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RESEARCH ARTICLE

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Abstract

We report here a proposed process water treatment design guide: selection of nanofiltration membrane, membrane test for model solutions and test for pre-treated industrial process water. We also suggest a complex evaluation method, which can help in decision-making process. Membrane selection experiments showed that high flux coupled with high enough rejection is favored to shorten treatment time and perform acceptable rejection. The effect of composition was studied during constant total salt concentration and it was revealed that the DL membrane had stable flux and high rejection. In case of pre-treated industrial process water a more complex effect could be observed: the counter ions present in the feed solution, moreover the complexing agents as well as other properties of the feed could lower the membrane's rejection, simultaneously decreasing the flux. Nanofiltration though still showed advantages, which allowed its implementation into an existing industrial scale technological chain. At a recovery rate of 0.2-0.5 all the environmental requirements could be fulfilled, and the permeate leaving the technology could be fed into the city sewer system.

Keywords

nanofiltration, process water treatment, membrane selection, salt removal, heavy metal removal

1 Introduction

The increasing population of the world requires increased demand of water, food, energy as well as welfare products to maintain or even increase living standards of humanity. This phenomenon is coupled however, with huge amount of wastes generated during the supply. To balance the enormous quantities of waste streams, focus is turned to prevention by means of reducing the volume of effluents if possible and releasing less harmful pollutants. Industry pushes effort into production of high-quality products with high yield, simultaneously aiming to generate less waste, even though the technology improvement is always a great challenge. Considering that production technologies cannot be changed easily, more focus is given on the efficient treatment of wastes to reduce volume and/or lessen the concentration of pollutants to reach the emission limits.

Enormous quantity of wastewaters is generated in the industrial sector (Table 1), especially in manufacturing industries (incorporating electrochemical industry, electroplating plants, mining or food and beverage industry). These wastewaters can be characterized according to their main constituents as: i) inorganic pollutant containing wastewaters called as process waters (effluents of electrochemical industry, electroplating plants, mining), or ii) organic compound-containing wastewaters (originating from food and beverage industry).

Table 1 Wastewaters generated by industry (million m³), selected examples [1]

Country	Industry total (million m ³)	Manufacturing industries (million m ³)	Inhabitants (million capita)	Specific release (m ³ /capita)
Hungary ¹	154	130	9.9	15.6
Belgium ²	530	240	11.2	47.3
Germany ³	1535	1181	80.6	19
Spain ³	6335	602	46.8	135.4
Bulgaria ⁴	154	91	7.3	21.0
Slovakia ⁴	192	163	5.4	35.6

¹ 2006

² 2009

³ 2010

⁴ 2011

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Focusing on process waters of group i) they represent extreme pH, salt content as well as ionic metal content. Due to these properties biological treatment must be avoided and the essential treatment should be executed via physicochemical methods. Several unit operations exist for the treatment of metal containing liquids like precipitation, electrolysis, evaporation, ion exchange, complex forming, *etc.*, but usually a combination of these represents the real solution for heavy metal removal. Among these methods, membrane processes are widely studied as environmental benign processes for heavy metal recovery because of their advantages; no (or low levels of) chemical addition is required, unlike conventional clarification, which generally relies on the addition of coagulants and flocculants; membranes are modular and compact; they can separate several molecules depending on their pore size; the driving force can be assured easily (especially in case of pressure-driven membrane filtration) [2]. Another advantage is that separation is achieved without requiring a change of physical state (*i.e.* liquid to gas), thus membrane processes are typically more energy efficient than evaporation. Due to the cross-flow filtration mode little accumulation takes place in the process, which makes it possible to operate continuously under steady state conditions without requiring regeneration cycles (as in ion exchange). In case of membrane processes the separation is usually performed at ambient temperature, thus allowing temperature-sensitive fluids to be treated without its constituents being damaged or chemically altered.

Dual goal can be achieved by process water treatment; to gain purified water and recover valuable compounds.

Some experts feel that traditionally membrane technologies have been considered too expensive for wastewater reclamation in most industrial processes. Although this situation is changing with the new generation of membranes (together with increasing implementation of modern techniques such as MBR technology) [2].

Nanofiltration (NF) is particularly interesting as it can be used in combination with existing unit operations like evaporation, distillation and extraction where recovery of solvent (mainly water) is important. NF is likely to be more viable than ultrafiltration (UF) or microfiltration (MF) as clean solvent is generated that can be readily re-used [3, 4]. Industrial applications of NF are spreading in metal finishing, electroplating, electrochemical industries where the aim is to recover single heavy metals from waste streams. The most common applications are special situations in which the chemicals separated from the water are valuable. An example is recovery of pure nickel from nickel-plating rinse tanks [5].

In the last twenty years, many different existing applications have combined one or several of the following removal capacities of nanofiltration:

- a) Dissolved mineral components: hardness and alkalinity (softening) [6-8], sulphate- [9, 10], nitrate ions, other inorganic micro-pollutants and metals (As, Cr, Cd, Fe, Mn, *etc.*) [11].

- b) Dissolved organic compounds: natural organic matter, organic color causing compounds, [12], biodegradable dissolved organic molecules [8, 13], biodegradable dissolved organic carbon (BDOC), assimilable organic carbon (AOC) [11].
- c) Organic micro-pollutants: pesticides [14], emerging organic micro-pollutants (endocrine disruptors, pharmaceuticals, *etc.*) [15], taste and odor causing components [8, 13].

NF is used as a purification process in different chemical sectors, for example in the production of salt from natural brine. Most chemical industries produce quite vicious wastes, from which valuable chemicals can usually be recovered by separation processes including NF. Nanofiltration technology offers unique separation opportunities for metals in acidic waste streams, which is common in winning, processing and industrial use of metals, because NF membranes typically have low rejections for acids. Thus NF is applied in mining, metal finishing and electroplating industries to recover the metal or spent acid (like sulfuric-, hydrochloric-, nitric- and phosphoric acid) rather than to treat wastewater streams. In gold processing NF is applied to gold-cyanide liquor, to separate the aurocyanide from other metal complexes present in the leach liquor. In the waste from uranium mining activities, uranium occurs as a completed uranyl ion species which will be efficiently rejected by most of the NF membranes [11].

Membrane selection is always a crucial point for treatment technology designers/engineers, because a membrane has to meet the following requirements: to be robust, provide stable flux under the process water's conditions (such as pH and temperature), have to have high flux to reduce treatment time and offer high rejection values for the components to be eliminated from the process water. Since high flux is usually coupled with low selectivity and *vice versa*, preliminary test experiments have to be carried out prior to the final selection.

We present here a three-step method: i) membrane selection studies, ii) study on the effect of feed composition and concentration on the rejection, and iii) laboratory scale implementation of nanofiltration into an existing technological chain (regarding also the effect of temperature), *via* the co-removal of copper and nickel from process waters can be executed.

2 Materials and methods

All experiments were carried out by a laboratory-scale stainless steel membrane apparatus (CM-CELFA Membrantrenntechnik AG P-28, Fig. 1), with variable membranes all having an effective area of 0.0028 m². In case of i) and ii) experiments the feed solution was kept at 25°C and temperature was controlled continuously, while it varied (15, 20, 25, 30°C) in case of iii) experiments. Driving force was maintained by inert nitrogen gas cylinder. Aiming reduced fouling, cross-flow filtration mode was applied, and by continuous feed flow rate the retentate was

recycled into the feed tank. Permeate left the membrane continuously and was collected in charges (4 or 5 charges) for further analysis. The concentrated retentate was removed from the feed tank after experiment like in batch mode.

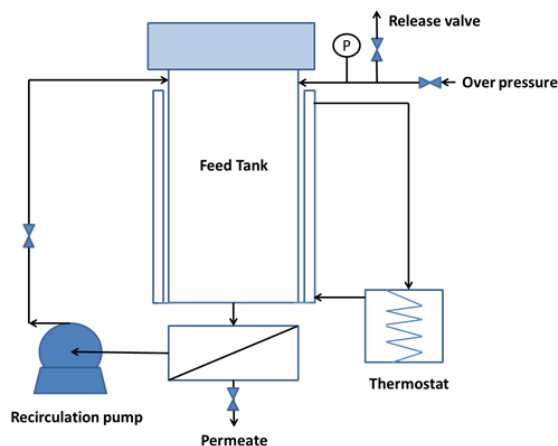


Fig. 1 Schematic drawing of Celfa P-28 test apparatus

Specific electric conductivity and pH of permeate were continuously measured by a WTW 340i pH/conductivity meter. Composition of feed solutions, permeates and retentates were determined by atomic absorption spectroscopy. In case of i) and ii) GBC 932 device was used applying air/acetylene flame at a wavelength of 213.9 and 351.5 nm for zinc and nickel, respectively. The acetylene and air flow rates were set to 2 and 8.5 dm³/min. In case of iii) Perkin Elmer 3000 device was used at 324.9 nm for copper and 342.1 nm for nickel analysis. The acetylene and air flow rates were set to 1:2 dm³/min ratio in case of the latter device. Each concentration was calculated as mean of 25 parallel measured concentrations working in a 0–20 mg/dm³ measuring range and the maximum of the standard deviation was always below 0.05% during the whole experiment. Chemical Oxygen Demand (COD_{Cr}) tests were carried out with Merck COD cell test and photometric determination, according to the ISO 15705 standard.

3 Experimental plan

Selected membranes were conditioned with distilled water before the experiments, under the same conditions as set for the real experiments, and their properties are illustrated in Table 3. Single cation containing model solutions were used to test the recovery of zinc and nickel ions of different membranes (i), and the effect of concentration (ii), prepared from analytically pure zinc sulphate (ZnSO₄·7H₂O) and nickel sulphate (NiSO₄·6H₂O). The influence of competing co-ions in the feed solutions and the effect of concentration on membrane rejection were tested at 1:2, 1:1 and 2:1 mass ratio for nickel and zinc, respectively (ii) keeping the total concentration of cations at 1100 ppm. Real pre-treated process water was provided by an operating metal plating plant and used for the implementation experiments (iii).

Simultaneously the effect of temperature was studied. Calcium-hydroxide was added to the genuine process water. Precipitates as metal-hydroxides and CaCO₃ encapsulated and/or adsorbed the bulk content of copper and nickel ions, then filtered out by a press filter. In spite of the lowered metal ion content in the water phase, the followed metal ion concentrations were still above the emission limits, moreover the water contained organic compounds too, determined as COD_{Cr}, which justified the need of further treatment. The summarised experimental plan is shown in Table 2.

4 Results and discussion

4.1 Membrane selection experiments (i)

Measured feed concentrations are shown in Table 4.

Permeate flux was calculated according to Eq. (1):

$$J = \frac{1}{A} \cdot \frac{dV}{dt} \quad (1)$$

where A is the active area of membrane, V is the volume of the permeate, t is the contact time (Fig. 2 and Fig. 3).

Table 2 Experimental plan

Series of experiments	Membrane/Supplier	Composition of feed	Applied pressure	Temp.
i)	RO 9100340361/Zenon	200 ppm Ni ²⁺	Const. 35 bar	Const. 25°C
	MPF 44/Koch Membrane Inc. DL /Sterlitech Corp.	or 200 ppm Zn ²⁺		
ii)	DL /Sterlitech Corp.	Ni ²⁺ : 200, 1100, 2000 ppm Zn ²⁺ : 200, 1100, 2000 ppm Ni ²⁺ - Zn ²⁺ : 360-740, 550-500, 740-360 ppm	Const. 35 bar	Const. 25°C
iii)	DL /Sterlitech Corp.	COD _{Cr} : 626 mg O ₂ /dm ³ , Cu ²⁺ : 0.790 ppm Ni ²⁺ : 0.528 ppm Spec. ele. conductivity: 30.3 mS/cm	Const. 35 bar	15, 20, 25, 30°C

Table 3 Properties of the tested membranes

Membrane	Operation pressure	pH range	Rejection or molecular weight cut-off
RO 9100340361/ Zenon	15-35 bar	2-10	Rejection 97% for NaCl
MPF 44/Koch Membrane Inc.	14-40 bar	2-10	MWCO 250 Dalton
DL /Sterlitech Corporation	7-35 bar	2-11	Rejection 96% for MgSO ₄ , or MWCO 150-300 Dalton

Table 4 Measured feed concentrations in case of experiment series i)

Membrane/Supplier	Ni ²⁺ [mg/dm ³]	Zn ²⁺ [mg/dm ³]
RO 9100340361/Zenon	186	242
MPF 44/Koch Membrane Inc.	193	192
DL /Sterlitech Corp.	182	214

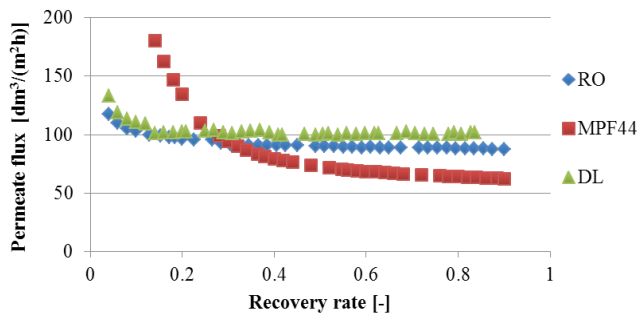


Fig. 2 Permeate flux vs recovery rate in case of 0.2 g/dm³ Zn²⁺ solution feed

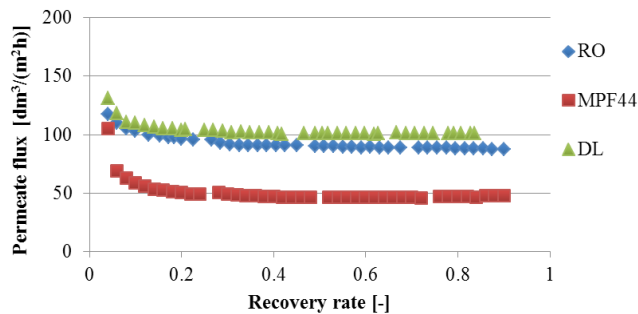


Fig. 3 Permeate flux vs recovery rate in case of 0.2 f/dm³ Ni²⁺ solution feed

The recovery rate was calculated as follows:

$$Y = \frac{V_p}{V_f} \quad (2)$$

where Y is the recovery rate (or yield), V_p is the volume of the permeate and V_f is the volume of the feed solution.

Concerning the permeate concentrations measured in 4 charges, the average concentrations (see Eq. (3)) were calculated and plotted versus the recovery rate (Fig. 4).

$$c_{Average} = \frac{c_1V_1 + c_2V_2 + c_3V_3 + c_4V_4}{V_1 + V_2 + V_3 + V_4} \quad (3)$$

where c_i are the followed ion's concentration in the permeate charges, V_i are the volume of the permeates.

Since the effluent charge limits to the sewer system are limited to 500 ppm both for nickel and zinc ions [16], all membranes fulfil the requirements. MPF44 membrane showed similar permeate concentrations both for nickel and zinc feed solutions, while RO and DL type membranes showed lower permeate concentrations for nickel than zinc, however this does not lead to the evidence of higher rejection to nickel ion in general. To compare the filtration efficiency of the membranes, the rejection values were calculated both for nickel and zinc ion according to Eq. (4), and compared (see Fig. 5).

$$R_i = \left(1 - \frac{c_{i,average}}{c_f}\right) \cdot 100\% \quad (4)$$

where c_f is the is the feed concentration.

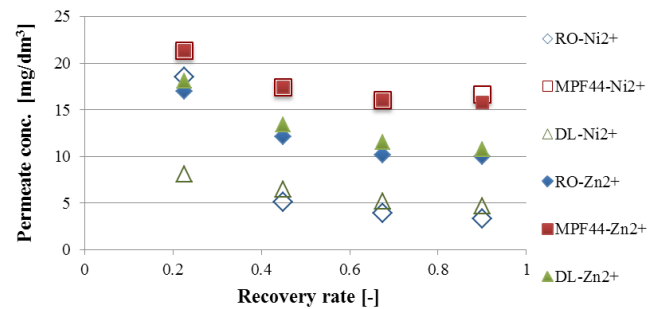


Fig. 4 Permeate concentrations

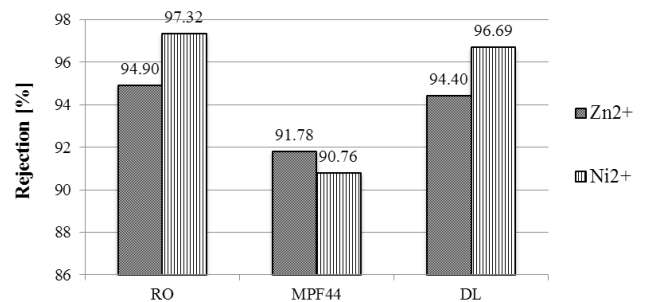


Fig. 5 Rejections of membranes p=35 bar, T=25°C

The RO membrane showed the highest rejections for both ions, as expected. Concerning nickel rejections RO and DL membranes provided 2% higher values for nickel than zinc, while in case of MPF44 this is reversed.

Critical evaluation of membrane properties revealed that DL type nanofiltration fits the best to the requirements: it has high enough flux coupled with high enough rejection values and good stability, which enhances its applications.

Table 5 Structured ranking of membranes by selected parameters: permeate flux (1: lowest, 3: highest), permeate concentration (1: highest, 3: lowest), rejection (1: lowest, 3: highest) and stability (1: least stable, 3: most stable) in general: highest score represents the most favorable case

	RO		MPF44		DL	
	Nickel	Zinc	Nickel	Zinc	Nickel	Zinc
Permeate flux	2	2	1	1	3	3
Permeate concentration	3	3	1	1	2	2
Rejection	3	3	1	1	2	2
Stability*	1	1	2	2	3	3
SUM	9	9	5	5	10	10

* stabilities were measured previously [17]

4.2 The effect of feed composition and concentration on the rejection (ii)

It is revealed earlier that for MPF44 membrane at constant pressure and temperature an increase of the feed copper ion concentration by ten-fold, decreases the flux by 16% [18, 19].

Although similar decreasing tendency could be observed in case of DL type membrane, a 10-fold increase in concentration decreased the flux insignificantly, only by 7% and 5% for zinc and nickel ions, respectively (Fig. 6 and Fig. 7).

Keeping the total cation concentration constant (1100 mg/dm³), the membrane showed constant rejection for zinc (94.48% ± 0.12%) and nickel (97.09 ± 0.11%) independently of the Zn²⁺:Ni²⁺ mass ratio (Fig. 8).

4.3 Implementation of nanofiltration into an existing technology chain (iii)

Based on the results of experiments i) and ii), DL membrane was tested as a final treatment step of process water originating from an electroplating plant. Ca(OH)₂ addition, precipitation enhanced with coagulation-flocculation and press filtration were applied as pre-treatment steps for the genuine process water, resulting in a moderate metal ion containing solution. After the pre-treatment, nickel and copper ion concentrations were still above the emission limits, which justified the necessity of further treatment. Composition of the pre-treated process water (the feed of nanofiltration) is shown in Table 6.

In contrast to the flux values of model process waters, the flux of the real pre-treated process water at different temperatures showed S-shaped curves illustrated in Fig. 9, beyond reasonable doubt of the continuous concentration concomitant increasing osmotic pressure difference. Therefore the decreasing driving force resulted in a dramatic and continuous decrease in flux as the solution got more concentrated. With increasing temperature the flux increased, however the effect of temperature seems insignificant compared to the effect of recovery rate.

Table 6 Composition of the pre-treated test solution

Parameter	Unit	Value
pH	-	6.87
Conductivity	mS/cm	30.3
COD _{Cr}	mg/dm ³	626
Cu ²⁺	mg/dm ³	0.790
Ni ²⁺	mg/dm ³	0.528
Na ⁺	mg/dm ³	2110

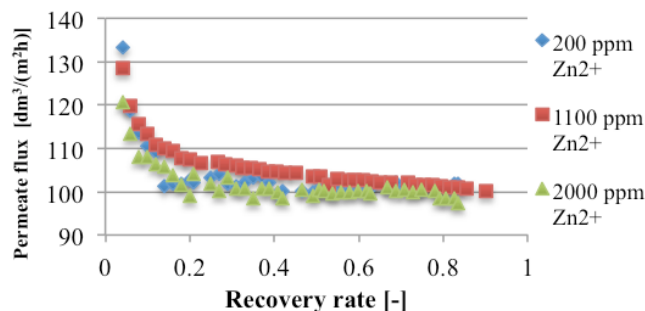


Fig. 6 Permeate flux vs recovery rate in case of 200, 1100, 2000 ppm Zn²⁺ solution feed

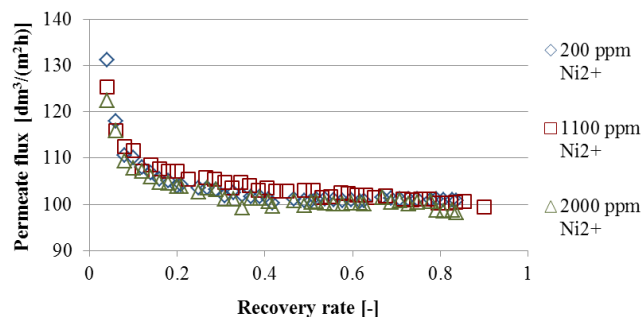


Fig. 7 Permeate flux vs recovery rate in case of 200, 1100, 2000 ppm Ni²⁺ solution feed

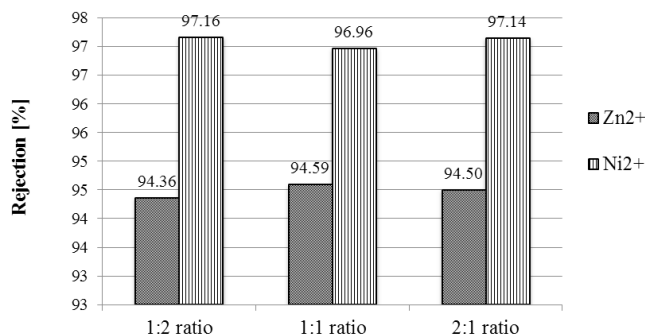


Fig. 8 Membrane rejection for zinc and nickel

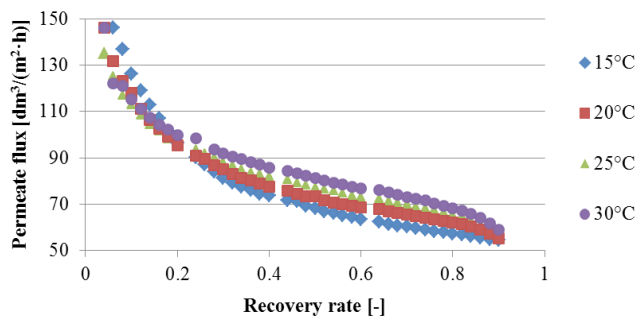


Fig. 9 Permeate flux vs recovery rate in case of the real pre-treated sample

It is clearly visible in Fig. 10 and Fig. 11 that the temperature applied in the range of 15-30°C has almost no effect on permeate concentrations and rejection both for copper and nickel. Effluent limit [16] was already reached at a recovery rate of 0.4, and 0.2 in case of copper and nickel, respectively. For complete evaluation of the efficiency of nanofiltration, the conductivity of permeates as well as their COD_{Cr} values were determined. Since NF membranes reject multivalent ions while let most of the monovalent ones through, the conductivity can provide an informative overview about the overall rejection of salinity.

For comparison the initial conductivity of the feed solution is indicated in Fig. 12 at zero recovery rate. The main components of the pre-treated process water were two monovalent ions, Na^+ and Cl^- , representing a high salinity. After the first drop in specific electric conductivity, a monotone increasing trend could be observed as the process proceeded, indicating that monovalent ions are rather pressed through the membrane from a more concentrated solutions than divalent ones. At the last charge actually the NF turned to an enrichment process, instead of elimination, due to such high concentrations that the ions were physically pressed through the membrane.

Considering COD_{Cr} values they stayed below the limit almost during the whole process. The required COD_{Cr} limit for effluents for electroplating plant effluents is $1000 \text{ mg } O_2/dm^3$, which can be kept approaching the recovery rate of 0.8, *i.e.* 80%. When the retentate is too concentrated, the complex-forming agent is pressed through the membrane resulting in an increased COD value (Fig. 13).

Rejection data shown in Fig. 14 were significantly higher in case of Ni^{2+} (71-76%) at all examined temperatures than observed for Cu^{2+} , (41-45%). These rejection values are much lower than those of model test solutions tested before [18], which were always above 90%. The explanation of this phenomenon is that in real process waters the existing other ions hinders the rejection of heavy metals. Highest rejection value was obtained at 15°C both for nickel and copper ions and at higher temperatures the rejections consequently dropped, though not significantly (only with an average of 5%).

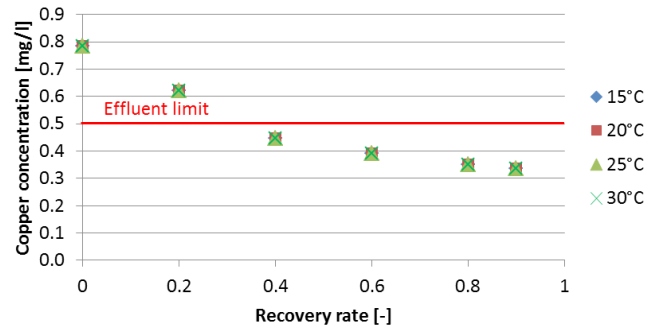


Fig. 10 Copper concentration vs recovery rate

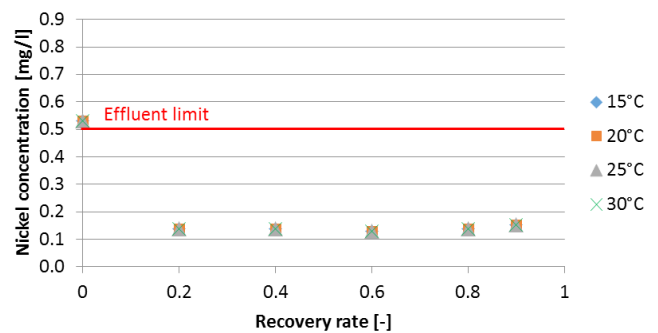


Fig. 11 Nickel concentration vs recovery rate

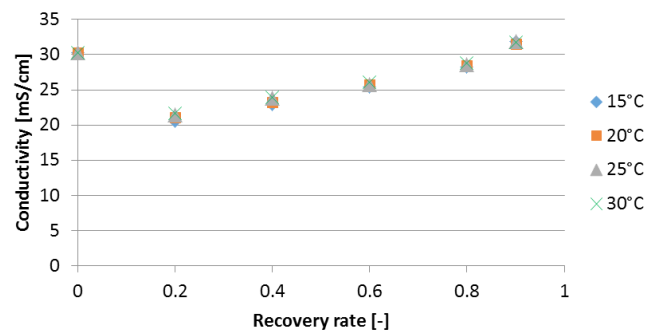


Fig. 12 Specific electric conductivity vs recovery rate

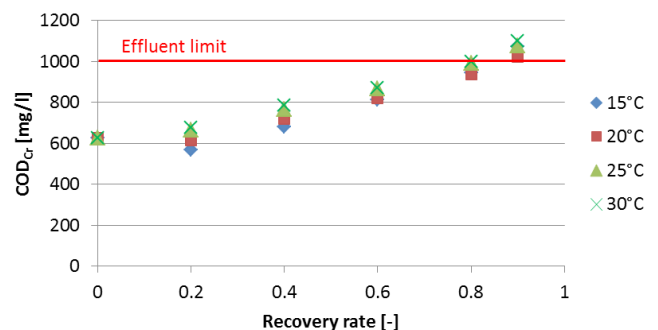
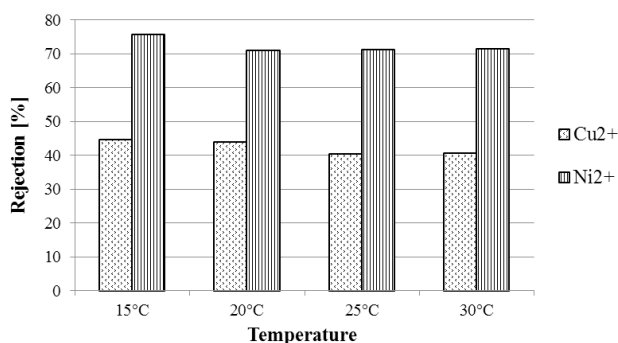


Fig. 13 COD_{Cr} concentration vs recovery rate

Table 7 The followed metal ions' relevant physical parameters

Metal ion	Ionic radius [pm] acc. to ref. [21]	Me-O bond length [pm] acc. to ref. [22]	Calculated hydrated ionic diameter [pm]	Hydrated ionic diameter [pm] acc. to ref [20]	Electro negativity acc. to ref. [23]
Ni ²⁺	72	210.8	613.6	808	1.91
Zn ²⁺	74	212.3	618.6	860	1.65
Cu ²⁺	69	212.1	613.2	838	1.90
Na ⁺	95	243.0 [24]	701.0	358	0.93

**Fig. 14** Copper and nickel rejections vs the temperature

Based on these results a batch nanofiltration unit can be implemented into the process chain, when a volume reduction ratio of 2 is applied, *i.e.* the half of the pre-treated process water can be further treated with nanofiltration membrane proving a drainable permeate which fulfil all the requirements of the emission limits. In case of technology extension, continuous nanofiltration can also be implemented into the process chain, however recycling the retentate and mixing with the feed is a crucial point of the technology. In case of continuous NF systems the recovery rate can be adjusted to 0.2 or 0.25, which avoids a severe concentration of retentate thus providing a longer operation time.

Experiments i), ii) and iii) can be evaluated according to the analysis of the hydrated ionic diameter. Considering the hydration of solutes in aqueous phase, ions with more coordinating water molecules and/or higher hydrated radii or diameter, prognoses higher rejection. Early studies provided higher calculated hydrated radii for Zn²⁺ (4.30 Å) than Cu²⁺ (4.19 Å) and Ni²⁺ (4.04 Å) [20], but newer ones determined the metal-oxygen bond length in the coordinated structures, providing lower values of hydrated radii (Table 7). By the application of these values in hexa-aqua complexes and limiting the structure of 3D-symmetry to the simplest *Th*-symmetry, the hydrated ionic diameter can be calculated as follows:

$$d_h = d_{ion} + 2 \cdot d_{Me-O} + 2 \cdot x \quad (5)$$

where d_{ion} is the diameter of bear ion, d_{Me-O} is the length of Me-O bond and x is the height of the isosceles triangle, which is the shape of a water molecule and can be calculated easily

knowing the bond angles and H-O bond length (in water molecule x is regarded as 60 pm).

By using the ionic radius of Ref. 21 and the Me-O bond provided by Ref. 22, the calculated hydrated ionic diameters in ascending order is as follows: Cu²⁺ < Ni²⁺ < Zn²⁺ = 613.2 pm < 613.6 pm < 618.6 pm. The order correlates with our observations concerning the rejections: the highest ionic diameter-possessing ion had the highest rejection, as expected.

Since the feed solution contained mono- and divalent ions as well, and monovalent ones definitely pressed through the membrane so their hydration have to be considered, too. Sodium forms 4-8 aqua complexes, and according to X-ray diffraction data, the length of Na⁺-O bond in hexa-aqua complex is estimated as 243 pm, resulting in a calculated hydrated ionic diameter of 701 pm which is greater than those of calculated for nickel, zinc or copper ions. In presence of high electronegativity ions, sodium ion was probably less hydrated, resulting in an increased transport through the nanofiltration membrane. Our calculations showed that with the assumption of hexa-aqua complexes and *Th*-symmetry the hydrated ionic diameter of nickel, zinc and copper were close to each other, thus our expectation was similar rejection values for all these metal ions. In concentrated solutions, however the *Th*-symmetry or even the hexa-aqua structure can be distorted resulting in different hydrated ionic diameter. In addition to steric properties of dissolved cations, counter ions could also influence the transport mechanism and the rejection. We think that an increase in total salinity, *i.e.* dissolved solid content, could increase the possibility of the ions pass through the membrane, reducing the rejection, while at constant salinity the electronegativity of the elements could have an influence on hydration and rejection. Our experiments verified that the higher the electronegativity of an ion, the higher the rejection was however, this statement requires more data and authentication. Based on these considerations the hydration is important, but not a critical influencing factor in rejection.

5 Conclusions

Regarding the performance parameters (rejection and average flux) of MPF44, DL and RO membranes, the last two were more efficient for recovery and separation of nickel and zinc ions from test solutions, showing higher rejection and high average flux at the same time. Considering the results of rejections of

nickel and zinc ions, they were all above 90% for all the three membranes tested. It can be concluded that nanofiltration is an appropriate method for recovery of nickel and zinc from process waters. Although the hydration properties of nickel and zinc ions dissolved in distilled water may have an influence on rejection of DL membrane, in case of concentrated solutions, moreover in complex, real process waters the hydration of ions seems to be the main determining factor in membrane rejection however, other properties such as electronegativity may also influence it.

Although in case of the pre-treated real process water significantly higher rejection could be observed for Ni²⁺ than Cu²⁺ at all examined temperatures, the rejection values were much lower than those of measured for model test solutions. In real process waters the negative effects of counter ions, and unidentified distortion in hydrated complexes could be observed resulting in a reduced rejection of heavy metal ions. The highest rejection value was obtained at 15°C for the real process water. The specific electric conductivity values of permeates raised significantly with the advancement of the NF process, indicating an enhanced transport of monovalent ions (especially sodium ions) through the DL membrane.

To conclude the implementation of NF to industrial process water treatment chain according to the laboratory scale experiments after an approximate 10-day-long initial conditioning phase, regular operation can start and reaching a recovery rate between 0.2-0.5 provides purified permeate that fulfills all the emission limits. This indicates the importance of combined technologies: in case of smaller loading more effective rejection and longer lifetime of a membrane can be achieved.

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