Methylated liquor treatment process in caffeine production

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Abstract. The caffeine production process produces a large amount of sodium methyl sulphate in the methylated mother liquor. In order to recycle this part of ingredient, we use the mother liquor of Shijiazhuang Xin Nuowei Pharmaceutical Co., Ltd. as the object of study, the use of "nanofiltration (NF) - Dish Type Reverse Osmosis (DTRO) " combination of membrane technology for desalination and concentration. The experimental results show that the concentration of sodium sulfate in the nanofiltration solution is 0.37 g • L -1, the rejection rate is 98%, and the concentration of sodium methyl sulfate in DTRO concentrated solution is 453.80 g • L -1, which meets the requirements of the enterprise.

1. Introduction
In the extraction process of caffeine production, there is a lot of residual sodium methyl sulphate in the mother liquor, also containing the sodium sulfate from the upstream process [1]. Sodium methyl sulfate is the main source of COD in waste water, and it is also a chemical product with high economic value. It can be used to prepare chemical products such as tromethamine, nitromethane and hydroxylamine hydrochloride [2-3]. Caffeine production enterprises are mostly remove the sodium methyl sulfate in the waste water by the biological method, which led to the waste of resources. In last decade nanofiltration(NF) and Dish-type reverse osmosis (DTRO) were extensively used for treatment of landfill leachate. Its removal efficiency of COD, ammonium and metals is up to 100%[4]. In this paper, desalination and concentration are carried out using the combined membrane process of "nanofiltration(NF) + Dish-type reverse osmosis (DTRO)" for the methylated mother liquor in caffeine production.

2. Materials and methods

2.1. Materials
The methylated mother liquor in caffeine production was provided by Shijiazhuang Pharmaceutical Group Xin Nuowei Pharmaceutical Co., Ltd., the pH of the solution was 7.65, the content of sodium methyl sulfate was 124.76 g • L-1, the content of sodium sulfate was 14.30 g • L-1.

2.2. Experimental process
The nanofiltration membrane used in the experiment was GE2540-1-600PSI, the effective membrane area was 2.5m², which was a roll membrane module. The diameter of the DTRO film was 8 inches, the length of the membrane was 1400mm, and there were 209 diaphragms and 210 diversion plates. It’s the high pressure disc type membrane column. The experimental device flow was shown in Figure 1.
In the beginning, the raw material liquid in the security filter and heater was driven by the feed pump, to achieve the initial filtration of raw material and heat transfer. The high pressure pump could provide pressure to the nanofiltration desalting process. The concentrate and the permeate were simultaneously returned to the feed tank. Nanofiltration membrane having selective permeability, monovalent salts were not completely trapped by the nanofiltration membrane, and the nanofiltration membrane had a high rejection for divalent salts. The sodium sulphate in the mother liquor was removed by the nanofiltration membrane and then the permeate liquid was fed to the DTRO for multiple enrichment. Reverse osmosis membrane could effectively retain all the inorganic salts, after treatment of the liquid could be re-used in the production process. Concentrated sodium methyl sulfate solution could be sent to the chemical plant for further processing, the permeate liquid was used in the production process.

2.3 Analysis and testing equipment
DTRO membrane, PT160-90P, Beijing Xin Bai Li Technology Development Co., Ltd.; nanofiltration membrane, GE2540, Beijing Xin Bai Li Technology Development Co., Ltd.; electronic balance (accuracy of 0.001 g), RP3002K, China; water quality monitor, CIC-100, China; ion chromatography, CIC-100, Qingdao Sheng Han Chromatography Technology Co., Ltd.

3. Experimental results and discussion
3.1 Effect of working pressure on nanofiltration desalination process
Under the condition of feeding flow rate of 8.0 L • min -1 and temperature of 25 ℃, the working pressure was changed to study the relationship between the indexes of the nanofiltration membrane and the working pressure. Calculate and collate the data, the results were shown in Figure 2, Figure 3 and Figure 4.

It could be seen from Figure 2, the pressure in the range of 2.2MPa to 2.6MPa. With the pressure rising, sodium sulfate retention rate gradually increased; and with the pressure change from 2.6MPa to 3.0MPa, the retention rate remained essentially unchanged. This was because the nanofiltration membrane was further compacted as the pressure increases, and the pore size of the membrane becomes smaller, and the charge density in the membrane surface and membrane pore size increased, thereby increasing the rejection of the nanofiltration membrane. And when the pressure reaches
Figure 2. Effect of working pressure on removal rate of sodium sulfate and penetration rate of sodium methyl sulfate.

Figure 3. Effect of working pressure on concentration of sodium sulfate and sodium methyl sulfate in the permeate liquid.

Figure 4. Effect of working pressure on membrane flux.

2.6MPa, the concentration polarization phenomenon was aggravated, which reduced the rejection rate of nanofiltration membrane [5]. The transmittivity of sodium methylsulfate increased over the entire pressure range. This was because the nanofiltration membrane was a kind of selective membrane, membrane pore size changes impact a little to the selection [6]. At the same time, the charge resistance of the monovalent ions was small and much easily penetrate the nanofiltration membrane into the permeate.

It could be seen from Fig. 3 that the concentration of sodium methyl sulfate in the permeate decreases gradually as the pressure increases. Because the increase in pressure, the amount of liquid passing through the nanofiltration membrane increase. The concentration of both sides of the membrane impact the flux of salt, not the pressure [7]. When the pressure increases, the amount of liquid through increase, salt flux was basically the same, so the concentration of sodium methyl sulfate solution decreased.

The content of sodium sulfate in the solution had been low throughout the pressure range. In the range of 2.0MPa to 2.8MPa, its content remained basically unchanged; when the pressure reached
3.0MPa, the concentration of sodium sulfate increased sharply. This was because the nanofiltration membrane had excellent trapping ability for divalent ions. Before 2.6MPa, the retention effect was the dominant factor, and the concentration in the permeated solution did not change much. After the pressure reaches 2.6MPa, the concentration of concentrated liquid was gradually reduced, and the salt concentration did not change much, so the concentration of concentrated solution increases. At the same time, the effect of high pressure was that the concentration polarization near the nanofiltration membrane was strengthened, with the concentration increased, the membrane performance remained unchanged, the retention rate remained essentially unchanged, resulting in the liquid concentration was also a corresponding increase.

As could be seen from Fig. 4, the membrane flux increases as the working pressure increases. This was because the driving force of nanofiltration separation was the pressure difference on both sides of the membrane, the pressure increases, and the driving force of the nanofiltration membrane separation process was enhanced. When the pressure reached 2.6MPa, the increase trend of membrane flux slowed due to the influence of concentration polarization and membrane contamination.

3.2 Effect of feeding flow on nanofiltration desalination process

![Figure 5. Effect of flow capacity on removal rate of sodium sulfate and penetration rate of sodium methyl sulfate.](image1)

![Figure 6. Effect of flow capacity on concentration of sodium sulfate and sodium methyl sulfate in the permeate liquid.](image2)

![Figure 7. Effect of flow capacity on membrane flux.](image3)
Under the condition of working pressure of 2.6MPa and temperature of 25 ℃, the feed flow was changed and the relationship between the indexes of the nanofiltration membrane and the feed flow was studied. Calculated and collated the data, the results were shown in Figure 5, Figure 6 and Figure 7.

It could be seen from Figure 5, with the increase in the flow rate, the sodium sulfate retention rate remained essentially unchanged, the sodium methyl sulfate transmittance gradually increased, when the flow reached 8.0 L • min -1, the transmittance increased trend slow down. This was because the increased of the flow rate made the solution flow rate on the surface of the nanofiltration membrane increase, could reduce the surface of the membrane deposition of various ions [8], so as to effectively reduce the nanofiltration membrane surface polarization and membrane contamination. But the feed flow should not be too high, because when the feed flow was too high, the membrane surface along the resistance loss will increase, affecting the size of membrane flux. So the flow rate should be 8.0 L•min⁻¹.

It could be seen from Fig. 6 and Fig. 7 that the concentration of sodium sulfate was not affected as the feed flow rate increases, and the concentration of sodium methylsulfate in the solution changes slowly before L·min⁻¹ after the drop significantly. This was because the feed flow rate was too large, the membrane surface along the resistance loss will increase, the membrane driving force decreases, the liquid concentration was also reduced accordingly.

### 3.3 Effect of temperature on nanofiltration desalination process

Under the condition of working pressure of 2.6MPa and feed flow rate of 8.0 L·min⁻¹, the feed flow was changed and the relationship between the indexes of the nanofiltration membrane and the temperature was studied. Calculate and collate the data, the results are shown in Figure 8, Figure 9 and Figure 10.

![Figure 8. Effect of temperature on removal rate of sodium sulfatend penetration rate of sodium methyl sulfate.](image_url)

It could be seen from Fig. 8 that the effect of temperature on the rejection of sodium sulfate and the transmittance of sodium methyl sulfate was very small. This was because the pressure and feed flow conditions were selected properly, the temperature changed on the permeability of the nanofiltration membrane is not obvious. It could be seen from Fig. 9 and Fig. 10 that the increase of the internal energy of the temperature would further reduce the viscosity of the solution and increase the diffusion coefficient of the solution [9], which reduced the influence of the concentration polarization, meanwhile the flow resistance of the solution would also be reduced, causing increased membrane flux. Taking into account the experimental operation and operation of the device and other factors, the operating temperature selected at 25 ℃.
3.4 Continuous experiment

According to the analysis, the optimum process conditions were obtained. The continuous nanofiltration membrane desorption experiment was carried out. The working pressure was 2.6 MPa, the feed flow rate was 8.0 L • min^{-1}, and the temperature was 25 ℃. The operation time is 28 minutes, and the results are shown in Figure 11 and Figure 12.

As could be seen from Figure 11, as time increases, the membrane flux begins to decrease. This was due to the solution concentration. Permeate volume gradually increased, while the concentration of concentrated liquid gradually decreased, the concentration of raw material gradually increased, concentration polarization and membrane fouling and other effects would be strengthened, indirectly increased the resistance of nanofiltration process, and caused a decrease in membrane flux [10-11].

As could be seen from Figure 12, the concentration of sodium methyl sulfate was increasing and the transmittance was almost constant. This was because the concentration of this experiment was not high, the concentration of sodium methyl sulfate in the osmotic pressure was basically the same, under certain conditions of pressure, its transmittance also remained unchanged. After the nanofiltration membrane was desalted, the components of the concentrate and the permeate were shown in Table 1.
Table 1. The result of continuous desalting experiment by nanofiltration membrane

| project       | volume V·L⁻¹ | C(Na₂SO₄)/ (g·L⁻¹) | C(CH₃SO₄Na)/ (g·L⁻¹) |
|---------------|--------------|---------------------|----------------------|
| Stock solution| 50           | 14.30               | 124.76               |
| Permeate      | 40           | 0.37                | 116.02               |
| Concentrate   | 10           | 60.71               | 153.83               |

The solution was sent to a DTRO device for concentration experiments. The working pressure was chosen to be 6 MPa, the feed flow rate was 5.4 L·min⁻¹ and the temperature was 25 °C. The operation time was 12 minutes, and the experimental data was sampled at a fixed time. The results were shown in Figure 13 and Figure 14.

![Figure 13](image1.png)  
**Figure 13.** The influence of time on membrane flux.

![Figure 14](image2.png)  
**Figure 14.** Effect of running time on concentration and removal rate of sodium methyl sulfate in the penetrating solution.

As could be seen from Fig. 13, the membrane flux remains constant as time increases. Concentration was carried out for 8 minutes, and the membrane flux began to decrease, which was due to the gradual increase in the volume of the permeated liquid as the concentration progressed, and the volume of the concentrate gradually decreased. DTRO membrane had a good concentration and anti-pollution properties, pre-membrane flux was basically unchanged. DTRO membrane had a good ability to concentrate, the liquid components were basically retained in the concentrated liquid, the concentration gradually increased.

It could be seen from Fig. 14 that under the condition of constant operating pressure, the effect of late concentration polarization and membrane fouling became more and more obvious, the membrane flux would begin to decrease and the rejection rate will gradually decrease, but the overall change was not Big. After concentration of DTRO process, the concentration of sodium methyl sulfate in the solution reached 453.80 g·L⁻¹, which meets the requirements of industrial use.

4. Conclusions
The effect of nanofiltration on the separation was studied. The experimental results showed that the nanofiltration membrane had a good ability to separate these two salts, and the optimum technological conditions for the nanofiltration operation were the working pressure 2.6MPa, feed flow rate 8.0L·min⁻¹, temperature 25 °C. After 28 minutes of continuous desalination, the concentration of sodium sulfate in the solution was 0.37 g·L⁻¹ and the rejection rate was 98%. After concentration of DTRO device, the concentration of sodium methyl sulfate in the solution reached 453.80 g·L⁻¹.
References

[1] Zhu Zhaoyou and Ma Yixin 2008 Treatment of Caffeine Nitrous Wastewater by Fenton Reagent J. Journal of Qingdao University of Science and Technology(Natural Science Edition) 29(3) 217-219

[2] Wang Guoping 2016 Synthesis of anisole from phenol and sodium methyl sulfate a by product from synthesis of medicine intermediates J. Petrochemical Technology 45(11) 1337-1340

[3] Yu Lu and Lu Tao 2000 The Improvement of Nitromethane Synthesis J. Chemical Engineering & Equipment 20(3) 38-41.

[4] Dolar, D., Košutić, K., & Strmecky, T. 2016 Hybrid processes for treatment of landfill leachate: coagulation/uf/nf-ro and adsorption/uf/nf-ro J. Separation & Purification Technology 168 39-46.

[5] Liu Dongfang, Chen Lu and Ji Tao 2003 Nanofiltration Membrane Concentration Polarization and Fouling for Treatment of High Concentration Industrial Waste Liquid J. Urban Environment & Urban Ecology 16(1) 16-18

[6] Li Wei, Zhan Xia, Li Jiding and Zheng Dongjtu 2011 Experimental Study on Nanofiltration Treatment of High-concentration Acrylonitrile Industrial Wastewater J. Chemical Engineering(China) 39(11) 79-82

[7] Zhang Xinhui, Yuan Qipeng, Fang Li and Yang Xiaojin 2004 Experimental Studies on Transport Flux and Rejection for Nanofiltration in Organic Solvents J. Journal of Beijing University of Chemical Technology 31(6) 5-8

[8] Yang Qingjuan, Wei Hongbin, Wang Zhihai, Zou Ping and Chen Liangcai 2009 Pilot Study on Removal of Inorganic Ions from Drinking Water by NF Membrane J. China Water & Wastewater 25(5) 52-55

[9] Li Yuxian, Zhang Jiale and Liu Jinhao 2011 Study on Optimum Route of Extrating Caffeine by Orthogonal Experiment J. Laboratory Science 14(2) 105-107

[10] Yin Jian, Tong Zhangfa, Chen Zhichuan and Peng Juan 2013 Study on Treatment of Micro-etching Wastewater by DK2540 Nanofiltration Membrane J. Science & Technology in Chemical Industry 21(4) 27-30

[11] Sha Wenbo, Feng Hui, Wu Huning, Yu Yue and Wang Xiaolin 2005 Desalination of Active Dye Solution with Nanofiltration Membrane J. Journal of Nanjing University of Technology 27(1) 97-100