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Characteristics and application of multiple membrane process in plating wastewater reutilization

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Abstract

A multiple membrane process aimed at reutilization of plating combined wastewater after physical and chemical pretreatment in mechanical industry was developed for selective separation to reduce cost and mitigated the increasing heavy metal pollution. The process was divided into three stages: firstly, microfiltration (MF) and ultrafiltration (UF) was used to separate the possible organic and suspended matters, secondly, electrodialysis (ED) was carried out for effective desalination, and thirdly, the concentrate from ED was treated by nanofiltration (NF) and reverse osmosis (RO) separately to increase the recovery rate of water. Results showed that filtration characteristics of UF membrane here was not so good as usually, even if compared with MF membrane. And RO performed better than NF in wastewater separation, especially in anti-compacting ability of membrane. Since the rejection rate of heavy metal ions and COD in ED/RO process is high, all the product water exceeded the related qualification and could be reused as cooling water in industry.

Keywords: Plating wastewater; Multiple membrane process; Separation; Reuse

1. Introduction

In mechanical industry, especially in plating sector, large amounts of wastewater which contains many chemical additives and heavy metals are often generated [1]. In order to meet legislative discharge requirements, plating wastewater is usually treated with physical and chemical method, or most commonly followed by biochemical ways such as the activated sludge method, but the treated wastewater is still highly saline and cannot be reused as industrial cooling water [2]. Therefore, in order to produce qualified water that can be recycled in production line, secondary effluents from ordinary wastewater plant needs more advanced and efficient treatments. One of them

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is the membrane separation, which has become increasingly attractive for treatment and recycling of wastewater in mechanical industry as it is highly efficient, easy to operate and of low cost [3].

Electrodialysis (ED) is an electromembrane process in which ions are transported through ion permeable membranes from one solution to another under the influence of a potential gradient. It has been an effective way for desalination of water and wastewater, for example, A. Guvenc et al. [4] used ED to remove silver ions from model solutions and wastewater. In spite of its significant desalting performance, fouling of ion-exchange membrane is one of the most important considerations in operation. It is known that most surfactants existing in effluent from plating plant have negative charges and thus anion-exchange membranes are often fouled by deposition. As pretreatment, microfiltration (MF) and ultrafiltration (UF) has been widely used for separating suspended solids and prevent membrane fouling [5]. Since the concentrate from ED has an equivalent volume to be diluted before charging, an application of reverse osmosis (RO) or nanofiltration (NF) can further be used for desalination and purification, for example, J.J. Qin et al. [6] reported a method for reclaiming wastewater containing copper, zinc and nickel from metal finishing using UF and RO combined processes together with precipitation, resulting in a high water recovery of 95%.

In this study, more combined processes with MF/UF, ED and NF/RO membranes were investigated, not only to improve the quality of recycling water as a feed in industrial cooling system, but also to increase the water recovery rate in wastewater treatment and cut down the increasing heavy metal pollution discharging from plating workshop.

2. Materials and methods

2.1. Industrial effluents tested

The secondary effluent from the Jiaxin Mechanical Factory sewage treatment plant was collected and used as feed water. The sewage was very complicated and usually contained high content of spent solvent, acid and plating rinses. The effluent was initially treated by screening, neutralization, sedimentation, flocculation/coagulation and sand filtration, but still contained a great deal of salt and a high COD up to 300 mg/L, which can not reach the legislative primary discharge standard of 100 mg/L [7].

2.2. Membranes and equipments

The main characteristics of the different membranes selected are shown in Table 1. All the

Table 1
Characteristics of different membranes

Filtration	Membrane type	Materials	Pore sizes/MWCO[a]
MF	CN-CA	Cellulose nitrated-cellulose acetate	0.45 μm; 1 μm; 3 μm
MF	N6	Nylon-6	0.45 μm; 1 μm; 3 μm
UF	PAN700	Polyacrylonitrile	70 kDa
UF	PES200	Polyethersulfone	20 kDa
NF	Desal DL-4040, Osmonics	Composite membrane	NA[b]
RO	BW36-4040, Filmtech	Composite membrane	NA[b]
ED	Ion exchange membrane, SCEF	Polystyrene	NA[b]

[a]Molecular weight cut-off.
[b]Not available.

membrane materials were chosen according to the former experiments and relative experience from past practice. MF/UF membrane (RDCWTT, Hangzhou and SINRAS, Shanghai, China) filtration experiments were conducted in a 15 cm^2 flat-sheet cell. NF/RO membrane (Filmtec and Hydraunatics, USA) filtration experiments were conducted in a 70 cm^2 unstirred cell (RDCWTT, Hangzhou, China) connected to a 2 L reservoir. ED experiments were performed in a membrane stack with 15 pairs of heterogeneous polystyrene ion exchange membranes (SCEF, Shanghai, China), whose area is 200 cm^2. The spacer of ED stack was specially designed with two tortuous paths. All the membranes were soaked in pure water for 24 h before use and then inserted to the cell or stack.

2.3. Experiment process

MF and UF cell were working under pressure of 0.03 MPa to separate the possible organic and suspended matters. The products were collected in a reservoir and then treated by ED to desalinate. In ED process, a constant current of 2 A was supplied in the ED stack for operation. Both the flow of feed inlet and concentrate inlet were controlled in the range of 200–300 L/h and then circulated for a set time to achieve a desired concentration [8]. The ED product usually met the standard for industrial cooling water and could be reused directly. The ED concentrate was further treated by NF/RO to aim at increasing the water recovery rate.

NF/RO experiments were carried out at a controlled temperature of 25°C. A high-pressure pump was used to ensure the transmembrane pressure. Usually, NF membrane worked under the pressure of 0.6–2.2 MPa, and RO membrane worked in the range of 2.2–3.0 MPa. The concentrate was recirculated to feed tank, and permeate was analyzed. This procedure is some different from engineering route, in which the concentrate would be pumped to the sewage reservoir to be mixed as feed and the permeate water would be reused in industrial cooling system together with the ED product. Fig. 1 shows the schematic route of experimental multiple membrane processes.

2.4. Sample analysis

The important parameters for water reuse were determined as chemical oxygen demand (COD), conductivity, chlorides, sulfates and heavy metal ions, according to the Water Quality Standard for Industrial Water (GB/T 19923-2005) [9]. The COD value was obtained by a HBA-100 chemical oxidization meter according to the GB11914-89 Standard of China [10]. Heavy metal ions were analyzed by an IRIS Intrepid ICP and anions such

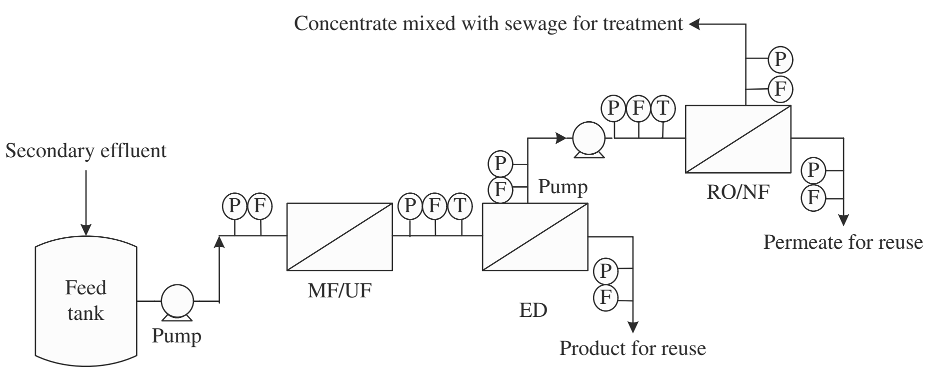

Fig. 1. Schematic route of multiple membrane processes.

as sulfates and chlorides were measured by ionic chromatography using a Metrohm 761 Compact IC with conductivity detection. The conductivity of solution was measured by a DDS-11A conductivity meter (Reiz, Shanghai, China).

3. Results and discussion

3.1. Characteristics of MF and UF filtration

MF/UF was a more effective way than sand filtration to remove the suspended solids and macro molecules of organics still contained in the effluent after secondary treatment of wastewater. This pretreatment procedure was also important for smooth operation of the following membrane separation processes and especially beneficial to avoid fouling of more expensive RO/NF membrane.

The results of the MF/UF experiments are presented in Fig. 2. As it can be seen, all of the membranes could cut down more than half of the COD contents in the feed and showed better separation efficiency than the above mechanical treatments. The CN-CA microfiltration membrane possessed a higher COD rejection rate than N6 membrane, which was very close to the value of PAN700 and PES200 ultrafiltration membrane. Although the UF membrane normally had a smaller pore size with a lower molecular weight cut off than MF membrane, it seemed that no extra performance appeared in treating this kind of secondary effluent from plating workshop. The weak correlation between membrane pore size and COD rejection demonstrated that the pollutant in the feed was either very big molecular organics, or very small dissolved matters such as organic and inorganic salts. This could partly be explained from the filtration results of both CN-CA microfiltration membrane with an average pore size of 0.45 μm and PAN700 ultrafiltration membrane with a molecular weight cut off of 70 kDa, in which the permeate was often accompanied by a significant amounts of dissolved salts when a middle rejection rate of COD of 60% was reached.

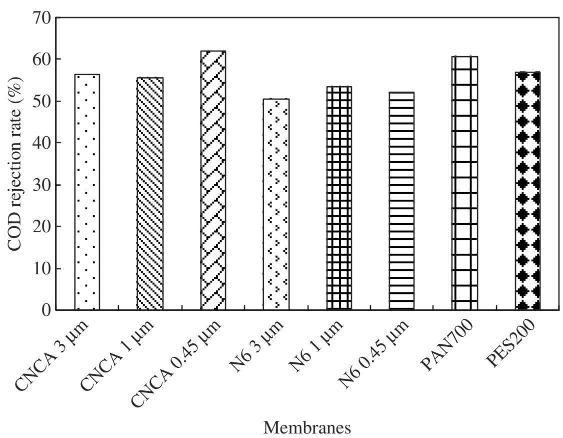

Fig. 2. COD rejection of different ultrafiltration and microfiltration membranes. The histogram refers to COD rejection rate and shows a comparison between MF and UF membrane with different pore size and different materials (operating pressure: 0.03 MPa).

3.2. Treatment with ED unit

3.2.1. Desalination performance

Variation of the effluent conductivity, ion concentration and COD with the operating time in the electrodialysis process is given in Fig. 3. The current was maintained around 2A according to the former experiments and the conductivity and ion concentration of product decreased sharply initially. After 60 min, conductivity leveled off, indicating that the desalting rate sharply decreased and the ED was then stopped and changed to polarity reversal operation to prevent concentration polarization and scaling. In ED step, about 97% of heavy metals, 95% of anions and 85% of COD were successfully removed, which demonstrated excellent separation efficiency. From Fig. 3, the dangerous heavy metals such as Cr^{3+}, Cu^{2+} and Zn^{2+} were quickly and almost completely cut off in products, even if the concentration of feed was very low for chemical sedimentation unable to settle down. The reason why COD could be

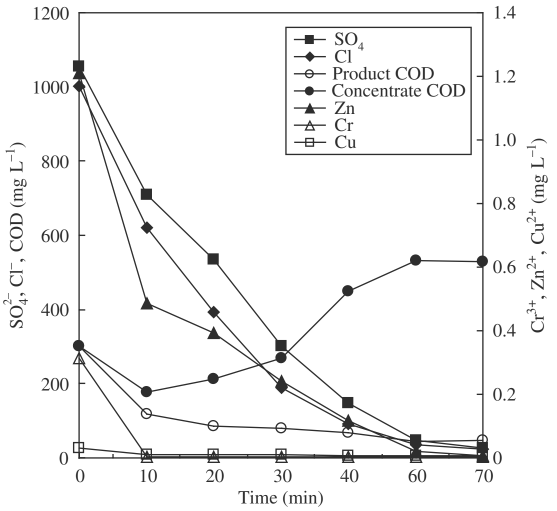

Fig. 3. Change of ion concentration and COD with operating time. The figure implies the varying tendency of concentration of different ions and COD through the ED process.

effectively reduced from the feed was that the pollutants in the solution should be charged dissolved organic or inorganic compounds which could freely migrate from feed to concentration under electric current. The concentrate from ED with a high content of salts, whose electric conductivity was 9600 μS/cm, was further processed in NF/RO treatment.

3.2.2. Relationship between concentration ratio of concentrate to product and current efficiency

A key factor determining the overall efficiency of an ED process is the energy consumed to perform the separation. Here the average current efficiency in circular process was expressed as a ratio of theoretical to practical energy consumption which worked to remove a certain amount of salts. It was then calculated by [11]:

$$\eta = \frac{V \times (C_{\mathrm{di}} - C_{\mathrm{do}}) \times F}{N \times I \times \Delta t} \quad (1)$$

where η is the average current efficiency (%), C_{di} and C_{do} are the concentration of dilute at different time (mol/L); V is the volume of dilute (L), F is the Faraday constant (96500 coulomb), I is the current (A), Δt is the time used (S) and N is the pairs of membranes. The relationship between concentration ratio of concentrate to dilute and current efficiency is given in Fig. 4. As it shows, the current efficiency drastically decreased when concentration ratio of concentrate to dilute increased. As the concentration of dilute turned to be very low, a majority of current might be used to electrolyze water to H^+ and OH^-, which substituted salt ions to transport current chargers, thus resulting in a low current efficiency. In the meantime, the large difference between the concentrate and the dilute often caused concentration polarization and would make a higher resistance for ion migration. Therefore, the ratio of concentrate to dilute should be controlled at an appropriate value for effective separation, for example, the conductivity of dilute was 1100 μS/cm with a low COD value around 70 mg/L and the current efficiency was 50% when the ratio was 7.

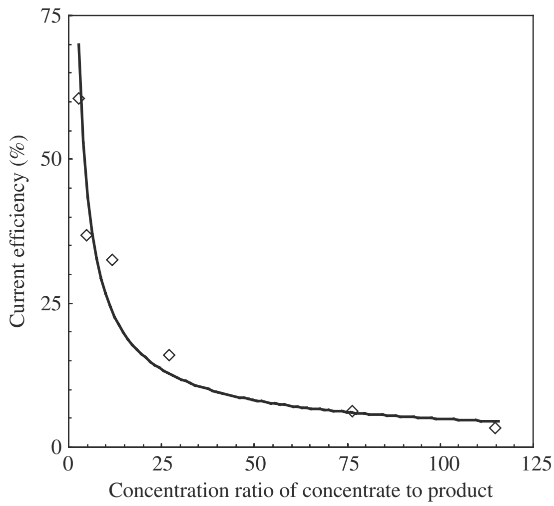

Fig. 4. Relationship between current efficiency and concentration ratio of concentrate to product.

The quality of dilute could easily meet the criteria of industrial cooling water.

3.2.3. Effect of energy consumption on salt rejection

The energy consumption of ED is composed of the energy demand for the separation of ions and the energy demand of pumping, which was not analyzed for the laboratory scale unit because of the unrealistic ratio between the size of the stack and that of the pump and pipe system. As to the separation of ions, energy is used for the transport of ions through solution and membrane and for overcoming the resistance of the electrode compartments. The resistance of the electrodes was not high in this case, because the concentration of NaCl solution used as cathode and anode feed was up to 1000 mg/L. So the electrical energy to transfer ionic species through solution and membrane was the main factor evaluated in the experiment and the relative influence could be described as [12]:

$$W = \frac{U \cdot I \cdot t}{L} \tag{2}$$

where W is the energy consumption (KWh/m^3), U is the voltage (V), I is the current (A), t is the time used (h) and L is the volume of dilute (m^3). The total salt rejection increased as the ED process went on, but the single-grade salt rejection at a set electric current was very different due to the polarizing effect at high concentrations. It can be observed from Fig. 5 that, as the energy consumption increased, the single-grade salt rejection at 2A increased from 30% to 45% first, then dropped below 30% fast with higher energy consumption on the stack. The result showed that the desalting process of ED in sewage treatment should be very different with the conventional one. In order to obtain higher separation efficiency and cut down the operating cost, different electric current should be charged on the stack before the highest salt rejection reached.

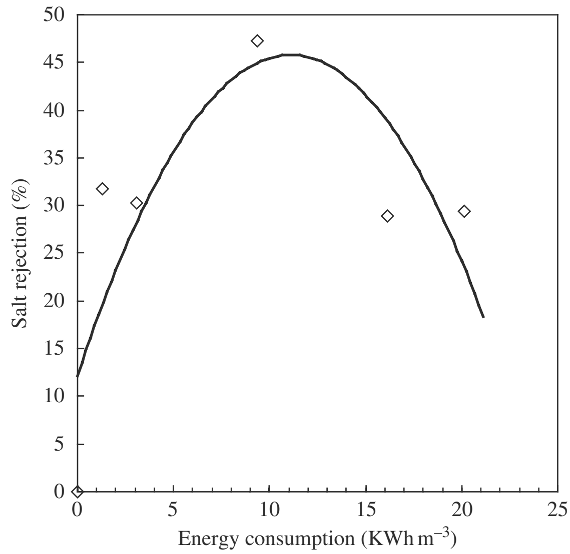

Fig. 5. Variation of salt rejection vs. energy consumption.

3.3. Desalination of NF/RO using ED concentrate as feed

3.3.1. Relationship between rejection and transmembrane pressure

Rejections of Cl^-, SO_4^{2-} and COD were measured in a different pressure range respectively for NF and RO, in which the desalination experiments using the ED concentrate as feed (Fig. 6). As the macromolecule membrane was compressed by increasing operating pressure, the resistance of objects passing through membrane increased, therefore the rejection increased. A wider range of NF is presented in Fig. 6 because NF membrane selected here could run at a very low pressure of 0.4 MPa while RO membrane started desalting at pressure of 1.7 MPa with a feed of 12,500 μS/cm. A steady rejection of COD up to 60.0% and SO_4^{2-} around 98.0% with a low rejection of Cl^- below 20% were also achieved in NF membrane. This certified again that NF membrane usually had excellent separation selectivity between the univalent and bivalent ions. Compared with NF, RO membrane showed good performance on

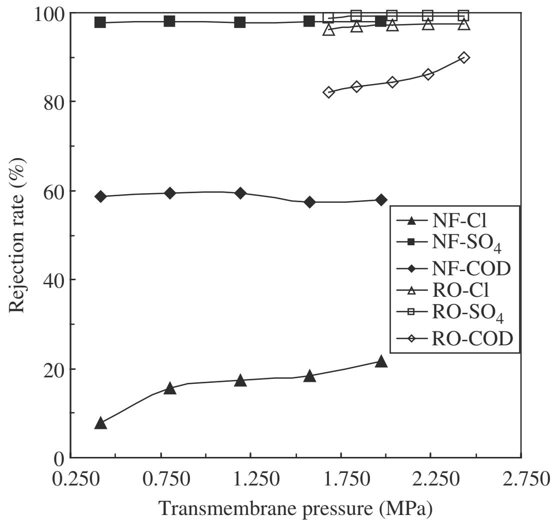

Fig. 6. Rejection rate of different ions and COD vs. transmembrane pressure for NF and RO membrane.

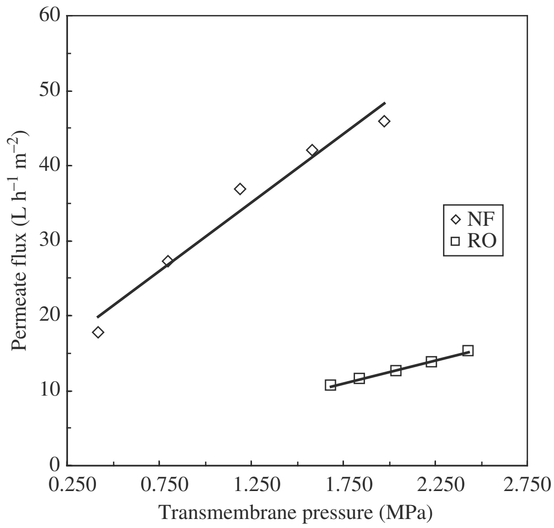

Fig. 7. Effect of transmembrane pressure on permeate flux.

rejection of almost all ions which was up to 98.0%. As RO achieved better COD rejection of 96.4% and its permeate could easily meet the criteria of water reuse while NF was hard to reach, RO membrane should be the first choice here, even if NF membrane could double or triple the permeate flux.

3.3.2. Effect of pressure on permeate flux

Permeate flux is an important parameter in design and economical feasibility analysis of membrane separation processed. When the level of solute rejection is met, the permeate flux becomes a fundamental factor in optimization of the process. The higher the permeate flux of membrane, the lower the filtration area necessary for a certain amount of solution to be processed. Fig. 7 shows that the flux for both NF and RO increased linearly with transmembrane pressure, indicating that the increase in operating pressure will enhance the driving force and then overcome the membrane resistance. The permeability of membrane which described by water transport coefficient can be calculated from following equation [13]:

$$F_w = A \times (\Delta P - \Delta\pi) \quad (3)$$

where F_w is water flux through the membrane (L h^{-1} m^{-2}), A is water transport coefficient, ΔP is transmembrane pressure (MPa), $\Delta\pi$ is osmotic pressure differential across the membrane (MPa). As expected, the permeability of NF at 18.25 L h^{-1} m^{-2} · MPa^{-1} was better than that of RO at 6.15 L h^{-1} m^{-2} · MPa^{-1}. This is consistent with the results that NF membranes usually have higher water flux than RO membranes since the surface of RO membranes are denser and tends to be more compacted to resist the obstacles in solution.

3.3.3. Flux attenuation coefficient

Influence of time on permeate flux was studied by keeping a constant operating pressure, such as NF at 1.4 MPa and RO at 2.8 MPa respectively, while the retentate was recycled to the feed tank. The specific fluxes of NF and RO membrane

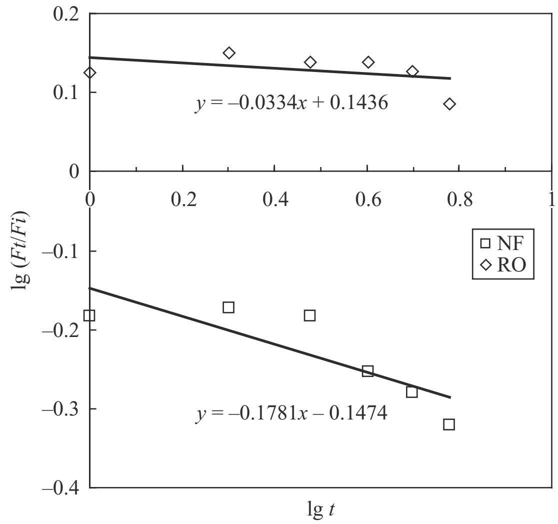

Fig. 8. Variation of lg(*Ft*/*Fi*) vs. lg *t*. The slope of the lines represents the flux attenuation coefficient of NF and RO respectively.

were compared after 6 h operation, and the same experiment were repeated 5 times for comparison. All the data showed a similar flux attenuation tendency. The flux attenuation coefficient (*m*) was then used to illustrate the membrane's compressibility and can be calculated by [14]

$$m = \frac{\lg Ft/Fi}{\lg t} \quad (4)$$

where *Ft* and *Fi* are the flux at t moment (L h^{-1} m^{-2}) and initial flux (L h^{-1} m^{-2}), *t* is the time used (h). The m_{NF} value of 0.1781 and m_{RO} value of 0.0334 can be obtained from the slope of the line in Fig. 8. The lower value of *m*, the slower the flux of membrane attenuates. Therefore, the RO membrane performed a better anti-compacting ability than NF here, which demonstrated that the RO membrane could more easily keep a stable

Table 2
Performance of different membrane processes in treating effluent

Parameter	MF	UF	ED	[a]NF	[b]RO	[c]Std	[d]Std
Conductivity (μs/cm)							
Feed water	–	–	4000	12,500	12,500	–	–
Permeate water	–	–	260	7900	200		
Rejection rate (%)	–	–	93.5	36.8	98.4		
COD (mg/L)							
Feed water	300.2	300.2	300.2	767.5	767.5	100	50
Permeate water	114	118.3	46.0	405.2	27.74		
Rejection rate (%)	62.0	60.6	84.7	47.2	96.4		
Cl^- (mg/L)							
Feed water	–	–	1001.7	1818.2	1869.1	–	250
Permeate water	–	–	23.5	1645.4	40.9		
Rejection rate (%)	–	–	97.7	9.5	97.8		
SO_4^{2-} (mg/L)							
Feed water	–	–	1054.6	2069.5	2180.6	–	250
Permeate water	–	–	27.6	39.9	12.8		
Rejection rate (%)	–	–	97.4	98.1	99.4		

[a]Operated under 1.4 MPa.
[b]Operated under 2.8 MPa.
[c]Integrated Wastewater Discharge Standard, China, GB 8978-1996.
[d]Reuse of recycling water for urban, Water Quality Standard for Industrial Water Consumption, China, GB/T 19923-2005.

permeate flux under pressure and behave better anti-fouling characteristics in sewage treatment. With the high salt rejection shown in Table 2, the final permeate from RO membrane had a fairly good quality to exceed the Water Quality Standard for Industrial Water Consumption (GB/T 19923-2005) of China, which showed the strong feasibility of multiple membrane process application in plating wastewater treatment.

4. Conclusion

New results of multiple membrane separation in plating wastewater treatment have been introduced, which showed a possible feasibility for industrial application in the near future. In the pretreatment step, cellulose nitrated-cellulose acetate MF membrane with 0.45 μm pore size and polyacrylonitrile UF membrane with a molecular weight cut-off of 70 kDa were found to be more suitable than other materials. Electrodialysis demonstrated an excellent performance with ion rejection above 97.0%, COD rejection of 84.7% and the concentration of heavy metal below 0.01 mg/L. In order to obtain higher separation efficiency and cut down the operating cost, the ratio of concentrate to dilute should be controlled around 7 and different electric current should be charged on the stack before the highest salt rejection reached. Aimed at a higher water recovery rate, ED concentrate was then used as feed in NF/RO desalination process. While the NF membrane usually had excellent separation selectivity between the univalent and bivalent ions and a higher flux under low operating pressure, the RO membrane showed better performance on salt rejection, anti-compacting behavior and therefore anti-fouling characteristics in sewage treatment.

Further work will focus on the investigations of membrane fouling and cleaning mechanism and the experiments of pilot system of multiple membrane processes applied in plating workshop.

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