Research on the Ultrafiltration and Removal of Aniline via the Compound of Sophorolipid and Rhamnolipid

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Abstract: In this paper, a biological surfactant composed of sophorolipid and rhamnolipid is used as an enhanced ultrafiltration treatment for simulated aniline wastewater and the impact of the surfactant concentration, feed liquid aniline concentration, surfactant compound ratio, solution pH value and operating pressure on the aniline rejection rate and permeation flux is analyzed. The research results showed that the biological surfactant compound was able to remove aniline. The removal effect of aniline was considerable when the aniline concentration was 150 mg/L, the surfactant concentration was 0.8 mmol/L and the surfactant compound ratio was 0.1. The pH value had a significant impact on the aniline rejection rate. However, the operating pressure had little impact on the aniline rejection rate, although it exerted a considerable influence on the permeation flux.

1. Introduction
Chemical production processes related to pharmaceutical production, printing, dyeing, petroleum refining, etc. produce a considerable amount of aniline wastewater that can cause serious pollution hazards to humans and animals in the case of direct discharge [1-3]. Aniline wastewater has a considerable influence on wild animals and humans because of its obviously toxic, carcinogenic and mutagenic properties. In addition, aniline wastewater can further accumulate in the body because of its biological insolubility and high water solubility. Aniline wastewater is classified as a persistent organic pollutant [3-4]. Therefore, the treatment of aniline wastewater is of great practical significance. The
treatment methods of aniline wastewater mainly include chemical oxidation, biochemical treatment, membrane separation, light degradation, etc. [5-10]. Among membrane technologies, micellar enhanced ultrafiltration (MEUF) technology is a high-efficiency hot water treatment technology. MEUF technology presents low energy consumption, is easy and simple to implement, and is capable of effectively removing refractory organics in wastewater [11-12]. MEUF technology has broad application prospects. Compared with chemical surfactants, biological surfactants are more suitable for application in MEUF because of their characteristics, including biological degradation, renewability, environmental protection, etc. [13]. In this study, an environmentally friendly biological surfactant compound of sophorolipid and rhamnolipid was used to remove the organic pollutant aniline and the impacts of the biological surfactant concentration (surfactant concentration for short), feed liquid aniline concentration, surfactant compound ratio (i.e., the proportion of sophorolipid in the total concentration of surfactants (α)), solution pH value and pressure on the aniline rejection rate and permeation flux were evaluated.

2 Experiments

2.1 Experimental reagents and devices
Reagents: Aniline was purchased from Shanghai Hushi Chemical Co., Ltd. and used as the analytical reagent; rhamnolipid was purchased from Huzhou Zijin Biotechnology Co., Ltd.; and sophorolipid was purchased from Xi’an Kono Chemical Co., Ltd.

Devices: The membrane device used in the experiment was the FlowMem-0015 ultrafiltration flat membrane small test equipment, which was provided by Xiamen Fumei Technology Co., Ltd. See [14] for the main performance parameters of the FlowMem-0015 ultrafiltration flat membrane small test equipment and ultrafiltration membrane.

2.2 Experimental process
At room temperature (25°C), a certain amount of rhamnolipid and sophorolipid were weighed and added to the simulated aniline wastewater, which was then evenly stirred and set aside for 20 minutes for ultrafiltration. Simulated wastewater entered the membrane module through a membrane pump. The concentrated solution reflowed to the feed chute for further ultrafiltration. The penetrating fluid was collected by a special container. Under a certain pressure, the permeation flux was measured after 20 minutes of operation, and then a moderate amount of penetrating fluid was collected to measure the concentration of aniline. See Figure 1. for the experimental process.
3 Experimental results and discussion

3.1 Impact of aniline concentration on MEUF

When the surfactant concentration in the feed liquid was 0.5 mmol/L, the α value was 0.1. The change in aniline rejection rate based on the initial concentration of aniline in the feed liquid is shown in Figure 2.

As the influent aniline concentration increased, the aniline rejection rate (RAN) first increased and then decreased. When the initial concentration of aniline was less than 150 mg/L, the RAN showed an increasing trend from 7.4% to 28.6% because a number of micelles were observed in the solution when the surfactant concentration was 0.5 mmol/L. When the initial concentration of aniline increased from 10 mg/L to 150 mg/L, the excessive micelles in the wastewater solubilized the aniline molecules and rejected more aniline. When the aniline concentration was greater than 150 mg/L, the interiors of the micelles in wastewater tended to be saturated. Therefore, the number of aniline molecules that could not be solubilized by micelles increased, which led to a decrease in the RAN.

Figure 1. Schematic of micelle enhanced ultrafiltration process.
Figure 2. Impact of the feed liquid aniline concentration on the aniline rejection rate and permeation flux.

The permeation flux ($J$) gradually decreased as the initial concentration of aniline in solution increased. When the aniline concentration changed between 10 mg/L and 200 mg/L, the $J$ decreased from 30 L/m$^2$·h to 19.6 L/m$^2$·h. Moreover, an increase in the initial concentration of aniline aggravated the membrane pollution.

3.2 Impact of surfactant concentration on MEUF

Figure 3. Impact of the surfactant concentration on the aniline rejection rate and permeation flux.

As displayed in Figure 3, the $R_{AN}$ first increased rapidly and then decreased as the surfactant concentration increased. The molecular weight of aniline in wastewater was much smaller than the molecular weight cut off (MWCO) of the ultrafiltration membrane. Therefore, aniline molecules would outflow through the ultrafiltration membrane when surfactants were not added to wastewater.
As a result, the $R_{AN}$ was close to 0, although it increased to 20.4% when the surfactant concentration increased from 0 to 0.3 mmol/L. The $R_{AN}$ increasing trend was gentle with the further increases in the surfactant concentration. When the surfactant concentration was 0.8 mmol/L, the $R_{AN}$ reached the maximum value of 24.4%. When the surfactant concentration varied from 1.0 mmol/L to 1.5 mmol/L, the $R_{AN}$ started to show a downward trend, which might have been related to a change in the shape of the micelles in wastewater under high surfactant concentrations. The particle size reduced from the previous spherically shaped micelles to slender rod-shaped micelles. Therefore, the micelles solubilizing aniline molecules could not be rejected by the membrane and would outflow along with water.

The $J$ was reduced by more than half when surfactants were initially added to the feed liquid. The declining rate of the $J$ decreased when the surfactant concentration was greater than 0.5 mmol/L. Initially, the $J$ presented a sharp drop, which might have been related to the absorption of the added surfactants by the ultrafiltration membrane or membrane pollution caused by the effect of concentration polarization, which then led to a decline in the membrane flux[15]. The particle size of the micelles gradually decreased with further increases in the surfactant concentration and might have led to the blockage of membrane pores by micelles with a similar size as the pores, which thus affected the $J$.

3.3 Impact of the surfactant compound ratio on MEUF

The impact of different $\alpha$ values on the $R_{AN}$ when the surfactant concentration was fixed at 0.8 mmol/L is shown in Figure 4. The $R_{AN}$ first increased and then decreased with an increase in the proportion of sophorolipid in the total concentration of surfactants. The $R_{AN}$ rate rose from 17.4% to 24.4% when the proportion of sophorolipid in the total concentration of surfactants increased from 0 to 0.1. The $R_{AN}$ gradually decreased when the proportion of sophorolipid in the total concentration of surfactants was greater than 0.1 because the dosage of added sophorolipid was too large, which produced a stereo-hindrance effect. Sophorolipid was rejected by the mixed system, which led to an increase in the CMC of the mixed system and a decline in the number of formed micelles; in addition, such conditions would reduce the diameter of the micelles in solution and cause part of the micelles to outflow through the membrane pores, thereby reducing the $R_{AN}$. The $R_{AN}$ was the largest when the sophorolipid concentration accounted for 0.1% of the total concentration of surfactants, which might have been related to the good combination of rhamnolipid and sophorolipid generating a small CMC in the compound system. Therefore, additional micelles could be generated and additional aniline could be solubilized under the condition of the same surfactant concentration.
Figure 4. Impact of the surfactant compound ratio on the aniline rejection rate and permeation flux.

The J first decreased and then increased as the $\alpha$ value increased, and it subsequently increased from 25.2 L/m$^2$·h to 58.9 L/m$^2$·h because of an increase in the proportion of sophorolipid in the total concentration of surfactants, a decrease in the number of micelles in solution and a reduction in the membrane pollution.

3.4 Impact of pH value on MEUF

As shown in Figure 5, the $R_{AN}$ first decreased and then slowly increased as the pH value of the feed liquid increased. The $R_{AN}$ presented a downward trend when the pH value varied from 4 to 7. The MEUF process had the best rejection effect on aniline, and the $R_{AN}$ was 41.1% when the pH value was 4 because aniline can hydrolyze a considerable amount of H$^+$ in water under acidic conditions and thereby generate positively charged aniline ions. Therefore, micelles in wastewater could not only remove aniline molecules through a solubilization effect but also absorb aniline ions on the surface of micelles via electrostatic adsorption and reject more aniline. Under alkaline conditions, the $R_{AN}$ increased, which might have been related to the good solubility of rhamnolipid under alkaline conditions and the subsequent increase in micelle formation and aniline solubilization.

The figure clearly shows that the J value continually increased as the pH value increased. When the pH value rose from 4 to 10, the J increased from 4.8 L/m$^2$·h to 33.7 L/m$^2$·h, which was mainly because the increase in pH value promoted the dissolution of rhamnolipid in solution and reduced the viscosity of the solution. Thus, the pH value had a significant impact on the J.
3.5 Impact of the operating pressure on MEUF

Changes in the $R_{AN}$ and $J$ value under changes in the operating pressure while the other operating conditions remained unchanged are shown in Figure 6. The $R_{AN}$ showed no obvious changes when the pressure rose from 0.2 MPa to 0.4 MPa. Thus, the operating pressure had no significant impact on the $R_{AN}$. The $J$ value also continued to increase as the operating pressure increased, and it presented a value of 25.2 L/m²·h when the pressure was 0.2 MPa and almost doubled to 51.1 L/m²·h when the pressure rose to 0.4 MPa.

Figure 5. Impact of the pH value on the aniline rejection rate and permeation flux.

Figure 6. Impact of the operating pressure on the aniline rejection rate and permeation flux.
4 Conclusions

- The RAN increased as the initial concentration of aniline varied from 10 mg/L to 150 mg/L and presented a downward trend when the initial concentration of aniline in the feed liquid was greater than 150 mg/L. The J value continually decreased as the initial concentration of aniline in wastewater increased.
- The RAN continued to increase when the surfactant concentration varied from 0 mmol/L to 0.8 mmol/L. The RAN started to decrease when the surfactant concentration was greater than 0.8 mmol/L, and the J value rapidly decreased and then slowly reduced as the surfactant concentration increased.
- The RAN showed an increasing trend when α varied from 0 to 0.1 and began to decrease when the α value was greater than 0.1. The J initially decreased and then increased with increases of α.
- The RAN first decreased and then slowly increased as the pH value of the simulated water increased. Under acidic conditions, the removal effect of aniline was good because acidic conditions were beneficial to the hydrolysis of aniline and thus produced positively charged aniline ions, which were absorbed by micelles via electrostatic adsorption. Thus, additional aniline was removed. Moreover, the J value continued to increase with increases in the pH value.
- The RAN showed almost no changes as the operating pressure increased. Pressure had a significant impact on the J value, which linearly increased as the operating pressure increased.

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