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Pilot scale membrane separation of plating wastewater by nanofiltration and reverse osmosis

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Abstract. Plating wastewater containing various heavy metals can be produced by several industries. Specifically, we focused on the removal of copper (Cu2+) and nickel (Ni+) ions from the plating wastewater because all these ions are strictly regulated when discharged into watershed in Korea. The application of both nanofiltration (NF) and reverse osmosis (RO) technologies for the treatment of wastewater containing copper and nickel ions to reduce fresh water consumption and environmental degradation was investigated. In this work, the removal of copper (Cu2+) and nickel (Ni+) ions from synthetic water was studied on pilot scale remove by before using two commercial nanofiltration (NF) and reverse osmosis(RO) spiral-wound membrane modules (NE2521-90 and RE2521-FEN by Toray Chemical). The influence of main operating parameters such as feed concentration on the heavy metals rejection and permeate flux of both membranes, was investigated. Synthetic plating wastewater samples containing copper (Cu^{2+}) and nickel (Ni^{2+}) ions at various concentrations(1, 20, 100, 400 mg/L) were prepared and subjected to treatment by NF and RO in the pilot plant. The results showed that NF, RO process, with 98% and 99% removal for copper and nickel, respectively, could achieve high removal efficiency of the heavy metals.

Keywords: nanofiltration; reverse osmosis; plating wastewater; heavy metal; rejection rate

1. Introduction

Plating industry is one of the major chemical processes that discard large amounts of wastewaters. These plating industrial wastewaters contain various types of harmful heavy metals and toxic substances such as chromium, zinc, nickel, copper, cyanide and degreasing solvents (Akbal 2011). Heavy metals are a serious environmental contaminant because they are environmentally persistent, have high toxicity and have a tendency to accumulate in body tissues (Mohammad 2004). Because of this, environmental regulations compel industries to reduce the concentration of heavy metals in their wastewater to within safe levels.

Numerous approaches such as physical, chemical and biological processes including adsorption, biosorption, precipitation, ion exchange, reverse osmosis filtration and other membrane separations are employed to treat wastewaters (Tchobanoglous 2003, Song 2018).

Precipitation of heavy metals in an insoluble form of hydroxides is the most effective and economical method to treat heavy metals wastewater (Agridiotis 2007). However, this process requires a large amount of treatment chemicals to decrease the heavy metals to levels imposed by the regulations. In addition, the sludge produced from the precipitation process needs dewatering and disposal into landfills, which adds an additional cost to the treatment process. Therefore, it is important to recover the valuable materials (metals and water) and prevent environmental degradation.

For plating wastewater treatment and reuse, the most widely used membrane processes included ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). All these processes are pressure-driven, thus require external energy to transport the water under pressure through the membrane system. Although membrane technologies have a high potential in producing pure water, wide applications are mostly hindered by the consideration of cost (Mohammad 2004). Membrane technology has the following advantages: (1) low energy requirements; (2) small volume of retentate that needs to be handled; (3) selective removal of pollutants with complexing agents and biocatalysts or by membrane surface modification; (4) the possibility of achieving 'zero discharge' with reuse of permeate water, binding media and removed compounds; (5) continuous operation; (6) modular design without

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significant size limitations; (7) discrete membrane barrier to ensure physical separation of contaminants; and (8) minimal labor requirement (Bes-pia 2003, Gozálvez-Zafrilla 2008, Ciardelli 2001, Rozzi 1999, Nam 2015)

In recent years, the use of NF and RO has increased rapidly in the chemical, petrochemical, biotech and desalination industries, since the high-pressure membrane technology overcomes operational problems that are associated with conventional techniques.

Several successful studies have been reported which have used NF membranes as tools for heavy metal removal (Al-Rashdi 2011). Most commercial NF membranes are thin-film composites made of synthetic polymers containing charged groups which can make them effective in the separation of charged metals from water. Additionally, the separation in NF occurs due to solution diffusion as well as sieving, the Donnan effect, dielectric exclusion and electromigration, which also makes it useful in the separation of both charged and uncharged organic solutes (Kotrappanavar 2011).

The feed pH can change the nature of the membrane surface charge and pore size, as well as that of dissolved metal species and therefore can affect the membrane separation efficiency. However, the investigation of several different heavy metals on the same membrane, under the same conditions gives much information about the membrane and its suitability at different conditions (i.e. pH, metal ions, feed pressure and concentration).

In this work retention of two metal solutions (Cu^{2+}, Ni^{2+}) was investigated using the NF and RO membrane. The effect of the following factors on membrane separation was studied: pressure (8, 20 bar), initial feed concentration (1, 20, 100, 400 mg/L) and pH 3 of the solution.

The purpose of this study is to evaluate the performance of the RO and NF processes in removing heavy metals from plating wastewater.

2. Materials and methods

2.1 Characterization of synthetic heavy metal wastewater

Synthetic samples of heavy metal wastewater were prepared by adding different amounts of copper and nickel as sulfates to distilled water. Copper(II) sulfate pentahydrate, Nickel(II) sulfate hexahydrate are the products of Kanto Chemical (Tokyo, Japan). Copper and Nickel standard solutions, with concentration ranging from 1, 20, 100, 400 mg/L, were prepared, immediately before use, by appropriate dilutions of a 1000mg/L stock solution. The pH of the solution was adjusted by HCl.

The wastewater was characterized for pH, Copper and Nickel and the data were presented in Table 1. To monitor the performance of the NF and RO processes, the heavy metals concentration was used as an indicator of performance. The content of copper and nickel in the solution was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin-Elmer, Optima 5300 DV) operating in the axial viewing mode. Argon, air and nitrogen were the used gases. The blank for the analysis was prepared by adding nitric acid to distilled water up to a HNO_3 concentration of 2% v/v. Similarly, before measurements, samples and standard Copper, Nickel solutions were acidified with nitric acid in order to obtain a final solution containing HNO_3 at 2% v/v. The system was equipped with an auto-sampler which automatically sent to the torch chamber the solution to be analyzed.

Table 1 Characteristics of synthetic wastewater

Characteristics	Value (mg/L)
Cu^{2+}	1, 20, 100, 400
Ni^{2+}	1, 20, 100, 400
pH	3.00 ± 0.2

The deviation of each measurement was of 2% from the average value.

$$R(\%)=\left[1-\left(\frac{C_P}{c_f}\right)\right]\times 100 \quad (1)$$

With c_p and c_f as permeate and feed concentration (ppm), respectively, was determined in each experiment.

2.2 NF/RO membrane module and pilot system

NF/RO experiments were performed by using two commercial nanofiltration (NF) and reverse osmosis(RO) spiral-wound membrane modules (NE2521-90 and RE2521-FEN by Toray Chemical). The characteristics of the membrane modules are summarized in Table 2.

A pilot scale skid mounted system (Filterrain, Korea), schematically shown in Fig. 2, was built by incorporating a thin film composite membrane with an inlet pressure of 60 bar inside the fiber-reinforced plastic (FRP) cylindrical pressure vessel with the dimension of 2.5 in. dia×21 in. length (the size of each of the module). The membrane-housing cell is made of stainless steel with two valves fastened together with high tensile bolts. The top half of cell contained the flow distribution chamber and the bottom half is used as the membrane support system. The membrane required support to prevent rupture at high hydrostatic pressures. A feed tank of 150 L capacity made of plastic was provided for storage and supply of effluent to the system as well as collection of the recycled concentrate.

150 liters of the feed were poured into the feed tank after thoroughly cleaning the membrane systems and then wetted the tap water. A high-pressure pump was employed to transport the feed to spiral wound membrane module and system pressure was adjusted at a value greater than the osmotic pressure by means of the restricting needle valve. The retentate flow rate was maintained constant throughout the experimental runs to ensure identical hydrodynamic conditions inside the membrane module. Feed pressure was varied from 8 and 20 bar by keeping the feed conductivity concentration constant. Permeate samples were collected after 10 min.

2.3 Membrane filtration experiments and analytical methods

Water flux was determined by measuring the permeate

Table 2 Membrane specifications used in the experiments

Characteristics	NF Membrane (NE2521-90)	RO Membrane (RE2521-FEN)
Membrane material	Thin Film Composite	Thin Film Composite
Membrane material	Polyamide(PA)	Polyamide(PA)
Element configuration	Spiral-Wound	Spiral-Wound
Permeate flow rate	0.91 m^3/day	1.1 m^3/day
Effective membrane area	12ft^2 (1.1m^2)	12ft^2 (1.1m^2)
Operating pH Range	2.0–11.0	2.0–11.0
Monovalent ion rejection (NaCl) %	85-97	-
Nominal salt rejection (%)	-	99.7
Divalent ion rejection $(CaCl_2)^2$ %	90-97	-
Maximum operating temperature (℃)	45	45
Maximum operating pressure (psi)	600	600

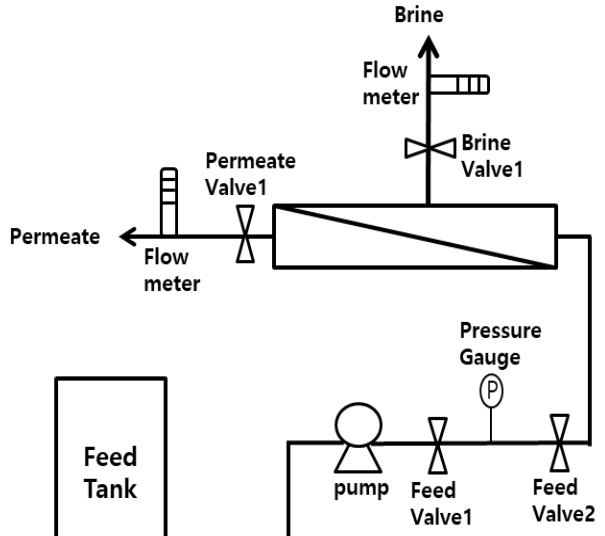

Fig. 1 Schematic diagram of the NF, RO membrane unit

water volume collected over a certain period in terms of liter per square meter per hour (L/m^2 h) and using the following equation:

$$J_w = \frac{V}{A \times \Delta t} \quad (2)$$

where J_w is the volumetric permeate water flux, A is the effective area of the membrane for permeation, and V is the volume of permeation over a time interval Δt.

The flux decline and water recovery were determined through the following equations of (3) and (4), respectively:

$$Flux\ decline = \frac{J_{w0} - J_{ws}}{J_{w0}} \times 100\% \quad (3)$$

$$Water\ recovery = \frac{J_{wc}}{J_{w0}} \times 100\% \quad (4)$$

in which, J_{w0}, J_{ws} and J_{wc} are the water fluxes of the fresh, filtrated and water cleaned membranes. The lower flux decline value means the better antifouling property, while the higher water recovery value indicates the higher cleaning efficiency.

3. Result and discussion

3.1 Membrane permeability

The tap water flux of the NF, RO membranes versus the TMP drop ΔP (in the range of 5, 8, 10, 12, 14, 16, 18, 20 bar) for tap water at different membrane types are shown in Fig 2. It can be seen that, at membrane type, the tap water flux increases linearly with increasing TMP drop as predicted by Eq. (5) of the solution diffusion model.

$$J_w = A\ (\Delta P - \Delta \pi) \quad (5)$$

The constant A is usually called the water permeability constant and is a function of the water concentration on the high pressure side of the membrane. ΔP is the pressure difference across the membrane, and Δπ is the difference in osmotic pressures of solutions that are outside the membrane and in contact with the high pressure side and the low pressure side of the membrane.

3.2 Water flux decline and operating pressure

Water flux is one of the key factors for evaluating the performance of membranes, which reflects the amount of permeate and product rate and is a factor demonstrating the membrane's efficiency. Fig. 3 gives the flux performance of the NF and RO membranes under the initial flux of 70.0 L/m^2 h and TMP of NF(8Bar), RO(20Bar). Under the same initial flux, the flux declines by about 3.2% and 5.7% for membranes NF and RO, respectively. The changes of permeate flux as a function of operating time for the two membranes at the operating pressure of NF(8Bar), RO(20Bar) are also shown in Fig. 3(A and B), from which

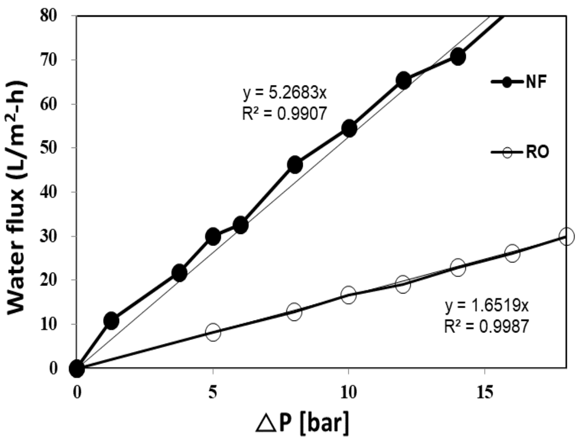

Fig. 2 Effect of TMP on tap water flux: NF membrane and RO membrane (temperature=25℃, pH = 7)

we can see that the permeate flux for each studied membrane declines slowly and ultimately reach a steady state. This can be taken as an indication of membrane fouling or due to osmotic pressure build up caused by the retained metal ions (Wang 2007, Tanninen 2006). A similar reduction in permeate flow using a similar range of pressure was observed by Chaabane *et al*. (Chaabane 2006). The metals ranked by the order which they caused membrane fouling is Cu^{2+}>Ni^{2+}. This may be due to the formation of a cake layer of copper hydroxide precipitate $Cu(OH)_2$.

From Fig. 4, where the contaminant concentration in the operating pressure was plotted against the time, it can be seen that the operating pressure increased with an increase in operating time.

Pressure increasing to 8.9-21.5 bar in NF and RO caused an increase in the removal rate (Fig. 5) and also proved that pressure is a decisive factor in the removal of all parameters. This phenomenon could be due to enhancement in the solvent passage that is derived from increasing pressure and as a result, increase in solutes rejection (Al-Rashdi 2013, Gherasim 2014). Results from a similar study showed that Ni rejection increased from 72 to 97%, when the pressure witnessed an increasing trend from 4 to 20 bar (Murthy and Chaudhari 2008).

3.3 Efficiency of NF and RO processes in removing copper and nickel ions

The efficiency of RO and NF processes in removing Cu^{2+}, Ni^{2+} from wastewater are presented in Fig. 5. As shown from Fig. 5(A), Cu^{2+} ions were successfully removed from the wastewater by both NF and RO. The concentration of Cu^{2+} in the product water (permeate) for RO was reduced to an average value 0.34 ppm with an average removal efficiency of 99.76%. On the other hand, the removal efficiency of Cu^{2+} by NF ranged from 79% to 98% for an initial feed concentration of 1 and 400 ppm, respectively.

The same result can be observed for Ni^{2+} ions (see Fig. 5(B)) where its concentration in the permeate from RO was reduced to 0.35± 0.6 ppm with average removal efficiency of 99.7%, while the Ni^{2+} removal efficiency of the NF ranged from 97.4 to 99.2%. This implies that membrane

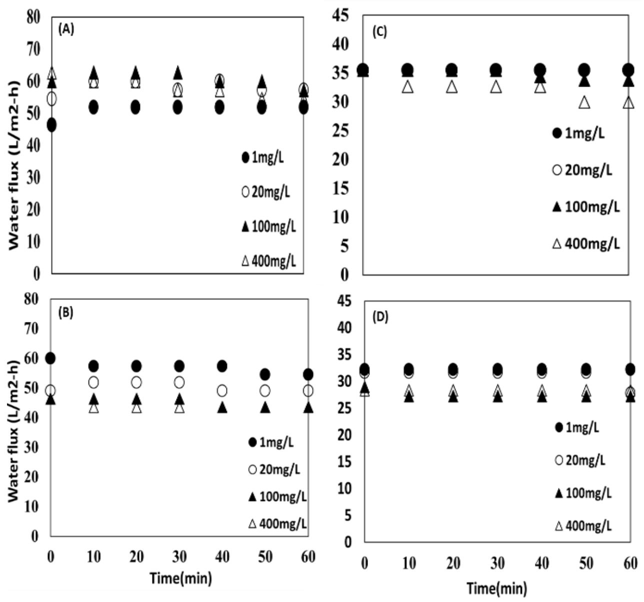

Fig. 3 Water flux with time at different metal concentration, experimental conditions: Metal concentration=NF(A) and RO(C) 1, 20, 100, 400 mg/L Copper, NF(B) and RO(D) 1, 20, 100, 400 mg/L Nickel, pH=3±0.2, operating time = 60min

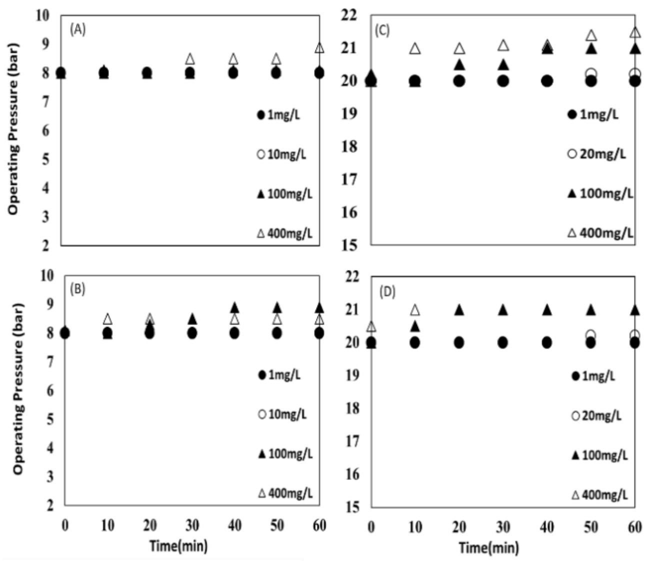

Fig. 4 Operating pressure with time at different metal concentration, experimental conditions: Metal concentration=NF(A) and RO(C) 1, 20, 100, 400 mg/L Copper, NF(B) and RO(D) 1, 20, 100, 400 mg/L Nickel, pH=3±0.2, operating time = 60min

techniques such as RO and NF are efficient processes for removing heavy metals from wastewater, to reclaim this water for further uses.

The results obtained also show that Ni^{2+} ions were removed at a slightly higher efficiency compared to Cu^{2+}. This might be due to the fact that the size of the Cu^{2+} is larger than that of Ni^{2+}. A somewhat similar result was found by Ujang *et al*. (Ujang 1996), who reported that Zn^{2+} ions can be removed at a slightly higher efficiency compared to Cu^{2+}.

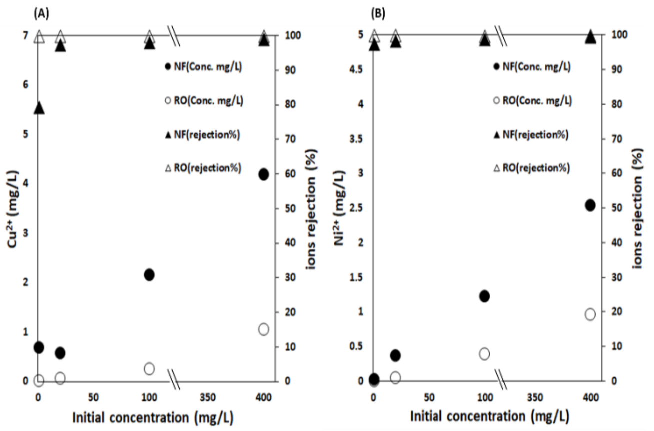

Fig. 5 Concentration of Cu^{2+}, Ni^{2+} in the permeate from NF (A) and RO (B) for different feed concentrations

These results indicate that both types of the membrane filtration are efficiency for Cu^{2+} and Ni^{2+} removal from plating wastewater. However, NF requires a lower pressure than RO, making NF more preferable due to its lower treatment costs (Mohammad 2004).

In general, NF membrane can treat inorganic effluent with a metal concentration of 2000 mg/L. Depending on the membrane characteristics, NF can effectively remove metal at a wide pH range of 3–8 and at pressure of 3–4 bar (Ahn 1999, Saffaj 2004).

4. Conclusions

This study shows that it is successful to remove copper and nickel ions from synthetic waste water using NF/RO membrane separation on a pilot scale.

The NF membrane has relatively high rejection capacity of specific divalent substances under lower pressure and achieved better permeate flux compared to RO membrane.

Furthermore, the heavy metal ions rejection of the NF membrane can be up to 98% and the conductivity value is low. It is also speculated that the ion penetration cross the membrane is due to the swelling plasticization effect of water on the polymer matrix.

Therefore, NF seems more suitable for large-scale industrial practice. The theoretical flux can be predicted and compare well with the experimental data.

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References

Agridiotis, V., Forster, C.F. and Carliell-Marquet, C. (2007), "Addition of Al and Fe salts during treatment of paper mill effluents to improve activated sludge settlement characteristics", *Bioresour. Technol.*, **98**(15), 2926-2934.

Ahn, K.H., Song, K.G., Cha, H.Y. and Yeom, I.T. (1999), "Removal of ions in nickel electroplating rinse water using low-pressure nanofiltration", *Desalination*, **122**(1), 77-84.

Akbal, F. and Camcı, S. (2011), "Copper, chromium and nickel removal from metal plating wastewater by electrocoagulation", *Desalination*, **269**(1-3), 214-222.

Al-Rashdi, B., Somerfield, C. and Hilal, N. (2011), "Heavy metals removal using adsorption and nanofiltration techniques", *Separation Purification Rev.*, **40**(3), 209-259.

Bes-Pia, A., Mendoza-Roca, J.A., Alcaina-Miranda, M.I., Iborra-Clar, A. and Iborra-Clar, M.I. (2003), "Combination of physico-chemical treatment and nanofiltration to reuse wastewater of a printing, dyeing and finishing textile industry", *Desalination*, **157**(1-3), 73-80.

Chaabane, T., Taha, S., Ahmed, M.T., Maachi, R. and Dorange, G. (2006), "Removal of copper from industrial effluent using a spiral wound module—Film theory and hydrodynamic approach", *Desalination*, **200**(1-3), 403-405.

Ciardelli, G., Corsi, L. and Marcucci, M. (2001), "Membrane separation for wastewater reuse in the textile industry", *Resour., Conserv. Recycling*, **31**(2), 189-197.

Gherasim, C.V. and Mikulášek, P. (2014), "Influence of operating variables on the removal of heavy metal ions from aqueous solutions by nanofiltration", *Desalination*, **343**, 67-74.

Gozálvez-Zafrilla, J.M., Sanz-Escribano, D., Lora-García, J. and Hidalgo, M.L. (2008), "Nanofiltration of secondary effluent for wastewater reuse in the textile industry", *Desalination*, **222**(1-3), 272-279.

Kotrappanavar, N.S., Hussain, A.A., Abashar, M.E.E., Al-Mutaz, I.S., Aminabhavi, T.M. and Nadagouda, M.N. (2011), "Prediction of physical properties of nanofiltration membranes for neutral and charged solutes", *Desalination*, **280**(1-3), 174-182.

Lin, Y.L., Chiang, P.C. and Chang, E.E. (2007), "Removal of small trihalomethane precursors from aqueous solution by nanofiltration", *J. Hazardous Mater.*, **146**(1-2), 20-29.

Mohammad, A.W., Othaman, R. and Hilal, N. (2004), "Potential use of nanofiltration membranes in treatment of industrial wastewater from Ni-P electroless plating", *Desalination*, **168**, 241-252.

Murthy, Z.V.P. and Chaudhari, L.B. (2008), "Application of nanofiltration for the rejection of nickel ions from aqueous solutions and estimation of membrane transport parameters", *J. Hazardous Mater.*, **160**(1), 70-77.

Nam, A., Kweon, J., Ryu, J., Lade, H. and Lee, C. (2015), "Reduction of biofouling using vanillin as a quorum sensing inhibitory agent in membrane bioreactors for wastewater treatment", *Membr. Water Treat.*, **6**(3), 189-203.

Rozzi, A., Antonelli, M. and Arcari, M. (1999), "Membrane treatment of secondary textile effluents for direct reuse", *Water Sci. Technol.*, **40**(4-5), 409-416.

Saffaj, N., Loukili, H., Younssi, S.A., Albizane, A., Bouhria, M., Persin, M. and Larbot, A. (2004), "Filtration of solution containing heavy metals and dyes by means of ultrafiltration membranes deposited on support made of Moroccan clay", *Desalination*, **168**, 301-306.

Song, W., Lade, H., Yu, Y. and Kweon, J. (2018). "Effects of N-acetylcysteine on biofilm formation by MBR sludge", *Membr. Water. Treat.*, **9**(3), 195-203.

Tanninen, J., Mänttäri, M. and Nyström, M. (2006), "Nanofiltration of concentrated acidic copper sulphate solutions", *Desalination*, **189**(1-3), 92-96.

Tchobanoglous, G., Burton, F.L. and Stensel, H.D. (2003), *Wastewater engineering treatment and reuse (No. 628.3 T252s)*, McGraw-Hill Higher Education, Boston, U.S.A.

Ujang, Z. and Anderson, G.K. (1996), "Application of low-pressure reverse osmosis membrane for Zn2+ and Cu2+

removal from wastewater", *Water Sci. Technol.*, **34**(9), 247-253.

Wang, Z., Liu, G., Fan, Z., Yang, X., Wang, J. and Wang, S. (2007), "Experimental study on treatment of electroplating wastewater by nanofiltration", *J. Membr. Sci.*, **305**(1-2), 185-195.

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