



Removal of heavy metals from aluminum anodic oxidation wastewaters by membrane filtration

Nuray Ates¹ · Nigmet Uzal²

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Abstract

Aluminum manufacturing has been reported as one of the largest industries and wastewater produced from the aluminum industry may cause significant environmental problems due to variable pH, high heavy metal concentration, conductivity, and organic load. The management of this wastewater with a high pollution load is of great importance for practitioners in the aluminum sector. There are hardly any studies available on membrane treatment of wastewater originated from anodic oxidation. The aim of this study is to evaluate the best treatment and reuse alternative for aluminum industry wastewater using membrane filtration. Additionally, the performance of chemical precipitation, which is the existing treatment used in the aluminum facility, was also compared with membrane filtration. Wastewater originated from anodic oxidation coating process of an aluminum profile manufacturing facility in Kayseri (Turkey) was used in the experiments. The characterization of raw wastewater was in very low pH (e.g., 3) with high aluminum concentration and conductivity values. Membrane experiments were carried out with ultrafiltration (PTUF), nanofiltration (NF270), and reverse osmosis (SW30) membranes with MWCO 5000, 200–400, and 100 Da, respectively. For the chemical precipitation experiments, FeCl₃ and FeSO₄ chemicals presented lower removal performances for aluminum and chromium, which were below 35% at ambient wastewater pH ~ 3. The membrane filtration experimental results show that, both NF and RO membranes tested could effectively remove aluminum, total chromium and nickel (>90%) from the aluminum production wastewater. The RO (SW30) membrane showed a slightly higher performance at 20 bar operating pressure in terms of conductivity removal values (90%) than the NF 270 membrane (87%). Although similar removal performances were observed for heavy metals and conductivity by NF270 and SW30, significantly higher fluxes were obtained in NF270 membrane filtration at any pressure that there were more than three times the flux values in SW30 membrane filtration. Due to the lower heavy metal (<65%) and conductivity (<30%) removal performances of UF membrane, it could be evaluated as pretreatment followed by NF filtration to protect and extend NF membrane life. The water treated by both NF and RO could be recycled back into the process to be reused with economic and environmental benefits.

Keywords Aluminum · Anodic oxidation · Heavy metal · Ultrafiltration · Nanofiltration · Reverse osmosis · Water reuse

Introduction

The aluminum industry contributes to the global economy and to the individual national economies of more than 30

countries. Primary aluminum production, the second most used metal in the world, has been recorded as 51 million tonnes (Das and Yin 2007; IAI 2013). Aluminum is used for varied applications in the construction industry, in transport, in electrical engineering, in packing, and in all kinds of equipment. Among them, production of fencing construction such as windows, doors, and wall and roof profile systems are common usages (Sergey 2011). Finished aluminum is produced by extrusion of the ingots and then the extruded pieces are anodized or covered (Dufour et al. 2001). The aluminum surface is converted to aluminum oxide in the anodizing process. Anodic coatings are impregnated with organic and inorganic dyes and pigments (Lyle et al. 2000) and sulfuric acid solutions are widely employed as electrolytes in anodizing

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✉ Nuray Ates
nuraya@erciyes.edu.tr

¹ Environmental Engineering Department, Engineering Faculty, Erciyes University, 38280 Kayseri, Turkey

² Civil Engineering Department, Abdullah Gul University, 38380 Kayseri, Turkey

(Sakon et al. 2005; Sanders 2012). The conventional anodizing process has environmental problems that producing huge amounts of wastewater with toxic reagents, heavy metals, and wide variation in pH (Sakon et al. 2005). Wastewater is one of the main issues for the aluminum industry because of significant environmental concerns and public health problems, since they usually contain a notable amount of heavy metals and even toxic elements with relatively high solubility (Agrawal and Sahu 2009). Heavy metals released into the environment bioaccumulate in living organisms and have a serious impact even in trace quantities (Lin et al. 2005; Murthy and Chaudhari 2008).

Nowadays, manufacturing industries have been under pressure for they have been faced with gradually stringent regulations on heavy metals wastewater discharges. Since heavy metals cannot be biologically degraded or destroyed (Gupta and Bhattacharyya 2008), physicochemical processes are more promising in treating these pollutants (Murthy and Chaudhari 2008). There are several methods in removing heavy metals from wastewater including chemical precipitation (Baltpurvins et al. 1996; Huisman et al. 2006), ion exchange (Dabrowski et al. 2004; Wingenfelder et al. 2005), adsorption (Lazaridis et al. 2001; Doyle and Liu 2003), membrane filtration (Bouranene et al. 2008; Katsou et al. 2011; Al-Rashdi et al. 2013), floatation (Waters 1990; Polat and Erdogan 2007; Yuan et al. 2008), and electrochemical treatment technologies (Ku and Jung 2001; Lambert et al. 2006; Heidmann and Calmano 2008).

Because of the simplicity and cost-efficiency of the process, chemical precipitation has been widely applied in heavy metals removal by adding lime (Peters et al. 1985; Karthikeyan et al. 1995; Huisman et al. 2006). In approximately 75% of electroplating facilities, basic precipitation of heavy metals as insoluble hydroxides, carbonates, or sulfides has been commonly applied to treat industrial wastewater (Karthikeyan et al. 1995; Huisman et al. 2006; Ozverdi and Erdem 2006). However, the requirement of large amounts of lime to increase and keep pH high enough for the removal heavy metals, besides producing secondary wastes such as metal hydroxides, is a major drawback of chemical precipitation (Matlock et al. 2002; Dabrowski et al. 2004; Qdais and Moussa 2004). Also, treated water might still have low levels of heavy metals up to a few mg/L after chemical precipitation (Dabrowski et al. 2004).

Among the other treatment processes, the membrane process, (MF, UF, NF, RO) exhibits a great assurance efficiency for removing heavy metals due to its high efficiency and convenient operation (Jakobs and Baumgarten 2002; Mohammad et al. 2004; Frares et al. 2005; Ghezzi et al. 2008; Murthy and Chaudhari 2008). In the membrane process, heavy metals are not only removed from wastewater but heavy metals and treated water can also be recovered and reused at greater

efficiencies (Heller et al. 1998; Yang et al. 2001; Wong et al. 2002; Castelblanque and Salimbeni 2004).

Although there are researches on removal of heavy metals by chemical precipitation and the membrane process, limited information is available on aluminum removal. The available studies in the literature focusing on heavy metal removal from industrial wastewater are usually using synthetic wastewater with individual heavy metals at low concentrations. Additionally, to the best of our knowledge, no study was found about the treatment using the anodizing plating process in aluminum production, especially, aluminum removal in low pH (e.g., pH ~ 3) wastewater. Therefore, the main focus of this study was to evaluate the removal of heavy metals (e.g., aluminum, nickel, and chromium) by the membrane processes from the anodizing plating process in the aluminum products manufacturing sector in Kayseri (Turkey). NF and RO membranes were mainly examined to determine the heavy metal removal performance. For this purpose, wastewater produced during the aluminum anodizing plating process was collected from an aluminum profile manufacturing facility. On the other hand, the UF membrane process was also investigated to assess its performance as a pretreatment step to prolong membrane life, to prevent fouling in short time for NF or RO, and to reduce sludge production for chemical precipitation within the treatment trail. Besides, the opportunity of reusing the treated water from membrane process in the production line was assessed, since recovering of valuable materials such as heavy metals and water has been crucial for sustainable and cleaner production in industries. Since the chemical precipitation process using iron-based chemical (FeCl_3) was currently used to treat the process wastewater in the facility, its performance was also evaluated. To improve the treatment system performance in the facility, variable chemical dosages, pH values, and different chemicals (FeSO_4 and $\text{Ca}(\text{OH})_2$) were tested in the chemical precipitation experiments. Thus, the performances of chemical precipitation could be compared with membrane filtration.

Materials and methods

Plant description and source of wastewater

The plant is one of the largest aluminum production facilities in Kayseri with 11.520 tonnes of aluminum profile production capacity, of which 7500 tones originates from the anodizing plating process. Anodizing plating process in the plant consists of cleaning, caustic etching, acid neutralization, aluminum anodizing, coloring, fixing, and drying. After each step, the product will be rinsed once or twice with deionized water except during the cleaning process. Cleaning of the aluminum profiles prior to anodizing is essential to have a uniform and attractive appearance of the final product. An organic based

cleaner (35–50 g/L Politoksal DG 16) is used for the cleaning purposes. Coloring involves the absorption of a colored dye into the pores of the oxide coating. In the coloring process, dyestuffs can bond to the oxide or metal ions in the anodized layer and the anodized work is dipped in a tank containing colored ions of other metals. In our process, nickel and tin solutions were used applying different contact periods for the intended color (bronze–black). A flow diagram of the aluminum profile production process with wastewater sources in the production line is given in Fig. 1.

The wastewater used in this work was collected from the main wastewater collector of the aluminum production facility. The wastewater was collected in 25 L polyethylene jerrycans at different times and they were shipped to the laboratory. Samples were kept in the dark at +4 °C until the experiments. The raw samples were filtered (1 μm glass fiber filters, Sartorius) prior to characterization, chemical precipitation, and membrane tests. The analyses of samples were repeated three times and average values were given in a range. Table 1 presents the physicochemical characteristics of wastewater used in experiments.

Membranes and filtration system

Three different flat-sheet membranes, PTUF (Sterlitech), NF270 (Dow–Filmtec), and SW30 (Dow–Filmtec) were tested in this study. PTUF membrane is made of polyethersulfone. NF270 membrane is composed of a semiaromatic piperazine-based polyamide layer on top of a polysulfone (PSF) microporous support reinforced with a polyester non-woven backing layer (Freger et al. 2002). RO membrane is made of polyamide with non-porous active skin layer (Tu et al. 2011). Properties of the tested membranes provided by manufacturers are presented in Table 2.

In the membrane experiments, a lab-scale cross-flow flat-sheet test unit (SEPA® CF II, Sterlitech, USA), which simulates hydraulic dynamics in commercial membrane elements, was used. The membrane cell body is made of stainless steel and the membrane test unit accommodates any 19 × 14 cm flat-sheet membrane for a full 140 cm² of effective membrane area. The equipment of membrane test system are a high

pressure pump equipped with digital variable frequency drive to adjust feed flow rates, pressure relief valve, membrane cell, membrane cell holder, high pressure concentrate control valve, hydraulic hand pump, and feed tank (10 L maximum solution volume, stainless steel). Temperature of the feed tank was kept constant by circulating cool tap water by chiller coil embedded in feed tank during the membrane tests (Fig. 2).

Experimental procedures

Membrane filtration

Membrane filtration experiments were designed to evaluate rejections of aluminum, nickel, and chromium at various operating pressures by UF (5 and 7.5 bar), NF (10, 15 and 20 bar) and RO (10 and 20 bar) membranes. In order to keep a constant concentration in feed, the experiments were conducted in total recycle mode in which both concentrate and permeate were channelized to the feed tank. Feed and permeate samples were collected during operation at different time intervals to monitor flux developing and rejection of heavy metals. All experiments were performed at feed water temperatures of 25 ± 5 °C.

In order to remove the organic and inorganic foulants from the membrane surfaces, membranes used in wastewater filtration tests were cleaned. The cleaning procedure was performed by clean-in-place method, i.e., the membranes were kept in the test unit while the cleaning solutions were circulated through the system consecutively each for 1 hour in the following order: nitric acid solution at pH of 3, deionized water, sodium hydroxide solution at pH of 9, and again distilled/deionized water under low pressure (2–3 bar). The flux was monitored as collecting samples in a graduated cylinder and calculating flux at each hour of operation using the following equation:

$$J = \frac{dV/dt}{A}$$

Where *J* is the flux (L/m²-h), dV/dt is the permeate flow rate (L/h), and *A* is the effective membrane area (m²).

Fig. 1 Flow diagram of aluminum profile production and sources of wastewater

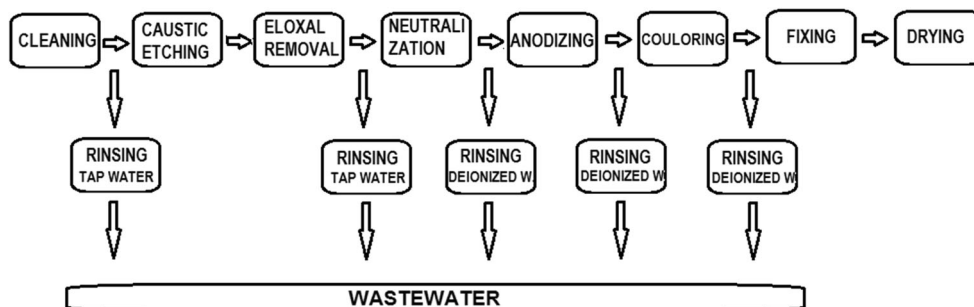


Table 1 Characterization of raw wastewater Intervals of three samples

Parameter	Value
pH	2.7–3.3
Conductivity ($\mu\text{S}/\text{cm}$)	3000–7600
Turbidity (NTU)	32–50
Suspended solids (mg/L)	160–190
Total organic carbon (TOC) (mg/L)	8.2–15.9
Oil/Grease (mg/L)	10–50
Aluminum (mg/L)	67–134
Nickel (mg/L)	3.2–5.3
Chromium (mg/L)	0.2–1.3

Chemical precipitation

Three inorganic chemicals ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$) (97% ACS reagent, Merck) were tested in a jar-test unit. Stock solutions of chemicals were prepared with 10 g of each chemical per liter of deionized water. Jar-tests were performed at different reaction conditions by varying coagulant concentrations (50, 100, 250, 500, 750, and 1000 mg/L) and different pH (3, 5, 6, 8, 9, and 11) so as to determine the optimum coagulant dosages and the pH condition with 500 ml of raw water. Besides, control experiments were conducted under stirring and settling without chemical addition to observe effect of only mixing and settlement. A laboratory flocculator was used and all experiments were repeated two times. After the chemical addition, all solutions were stirred for 2 min at 120 rpm, then it was stirred for 20 min at 30 rpm, and then 60 min was allowed for settling. The pH value was adjusted to the desired value with H_2SO_4 and NaOH was used to adjust the desired pH value before adding chemical. The supernatant was separated from the precipitate by filtration through a 0.45- μm filter paper.

Analytical methods

Furnace atomic absorption spectrometry (Shimadzu Corp., Kyoto, Japan) was used for aluminum, nickel, and chromium determination according to SM 3500 Al, Ni, and Cr, respectively (APHA/AWWA/WEF 1998). The surface morphologies of virgin and fouled membranes were observed with an environmental scanning electron microscope (SEM, LEO 440 computer controlled digital) and an atomic force

microscopy (AFM, VEECO MULTIMODE 8. TOC-VCPN analyzer (Shimadzu Corp., Kyoto, Japan), which utilizes high-purity air as the carrier gas and for sample sparging, was used for TOC analysis based on the high-temperature combustion method according to SM 5310B. The minimum quantification limit of the analyzer was 0.004 mg/L. All standards were prepared in deionized water (Milli-Q plus, Millipore, Molsheim, France) using ACS-grade chemicals. Oil/grease analysis was performed based on EPA 1664B method by Wilkser InfraCal Model HATR-T2 (USEPA 2010). Conductivity and pH analyses were measured directly using Hach HQ40D pH/Conductivity/DO meter according to SM 2510 B and SM 4500-H+, respectively (APHA/AWWA/WEF 1998).

Results and discussion

UF application

Removal of metals by membrane filtration (UF, NF, RO, and electro dialysis) has become a promising process because of its high removal efficiency, easy operation, and minimal use of space. But the size of metal precipitates in the form of hydroxides are much smaller than the pore size of UF membranes, thus these metals can pass easily through the pores of the UF membranes and these membranes exhibit low removal efficiencies for metals (Fu and Wang 2011). UF experiments were performed with 5000-Da sized polysulfone membranes at 5 and 7.5 bar pressures. The removal performances of UF membranes on aluminum, chromium, and nickel and the conductivity are given in Fig. 3. As seen in the figure, reductions in metal concentrations in permeates are improved by increasing the operation pressure from 5 to 7.5 bar on the contrary of conductivity. By UF membrane at 5 bar pressure, 24, 34, and 46% removal efficiencies in average were obtained for aluminum, nickel, and chromium, respectively. During filtration, aluminum, nickel and chromium were reduced from 74.3 to 34.2 mg/L, from 3.6 to 1.4 mg/L, and from 0.6 to 0.2 mg/L, respectively, at 7.5 bar operation pressure. While different removal performances were observed in aluminum, nickel, and chromium at 5 bar pressure, the metal removal efficiencies were similarly varied between 54 and 62% at 7.5 bar pressure. Although the difference in removal performances for aluminum and nickel between pressures of 5 and 7.5 bar

Table 2 Properties of the membranes used in this study

Class	Polymer structure	Designation	Rejection size (MWCO) (Da)	Pure water flux/pressure ($\text{L}/\text{m}^2\text{-h}/(\text{bar})$)	Contact angle (degrees)
UF	Polyethersulfone	PT	5000	153/3.5	59
NF	Polyamide	270	200–400	2930–3980/9	29
RO	Polyamide	SW30	100	700–977/56	62

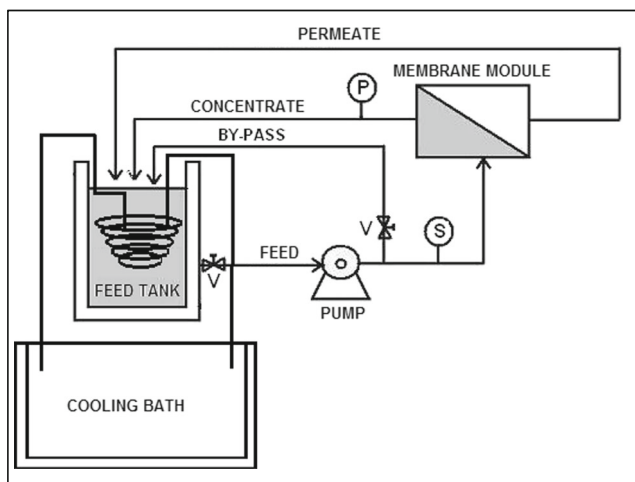


Fig. 2 Schematic diagram of the lab-scale membrane system (P: pressure gauge, S:suction gauge, V: valve)

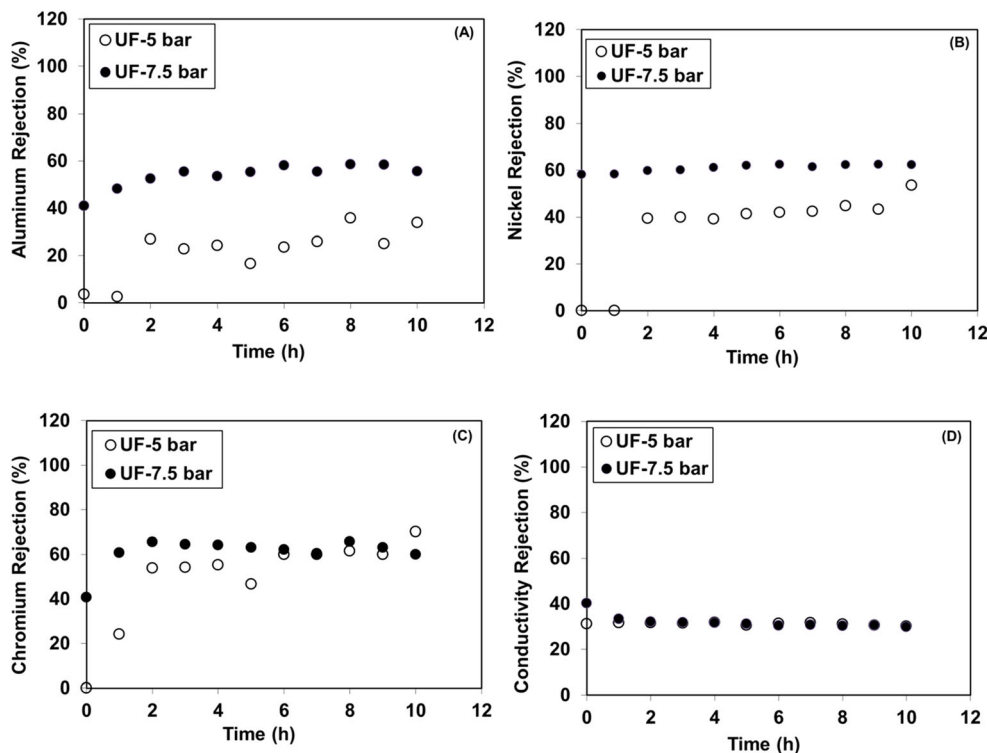
were higher, the removal performances of chromium were slightly varied up to 6 h, and then they were similar at these pressures. Contrary to this study, Srisuwan and Thongchai (2002) reported that the removal efficiencies are decreased by increasing the operation pressure from 0.5 to 2 bar. On the other hand, change in pressure did not affect removal of conductivity, which was 32% in both pressures. The removal of metals and conductivity did not change with time; a steady state was reached almost after 2 hours from the beginning of filtration. Besides metals and conductivity, organics (as TOC) coming from the cleaning of profiles were also observed in UF process. The TOC value was 15 mg/L in raw wastewater,

which was caused by the organic based cleaner used in cleaning process. TOC removal did not significantly vary with respect to pressure and it was decreased to 11.2 and 10.5 mg/L at the steady state for 5 and 7.5 bar, respectively and corresponding TOC rejections were 25% (5 bar) and 30% (7.5 bar). Moreover, TOC rejections were stable during the membrane filtration for both applied pressures. Relatively promising metal removals were reported by Katsou et al. (2011), treating by polyvinylidene fluoride membrane with a molecular weight cutoff of 200 kDa. The removal performances were as followed in order for lead, copper, zinc, and nickel as 60, 40, 25 and 15%, respectively. The possible reason for a much lower nickel removal observation with respect to our results is that the membrane molecular weight cutoff is much higher (5000 Da) than the one used in this study. Gohari et al. (2013) reported higher than 90% of lead removal from synthetic solution simulating electroplating wastewater by polyethersulfone UF membrane having 24 kDa molecular weight cutoff at 0.5 bar pressure.

NF application

The separation of ions by NF is achieved both by size exclusion and by electrical interactions between the ions in the feed aqueous solution and the charged NF membranes (Linde and Jonsson 1995; Gherasim and Mikulasek 2014). The aim of the NF experiments was the removal of heavy metals and conductivity from the wastewater. In the NF experiments, NF 270 membrane was employed at 10, 15, and 20 bar

Fig. 3 The impact of pressure on time dependent rejection of aluminum (a), nickel (b), chromium (c), and conductivity (d) by PTUF



transmembrane pressures and the decreasing of conductivity, aluminum, nickel, and chromium heavy metals were determined for the first 10 h of operation and the results of removal tests were given in the Fig. 4.

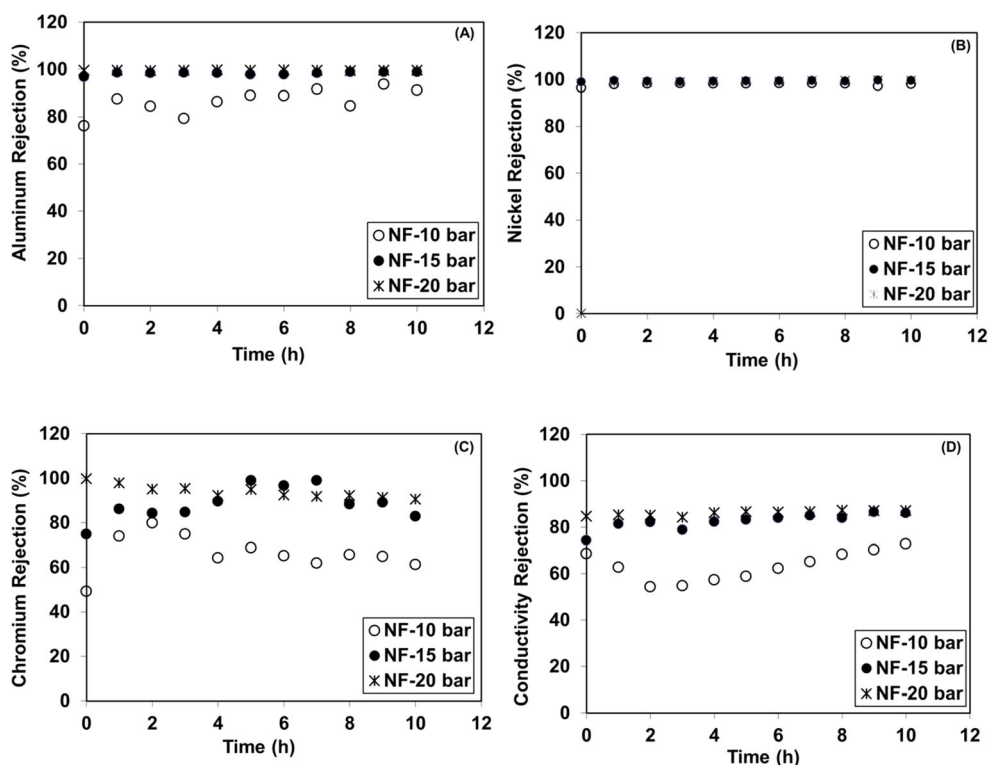
As seen in Fig. 4, for the NF experiments at 10 bar pressure, conductivity values decreased from 2.82 to 0.98 mS/cm. TOC values decreased from 13.9 to 6.8 mg/L (data not shown). After 2 h of membrane operation, TOC was stabilized and varied between 6.6 and 6.9 mg/L. The removal values for TOC and conductivity at steady state were 65 and 51%, respectively. During the NF experiments, aluminum, nickel and chromium decreased from 64.9 to 1.5, 4.6 to 0.1, and 0.2 to 0.06 mg/L, respectively. According to these results, aluminum, nickel, and chromium heavy metals were removed 91, 97, and 66% by NF270, respectively. Thus, aluminum and nickel heavy metals were almost completely removed from the raw wastewater with the NF270 membrane.

For the 15 bar of NF tests, conductivity values decreased from 3.38 to 0.63 mS/cm and TOC values (data not shown) decreased from 8.2 to 4.1 mg/L. The removal rate for conductivity and TOC were 81 and 70%, respectively, by NF at 15 bar. Organic constitutes (TOC) in the permeate did not change significantly corresponding to time. While aluminum values decreased from 116.4 to 15.4 mg/L and the removal rate for aluminum was 98%, nickel was removed with 99%, and it was 89% for chromium by NF270 at 15 bar. According to these results, increasing TMP from 10 to 15 bar had the

most impact on chromium removal that chromium removal increased from 66 to 89%.

For the 20 bar of NF tests, conductivity values decreased from 3.33 mS/cm to 0.46 mS/cm and TOC values (data not shown) decreased from 13.7 mg/L to 5.2 mg/L. Similar to 10 bar of NF270, TOC values reached a steady state condition in 20 bar NF270 after almost 30 min. For 20 bar of NF270 tests, conductivity and TOC removals at steady state were 86 and 61%. In NF process, aluminum values decreased from 129.3 to 0.53 mg/L, nickel values decreased from 5.33 to 0.05 mg/L, and chromium values decreased from 0.60 to 0.04 mg/L. The removal performances of copper, cobalt, manganese, lead, and arsenic were also investigated by Al-Rashdi et al. (2013) using NF 270 membrane. The rejection of NF270 membrane was in the order of $Cu^{2+} > Cd^{2+} \approx Mn^{2+} > Pb^{2+} \approx As^{3+}$. Although NF270 membrane could not retain As^{3+} , the rejections of membrane were about 100, 99, 89 and 74% for the removal of Cu^{2+} , Cd^{2+} , Mn^{2+} , and Pb^{2+} , respectively. In another study performed by Bouranene et al. (2008), as the removal rate was 96% for cobalt, it was 79% for lead at pH 4.0. In accordance with the literature, heavy metal removals with NF 270 membrane at 20 bar pressure were 99% for aluminum, 99% for nickel, and 94% for chromium. Aluminum, nickel, and chromium heavy metals were almost completely removed by NF270.

Fig. 4 The impact of pressure on time dependent rejection of aluminum (a), nickel (b), chromium (c), and conductivity (d) by NF270



RO application

RO tests were performed for 12 h of operation with SW30 membrane at two different pressures (10 and 20 bar) and TOC, conductivity and heavy metal (aluminum, nickel, and chromium) removal values were obtained. For the 10 bar of RO operation, conductivity values decreased from 3.9 to 0.68 mS/cm (Fig. 5) and TOC values decreased from 15.9 to 2.3 mg/L (data not shown) and the removal of conductivity and TOC at steady state were reached up to 89 and 86%, respectively. TOC did not vary with respect to time that the steady state condition was reached in 30 min. In Fig. 5, the removal performances of aluminum, nickel, and chromium are given. As illustrated in the figure, nickel values decreased from 5.0 to 0.14 mg/L, chromium values decreased from 1.3 to 0.01 mg/L, and aluminum values decreased from 134.6 to 1.1 mg/L during the RO filtration process. Aluminum, nickel, and chromium heavy metals were almost completely removed for SW30 membrane at 10 bar and the removal ratios were 99, 99, and 97%, respectively.

For the 20 bar of RO operation, conductivity values decreased from 3.05 to 0.35 mS/cm (Fig. 5) and TOC values decreased from 8.6 to 0.5 mg/L (data not shown) and the removal of conductivity and TOC at steady state were reached up to 94 and 89%, respectively. As with the other parameters, the TOC did not change with time and reached equilibrium within the first half hour. During the 20 bar of RO membrane tests, aluminum values decreased from 100.81 to 0.50 mg/L, nickel values decreased from 3.80 to 0.03 mg/L and

chromium values decreased from 0.35 to 0.02 mg/L, as shown in Fig. 5. Heavy metals were removed almost completely for SW 30 membrane at 20 bar and removal ratios at steady state conditions were obtained as 99% for aluminum, 99% for nickel and 94% for chromium.

Garcia et al. (2013) applied RO/NF membranes for metal removal from a municipal wastewater treatment plant and a MBR pilot plant. The heavy metal rejections were between 94.5–99%, with copper and nickel concentrations of 0.01–0.7 µg/L and zinc concentration of 0.7–5.7 µg/L in permeate. The results of RO experiments showed that SW30 membrane as the RO membranes metal removal efficiency was better than the NF270 membrane. This is in accordance with the literature and Qdais and Moussa (2004) examined the performance of RO and NF membranes for cadmium and copper removal and found that the RO system showed higher than 98% removals for both metals and the NF unit achieved metal removal ratios higher than 90%.

Flux development

Clean water and raw water fluxes of membranes tested with respect to applied pressures were given in Table 3. The clean water fluxes of PTUF, NF270, and SW30 membranes were compatible with fluxes provided by manufacturer (Table 2). On the other hand, contact angle values of membranes also support the flux trend that PTUF (59°) (Benitez et al. 2009) and SW30 (62°) (Tu et al., 2011) membranes present hydrophobic surface, while NF270 (27°) (Tu et al. 2011) membrane

Fig. 5 The impact of pressure on time dependent rejection of aluminum (a), nickel (b), chromium (c), and conductivity (d) by SW30

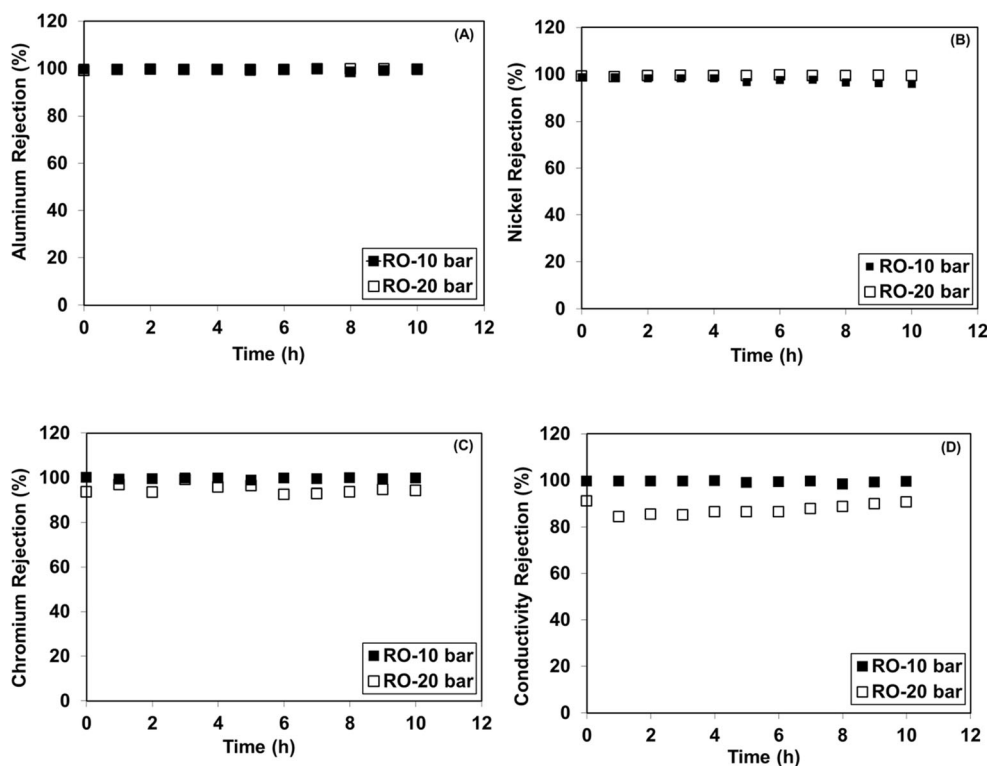


Table 3 Clean and raw water fluxes and flux recovery of UF, NF, and RO membranes at steady state conditions

Membrane	Operating Pressure (bar)	CWF-BT (L/m ² h)	RWF (L/m ² h)	CWF-AT (L/m ² h)	Flux decline (%)	Flux recovery (%)
PTUF	5	506	432	431	15	85
	7.5	560	499	531	11	95
NF270	10	2392	2099	2390	12	99
	15	2378	2358	2394	1	100
	20	2773	2747	2740	1	99
SW30	10	1023	566	730	44	71
	20	1392	830	1248	40	90

CWF-BT clean water flux before treatment, *RWF* raw water flux, *CWF-AT* clean water flux after treatment

is relatively hydrophilic. Flux decline for each membrane type was determined based on the differences between clean water and raw water fluxes at steady state. By increasing pressure, both clean and raw water fluxes increased especially in PTUF and SW30 membranes. The highest flux decline was observed in SW30 experiments by 44 and 40% at 10 and 20 bar pressures, respectively. On the other hand, the flux decline between clean and raw water in PTUF membrane was 15% for 5 bar and 11% for 7.5 bar. In contrast to PTUF and SW30 membranes, no significant flux decline (~ 1%) was observed for NF270 membrane at 15 and 20 bar pressures, however the flux decline was 12% at 10 bar. The fluxes were easily almost completely recovered in NF270 membranes at any pressures by recirculating clean water. However, chemical cleaning was required to recover fluxes in PTUF and SW30 membranes. The flux of PTUF at 5 bar could not be recovered, while 95% of flux could be recovered at 7.5 bar. A similar result was also reported in the study of Ates et al. (2009) that partially irreversible fouling was observed for PTUF membrane during filtration of surface water containing natural organic matter composed of low molecular weight organics (<2 kDa MWCO) and low molecular weight organics (>5 kDa MWCO). For SW30 membrane, 71% of flux at 10 bar and 90% of flux at 20 bar could be achieved after chemical cleanings. Based on these results, it is considered that the fouling in the NF270 membrane was reversible fouling and mainly resulted from cake layer formation on the membrane surface. Therefore, the flux was recovered by cleaning of membranes. On the other hand, the fouling developed in PTUF and SW30 membranes were partially reversible that the fluxes were recovered to the certain point; unrecovered portion was irreversible which was developed by pore blocking and metal ion interaction with membrane surface. The fouling characteristics of membranes were also clearly shown from AFM and SEM images in Figs. 6 and 7 for NF270 at and SW30 membranes, respectively. As seen in Fig. 6(a, b), the roughness of the virgin NF270 membrane was reduced corresponding to NF270 operated at 20 bar pressure. On the other hand, the accumulation of metal precipitations could be seen in Fig. 6(c, d). No such accumulation was

observed on SW30 membrane surface as it was in the NF270 membrane (Fig. 7d). This consideration is also supported in the literature (Tansel et al. 2000; Van der Bruggen et al. 2005; Zahrim et al. 2011) that can lead to cleaning of reversible fouling. In contrast to reversible fouling, which was to easily get rid of by changing operational parameters, irreversible fouling demand chemical cleaning. The studies also stated that the contributions of reversible fouling and irreversible fouling could be up to 18% and 6–46% of permeate flux reductions, respectively (Van der Bruggen et al. 2005).

Recovery and reuse potential of membrane treated water

Anodizing plating process in the plant consists of cleaning, caustic etching, acid neutralization, aluminum anodizing, coloring, fixing, and drying. After each step, the product has been rinsed once or twice with deionized water except during the cleaning process. Aluminum production by anodic oxidation process requires deionized water in all steps especially after the acid neutralization process. To produce deionized water, a softening process consisting of coarse filter, activated carbon, demineralization (RO membrane), and deionization (ion exchange) is operated. To evaluate the possibility of treated wastewater coming from aluminum production process, the characterization of waters softened (deionized), which is used in production anodic oxidation process, and water treated by membranes (UF, NF, and RO) were compared in Table 4. The most important parameter for water quality to be used in the rinsing bath after the neutralization process is conductivity and it should be lower than 50 $\mu\text{S}/\text{cm}$. In terms of metal concentration, permeates of NF and RO membranes were acceptable to use in the process. However, the conductivity of NF and RO membranes were higher than the conductivity of water produced in deionization. In the view of these results, the membrane-treated water could be reused in two lines. The first line is the rinsing bath of the cleaning and caustic etching processes. Because in these processes the water used in rinsing is tap water. The membrane-treated water qualities of NF and RO permeates and even UF permeates are suitable for these

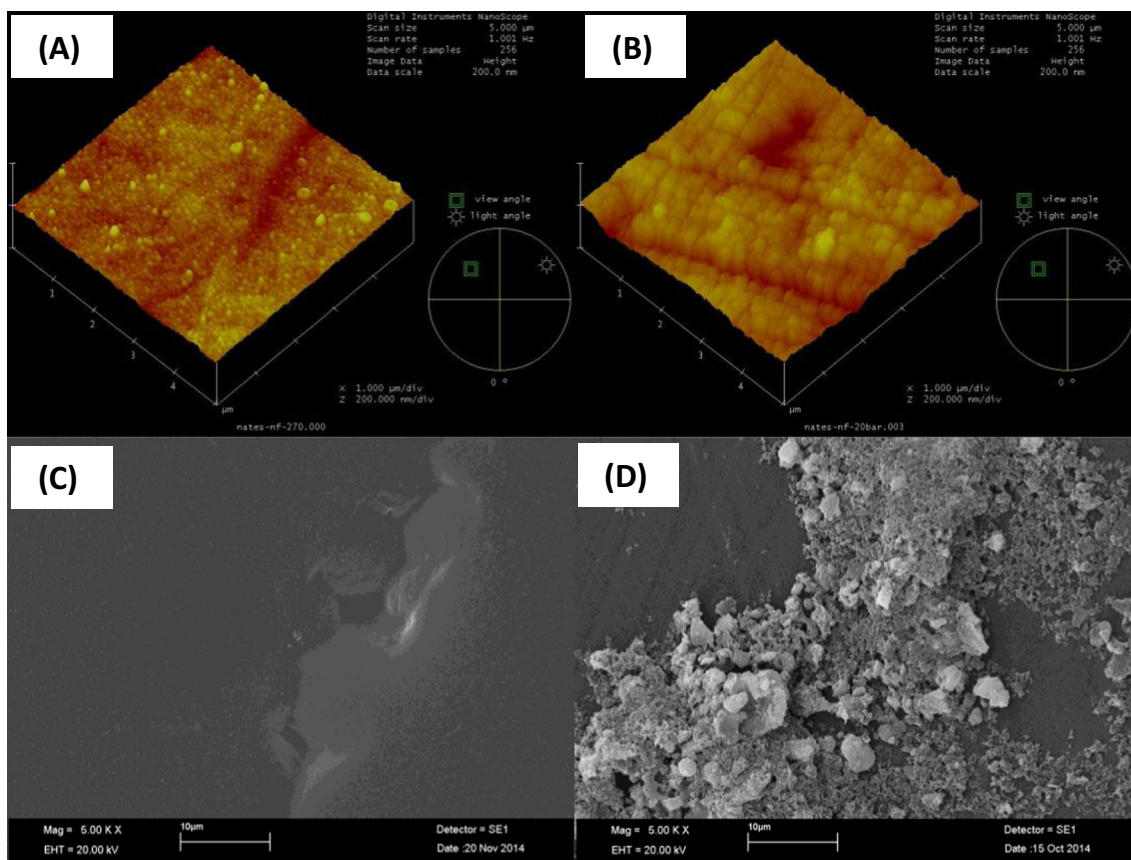


Fig. 6 The AFM and SEM images for virgin and used (at 20 bar pressure) NF270. **a** AFM of virgin NF270. **b** AFM of used NF270. **c** SEM of virgin NF270. **d** SEM of used NF270

processes. Although heavy metal concentrations in the UF permeate are higher than in tap water, aluminum profiles product quality is not affected by the presence of heavy metals in the rinsing bath following the cleaning and caustic etching processes. Besides heavy metals, there no other standard for conductivity of feed water. The other line might be the use of membrane-treated water as raw water for the softening process. In this line, NF or RO permeates should be channeled directly to the demineralization or deionization process. Nevertheless, the point to be noted in the pH of permeates is that the pH of raw water treated in membranes is about 3. Therefore, the pH of permeates should be neutralized to a pH of 7. In this manner, the wastewater could be treated and the treated water recovered and reused at the onsite plant area.

Chemical precipitation

The results of heavy metal removals by chemical precipitation based on chemical dose were given in Fig. 8. In general, removal rates of aluminum, nickel, and chromium increased with increasing chemical dose for all chemicals; however, the most prominent chemical was $\text{Ca}(\text{OH})_2$. There was no aluminum, nickel, and chromium removal observed in the control samples. Similar removal performances for aluminum

by FeCl_3 and FeSO_4 were observed. Even so, FeSO_4 assured lower aluminum removal than FeCl_3 at lower dosages. Aluminum removals varied between 15 and 28% by FeSO_4 except at the last sample, somehow, aluminum removal decreased to 9% at 1000 mg/L (Fig. 8a). A slight improved trend was observed with FeCl_3 in that aluminum removal increased from 29 to 34% by increasing FeCl_3 doses from 50 to 750 mg/L. The highest aluminum removal as expected was attained between 33 and 100% by $\text{Ca}(\text{OH})_2$. The lowest removal performance for chromium was observed when using FeCl_3 coagulant that almost no removal was obtained in lower FeCl_3 doses and the highest removal was 8% at 750 mg/L dose. Chromium removals varied from 37 to 67% by FeSO_4 and 28 to 100% by $\text{Ca}(\text{OH})_2$ (Fig. 8b). Similar to aluminum removal, FeSO_4 showed worse performance on nickel removal (0–9%). Nickel was removed by FeCl_3 with 3–17%, it was removed by $\text{Ca}(\text{OH})_2$ with 3–69% (Fig. 8c).

For most of the metals, hydroxide and sulfide precipitations are common applied precipitation methods with other salts, carbonate, chloride, etc. (Karthikeyan et al. 1995; Huisman et al. 2006; Ozverdi and Erdem 2006). In the coagulation process, metal-based coagulants are usually applied to the system and these metals are removed by formation of metal hydroxides as precipitated. As reported in the literature, FeCl_3

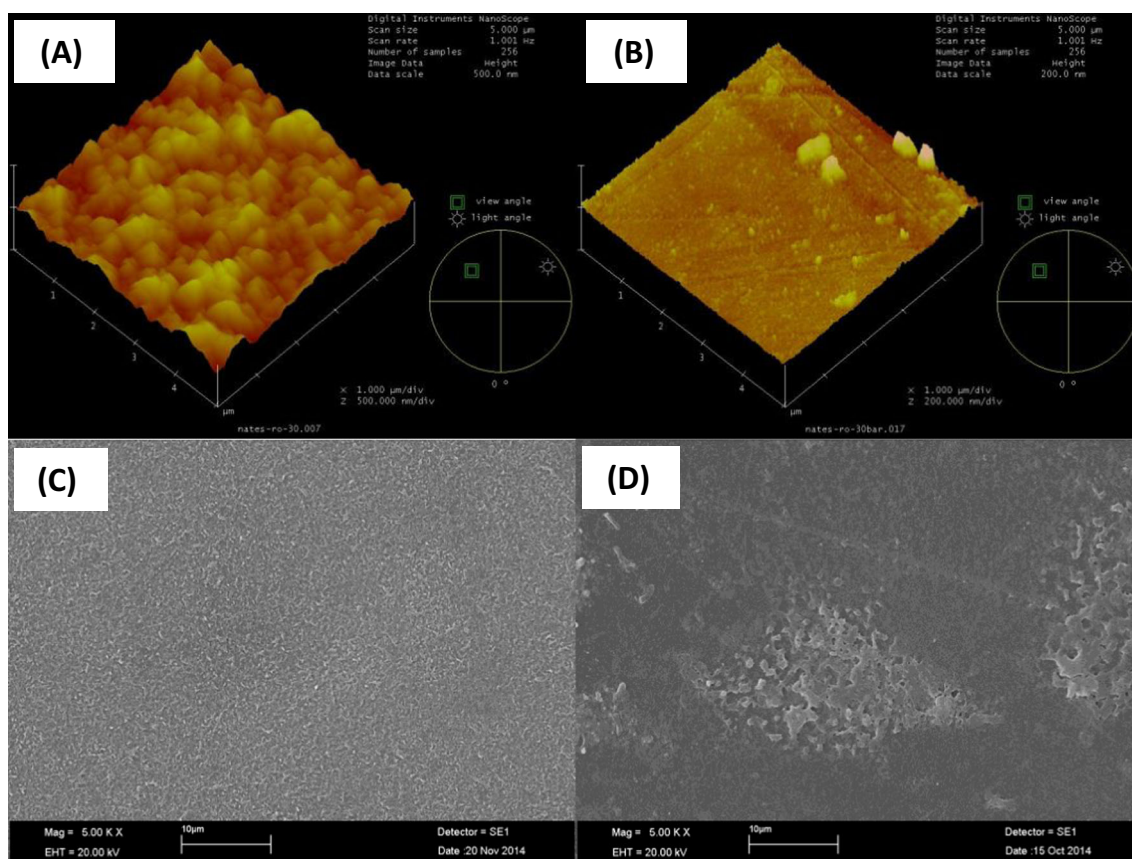


Fig. 7 The AFM and SEM images for virgin and used (at 20 bar pressure) SW30. **a** AFM of virgin SW30. **b** AFM of used SW30. **c** SEM of virgin SW30. **d** SEM of used SW30

and FeSO_4 are the most used coagulants to remove especially suspended solids in natural waters or industrial wastewaters. During the coagulation process, some extent of heavy metal removal can be expected by chemical precipitation, entrapment and co-precipitation. In an appropriate pH range, metal

hydroxide formation has been a result of chemical precipitation (Fu and Wang 2011). Indeed, it is expected that there are lower removal efficiencies for heavy metals by coagulants, i.e., FeSO_4 or FeCl_3 , because of the pH value (~ 3) of the solution in which most of the heavy metals are soluble. The

Table 4 The characterization of water samples in the water softening process and membrane filtration

Sample point	pH	Conductivity ($\mu\text{s}/\text{cm}$)	TOC (mg/L)	Alkalinity (mgCaCO ₃ /L)	T. hardness (CaCO ₃ /L)	Al (mg/L)	Ni (mg/L)	Cr (mg/L)
Tap water	7.8	199	0.52	79	252	6	<1	<1
Sand filter	8.1	198	0.42	61	191	6	<1	<1
Activated carbon	8.1	198	0.64	49	173	4	<1	<1
Demineralization	8.1	197	0.52	37	112	<0.1	<0.1	<0.1
Deionization	7.9	24	0.21	24	76	<0.1	<0.1	<0.1
Rinsing water ^a	7.0–8.5	<50	<0.5	–	–	<0.1	<0.1	<0.1
PTUF permeate	7.0	680	11.3	ND	ND	74.3	34.2	3.6
NF270 permeate (20 bar)	7.0	460	5.2	ND	ND	0.53	0.05	0.04
SW30 permeate (20 bar)	7.0	350	0.5	ND	ND	0.5	0.03	0.02

^a The characterization parameters of rinsing water used in the rinsing baths after the neutralization process

ND not detected.

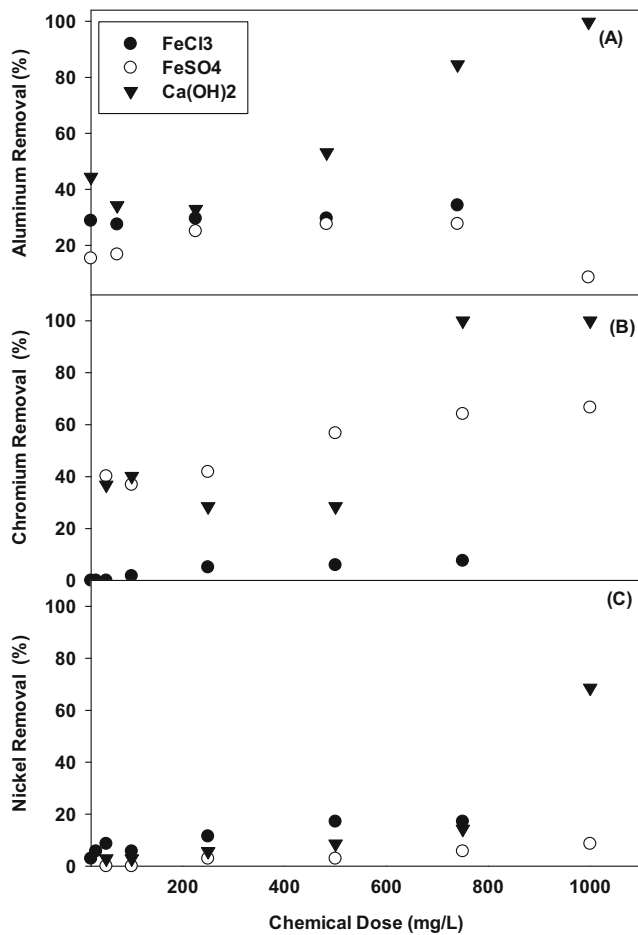


Fig. 8 The impact of chemical dose on aluminum (a), chromium (b), and nickel (c) removal

solubility of Fe(II) and Fe(III) is limited in the pH range of 5 to 8 and Fe precipitates as amorphous hydroxide form. In this pH range, relatively stable Fe(OH)₃ exists as colloidal suspension. Therefore, Fe has important role in efficient coagulation and flocculation. Commonly, co-precipitation and/or adsorption of metal hydroxides accompany formation of metal hydroxides and yields mixed precipitates (Karthikeyan et al. 1995; Feng et al. 2000; Blais et al. 2008). The possible explanation for the removal of aluminum, nickel, and chromium by iron species is that aluminum, nickel, and chromium was adsorbed onto precipitated phase of amorphous iron hydroxide to a certain extent. In fact, this phenomenon was also reported by El Samrani et al. (2008) for the removal of Cu, Pb, and Zn metals. Similarly, possible explanation for decreasing bromide concentration was its adsorption on the hydroxide flux (Feng et al. 2000). The mechanism of metal sorption onto hydrolyzed iron could be explained by interaction of metals with hydrolyzed iron leading some oxidative dissolution (Richmond et al. 2005), then replacement of metals by exchangeable ions associated with flux (Jung et al. 2005) or cation adsorption on oxide surfaces (Duan and Gregory 2003).

In the next step, heavy metal removal performances was observed in a different range of pH (3–11) at constant chemical dosages which were 50 mg/L of FeCl₃, 100 mg/L of FeSO₄ and 100 mg/L of Ca(OH)₂. According to these results, the optimum pH value was determined to obtain the highest heavy metal removal for aluminum, nickel, and chromium. Indeed, the one of the major drawback of hydroxide precipitation of heavy metals, which are mostly amphoteric, is that removal of one metal can be enhanced as removal of the other might be worsened. Since optimum pH for precipitation of heavy metals differ, mixed metals in solutions creates problems when using hydroxide precipitation (Fu and Wang 2011). Aluminum and chromium removal significantly increased after the pH 6. The aluminum removal was at 72, 90, and 100% by FeCl₃, FeSO₄, and Ca(OH)₂ at pH 6, respectively (Fig. 9a). Similarly, increasing pH led to the improvement of chromium removal that chromium was completely treated by all chemicals (Fig. 9b). On the contrary, almost no nickel removal (3% by FeCl₃ and 6% by FeSO₄) was obtained up to pH 6 (Fig. 9c). As seen in Fig. 9, the removal performance increased by increasing pH value for all metal ions. Notably, employing Ca(OH)₂ as an acting pH promoter

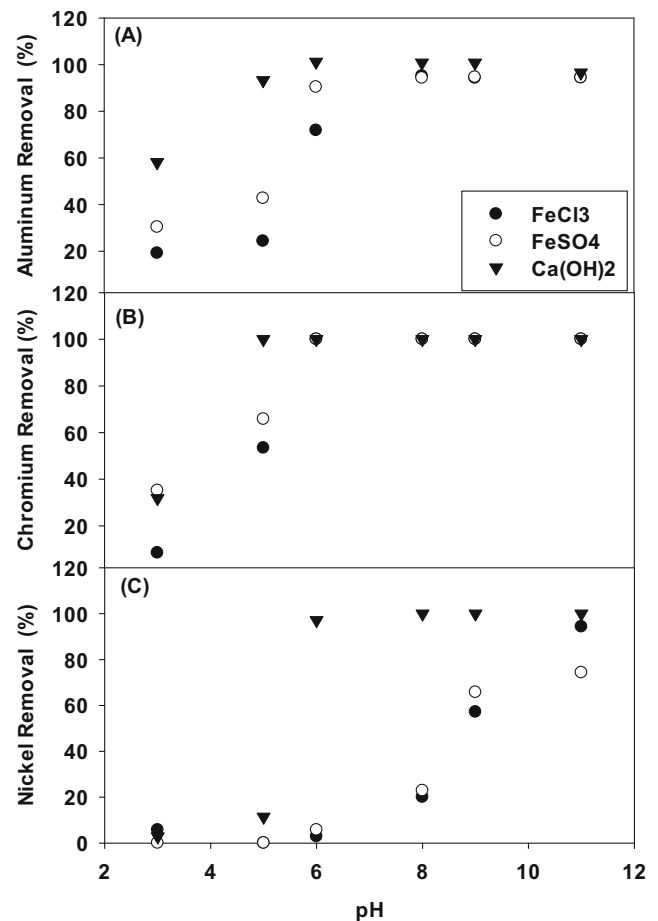


Fig. 9 The impacts of pH on aluminum (a), chromium (b), and nickel (c) removal

remarkably increased heavy metal removal because of its basic characteristics with respect to other chemicals. Nevertheless, $\text{Ca}(\text{OH})_2$ dosages were so low (100 mg/L) that it did not affect the pH values of samples for pH 3 and it raised the pH only from 5.05 to 5.39. The transition forms of aluminum are from the octahedral hexahydrate $\text{Al}^{3+} \cdot 6\text{H}_2\text{O}$ at $\text{pH} < 8.05$ to the tetrahedral $\text{Al}(\text{OH})_4^-$ at $\text{pH} > 8.10$ based on the pH values of the solution. Electrically neutral aluminum hydroxocomplexes as pure aluminum hydroxide is found only within narrow pH values, which are 8.05–8.10 (Duan and Gregory 2003; Savenko and Savenko 2011). Therefore, aluminum removal is promising beyond pH of 6. While aluminum removal was completed by $\text{Ca}(\text{OH})_2$, 72 and 90% of aluminum removal were achieved by FeCl_3 and FeSO_4 , respectively. The reason of the reduction in removal performances with respect to chemicals at the same initial pH value (e.g., pH: 6) is because of pH decrease by forming hydroxide precipitation of coagulants. As the chromium is precipitated in the intermediate pH range (6–11) (Rai et al. 1987), removal of chromium has been increased beyond pH of 6 especially for $\text{Ca}(\text{OH})_2$ addition. As seen in Fig. 9, the complete removal of chromium corresponding with aluminum or nickel removal was obtained with all chemicals although the addition of coagulants decreased pH to certain point. The reason is that optimum precipitation pH range of chromium is much wider and lower than aluminum or nickel. Contrary to this study, Mirbagheri and Hosseini (2005) observed maximum precipitation of Cr(III) at pH 8.7 with the addition of $\text{Ca}(\text{OH})_2$. Nickel precipitation occur the pH values between 7.5 and 12, and it maximizes at around pH 10 (Christensen and Delwiche 1982). Therefore, as chromium was removed almost completely at around pH 5, nickel precipitation was observed beyond pH 6. Besides, nickel removal was very low below pH 6 by applying $\text{Ca}(\text{OH})_2$. On the contrary of chromium and aluminum removal, nickel removal was poor below pH 8 in application of FeSO_4 or FeCl_3 . Since nickel is generally not known to be amphoteric unlike aluminum and chromium, co-precipitation or adsorption of nickel oxides onto iron oxides is not efficient as observed in Fig. 9 in different chemical dosages tests. Therefore, mixed metals in industrial wastewaters cannot be removed efficiently at a single pH level since the minimum solubility's of metals are varied at different pH values (Feng et al. 2000).

Conclusions

In this study, the treatment and reuse approaches of wastewater of the anodic oxidation coating process of the aluminum industry using UF, NF, and RO membranes were investigated. Chemical precipitation was also studied to observe the removal of heavy metals. The summary of findings are stated as follows:

- The wastewater generated by anodic oxidation during aluminum profile manufacturing leads to harsh characteristics regarding pH, heavy metal concentration, and conductivity.
- Low rejection performances were achieved by PTUF membrane with 5000 Da MWCO that the removal efficiencies of aluminum, nickel, and chromium were similar and varied between 54 and 62% at pressure of 7.5 bar. Increase in pressure improved aluminum and nickel rejection but not chromium rejection. Conductivity and TOC removals at 7.5 bar pressure were about 30%.
- The heavy metals of aluminum and nickel were almost completely removed from the raw wastewater with NF270 membrane at pressure of 20 bar. The removal efficiencies of aluminum, nickel, and chromium were 99, 99 and 94%, respectively. Increase in pressure significantly increased the rejection of chromium that the rejection was improved from 66 to 94% at 10 bar and 20 bar pressures, respectively.
- Similar to NF270 membrane, SW30 RO membrane was highly successful to remove heavy metals that aluminum and nickel were almost completely treated by SW 30 membrane. At steady state conditions, 99% for aluminum, 99% for nickel and 94% for chromium rejections were observed.
- The experimental results show that, both NF and RO membranes tested could effectively remove aluminum, total chromium, nickel (>90%) from the aluminum production wastewater. The RO (SW30) membrane showed slightly higher performance at 20 bar operating pressure in terms of conductivity removal values (90%) than the NF 270 membrane (87%). Although similar removal performances observed for heavy metals and conductivity by NF270 and SW30, significantly higher fluxes (more than three times) were obtained in NF270 membrane filtration at any pressures. For treatment of aluminum production wastewater, UF membrane should be used as pretreatment followed by NF filtration to protect, extend NF membrane life and retard membrane fouling.
- Positive impact of operational pressure was observed that fluxes for all membrane got higher as increasing pressure. Although the flux declines were between 11 and 15% for PTUF membrane and 40–44% for SW30 membrane with respect to the applied pressures, the flux decline (~ 1%) was insignificant for NF270 membrane. Fouling investigations revealed that the fouling of PTUF and SW30 was partially reversible and the cause of irreversible fouling was likely pore blocking and metal ion interaction with the membrane surface. NF270 membrane was more likely affected by the cake/gel layer formation that the flux was recovered by cleaning of membranes.
- By treating wastewater with both NF and RO, it could be recycled back into the process to be reused with economic

and environmental benefits. The recovered/treated water could be used instead of tap water in the rinsing bath following the cleaning and caustic etching process or could be used as feed water for the demineralization/deionization process.

- FeCl_3 and FeSO_4 chemicals presented similar removal performances for aluminum and chromium which was below 35% at pH~3 (ambient pH of wastewater). On the contrary, removal performances of aluminum, chromium, and nickel were improved by increasing pH of solution. The results obtained in this study revealed that the existing chemical precipitation treatment system using FeCl_3 does not satisfy the discharge limits (Kayseri Industrialized Zone discharge limits for sewer system) with respect to heavy metal concentrations and conductivity. Therefore, $\text{Ca}(\text{OH})_2$ should be preferred as an alternative chemical for the treatment or the whole system should be replaced with the membrane system to comply with the discharge standards and also to enable the reuse of treated water into the production lines.

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