisoning incidents[4]. When eutrophic water is used as a water supply source, it will bring a series of problems to the water plant. Due to the dense algae in the surface water of the water source, it is difficult for sunlight to penetrate into the deep layers of the lake, so that the photosynthesis of algae is obviously inhibited, and the source of dissolved oxygen is reduced. Algae continue to deposit after death, decompose and decompose, consume a large amount of dissolved oxygen in deep water bodies, and even cause anaerobic conditions in water bodies, trigger or accelerate the release of nutrients accumulated in the sediment, resulting in high load of nutrients in water bodies and formation of eutrophic water bodies. Vicious circle [5].

The harm of microcystins

The main hazard caused by water pollution is the release of many different types of algal toxins into the water after the rupture of toxic cyanobacteria cells. Microcystins (MCs) are the most frequently occurring in cyanobacterial blooms. The most abundant and most harmful species of algal toxins [6]. The degree of toxicity of MCs to organisms is mainly related to water

bloom density, water toxin content, and also to biological species and size. Animals are poisoned or killed by contact or drinking water containing MCs. The symptoms of poisoning include coma, pale skin, shortness of breath, diarrhea, coldness of the limbs, and muscle spasms. MCs also endanger human health. Human direct contact with toxin-containing blooms can cause skin, eye irritation, fever and acute gastroenteritis. If you are exposed to water containing toxins, it can cause skin cancer, hepatitis, and even death.

Current status of ultrafiltration technology in eutrophication water purification

Advantages and disadvantages of current common methods:The common methods for removing algae cells and their secretions from eutrophicated source water are classified into physical, chemical and biological[7].

Physical method

The physical method mainly includes air flotation, coagulation, micro-electrolysis and direct filtration to remove algae.

The removal rate of algae cells by air floatation method can reach more than 90%. The air floatation method covers a large area, and the floating scum is difficult to handle. The odor is often emitted around the air floatation basin, which makes the application of air flotation subject to the limitation of air flotation. The raw water has a low suspended solids content, and it is generally required to add chlorine before air flotation, which may endanger the safety of the effluent.

The coagulant mainly includes aluminum sulfate, polyacrylamide, iron sulfate and ferric chloride. The algae cells are different from the colloidal particles, and the dosage must be increased. This also increases the cost of water treatment and increases the concentration of metal ions in the water. , causing secondary pollution of water quality.

The principle of micro-electrolysis to kill algae is to obviously destroy the structure of chloroplasts in algae cells, so that the algae completely lose the ability of photosynthesis. Even under sunny conditions, the respiration is far greater than photosynthesis, and the dissolved oxygen drops sharply. good results. [8]

Chemical method

Chemical method: mainly includes the addition of oxidants and other chemical agents to kill algae. Commonly used oxidants (such as Cl2, ClO2 and O3) can destroy the physical form of algae cells under oxidative conditions, effectively eliminate algae cells and remove odor, but oxidants are generated when contacted with algae cells and dissolved organic matter in raw water. Disinfecting by-products harmful to the human body, which contain a large amount of tri-materials (carcinogenic, mutagenic, teratogenic), such as trihalomethanes and other carcinogens, reduce the safety of effluent. [9]

Biological methods:

The method utilizes stocked filter-feeding fish (such as squid) or aquatic plants to reduce the number of algae cells in the environment by swallowing algae, or by absorbing, migrating, and metabolizing eutrophic substances in the water to inhibit the growth of algae cells. The method makes full use of the interaction of various organisms in the ecosystem, and can effectively control the growth of algae without any negative effects [10]. The main disadvantage of the biological method is that the structure has a large area, long residence time and slow effect, which is not conducive to dealing with unexpected events.

Ultrafiltration technology application

Basic principle

The ultrafiltration membrane is a water treatment technique between the microfiltration and the nanofiltration, and the ultrafiltration membrane has a pore size ranging from 0.001 μm to 0.22 μm [11]. The basic principle is that the selective permeable membrane is a separation medium, and the raw material side component is selectively driven through the membrane by a pressure difference or a concentration difference, thereby achieving the purpose of separation or purification. Ultrafiltration technology is mainly to remove macromolecular substances, colloids, proteins, etc. in water. The smallest molecule that can be filtered has a molecular weight of thousands, and its water purification capacity is superior to that of activated carbon. At present, ultrafiltration membranes mainly include flat ultrafiltration membranes, tubular ultrafiltration membranes, capillary ultrafiltration membranes, hollow fiber ultrafiltration membranes, and porous ultrafiltration membranes.

Application status in engineering

In 2004, ultrafiltration began to be used in urban water purification plants. In recent years, with the continuous decline of membrane prices and the accumulation of operating experience, ultrafiltration has become more and more widely used in Chinese urban water purification plants, and the production rate of ultrafiltration water plants has accelerated. Water plants that use ultrafiltration to replace traditional filtration in China include Macao Dashui Pond Water Plant, Shanghai Xujing Water Plant, Urumqi Red Goose Pond Water Plant, and Zhaoqing High-tech Zone Water Plant. Almost every year, a large-scale ultrafiltration water plant with a water production of more than 10×104 m3/d is completed and put into operation, and the scale of the water plant is continuously expanding. Therefore, the replacement of traditional urban water treatment technology with ultrafiltration technology will become more and more popular [12].

Ultrafiltration technology distributes the average rate of use in MBR, seawater desalination pretreatment and wastewater reuse, accounting for about 30% of the market water treatment [13], and considering that technology has been used in wastewater treatment in other industries. For example, the power industry, the steel industry and the chemical industry provide technical support for solving water pollution and water shortage problems. Therefore, ultrafiltration technology has broad application prospects in the future sewage treatment industry.

Drinking water treatment process

The first generation of water treatment processes to prevent the spread of infectious diseases before the 20th century mainly included processes such as coagulation, filtration, sedimentation and chlorine disinfection. In the 1970s, the second generation of water treatment process newly added ozone activated carbon treatment process; the third generation was a combined process based on ultrafiltration technology developed to remove algae or other secretory interferences in water.

It can be seen from Table 1 that the third-generation water treatment process has a good removal effect, which can basically meet the basic requirements of modern people for drinking water quality, the rapid development of ultrafiltration membrane materials and the reduction of cost, ultrafiltration and its combined process. It is widely used in the interception of particles and microorganisms in drinking water

treatment. Because the pore size of the ultrafiltration membrane is much smaller than the diameter of algae cells, ultrafiltration membrane technology can effectively retain particles and algae cells, but can not effectively remove dissolved organic matter, such as algal toxins, odor and other substances [14]. The combination process with ultrafiltration as the core is diverse. The difference is that the pretreatment method is different. According to the difference of raw water quality, a suitable combination process is selected. The combination of pretreatment and ultrafiltration technology makes the effluent water quality reliable and safe. Hot spot. The following table is a comparative analysis between the current popular combination processes. As shown in Table 2 below：

Table 1 Comparison of the removal effects of the third-generation process on related key indicators

Removal rate（%） / Process algebra	Pathogenic microorganism	Turbidity	COD	UV_{254}	Algae
First generation	50%	80%	10%	30%	10%
Second generation	70%	90%	30%	70%	60%
Third Generation	95%	98%	50%	90%	90%

Table 2 Comparative analysis of various pretreatment techniques

Pretreatment method	Basic mechanism and advantages	Disadvantage
$CuSO_4$-UF	Copper sulfate is the earliest algicide for research and application. Copper is a heavy metal. When it enters the cell body, it will undergo oxidation reaction to destroy intracellular substances such as chloroplasts, which directly affect the photosynthesis, respiration and enzyme activities of algae cells and inhibit algae growth [15].	Excessive use of copper sulfate will cause the copper ion content in the water to exceed the standard, destroying the aquatic state, and copper sulfate will destroy the algae cells, causing most of the algal toxins in the cells to penetrate into the water body, causing the water body to re-contaminate.
$KMnO_4$-UF	The oxidation performance of KMnO4 increases the algae inactivation rate; the hydrated manganese dioxide produced by reduction will deposit on the surface of algae cells to increase the specific gravity and improve its sedimentation performance;	However, adding KMnO4 at the same time will increase the color of raw water, and excessive dosing may cause manganese ion to exceed the standard [16].
O_3-UF	The ozone oxidation ability is strong, the reaction speed is fast, the molecular state O3 can diffuse into the algae cells, destroy the cell organ function, inactivate the algae; and the secondary	The ozone process has defects in equipment and infrastructure investment, high operation and management costs, and bromate formation. At the same time,

	oxidation groups such as hydroxyl radicals and new ecological oxygen atoms generated by decomposition are extremely active. Acting on the surface of algae cells to kill algae [17]	algae kills algae cells while causing algae to release intracellular organic matter, which is harmful to water safety.
PAC-UF	Activated carbon has a good removal effect on color, smell, most organic pollutants and mutagens and carcinogens in water. [18]	Adsorption pretreatment technology has the problem of recycling and reuse. If the adsorbent is not effectively recycled, it will increase the cost of the process and increase the subsequent process load.
AOPs-UF	At present, AOPs technology is widely used in algae removal. OH• is highly oxidizing, so it can react rapidly with most organic and inorganic substances in water; OH• reacts with organic matter with low selectivity and completely oxidizes organic matter. When the organic matter is completely oxidized, most of the organic matter can be completely oxidized to carbon dioxide and water. No by-products are produced. [6]	The construction investment and operating costs of AOPs are extremely high, especially for large-scale applications. It also produces harmful by-products

Membrane fouling mechanism and prevention measures

Membrane fouling mechanism summary

Ultrafiltration membrane fouling and limited interception of dissolved organic matter severely hinder the further promotion of ultrafiltration membrane processes in drinking water treatment [19]. Therefore, strengthening the pre-treatment of membranes to alleviate membrane fouling is of great significance for the application of ultrafiltration membranes. It is agreed in the literature that colloidal particles, solute macromolecules, microparticles and membranes in the raw material liquid have different effects (physical, chemical, biochemical or mechanical), and are adsorbed on the surface of the membrane for a long time or deposited in the pores of the membrane, resulting in a decrease in membrane water production. . It is generally believed that membrane fouling is mainly divided into three parts: concentration polarization, membrane surface contamination (formation and compression of the filter cake layer), adsorption and clogging in the pores of the membrane [20]. In the process of clean water treatment of drinking water with surface water as the source of water, natural organic matter (NOM) is considered to be the main substance causing membrane fouling, and substances of different components in NOM cause different forms of pollution. Algae organic matter and microbial source organic matter are endogenous organic pollutants, and extracellular organic matter, intracellular organic matter and algal cell residues released by algae can cause ultrafiltration membrane contamination [21].

5.2 main measures to prevent membrane fouling

The control of membrane fouling generally starts from two aspects. One is to improve the performance of the membrane itself to delay membrane fouling, and the other is to reduce the membrane fouling by increasing the turbidity and organic content of the raw water by increasing the pretreatment unit.

(1) Improvement of film properties (membrane material modification) adsorption of organic substances, precipitation of insoluble inorganic substances, and adhesion of microbial cells on the surface of the membrane may cause membrane fouling. First, a hydrophilic membrane material is preferred when selecting a membrane material. Membrane material modification generally has chemical modification, photochemical modification and plasma modification [22].

(2) Raw water pretreatment

The water quality characteristics of the raw water will affect the degree of membrane fouling. Therefore, the physical, chemical, and biological properties of the raw water can be changed in advance, and the raw water is likely to cause membrane fouling by coagulation, filtration, adsorption, and oxidation processes to reduce the raw water. Degree of contamination of membrane modules [23].

At the same time, some scholars have developed a new type of active cross-flow filtration integrated equipment based on the principle of cross-flow filtration. It is applied to rural distributed water supply. The basic principle of the equipment is that the membrane inlet water is perpendicular to the infiltration direction, and the membrane module is produced during the tangential operation. Shear force, centrifugal force and turbulent flow of the filtrate promote the reverse movement of the solute on the surface of the membrane to the liquid body, making full use of the rotation to generate the shearing force and the turbulent flow of the filtrate, preventing the generation of the filter layer, and effectively preventing the membrane from clogging without aeration and backwashing. And delay membrane fouling [24]. It can effectively eliminate concentration polarization and increase membrane flux, which can extend the membrane cleaning cycle.

Membrane cleaning

Although the membrane fouling is controlled according to the principle, in the actual water treatment, as the membrane equipment runs longer, the transmembrane pressure difference increases, and the membrane flux decreases. If the membrane separation equipment is not cleaned, the equipment may be difficult to operate. Go on. At present, membrane cleaning technologies mainly include physical cleaning, chemical cleaning, and biological cleaning. (1) Among the traditional physical cleaning techniques, the flow method and the back pressure cleaning method are mainly used at low pressure. New types include ultrasonic cleaning and pulsed electric field cleaning technology [25]. (2) Chemical cleaning technology utilizes multiple reactions between the cleaning agent and contaminants on the surface of the membrane or pores to remove contaminants [26]. Common chemical cleaning reagents have different concentrations of NaOH, HCl, NaClO, H2O2, hydrochloric acid, sulfuric acid, and the like. In the actual water treatment process, depending on the source of water being treated, who chooses the matching cleaning reagent. (3) Bio-cleaning technology utilizes biologically active enzymes or biological agents to decompose or remove certain high-molecular organic substances, such as proteins, from ultrafiltration membrane pollutants.

Polysaccharides and the like. Enzymes or biologic agents with high biological activity can cleave protein chains and rapidly dissolve small loose protein fragments [27]. The biological cleaning method mainly involves cleaning the enzyme or biological agent as a cleaning agent

or fixing the biological agent on the membrane by a special method to enhance the anti-pollution energy of the membrane.

Conclusion

The combination of ultrafiltration as the core process for the treatment of eutrophicated source water to remove UV254 and algae in water has good effects, low energy consumption, simple process and easy control, and has broad application prospects in the future water treatment industry. In practical engineering applications, as long as the pretreatment process is not to be polluted by by-products, secondary pollution is not generated in the whole process, and the quality and stability of the effluent are grasped. This process is highly feasible. However, membrane fouling is the main obstacle to the promotion of membrane separation technology. Therefore, there are still huge research fields in membrane fouling mechanism and pre-membrane pretreatment.

Research progress space. For ultrafiltration membrane technology, there are many problems. One is the ultrafiltration membrane to remove dissolved organic pollutants. The other is the phenomenon that the ultrafiltration membrane will break during the use process, so that the raw water can pass through the filtration directly. Membrane, in which the solid matter can not be removed, reducing water quality; third, the ultrafiltration membrane is susceptible to temperature, when the room temperature is higher, the water viscosity increases, the water reverse flow is easy, the temperature is low, and even the water freezes. It is easy to cause damage to the ultrafiltration membrane; fourthly, the ultrafiltration membrane technology directly passes the raw water through the ultrafiltration membrane, and the inorganic salt in the water will contaminate the ultrafiltration membrane, and some chemicals can degrade the membrane. For the problems in these ultrafiltration technologies, the future research directions of scholars are prompted as follows: First, based on some pollutants present in the water, a kind of organic pollutants capable of removing soluble substances and improving the ability of membrane purification water are developed. Second, the development of a high-low temperature ultrafiltration membrane to reduce the impact of temperature on the membrane water purification capacity; the third is to develop new ultrafiltration membrane materials, optimize the membrane components, improve membrane toughness, reduce wire breakage The phenomenon occurs; the fourth is the development of membrane cleaning agent, targeted cleaning of some of the pollutants; the fifth is in the existing membrane module production process, improve membrane system configuration technology and operating conditions, improve product quality and output.

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