Study on Treatment of Preserved Wastewater by Combined Ultrafiltration-Nanofiltration

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Abstract. The treatment process of preserving soaking waste water by combined ultrafiltration-nanofiltration process was investigated. In the nanofiltration experiment, measuring the effects of different enrichment times on the flux, COD, total phosphorus and ammonia nitrogen to analyze the characteristics of the nanofiltration process and membrane fouling problems during nanofiltration. The results indicated that when the enrichment multiple was 4 times, the removal rate of COD was up to 87%, the removal efficiency of total phosphorus was above 90% and the removal rate of ammonia nitrogen was up to 63%, besides the membrane flux could be maintained at a better level. With prolonged operation, membrane flux decreased by 71%. After being soaked and cleaned with sodium hydroxide solution, membrane flux can be restored to more than 73% of the original. The concentrated waste water soaked by nanofiltration can be treated with advanced oxidation process, and the filtrate can reach the standard for reuse water.

1. Introduction
Candied soaking wastewater has low pH value, high salinity and high molecular weight of organic pollutants[1], and these are the key factors that affect the operation and stability of the wastewater treatment system. In this paper, on the basis of characteristics of preservative soaking wastewater, combined with the decontamination advantages of ultrafiltration and nanofiltration to research treatment process of preservative soaking wastewater with “combined ultrafiltration-nanofiltration”. Ultrafiltration membrane has been widely used in wastewater treatment, and it has a very high removal rate of suspended particulate matter, microorganisms and turbidity in water, but the ultrafiltration membrane itself belongs to mesoporous membrane[2]. It’s removal effect on dissolved salts, dissolved organic matter and some small organic molecules in the water is not good, while organic pollutants part of preservative soaking wastewater are small molecules[1]. Nanofiltration can not only effectively remove most of the organic matter in water, but also has a certain removal effect on some monovalent ions[3]. In this paper, through the actual wastewater operation test, we optimized the concentration multiples and membrane cleaning program to obtain efficient and stable treatment process, so as to provide some references and basis for solving the pollution of candied fruit soaking wastewater.

2. Experimental system and water quality
2.1. Experimental system

Figure 1 is experimental system diagram of the combined ultrafiltration - nanofiltration, preservative soaking wastewater firstly got into the ultrafiltration membrane, the effluent from the ultrafiltration membrane enters the nanofiltration membrane for concentration treatment. The transmembrane pressure of the ultrafiltration membrane is 0.2-0.4 MPa and the transmembrane pressure of the nanofiltration membrane is dominated as 2.0 MPa[4]. Before the experiment, ultrafiltration membrane and nanofiltration membrane were rinsed with pure water to reduce the impact of membrane fouling on the experiment.

Figure 1. UF-NF system

Ultrafiltration system: The ultrafiltration membrane selected by the ultrafiltration system is 181 tube ultrafiltration ceramic membrane, the operating pressure of equipment is 0.35 Mpa. First of all filling the waste tank with clear water, connect the electric source, turn on the machine, after adjusting the parameters, waiting for the machine to run for a period of time, test the water membrane flux of ceramic membrane. Turn off the machine, drain the water and pour the preservative soaked waste water into the two-thirds of the original liquid tank, re-open the machine to run under the specified parameters for 5mins, taking the filtrate to determine its parameters.

Nanofiltration system: 250 composite membrane is selected by nanofiltration system, the operating pressure of equipment is 1.5 Mpa. First of all filling the waste tank with clear water, connect the electric source, turn on the machine, after adjusting the parameters, waiting for the machine to run for a period of time, test the water membrane flux of ceramic membrane. Turn off the machine, drain the water and pour the preservative soaked waste water into the two-thirds of the original liquid tank, re-open the machine to run under the specified parameters for 5mins, taking the filtrate to determine its parameters.

Cleaning scheme of membrane: During actual membrane treatment, the permeate flux will decrease with prolonged operation[5], and membrane fouling problems will emerge. The experiment used different chemical reagents: such as sodium hypochlorite, sodium hydroxide and so on to clean the contaminated film, according to the cleaning effect of membrane, so as to determine the best cleaning method.

3. Experimental drugs and equipment

3.1. Materials

Sulfuric acid and sodium hydroxide, analytical reagent, Xilong Chemical Co., Ltd., ultrafiltration membrane material is the 181 tube ceramic membrane, molecular weight cutoff is $5 \times 10^4$ U; nanofiltration membrane is GE osmosis membrane, molecular weight cutoff is $3 \times 10^2$ U.
3.2. Experimental water quality
The experimental wastewater was collected from a salt immersion pond of a preserves plant in Yongtai County. The water samples showed a light yellow color and a large viscosity. Contents of COD, chloride and organic acid are high, the water quality index of experimental wastewater is shown in Table 1.

| COD (mg/L) | NH3-N (mg/L) | TP (mg/L) | pH | Cl- (mg/L) |
|-----------|--------------|-----------|----|------------|
| 4800      | 112          | 25.2      | 4.6| 8750       |

4. Results and discussion

4.1. Ultrafiltration of preservative soaking wastewater
The experiment selected the ceramic membrane for ultrafiltration pretreatment, the device is simple and easy to operate. Firstly pouring waste water into the original liquid tank, the operating equipment began to filter, until all the wastewater was filtered out, taking the supernatant to measure its parameters, the results are shown in Table 2:

| COD (mg/L) | NH3-N (mg/L) | TP (mg/L) | pH | Cl- (mg/L) |
|-----------|--------------|-----------|----|------------|
| 3650      | 102          | 23        | 4.6| 8550       |

From the experimental results, it can be seen that the removal efficiency of COD can reach 24% after the preservative soaking wastewater was ultrafiltrated, with little change in other parameters. However, the viscosity of water reduced from 2.1CP to 1.2CP, the effluent is more clear, which can effectively avoid membrane fouling during subsequent film process.

4.2. Effect of concentration ratio on the water quality of preservative wastewater during the process of nanofiltration
In this experiment, the ultrafiltration permeate was subjected to nanofiltration concentration experiment under the conditions of operation pressure 15 bar and the temperature 25-40 °C. The operation mode of all retentate recycle was adopted. The volume of each batch of feed liquid is 20L, and the membrane is not rinsed during the concentration of the feed liquid. In the nanofiltration filtration process, the concentration multiplier has a great influence on the treatment effect. This article investigated different concentrations of dialyzate influenced on the chemical oxygen demand COD, total phosphorus TP, ammonia nitrogen [NH 3-N] Through flux and so on.

4.2.1. Influence of concentration ratio on COD. This experiment use potassium dichromate titration method to measure the COD of dialyzate with different concentration times.
As shown in Figure 2, during the process of nanofiltration, the COD value of dialyzate gradually increased with the increase of concentration times. The COD value was 562 mg/L when the dialyzate was concentrated to 2 times, while the COD value increased slowly when the dialyzate was concentrated from 2 times to 4 times. When the concentration times of dialysate reaches 5, the COD value reached 645 mg/L. The upward trend of COD is more obvious when it is concentrated up to 6 times. This is mainly because the nanofiltration is a recycling process. The concentration times of organic pollutants in preservative soaking wastewater increases with the increase of operating time. The increase of concentration of concentrated side liquid leads to the continuous increase of COD concentration on the dialysis side. When the concentration times was 4 times, interception rate of COD was 87% or more, which can ensure better effluent quality and improve processing efficiency.

4.2.2. Effect of concentration times on total phosphorus

The effect of nanofiltration concentration times on total phosphorus is shown in Figure 3. After ultrafiltration treatment, total phosphorus concentration of preservative soaking wastewater was 23 mg/L. During the process of nanofiltration, the concentration of total phosphorus decreased obviously after treatment by nanofiltration membrane. With the increase of concentration times, the total phosphorus concentration of dialyzate increased gradually, but it was basically below 2.5 mg/L and the removal efficiency was over 90%.
4.2.3. Effect of concentration times on ammonia nitrogen. The experiment uses ultraviolet spectrophotometry to determine the concentration of ammonia in different dialyzate.Due to the high concentration of ammonia nitrogen in the dialyzate, this experiment was measured by the dilution method, ammonia concentrations of dialysate with different concentration times are shown in Figure 4.

![Figure 4. Influence curve between concentration multiple and NH3-N](image)

The results showed that the initial concentration of ammonia nitrogen in the ultrafiltrate effluent of preservative soaking wastewater was 102.0mg / L. After treatment through nanofiltration membrane, the concentration of ammonia nitrogen in the dialyzate was reduced to 23mg / L ~ 60mg / L. During the nanofiltration concentration, With the increase of concentration, dialyzate ammonia concentration gradually increased. When nanofiltration is concentrated at about 4 times, ammonia nitrogen removal rate of nanofiltration effluent was 63%. Thus, Nanofiltration membrane has high efficiency of ammonia nitrogen treatment, with less energy consumption and stable treatment results.

4.2.4. Influence of concentration ratio on permeation flux. In this experiment, under the condition of temperature 25 °C with the operating pressure was fixed to 2.0MPa at the same time, then all the intercepted liquid was used with the operation mode of internal circulation to conduct the nanofiltration concentration experiment on preservative soaking wastewater. The volume of each batch of feed is 20L, and the membrane is not rinsed during a complete feed concentration. The change of nanofiltration membrane permeation flux with concentration factor is shown in Figure 5.

![Figure 5. Influence curve between concentration multiple and NF membrane permeate flux](image)
At the beginning of nanofiltration, the membrane permeation flux was larger, which was 41.67 L/(m²·h). As can be seen from Figure 5, with the increase of the concentration factor, the permeation flux decreases rapidly, which is due to the feed concentration gradually increased, the viscosity also increased, then the membrane permeation flux decreased owing to intensification of concentration polarization. Concentration polarization will increase the osmotic pressure inside the membrane, reducing the effective operating pressure. In addition, the phenomenon of concentration polarization can cause the solute to form a resistance layer on the membrane surface and also prevent the solvent from passing through. That is, the concentration polarization can reduce the permeation flux of the nanofiltration membrane. The effect of concentration polarization layer on the solute permeability is relatively complex. The concentration of some solutes in the concentration polarization layer is higher than that in the bulk liquid material, increasing the driving force of these solutes when they through the nanofiltration membrane, thus the rate of interception is reduced. At the same time, due to the existence of the concentration polarization layer, diffusion resistance of some solutes increase, so that the permeability of these solutes is reduced.

When concentrated to 3 to 4 times, the nanofiltration membrane flux gradually stabilized. The main reason is that as the concentration proceeds, due to the formation of the solute-gel layer on the surface of the membrane, the rate of reverse diffusion of solute tends to be balanced with the concentration polarization, and the secondary resistance of the gel is basically unchanged, so that the permeation flux of the membrane Gradually stable.

After concentration to 5 to 6 times, the permeation flux of the membrane decreased, which is due to membrane fouling caused by the decrease of membrane flux. Membrane fouling is reversible (or irreversible) deposition (including plugging, adsorption, the formation of filter cake, precipitation, etc.), in the membrane surface or in the membrane pores due to mechanical or physicochemical interactions existed among trapped micelles, particles, suspensions, milk filtrates, salts and macromolecules, resulting in smaller or blocked membrane pore size to make an irreversible change in membrane separation and permeation flux.

4.3. Membrane fouling and cleaning
After the end of the experiment, then clear water permeation flux of nanofiltration membrane was measured through the water with the experiment. It is calculated that through the clear water permeation flux J was 40.91 L/(m²·h), the membrane flux is reduced by 71%. The data show that during the nanofiltration concentration process with preservative soaking wastewater, the original nanofiltration membrane is easily contaminated by some pollutants in the wastewater, which leads to the decrease of separation performance and the increase of operation cost, and the pollutants include organic pollutants, microorganisms pollutants, inorganic contaminants, etc[6].

Chemical cleaning is an important way to reduce pollution, and the concentration and cleaning time of chemical reagent depends on the chemical resistance of nanofiltration membrane. Common chemical cleaning methods include chelant cleaning, acid-base cleaning, surfactant cleaning and oxidant cleaning, Enzyme cleaning and salt washing[7]. In membrane separation operations, contamination begins when the feed is in contact with the membrane. When the membrane module is operated for a period of time, the permeation flux and the separation performance of the membrane are both decreased. Membrane cleaning can make the membrane performance parameters to restore as much as possible and prolong the service life of the membrane[8].

The two stage cleaning method is used in this experiment. That is, firstly the nanofiltration membrane is immersed in 0.1% sodium hypochlorite for 6 hours, and the sodium hypochlorite of the same concentration is exchanged once among these six hours to measure the permeation flux of the nanofiltration membrane; Then making the nanofiltration membrane immersed in clean water for 6 hours one more time, change the clear water every 2 hours to measure the permeation flux of the nanofiltration membrane; Finally, making the nanofiltration membrane immersed in sodium hydroxide solution for 6 hours to measure the permeation flux of the nanofiltration membrane. After 6 hours, the
membrane was rinsed with deionized water to remove organics from the membrane surface and residual sodium hypochlorite, which is as shown in Figure 6.

![Figure 6. Chart of permeate flux before and after NF membrane pollution](image)

It can be seen from Figure 6 that after using sodium hypochlorite solution to wash, the permeation flux of the nanofiltration membrane was recovered to 90.64 L/(m²·h); after it was soaked in clear water, using sodium hydroxide solution to clean it, so that the permeation flux of the nanofiltration membrane was restored to 102.85 L/(m²·h), corresponding to 73.76% of the new membrane. The analysis suggests that the decrease of membrane permeation flux is mainly caused by organic matter and microorganisms blocking membrane pores and accumulating on the membrane surface to form cake layer. Simple physical cleaning can only remove the loose physical adsorption adsorbed on the membrane surface; sodium hypochlorite and sodium hydroxide are commonly cleaning agents, which can effectively remove the formation of pollution formed by the adsorption and adhesion of organic layer and microorganisms in the membrane surface. However, there is still some membrane permeation flux can not be restored, and the irreversible pollution is a number of small molecular weight organic matter and microorganisms plug the membrane pores, so that the membrane pores become smaller and the membrane resistance increase, both of which make the water flux decrease, this part of the pollution is difficult to remove by physical and chemical cleaning.

5. Conclusion
In this study, the preservative soaking wastewater was treated by combined ultrafiltration-nanofiltration, and analyse the influence of different concentration times of dialysates on on the COD of dialyzate, total phosphorus, ammonia nitrogen and membrane permeation flux after the wastewater was concentrated by nanofiltration, besides the influence of operating conditions on the performance of nanofiltration membrane was investigated. The main conclusions are as follows:

Through chemical analysis, some components in preservative soaking wastewater were discussed. Through the combined ultrafiltration-nanofiltration, the membrane flux can be kept at a good level when the concentration ratio is 4 times, the COD removal rate can reach 87%, the total
phosphorus removal rate can reach 90%, and the ammonia nitrogen removal rate can reach 63%. With prolonged operation, membrane permeation flux will decrease. After soaked and cleaned with sodium hydroxide solution, membrane permeation flux can recover to 73.76%.

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