

# Comparison of hybrid membrane systems in electroplating wastewater treatment

Jianyang Zhu<sup>a</sup>, Qiang Jin<sup>a,\*</sup>, Aimin Li<sup>b</sup>, Fuqiang Liu<sup>b</sup>, Aidang Shan<sup>a</sup>

<sup>a</sup>School of Environmental and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China, Tel. +86-18621863638; Fax: +86-21-54740825; emails: qiang.jin@outlook.com (Q. Jin), casstile0325@163.com (J. Zhu), adshan@sjtu.edu.cn (A. Shan) <sup>b</sup>State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210093, People's Republic of China, emails: liaimin@nju.edu.cn (A. Li), jogia@163.com (F. Liu)

Received 21 September 2016; Accepted 16 February 2017

#### ABSTRACT

Studies were conducted to disclose the feasibility of membrane in simulated electroplating rinse wastewater. Single nanofiltration (NF) and reverse osmosis (RO) membrane were carried out under different operation pressure, temperature and feed Ni<sup>2+</sup> concentration. These four hybrid systems, built in concentrate staging, were investigated under optimized conditions. The results demonstrated that permeate flux of NF membrane, which was substandard (>0.5 mg/L), was almost double that of RO membrane. The values obtained for water recovery were 39.00%, 0%, 20.00% and 18.33%, concentration ratio were 1.60, 4.90, 2.45 and 2.45. The total exergy loss of four systems was 0.241, 0.460, 0.350 and 0.362MJ/h for RO–RO, NF–NF, RO–NF and NF–RO system, respectively. The specific entropy production (SEP) and unit production water cost were 0.69, 2.01 and 2.19 MJ/m<sup>3</sup> and 0.38, 0.46 and 0.50 \$/m<sup>3</sup> for RO–RO, RO–NF and NF–RO system, respectively. So RO–RO system had the highest freshwater flow rate, lowest exergy loss and SEP, but NF–NF system had the highest concentration and the highest exergy loss. In total, RO–NF and NF–RO system integrated the performance of the first two; furthermore RO–NF system was superior to NF–RO system as a whole.

*Keywords*: Electroplating wastewater; Reverse osmosis membrane; Nanofiltration membrane; Recovery; Exergy; Cost analysis

# 1. Introduction

The electroplating industry in China produces 4 billion m<sup>3</sup> of rinse water for electroplating parts that causes critical pollution problems [1]. The used rinse wastewater consists of many kinds of heavy metals that are toxic and carcinogenic as they tend to accumulate in the living organisms [2]. Due to increasing environmental awareness and tighter legislation, wastewater containing heavy metals can no longer be discharged into rivers or the sea in most countries. Therefore, it is necessary to treat electroplating rinse wastewater prior to its discharge.

The conventional treatment processes like chemical precipitation, ion exchange, adsorption, coagulation and flocculation, electrodialysis have significant disadvantages [2,3]. Chemical precipitation generates large volumes of sludge of low density, which can contribute to dewatering [4] and disposal problems [2]. Ion-exchange resins must be regenerated by chemical reagents when they are exhausted and the regeneration causes serious secondary pollution [2].

The membrane separation processes, such as reverse osmosis (RO), microfiltration, ultrafiltration and nanofiltration (NF), are now the main options to conventional treatment in order to treat water [5–8]. The latter technologies have become increasingly attractive for the treatment and recycling of wastewater in metal-plating industry as they are highly efficient, easy to operate and cost-effective [9–12]. Kamizawa et al. [13] reported a method for recovering gold and rinsing water in an electroplating process using an RO membrane. Ahn et al. [14] made use of low-pressure NF to recycle nickel ion in nickel electroplating rinse water.

<sup>\*</sup> Corresponding author.

<sup>1944-3994/1944-3986 © 2017</sup> Desalination Publications. All rights reserved.

Mehdipour et al. [15] applied a polyamide NF membrane to study the influence of ion interaction on lead removal. These methods were used not only to solve the problem of heavy metal pollution, but also to deal with the metal loss in wastewater. NF membrane used to increase the performance of RO membrane and composite NF/RO membrane module was studied by many studies [16-18], by exploiting the concentrate staging configuration [19,20]. In addition to this, increase in recovery employing concentrate staging has also been investigated earlier resulting in a significant reduction in specific energy consumption, henceforth the overall system cost [21]. The performance and overall cost of such systems have been evaluated on the basis of water recovery, rejection capability and energy consumption. However, RO membrane needs lower feed concentration and higher operation pressure than NF membrane, so RO membrane used as second stage would consume more exergy but produce less freshwater in theory. Besides, the comparison of exergy and economic assessment of different hybrid membrane systems in was not studied by exploiting the concentrate staging configuration before. Besides, the study above could help to improve wastewater treatment technology.

A pilot study using simulated electroplating rinse wastewater was introduced to study the performance of NF and RO membranes and four hybrid membranes systems, NF membrane as the subsequent RO membrane (RO–NF) system, RO–RO system, NF–NF system and NF–RO system were built on the basic process. Difference of treatment performance among four systems was compared and the effect of operation pressure, feed temperature and Ni<sup>2+</sup> concentration were studied. The advantages and disadvantages in many aspects were compared in the last part by analyzing these results.

### 2. Materials and methods

## 2.1. Experimental system description

The system comprised of a temperature unit, a feed tank, two low pressure feed pumps, security filter, a high pressure pump and a membranes module. Low pressure pump provided enough pressure to pass the feed water through the security filter to the high pressure pump, which could adjust the pressure for the feed water to get through the membrane module. Ultimate permeate and concentrate streams were recycled back to tank because of the limit of the operation scale. Details are depicted in Fig. 1(a). The NF membrane ESNA1-4040 and RO membrane ESPA2-4040 made by Hydranautics Company (Oceanside, California, USA) were used in the present study. The different operation parameters and specifications of these membranes for limiting the range of input parameters from official website are illustrated in Table 1.



Fig. 1. Main operation system and four combination forms. (a) Different schemes of hybrid membrane module experimental setup; A – feed water tank, B – low pressure pump, C – security filter, D – high pressure pump, E – membranes module, 1 – temperature controller, 2 and 2' – valve, 3 – concentrate stream, 4 – permeate stream. (b) RO–RO system, (c) NF–NF system, (d) RO–NF system and (e) NF–RO system.

106

Table 1 Different operation parameters and specification of RO and NF membranes used in experiments

Membrane type	RO membrane	NF membrane
Model	ESPA2-4040	ESNA1-4040
Configuration	Spiral wound	Spiral wound
Membrane	Composite	Composite
polymer	polyamide	polyamide
Maximum operating	4.14	4.14
pressure (MPa)		
Membrane	7.9	7.9
filtration area (m <sup>2</sup> )		
Maximum	45	45
operating temperature (°C)		
pH range	2-10.6	3-10
Maximum feed flow rate	60	60
(LPH)		
Minimum ratio of	5:1	5:1
concentrate to permeate		
flow for any element		
Maximum pressure drop	0.1	0.07
for each element (MPa)		
Maximum feed water silt	5.0	5.0
density index (15 min)		
Maximum feed water	1.0	1.0
turbidity (NTU)		

In order to maximize the treatment process performance, combination sequence was altered three times in the experiment. The first hybrid configuration (NF-NF) consisted of high flux NF membrane in first stage and the same NF membrane in the second stage (Fig. 1(b)). The second combination was double-stage same RO membrane (Fig. 1(c)). In the third hybrid configuration (Fig. 1(d)), NF membrane was subsequent to RO membrane. And at the last stage, the layout of NF and RO membranes were exchanged (Fig. 1(e)). The concentrated stream from first stage was used as feed water in subsequent stage, and the resulting concentrated stream of second stage could be used as alimentative electroplating solution after the further treatment. Ultimate permeate and concentrate streams were recycled back to tank because of the limit of the operation scale. Details are shown in Fig. 1(a).

#### 2.2. Experimental design

Experiment was carried out under different operation pressure, feed temperature and feed Ni<sup>2+</sup> concentration, so as to study the performance of NF membrane and RO membrane. Operation pressure ranged from 0.5 to 1.3 MPa, feed temperature was adjusted from 20°C to 36°C and feed Ni<sup>2+</sup> concentration varied from 250 to 600 mg/L based on the raw wastewater from Da Fu Technology Limited Company in Anhui, China.

In order to study the performance of four systems in detail, the process analysis of four systems under certain conditions was carried out. Four different kinds of study experiments were carried out to maximize water recovery and Ni<sup>2+</sup> rejection. Moreover, specific entropy production (SEP) of membrane process was minimized by using operation pressure, feed temperature and concentration of feed solution as input parameters.

#### 2.3. Analytical procedure

The concentration of nickel ion was measured by UV– VIS Spectrophotometer based on National Standard 11910-89, and the measuring wavelength was 520 nm [22]. The flux was measured by using pressure gauges and flow meters, respectively, Temperature control unit was used to adjust feed water temperature as well as to avoid heat generated by system. The detection limit of heavy metal was 0.25 mg/L for Ni in the experiment.

Each set of experiments of single membrane system was conducted for five times to get a series of data. Deviation analysis of the data from same operation condition was carried out, and the deviation was <1%. All the data displayed in the section of single membrane system was the mean calculated after data analysis.

Experiments of hybrid membrane system which were carried out in a controlled optimized condition (operation pressure=0.70MPa, temperature=20.0°C, feed flux=15.0 L/min and Ni<sup>2+</sup> concentration = 250.0 mg/L) for five times. The standard deviation of a series of data measured and calculated was obtained <1%, so the corresponding mean of data was used in the study.

## 2.4. Exergy theory

In order to calculate energy consumption, the study makes use of the exergy, which is part of the energy that is convertible into all other forms of exergy and represents the useful part of exergy for a system in its environment [23–25].

Exergy for a flow stream consist of three parts, namely temperature, pressure and concentration contribution [25–28]:

$$Ex = Ex^T + Ex^P + Ex^C \tag{1}$$

where the temperature, pressure and concentration terms are defined as:

$$Ex^{T} = G[(h - h_{0}) - T_{0}(s - s_{0})]$$
<sup>(2)</sup>

$$Ex^{P} = G\left(\frac{P - P_{0}}{\rho}\right)$$
(3)

$$Ex^{C} = -G(N_{s}RT_{0}\ln x_{1}) \tag{4}$$

where  $Ex^T$ ,  $Ex^P$  and  $Ex^C$  stand for exergy provided by temperature, pressure and concentration.

The subscript *o* stands for reference state; *h* is the mass specific enthalpy, kJ/kg; *s* is the mass specific entropy, kJ/kg/K;  $T_o$  is the preference temperature, K; *R* is the gas constant (mass base), kJ/kg/K; *P* and  $P_o$  are pressure and preference pressure, respectively, MPa;  $N_s$  is the solvent concentration

(mol/kg solution);  $\rho$  is the solution density, kg/m<sup>3</sup>; *G* is the mass flow rate of a stream, kg/h; MW<sub>s</sub> and MW<sub>i</sub> are the molecular weight of solvent and of the *i*-component, respectively, g/mol;  $c_i$  is the weight concentration of the *i*-component per litre of solution and  $\beta_i$  is the number of particles generated by the dissociation of the component *i* in the solution.

$$N_s = \frac{1000 - \sum c_i / \rho}{MW_s} \tag{5}$$

And  $x_1$  is the solvent mole fraction:

$$x_{1} = \frac{N_{s}}{\left(N_{s} + \frac{1000}{\rho} \sum \frac{\beta_{i}c_{i}}{MW_{i}}\right)}$$
(6)

Besides, using the second law of thermodynamics, the exergy balance for a whole plant or system can be written as [25–28]:

$$R_s T_0 = W_u - \Delta E_x \tag{7}$$

where the left-hand side of Eq. (7) represents the rate of entropy production, and is the net exergy difference between all inlet and outlet streams of the plant, kJ/h.

 $W_{\mu}$  is the electrical exergy supplied to the plant:

$$W_u = G \frac{\Delta P}{\rho} \tag{8}$$

where  $\Delta P$  is the difference between before and after the pump pressure, MPa.

SEP is defined as the amount of entropy production per unit mass of product water in a membrane desalination plant which is equal to the amount of lost work in the desalination plant per unit mass of water product:

$$SEP = \frac{R_s T_0}{Q_P} \tag{9}$$

where  $Q_p$  is the rate of water production in the membrane desalination plant, m<sup>3</sup>/h.

The convenience of process with respect to a conventional one can be evaluated in terms of the exergitic efficiency of the process ( $\epsilon$ ), defined as:

$$\varepsilon = \frac{E_{x_{output}}}{E_{x_{input}}} \cdot 100(\%) \tag{10}$$

Though Ex,  $Ex^{T}$ ,  $Ex^{P}$ ,  $Ex^{C}$ ,  $N_{s'} x_{1}$ ,  $R_{s}T_{o}$ ,  $W_{u}$  and  $\Delta E_{x}$  cannot be measured directly, their values can be calculated based on the measurable parameters, such as mass flow rate of a stream (G), temperature (T), pressure (P), concentration (C) and density ( $\rho$ ).

## 3. Results and discussion

## 3.1. Performance analysis of single membrane system

### *3.1.1. The performance of metal recovery*

The plots for metal rejection are depicted in Fig. 2. Metal rejection almost came to 100% and kept constant with the

change of pressure from 0.5 to 1.3 MPa for RO membrane, while rejection of NF membrane had an obvious downtrend, from 97.00% to 90.06%, when the operation pressure was larger than 0.7 MPa (Fig. 2(a)). The solution-diffusion model [29] implied the mass transports by diffusion, while irreversible thermodynamic model [30] indicated the transport of mass relied on convection. As mentioned by Van der Horst et al. [31], a high diffusive transport of salts through the membrane compared with convective transport was the reason for low retention at low pressure. With increasing pressure, convective transport became more important and retention would, therefore, also increase. However, concentration polarization would also increase with increasing pressure, which resulted in a decrease in retention. Counteracting contributions of increased convective transport and increased concentration polarization resulted in a constant retention value for RO membrane in the pressure range 0.5-1.3 MPa, but caused the decrease of rejection for NF membrane.

Fig. 2(b) depicts the metal rejection at various temperatures. Although the permeate flux increased with the increase of temperature, metal rejection tending to 100% did not show any obvious change for RO membrane. But the rejection of NF membrane decreased from 96.57% to 95.29%. This was because though both the permeability coefficient and the permeability constant [29,30] increased with temperature, the mass transfer coefficient of salt and salt permeability coefficient enhanced with increasing temperature [32]. Consequently, the temperature dependence of salt rejection would be determined by a trade-off between temperature dependence of the permeability coefficient [33]. The stability of salt rejection of RO membrane as temperature increases implied that the temperature dependence of the permeability coefficient kept balance on that of the permeability coefficient while the temperature dependence of the permeability coefficient for NF membrane brought the decrease of rejection. Metal rejection decreased with feed Ni<sup>2+</sup> concentration ranging from 250 to 600 mg/L for NF membrane (Fig. 2(c)), which was caused by high feed salinity, metal passage increases [34]. However, performance of RO membrane still keeps stable regardless of the variation of Ni<sup>2+</sup> concentration.

Thus, it was evident that there was no significant difference in terms of rejection of RO membrane under variable operation condition, which was similar to the study of Arkhangelsky et al. [35], but the rejection of NF membrane decreased obviously. Besides, the rejection of RO membrane was higher than NF membrane.

#### 3.1.2. The performance of water recovery

The comparative plots for water recovery are shown in Fig. 2. The results in Fig. 2 indicate that water recovery increased almost linearly with pressure both for NF and RO membrane (Fig. 2(d)). Water recovery increased from 13.33% to 38.33% for RO membrane, and about 30.67% to 61.67% for NF membrane. The reason for the increase could be explained by using the solution–diffusion model [29] and irreversible thermodynamic model [30]. According to the above models, permeate flux increased proportionally to the difference between the applied pressure and the osmotic pressure, but



Fig. 2. The performance of NF and RO membrane: (a)–(c) Metal rejections at different pressures, temperatures and concentrations respectively; and (d)–(f) Water recoveries at different pressures, temperatures and concentrations respectively.

solute flux did not. Water recovery increased because higher pressure allowed enhanced flow of water through the membrane [36]. As shown in Fig. 2(e), water recovery increased with temperature ranging from 20°C to 36°C for both membranes at the rate of 0.7 MPa. RO membrane increased from 20.00% to 32.00% and NF membrane increased from 41.67% to 55%. This was because water permeability coefficient increased when the temperature was raised [30], which in turn resulted in the increase of the permeate flux for both the systems.

However, at low pressure and temperature, water recovery decreased with the increase of concentration for both membranes (Fig. 2(f)), but the downtrend was inevident. It was from 20.00% to 18.33% for RO membrane and 41.67% to 37.33% for NF membrane. The reason for lower water recovery was that higher salt concentration caused the negative effect of concentration polarization and in turn decreased the membrane water flux [37], according

to the solution–diffusion model and irreversible thermodynamic model.

#### 3.2. Performance of hybrid membrane systems

In order to increase the output, a desalination system could be modified in various ways. The most common approach was to combine one membrane with another in a module and the arrangement of the modules was often the key factors affecting in treatment performance. Nemeth [38] used a double-stage system to improve the performance of a conventional brackish water reverse osmosis plant, the average flux was increased up to 10%, and the permeate total dissolved solids decreased by around 20% by utilizing a hybrid combination of ultra-low pressure and conventional membranes.

After the study of two membranes under the operation conditions, four hybrid membrane systems were used to

perform validation run under certain conditions as follows: feed Ni<sup>2+</sup> concentration 250 mg/L, operation pressure 0.7 MPa and feed temperature 20°C. Performance data of the four systems are shown in Fig. 3. Fig. 3 demonstrates that permeate of NF membrane was higher than RO membrane under the experimental conditions. However, the Ni2+ concentration (>1 mg/L) in permeate of NF membrane process exceeded the criterion, which claimed that Ni2+ concentration of reuse water was <0.5 mg/L according to the China legislation. But Ni<sup>2+</sup> concentration in the permeate of RO membrane was <0.5 mg/L. Similar phenomenon was mentioned in other research [39], which showed that NF membrane ESNA1 was not adequate under experimental condition. So the resulting permeate stream of NF membrane was refluxed back to the tank but permeate stream of RO membrane was reused as countercurrent rinsing water, respectively, as shown in Figs. 3(a)–(d).

Thus, it could be calculated that water recovery was 39.00%, 0%, 20.00% and 18.33% for RO–RO system, NF–NF system, RO–NF system and NF–RO system, respectively. RO–RO system had the largest water recovery followed by RO–NF system. NF–NF system produced water with a high Ni<sup>2+</sup> concentration, so water recovery was equal to 0. When it came to water recovery, RO–RO system was the best choice. As mentioned previously, RO and NF membrane was about 20.00% and 0%, respectively, so RO–RO system was better than single RO membrane, but RO membrane was similar with RO–NF system while a little better than NF–RO system.

#### 3.3. Metal recovery analysis of the four hybrid systems

Nickel is heavy metal and it is expensive, so the recovery or reuse of nickel can not only decrease water pollution but also reduce the waste of heavy metal and cost. The concentrate stream of membrane was very high and much higher than the discharge criterion, but it could be recycled by further enrichment. Previously, studies showed the feasibility of recovery of heavy metal using multi-stage membranes, for example, the use of double-stage NF membranes [40]. So the metal recovery of two single membrane systems was analyzed under the optimized conditions as mentioned previously. In the split parting systems, the concentrate stream of the first pass [38] was fed to the second pass as shown in Fig. 3. The figure depicted that metal recovery of RO membrane was higher than NF membrane, this was because the rejection and permeate of RO membrane were higher than NF membrane according to Fig. 2, so the total mass of ions crossing NF membrane was larger than RO membrane. It was evident that metal recovery was better when using RO membrane in the second stage.

However, the Ni2+ concentration of concentrate stream of NF membrane was higher than RO membrane, thus, NF membrane could contribute to get higher concentration of metal ions. Besides, the concentrate ratio was 1.25 and 1.69 for RO and NF membrane, respectively. Considering the reuse of heavy metal, Ni2+ concentration of concentrate stream in the second stage was the main parameter, which determined the metal reuse efficiency of whole system. The Ni<sup>2+</sup> concentration in the second stage was 400.92, 1,223.91, 613.25 and 613.68 mg/L and concentrate ratio was 1.6, 4.9, 2.45 and 2.45 for RO-RO, NF-NF, RO-NF and NF-RO system, respectively. So NF-NF system could condense metal ion most effectively, and NF-RO and RO-NF system had the similar effect to condense metal ion, while RO-RO system performed poorly. Furthermore, hybrid membrane systems had an advantage in metal recovery in comparison with single membrane systems.



Fig. 3. Change of major components at main process for four systems: (a) RO–RO system, (b) NF–NF system, (c) RO–NF system, and (d) NF–RO system.

Stream	I	II	III	IV	V	IV
RO-RO system						
G (kg/h)	900	900.23	179.72	720.28	561.36	138.88
C (g/L)	0.25	0.25	2.4e-4	0.313	0.401	2.5e-4
P (MPa)	0.1	0.7	0.1	0.68	0.65	0.1
T (K)	293.15	293.15	293.15	293.15	293.15	293.15
Ex (MJ/h)	0.162	0.702	0.03	0.538	0.402	0.029
NF–NF system						
G (kg/h)	900	900.23	375.01	525.22	178.1	347.11
C (g/L)	0.25	0.25	8.75e-3	0.423	1.223	3.02e-4
P (MPa)	0.1	0.702	0.1	0.67	0.62	0.1
T (K)	293.15	293.15	293.15	293.15	293.15	293.15
Ex (MJ/h)	0.162	0.702	0.062	0.388	0.122	0.058
RO–NF system						
G (kg/h)	900	900.23	179.72	720.28	360.22	360.06
C (g/L)	0.25	0.25	2.4e-4	0.313	0.614	1.07e-2
P (MPa)	0.1	0.7	0.1	0.68	0.63	0.1
T (K)	293.15	293.15	293.15	293.15	293.15	293.15
Ex (MJ/h)	0.162	0.702	0.03	0.538	0.262	0.06
(d)NF-RO system						
G (kg/h)	900	900.23	375.01	525.22	360.22	165
C (g/L)	0.25	0.25	8.75e-3	0.423	0.616	3.02e-4
P (MPa)	0.1	0.7	0.1	0.67	0.64	0.1
T (K)	293.15	293.15	293.15	293.15	293.15	293.15
Ex (MJ/h)	0.162	0.702	0.062	0.388	0.25	0.028

Table 2 Calculated and operative parameters for each stream

#### 3.4. Exergy distribution of hybrid membrane systems

In order to analyze energy at main states of systems, exergy theory was used to analyze the four processes. Exergy evaluations were carried out by using the equations reported previously and the experimental conditions were same as mentioned before. Four systems contributing to the total exergy, the operation parameters and the overall Ni<sup>2+</sup> concentration of each stream are reported in Table 2.

Exergy distribution throughout the system components was quantified as depicted in Table 2, thereby providing the main exergitic parameters calculated for each stream. It was easy to find that two systems need only electrical energy, so the exergy loss was based on the electrical energy and the introduction of membranes module consumes the most exergy.

As seen from Table 2, there was a total of 0.702 MJ/h exergy input to the systems through the pump, which included the exergy of stream before the pump based on Eq. (1) and the exergy provided by high-pressure pump based on Eq. (8). About 76.9% of exergy input was supplied by the high pressure pump and the remaining 23.1% was contributed by the feed process, which was not shown in the pictures. Some of this exergy was destroyed in the component, and the remaining was discharged from the systems. The exergy destruction

resulted from the pressure drops in the membrane module. Because the first stage was located in same RO and NF membrane, the performance of RO membrane in RO-RO system was similar with that in RO-NF system, and the performance of NF membrane in NF-NF system was same as it in NF-RO system. When process water passed through the first stage, the exergies of 0.134 and 0.252 MJ/h were destroyed for RO and NF membrane, and these loses corresponded to 19.1% and 35.9% of the total exergy input. The transmission of the concentrate stream through the first stage membrane resulted in 0.67 and 0.68 MPa pressure drop. The concentrate stream from the first stage fed into the second stage, and the exergy destroyed was 0.107, 0.208, 0.216 and 0.11 MJ/h and these loses accounted for 15.2%, 29.3%, 30.8% and 15.7% of the total exergy input for the four systems, respectively. Besides, the pressure drops from the second membrane were 0.65, 0.62, 0.62 and 0.64 MPa, respectively. So the total exergy loss of four systems was 0.241, 0.460, 0.350 and 0.362 MJ/h, respectively, and accounted for 34.3%, 65.2%, 49.9% and 51.60% of exergy input, respectively. The remaining left the systems with concentrate stream and the permeate streams. Hence, the second law of efficiency of these systems was determined by dividing the salinity by the total exergy input provided by the pump [41], and it was calculated as 65.7%, 34.8%, 50.1%

and 48.4%, respectively, using Eq. (10). The largest exergy loss took place in NF–NF system, and the lowest was RO–RO system. RO–NF and NF–RO system had no significant difference at exergy loss under the current operation conditions.

Note that the exergy discharged accounted for a big proportion of exergy input, if the remaining exergy could be recovered, energy consumption would decrease, which could reduce the consumption of fossil energy, save the fossil energy and reduce the emissions of greenhouse gas as well as hydrocarbon pollution. Based on this, the system with less exergy loss would have less impact on the environment.

However, though the evaluation of exergy loss was a key factor to judge the system, but it was not a determined factor in the choice of the solution to be used in desalination operations. Production water and brine disposal were two important factors that should be taken into account. SEP of RO–RO system was just 0.69 MJ/m<sup>3</sup>, but SEP of RO–NF and NF–RO system was 2.01 and 2.19 MJ/m<sup>3</sup>. Since production water flow rate of NF–NF system was 0 as studied previously, it was not significant to study the SEP. So RO–RO system had the least exergy loss and exergy input of NF–NF system was destroyed worst.

#### 3.5. Economic assessment

Table 3

For each flow sheet proposed, an economic evaluation had been done by taking into account the major factors

Equations and assumptions for economic evaluation

affecting the product water cost. The operation parameter and results for four systems were reported in Table 2. All calculations were based on recent data extracted from actual field data and from design studies in literature (Table 3) [42]. The cost of NF–NF system was not taken into consideration because of the low permeate quality according to the above analysis in this study.



Fig. 4. The comparison of unit production water cost for RO–RO, RO–NF and NF–RO system.

Electric power cost	$A_e = c \cdot w \cdot f \cdot m \cdot 365$
	where <i>w</i> : special consumption of electric power (kWh/m <sup>3</sup> ); <i>c</i> : electric cost =
	0.2\$/kWh; <i>m</i> : plant capacity (m³/d); <i>f</i> : plant availability (=0.9)
Annual labour cost	$A_{la} = \gamma \cdot f \cdot m \cdot 365$
	where $\gamma$ : specific cost = 0.03\$/m <sup>3</sup>
Membrane replacement	$A_{\rm mem}$ : replacement rate = 10% per year
Maintenance and spare parts	$A_{sn} = p \cdot m \cdot f \cdot 365$
	where <i>p</i> : specific = $0.033$ /m <sup>3</sup>
Indirect costs	10% of direct capital costs on annual basis
Annual amortization or fixed charge	Amortization factor:
	$i(1+i)^n$
	$\alpha = \frac{1}{(1+i)^n - 1}$
	Annual fixed charge:
	$A_{\text{fived}} = \alpha \cdot DC$
	where <i>n</i> : plant life = 30 years; <i>i</i> : interest rate = 5%; DC: direct capital cost (\$)
Annual cost for chemicals	$A_{\pm} = k \cdot m \cdot f \cdot 365$
	where k: specific chemicals cost = $0.025$ /m <sup>3</sup>
Annual brine disposal cost	$A_{i} = b \cdot B \cdot f \cdot 365$
1	where b: specific cost of brine disposal = $0.0015$ /m <sup>3</sup> ; B: brine flow rate (m <sup>3</sup> /d)
Annual profit for the sale of the salts	$profit = Salt \ price \cdot Salt \ flow \ rate \cdot f \cdot 365$
I	Salt price = 1.89 \$/kg
Annual profit for the sale of the freshwater	profit = Water price $\cdot$ Water flow rate $\cdot f \cdot 365$
1	Water price = $0.89 $ \$/m <sup>3</sup>
Total annual cost	$A_{\text{total}} = A_e + A_{la} + A_{sp} + A_{\text{che}} + A_{\text{brine}} + A_{\text{mem}}$
Unit product water cost	$A_{\text{unit,p}} = A_{\text{total}} / (f \cdot m \cdot 365)$

The cost ranged from 0.38 \$/m<sup>3</sup> for RO–RO system to 0.5 \$/m<sup>3</sup> for NF–RO system as illustrated in Fig. 4, which implied the correctness of previous studies that in all the flow sheets examined, the freshwater cost of membrane processes was lower than that of thermal desalination processes (1.5 \$/m<sup>3</sup>) [43]. The lower water cost in the RO–RO system was due to the higher water recovery, which was based on the introducing of standard of water reuse that abandoned the permeate of NF membrane.

### 4. Conclusions

Based on the study, NF membrane had much higher permeate flux but lower rejection than RO membrane. Besides, the combination of NF membrane and RO membrane was a promising solution to deal with electroplating wastewater, and the different configuration could satisfy different need. The RO–RO system could help get more freshwater with low exergy loss and SEP, and NF–NF system had a better performance to condense the metal ion concentration. The RO–NF and NF–RO system had a moderate performance, but the former was better than the latter in general trend. Besides, the cost of was 0.38, 0.45 and 0.50 \$/m<sup>3</sup> for RO–RO system, RO–NF system and NF–RO system, respectively.

#### Acknowledgements

This work was supported by the National Water Pollution Control and Treatment Project of China (2014ZX07204-008) and National Natural Science Foundation of China (21476139). We would like to thank all those involved in this project.

## References

- H. Rui-guang, The development trend of electroplating wastewater treatment in 21st century, Plat. Finish., 22 (2000) 1–2.
- [2] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: a review, J. Environ. Manage., 92 (2011) 407–418.
- [3] Q. Jin, Y. Yang, X. Dong, J. Fang, Site energy distribution analysis of Cu (II) adsorption on sediments and residues by sequential extraction method, Environ. Pollut., 208 (2016) 450–457.
- [4] N. Kongsricharoern, C. Polprasert, Electrochemical precipitation of chromium (Cr<sup>6+</sup>) from an electroplating wastewater, Water. Sci. Technol., 31 (1995) 109–117.
- [5] A. Maher, M. Sadeghi, A. Moheb, Heavy metal elimination from drinking water using nanofiltration membrane technology and process optimization using response surface methodology, Desalination, 352 (2014) 166–173.
- [6] V. Coman, B. Robotin, P. Ilea, Nickel recovery/removal from industrial wastes: a review, Resour. Conserv. Recycl., 73 (2013) 229–238.
- [7] P. Goh, T. Matsuura, A. Ismail, N. Hilal, Recent trends in membranes and membrane processes for desalination, Desalination, 391 (2016) 43–60.
- [8] T.Z. Sadyrbaeva, Separation of cobalt(II) from nickel(II) by a hybrid liquid membrane–electrodialysis process using anion exchange carriers, Desalination, 365 (2015) 167–175.
- [9] X. Chai, G. Chen, Y. Po-Lock, Y. Mi, Pilot scale membrane separation of electroplating waste water by reverse osmosis, J. Membr. Sci., 123 (1997) 235–242.
- [10] D.E. Hewitt, T.J. Dando, Water Recycle Treatment System for Use in Metal Processing, Aug 1976: US03973987, 1976, p. 6.
- [11] T. Sato, M. Imaizumi, O. Kato, Y. Taniguchi, RO applications in wastewater reclamation for re-use, Desalination, 23 (1977) 65–76.
- [12] F.-S. Wong, J.-J. Qin, M. Wai, A. Lim, M. Adiga, A pilot study on a membrane process for the treatment and recycling of spent

final rinse water from electroless plating, Sep. Purif. Technol., 29 (2002) 41–51.

- [13] C. Kamizawa, H. Masuda, M. Matsuda, T. Nakane, H. Akami, Studies on the treatment of gold plating rinse by reverse osmosis, Desalination, 27 (1978) 261–272.
- [14] K.-H. Ahn, K.-G. Song, H.-Y. Cha, I.-T. Yeom, Removal of ions in nickel electroplating rinse water using low-pressure nanofiltration, Desalination, 122 (1999) 77–84.
- [15] S. Mehdipour, V. Vatanpour, H.-R. Kariminia, Influence of ion interaction on lead removal by a polyamide nanofiltration membrane, Desalination, 362 (2015) 84–92.
- [16] E. Drioli, E. Curcio, G. Di Profio, F. Macedonio, A. Criscuoli, Integrating membrane contactors technology and pressuredriven membrane operations for seawater desalination, Chem. Eng. Res. Des., 84 (2006) 209–220.
- [17] H. Mehdizadeh, Membrane desalination plants from an energy-exergy viewpoint, Desalination, 191 (2006) 200–209.
  [18] W.L. Ang, A.W. Mohammad, N. Hilal, C.P. Leo, A review on
- [18] W.L. Ang, A.W. Mohammad, N. Hilal, C.P. Leo, A review on the applicability of integrated/hybrid membrane processes in water treatment and desalination plants, Desalination, 363 (2015) 2–18.
- [19] T. Qiu, P.A. Davies, Comparison of configurations for highrecovery inland desalination systems, Water, 4 (2012) 690–706.
- [20] E. Alayemieka, S. Lee, D. Kim, Effect of membrane surface characteristics on hydraulic flux balance and feed stream translation in concentrate multi-stage system, Desalination, 247 (2009) 64–76.
- [21] M.C. Garg, H. Joshi, Optimization and economic analysis of small scale nanofiltration and reverse osmosis brackish water system powered by photovoltaics, Desalination, 353 (2014) 57–74.
- [22] GB11910-89, Water quality determination of nickel dimethylglyoxime spectrophotometric method [S]. Beijing: Standardization Administration of the People's Republic China, 1989.
- [23] V. Calabro, G. Pantano, M. Kang, R. Molinari, E. Drioli, Experimental study on integrated membrane processes in the treatment of solutions simulating textile effluents. Energy and exergy analysis, Desalination, 78 (1990) 257–277.
- [24] E. Drioli, F. Lagana, A. Criscuoli, G. Barbieri, Integrated membrane operations in desalination processes, Desalination, 122 (1999) 141–145.
- [25] R. Molinari, R. Gagliardi, E. Drioli, Methodology for estimating saving of primary energy with membrane operations in industrial processes, Desalination, 100 (1995) 125–137.
- [26] A. Criscuoli, E. Drioli, Energetic and exergetic analysis of an integrated membrane desalination system, Desalination, 124 (1999) 243–249.
- [27] M.J. Moran, H.N. Shapiro, D.D. Boettner, M.B. Bailey, Fundamentals of Engineering Thermodynamics, John Wiley & Sons, New Jersey, 2010.
- [28] E.J. Henley, J.D. Seader, D.K. Roper, Separation Process Principles, Wiley, New York, 2011.
- [29] J. Wijmans, R. Baker, The solution-diffusion model: a review, J. Membr. Sci., 107 (1995) 1–21.
- [30] K.S. Spiegler, O. Kedem, Thermodynamics of hyperfiltration (reverse osmosis): criteria for efficient membranes, Desalination, 1 (1966) 311–326.
- [31] H. Van der Horst, J. Timmer, T. Robbertsen, J. Leenders, Use of nanofiltration for concentration and demineralization in the dairy industry: model for mass transport, J. Membr. Sci., 104 (1995) 205–218.
- [32] H. Hyung, J.-H. Kim, A mechanistic study on boron rejection by sea water reverse osmosis membranes, J. Membr. Sci., 286 (2006) 269–278.
- [33] K.L. Tu, L.D. Nghiem, A.R. Chivas, Boron removal by reverse osmosis membranes in seawater desalination applications, Sep. Purif. Technol., 75 (2010) 87–101.
- [34] C. Bartels, R. Franks, S. Rybar, M. Schierach, M. Wilf, The effect of feed ionic strength on salt passage through reverse osmosis membranes, Desalination, 184 (2005) 185–195.
- [35] E. Arkhangelsky, D. Kuzmenko, V. Gitis, Impact of chemical cleaning on properties and functioning of polyethersulfone membranes, J. Membr. Sci., 305 (2007) 176–184.

- [36] A. Sharma, V. Pareek, D. Zhang, Multi-Scale modelling of biomass pyrolysis processes, Comput. - Aided Chem. Eng., 30 (2012) 1133–1137.
- [37] I. Koyuncu, M. Yazgan, D. Topacik, H. Sarikaya, Evaluation of the low pressure RO and NF membranes for an alternative treatment of Buyukcekmece Lake, Water. Sci. Technol. Water Supply, 1 (2001) 107–115.
- Supply, 1 (2001) 107–115.
  [38] J.E. Nemeth, Innovative system designs to optimize performance of ultra-low pressure reverse osmosis membranes, Desalination, 118 (1998) 63–71.
- [39] H. Laborde, K. Franca, H. Neff, A. Lima, Optimization strategy for a small-scale reverse osmosis water desalination system based on solar energy, Desalination, 133 (2001) 1–12.
- [40] J. Castelblanque, F. Salimbeni, NF and RO membranes for the recovery and reuse of water and concentrated metallic salts from waste water produced in the electroplating process, Desalination, 167 (2004) 65–73.
- [41] Y. Cerci, Exergy analysis of a reverse osmosis desalination plant in California, Desalination, 142 (2002) 257–266.
- [42] F. Macedonio, E. Curcio, E. Drioli, Integrated membrane systems for seawater desalination: energetic and exergetic analysis, economic evaluation, experimental study, Desalination, 203 (2007) 260–276.
- [43] H.M. Ettouney, H.T. El-Dessouky, R.S. Faibish, P.J. Gowin, Evaluating the economics of desalination, Chem. Eng. Prog., 98 (2002) 32–40.