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Treatment of landfill leachate by membrane processes of nanofiltration and reverse osmosis

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ABSTRACT

Landfill leachate from Jakuševec, Zagreb, Croatia was treated by membrane processes of nanofiltration (NF) and reverse osmosis (RO). Different types of membranes were selected to obtain the parameters of leachate contaminants below maximum concentration levels (MCLs), defined by the Croatian law and EU directive. As a pretreatment of landfill leachate, coagulation and filtration were used. Parameters of total carbon, total organic carbon (TOC), inorganic carbon, chemical oxygen demand (COD), pH, turbidity, conductivity, concentration of different inorganic ions, heavy metals, etc., were analyzed in all steps. The landfill leachate was relatively low loaded with organic substances and ammonia; COD, TOC, and NH_4^+-N of real sample were 1,720.0 $mgO\,L^{-1}$, 1,260.5 $mgC\,L^{-1}$, and 1,147.6 $mg\,L^{-1}$, respectively. Their concentrations decreased after coagulation for 27.9, 58.6, and 7.9%, respectively. RO/NF membranes (NF270, NF90, and XLE) additionally decreased COD and TOC for >94.6% and >92.5%, respectively. Ammonium ions decreased in the range of 37.1% (NF270)–88.9% (XLE).

Keywords: Landfill leachate; Coagulation; Nanofiltration; Reverse osmosis; MCLs

1. Introduction

In most cases around the world, municipal solid waste (MSW) is disposed to landfills. During this period, the MSW undergoes a number of hydrodynamic, physicochemical, and biological processes, producing the landfill leachate. Therefore, the landfill leachate contains a complex of organic substances (biodegradable, but also refractory to biodegradation), inorganic substances, and heavy metals, which are toxic to living organisms and ecosystems. Its characteristics and the rate of generation strongly depend on the climate, type of waste, and landfill age. Three types of leachate can be classified by landfill age: young, intermediate, and stabilized [1,2].

The removal of organic material based on chemical oxygen demand (COD), biological oxygen demand (BOD), and ammonium from leachate is a usual prerequisite before discharging the leachate into natural waters. The treatment of landfill leachate is nowadays recognized as one of the most urgent environmental issues [3]. The leachate should be treated before reaching natural water (surface and ground) because it can

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accelerate algae growth due to its high nutrient content, deplete dissolved oxygen in the streams, and cause toxic effects in the surrounding water life [4].

In the last decade, nanofiltration (NF) and reverse osmosis (RO) were frequently used for treatment of landfill leachate [5–8]. Hasar et al. [4] used RO as a tertiary treatment and showed decrease in conductivity and COD by 99.7 and 99.2%, respectively. Singh et al. [9] obtained >99% removal of dissolved organic matter and 93% of salts by NF and RO membranes. Mariam and Nghiem [10] used NF270 and SR2 membranes for treatment of the landfill leachate. They monitored total nitrogen (TN), total organic carbon (TOC), and turbidity with removal of 10–16%, around 90 and 95%, respectively.

However, a wide spectrum of substances (dissolved organic and inorganic, colloidal, and suspended particles) may contribute to the membrane fouling. Amokrane et al. [1] and Singh et al. [9] showed a permeate flux reduction when treating raw leachate using membranes. The latter one obtained flux reduction of 23% and 15% using NF and RO membrane, respectively.

Therefore, the appropriate pretreatment has to be used to reduce the membrane fouling. Various methods were used, like coagulation/flocculation [1,3,11–14], adsorption [14,15], Fenton treatment [16,17], etc. [2].

The objective of the presented study was to investigate the use of coagulation with ferric (III) chloride ($FeCl_3$) as a pretreatment for the landfill leachate treatment using NF and RO membranes and to fulfill maximum concentration levels (MCLs) values for discharging the treated water to natural aquifers (surface water), according to the Croatian Environmental Protection Act (Official Gazzette no. NN 94/2008). Firstly, optimal concentration of Fe^{3+} was determined by Jar test. The final step was treatment of pretreated water with nanofiltration (NF270 and NF90) and RO (XLE) membranes.

2. Materials and methods

2.1. Landfill Jakuševec, Zagreb

Fresh landfill leachate was collected from the Jakuševec landfill (Zagreb, Croatia). About 800 tons of MSWs are disposed of daily. This is an active landfill with a leachate production of minimum 1,000 m^3 and maximum 21,000 m^3 per day during summer and winter, respectively. Leachates are collected in two connected basins ("north" and "south") and currently treated with biological sequencing batch reactor (SBR). The SBR is not efficient enough, since it does not meet MCLs values for discharging into surface waters.

Leachate samples were collected from the basin in the landfill site without any pretreatment in a 25-L plastic container. The sample was then transported to the laboratory and stored in refrigerator at around 7°C. Leachate samples were removed from refrigerator and placed for a few hours in the ambient temperature.

Landfill leachate was treated with coagulation ($FeCl_3$), filtration, and NF/RO, as shown in Fig. 1.

2.2. Chemical coagulation

The coagulation process was performed in a Jar test comprising of six paddle rotors, equipped with 6 beakers of 1 L each. Firstly, fresh leachate was placed in beaker and a predetermined concentration of $FeCl_3$ was added as a coagulant to the leachate. The initial rapid mixing stage was 3 min at around 220 rpm, followed by 30 min of gentle mixing at stirring speed of around 30 rpm. Stirring was then discontinued, flocs were allowed to settle for 1 h and the supernatant was carefully extracted by plastic syringe about 2 cm below the liquid level.

2.3. Filtration

Filtration was performed with Munktell filter paper. Grade 389 and 391 with typical retention of 8–12 and 2–3 μm, respectively, were used [18].

2.4. Membrane treatment

Commercially available membranes with different characteristics examined in this experiment included one RO membrane: the XLE (Dow/Filmtec, Midland, MI, USA), and two NF membranes of the same manufacturer: NF90 and NF270. All membranes were stored in a dark, cold place (refrigerator) before they were used. The main nominal and physicochemical characteristics of the membranes used are presented in Table 1. The treatment of landfill leachate was tested in a laboratory setup [19] at a working pressure of 15 bar and flow rate of 750 mL min^{-1}. The surface area of the membranes was 10.7 cm^2. The experiment was conducted in the batch circulation mode (permeate and concentrate streams circulated back to the feed tank). Virgin preserved membranes were washed with demineralized water without pressure and then pressurized at 20 bar for 3 h in order to stabilize the permeate flux. Then, membranes were tested with NaCl (300 mg L^{-1}). The next step involved the treatment of landfill leachate until a sufficient amount of samples was collected for analysis. As the final step,

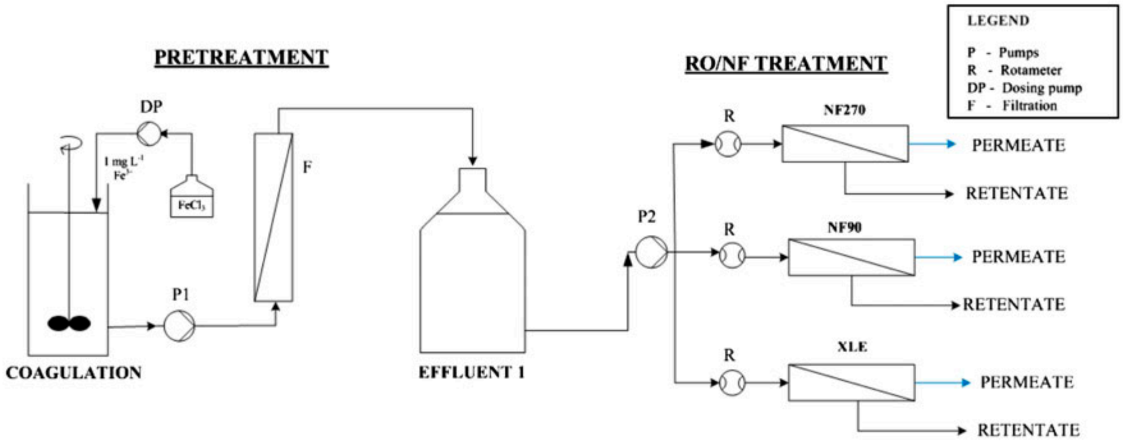

Fig. 1. Schematic representation of landfill leachate treatment.

Table 1
The main characteristics of the membranes

	NF270	XLE	NF90
Membrane type	polyamide	polyamide	polyamide
Max. operating temperature (°C)	45	45	45
Max. operating pressure (bar)	41	41	41
pH range	2–11	2–11	2–11
NaCl retention[a] (%)	23.82 ± 3.65	90.00 ± 5.67	81.56 ± 9.16
CaCl retention[a] (%)	59.19 ± 7.98	96.11 ± 2.24	98.01 ± 0.50

[a]Obtained in this study (concentration 300 mg L^{-1}, working pressure 15 bar).

membranes were washed with demineralized water (25 L) and cleaned with alkaline agent (1.5% NALCO 99). The cleaning agent (temperature between 34 and 37°C) was circulating for 30 min followed by soaking the membrane for 30 min in the same agent.

2.5. Analytical methods

The main characteristics such as pH, COD, conductivity (κ), turbidity, TOC, total carbon (TC), inorganic carbon (IC), ammonium (NH_4^+-N), chloride (Cl^-), fluoride (F^-), nitrite (NO_2^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), bromide (Br^-), and heavy metals of the leachate were determined.

Conductivity was determined by conductometer (SCHOTT Instruments Lab 960, Germany). Concentrations of TOC, IC, and TC were determined by Shimadzu TOC-V_{WS} carbon analyzer (Japan), while turbidity was measured using WTW Turb 430 (Germany) turbidimeter. Furthermore, ammonium ions were determined with Varian Cary 100 UV–vis spectrophotometer (Australia) at 655 nm, while anions were measured by ion chromatography using a Dionex CS 600 (USA). Finally, concentrations of heavy metals were examined using a Perkin Elmer Elan DRC-e (USA) inductively coupled plasma mass spectrometer (ICP-MS).

All characteristics during this study were analyzed according to Standard methods for the examination of water and wastewater [20].

3. Results and discussion

3.1. Leachate characterization

The characteristics of raw leachate from Jakuševec landfill are presented in Table 2. Noticeably, these characteristics include relatively low COD (1,720 mg L^{-1}), slightly basic (pH 8.05) character, high turbidity (39.3), high conductivity (13,170 μS cm^{-1}), and high TOC (1260.5 mg L^{-1}). Therefore, the landfill leachate can be classified as old or stabilized [2,21].

The leachate, as shown in Table 2, also contained inorganic substances such as metals. Some metals had very high concentrations but only Fe (6.41 mg L^{-1}) and B (7.36 mg L^{-1}) had concentration higher than MCLs. Since Jakuševec landfill receives domestic waste, the high concentration of Fe was expected. Other metals

Table 2
Characteristics of raw landfill leachate

Parameter	Concentration (mg L^{-1})[a]	MCLs (mg L^{-1})	Parameter	Concentration (mg L^{-1})[a]	MCLs (mg L^{-1})
Color	Very dark brown	No color	Co	6.38×10^{-2}	1.0
COD (S.D.)	1,720 (261)	125	Cr	2.86×10^{-1}	0.5
NH_4^+-N	1,147.6	10	Cu	3.71×10^{-2}	0.5
Turbidity/NTU	39.3	–	Fe	6.41	2.0
pH	8.05	6.5–9.0	Hg	$<1.0 \times 10^{-7}$	0.01
TC	2,443.5	–	K	748.83	–
IC	1,183.0	–	Mg	127.49	–
TOC	1,260.5	30	Mn	8.50×10^{-1}	2.0
κ / µS cm^{-1}	13,170	–	Na	1,373.84	–
Cl^-	18,124.32	–	P	5.65	–
F^-	19.59	10.0	Pb	5.08×10^{-2}	0.5
NO_2^-	1,711.69	1.0	Pt	3.41×10^{-4}	–
NO_3^-	50.96	2.0	Rb	5.38×10^{-1}	–
SO_4^{2-}	131.58	250	Se	2.07×10^{-2}	0.02
Br^-	25.36	–	Si	14.75	–
Ag	1.26×10^{-4}	0.1	Sn	4.52×10^{-2}	2.0
Al	4.48×10^{-1}	3.0	Sr	7.75×10^{-1}	–
As	5.92×10^{-2}	0.1	Th	$<1.0 \times 10^{-7}$	–
Au	4.04×10^{-2}	–	Ti	3.54×10^{-1}	–
B	7.36	1.0	U	$<1.0 \times 10^{-7}$	–
Bi	1.14	–	V	7.51×10^{-2}	0.05
Ca	102.04	–	W	1.56×10^{-2}	–
Cd	3.18×10^{-5}	0.1	Zn	1.06×10^{-1}	2.0

[a] Concentrations are in mg L^{-1} or otherwise written.
S.D. – Standard deviation.

with extremely high concentrations were Na, K, Mg, and Ca in concentration of 1,373.84, 748.83, 127.49, and 102.04 mg L^{-1}, respectively, but MCLs values are not defined by the law.

3.2. Coagulation processes

3.2.1. Optimal coagulant dose

In the chemical coagulation process, the selection of coagulant concentration is very important and it depends upon the nature of the suspended solid to be removed, the raw water conditions, the facility design, and the cost of the amount of chemical necessary to produce the desired result [12]. The dosage of coagulant was determined as a function of turbidity, TOC, TC, and IC removal.

Before experiments, leachate was characterized (all data were obtained by a measurement agency) by an average COD value of 2,308 mg L^{-1}, an average BOD value of 480 mg L^{-1}, and a BOD/COD ratio below 0.27, which excluded the possibility of biological treatment [3,5,16]. Therefore, physicochemical method, coagulation, was employed.

Experiments were conducted without prior adjustment of pH (8.05) with $FeCl_3$. The previous researches revealed that iron salts were more effective with a lower dosage, they coagulate in a wider pH range and form heavier flocs than aluminum [1–3,13,21]. Therefore, only $FeCl_3$ was used. Also, iron-based coagulants pose less health risks than aluminum in the event of an overdose [3]. Since the amount of ammonium present in the leachate was significant, it could have not been treated by conventional biological processes, because ammonium inhibits nitrification when subjected to such treatments [16].

The optimal concentration of Fe^{3+} ion was determined between 0.05 and 5.0 g L^{-1}. Fig. 2 presents removal rates of conductivity, turbidity, TC, IC, and TOC vs. dosage of Fe^{3+} ions together with pH value of the effluent.

Concentrations of Fe^{3+} ions used in Jar test were 0.05, 0.1, 0.5, 1.0, 2.0, 3.0, and 5.0 g L^{-1}. With the increase in the coagulant dose, the very dark brown color of raw leachate turned to brown and then to yellow for the coagulant dose near the optimal value. As for concentrations of 2.0, 3.0, and 5.0 g Fe^{3+} L^{-1}, no visible effect was observed (color was still dark brown with no flocs).

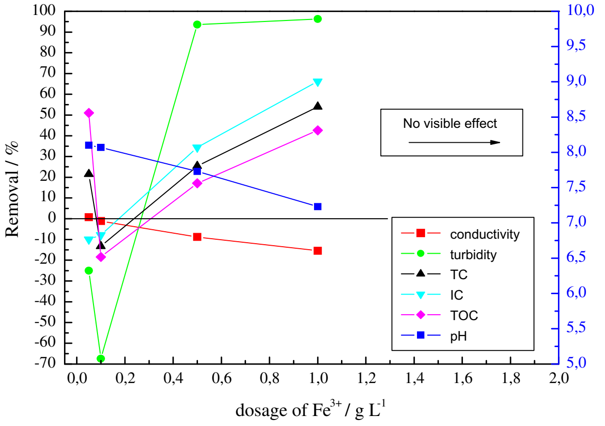

Fig. 2. Removal of conductivity, turbidity, TC, IC, and TOC vs. dosage of Fe^{3+} with pH.

Therefore, parameters shown in Fig. 2 were not measured. As for the concentration of 0.1 g L^{-1}, all parameters increased. It is assumed that this might represent an experimental mistake.

The pH value decreased with the dosage increase and moved from slightly basic (8.05) to neutral (7.23). Amokrane et al. [1] explained it with acidic character of Fe^{3+} (acid of Lewis). By reacting with OH^--ions of leachate, iron precipitates in form of $Fe(OH)_3$ or $Fe(OH)_4^-$ [1,14]. Conversely, conductivity increased (up to 15.5%) with the coagulant dosage increase. Such results were expected, since iron salts were added into leachate. With the coagulant dosage value of 0.05 and 0.1 g L^{-1}, turbidity increased to 25.2 and 67.4%, respectively. Also, turbidity decreased up to 96.3% with increasing concentration of iron salts and was 1.45 NTU at 1 g L^{-1}. Aziz et al. (2007) [13] showed 95% turbidity removal at 1.2 g L^{-1} of $FeCl_3$. The concentration of carbon was expressed with TOC, TC, and IC. It can be perceived that these parameters decreased with the increasing coagulant dosage. The highest decrease was for IC, TC, and TOC in the amounts of 66.2, 54.0, and 42.6%, respectively, for concentration of 1 g $Fe^{3+} L^{-1}$. All these results suggest that optimal coagulant dosage was 1 g L^{-1}, which was used in further investigation.

3.3. Coagulation and filtration (CF)

Coagulation with iron salt (1 g $Fe^{3+} L^{-1}$) with conventional filtration was used as a pretreatment to RO and NF. Results in Table 3 show the efficiency of this step. The color of the effluent was yellow with neutral pH (7.76). Turbidity was still relatively high (15.8), i.e. it was decreased to 59.8% and was much higher than turbidity accomplished during Jar test. Conductivity increased (to 12.7%), due to iron salts addition, and was quite similar to the increase obtained in Jar test. Nevertheless, removal of TC, IC, and TOC was 63.3, 68.2, and 58.6%, respectively, and was higher than obtained in Jar test. The removal of TOC (58.6%) was higher than the removal (34.6%) obtained by Abood et al. [12].

After the pretreatment, COD was 1,240 mg $O_2 L^{-1}$, i.e. it decreased to 27.9%. Li et al. [14] and Castrilln et al. [22] obtained even smaller COD removal (16 and 5.9%) at slightly basic pH (8.5 and 8.6). However, higher COD removal (50–73%) was accomplished [1,12–14,22] but with prior adjustment of pH to acidic (pH between 3 and 5.5). The reason lies in different hydrolyzed species of ferric [14].

As mentioned before, $Fe(OH)_3$ or $Fe(OH)_4^-$ can be formed in basic condition, while in the acid condition, ferric can hydrolyze and form polynuclear cation ($Fe(OH)^{2+}$, $Fe_2(OH)_2^{4+}$, $Fe_3(OH)_4^{5+}$, or other positive species). At higher pH values, OH^- and organic anions are competing for interaction with metal hydrolysis products. Therefore, the precipitation of metal hydroxides occurs mainly by co-precipitation, since OH^- competes with organic compounds for metal adsorption sites [23].

It is evident from Table 2 that ammonium (1,147.6 mg N L^{-1}) was present in significant amount and is much higher than MCLs. Some researchers claim this to be the primary cause of acute toxicity of municipal landfill leachates [24,25]. The coagulation and filtration (CF) treatment decreased it to 7.9% since the coagulation process does not remove it directly. It is strongly related to the removal of colloidal matter present as albuminoid nitrogen [26], which was probably absent since the leachate was evidently stabilized.

All anions were high removed (>95.4%), except Cl^-, F^-, and Br^- in amount of 79.1, 87.7, and 87.2%, respectively. After CF, only nitrite had concentrations much higher than MCLs. Nitrate was almost below this level, while concentration of fluoride was below MCLs.

In raw leachate, only boron and ferrum had concentrations higher than MCLs. Nevertheless, measuring and decreasing concentration of metals is important for reducing the impact on the environment. The concentration of boron increased to 3.3%, while ferrum reduced below MCLs since filtration was used. In some cases, concentrations of metals (B, Cd, Cu, Mn, Pb, Se, and Zn) increased, i.e. they seem to be refractory to this stage of the treatment, while in the majority of cases, their concentrations increased. Most metals at high pH of the leachate (pH 8.05) might be adsorbed onto suspended solids [16].

Table 3
Concentrations of the effluent and removal rates after CF treatment

	Concentration (mg L^{-1})^a	Removal (%)		Concentration (mg L^{-1})^a	Removal (%)
Color	yellow	–	Co	4.62×10^{-2}	27.6
COD (S.D.)	1,240 (100)	27.9	Cr	7.22×10^{-2}	74.7
NH_4^+-N	1,056.9	7.9	Cu	3.88×10^{-2}	−4.6
Turbidity/ NTU	15.8	59.8	Fe	4.97×10^{-1}	92.2
pH	7.76	–	Hg	$<1.0 \times 10^{-7}$	–
TC	897.0	63.3	K	740	1.2
IC	375.6	68.2	Mg	112	12.1
TOC	521.4	58.6	Mn	4.57	−437.6
κ / µS cm^{-1}	14,840	−12.7	Na	1,270	7.6
Cl^-	3,789.79	79.1	P	$<1.0 \times 10^{-7}$	>99.9
F^-	2.41	87.7	Pb	5.65×10^{-2}	−11.2
NO_2^-	78.74	95.4	Pt	2.85×10^{-4}	16.4
NO_3^-	2.14	95.8	Rb	5.04×10^{-1}	6.3
SO_4^{2-}	5.53	95.8	Se	2.08×10^{-2}	−0.5
Br^-	3.25	87.2	Si	10.6	28.1
Ag	$<1.0 \times 10^{-7}$	>99.9	Sn	2.76×10^{-3}	93.9
Al	4.51×10^{-2}	89.9	Sr	3.09×10^{-1}	60.1
As	1.73×10^{-2}	70.8	Th	$<1.0 \times 10^{-7}$	–
Au	2.04×10^{-2}	49.5	Ti	5.19×10^{-2}	85.3
B	7.60	−3.3	U	$<1.0 \times 10^{-7}$	–
Bi	4.56×10^{-1}	60.0	V	2.23×10^{-2}	70.3
Ca	55.00	46.1	W	3.32×10^{-3}	78.7
Cd	1.17×10^{-4}	−267.9	Zn	2.66×10^{-1}	−150.9

[a] Concentrations are in mg L^{-1} or otherwise written.
S.D. – Standard deviation.

3.4. Membrane treatment

CF was used as a pretreatment to RO/NF processes in order to remove non-biodegradable organic matter and heavy metals. The RO and NF processes have the ability to remove particles with a molecular weight higher than 100 Da and 200–300 Da, respectively, as well as inorganic substances through electrostatic repulsion and attraction. Two nanofiltration (NF90 and NF270) and one RO (XLE) membranes were used to treat effluent after CF. The permeate characteristics with additional removal rates are described in Table 4.

After the RO/NF treatment, the permeate was clear and colorless. The pH value varied between 7.36 (XLE) and 8.22 (NF90) and was in the MCLs range. After the CF treatment, turbidity was high (15.8) and decreased for over 99.0% with investigated membranes.

The conductivity decrease was highest for RO XLE membrane (94.1%) and the smallest for loose nanofiltration NF270 membrane (25.5%). Hasar et al. [4] also used RO membrane (AG4021FF by Desal Osmonics) and obtained somewhat higher removal (99.7%). The reason for such result could be the half smaller initial concentration.

After the treatment with RO/NF membranes, COD was in the range of the environmental norms applied in Croatia. For NF90 and XLE, the COD was similar (around 22 mg L^{-1}), while the effluent of NF270 membrane had the highest value (67 mg L^{-1}). Therefore, NF and RO reduced COD of treated leachate for more than 94.6%. This is comparable with results obtained by previous researchers [2,4,21].

If discharged into environment, ammonium represents a huge problem. The high concentration of ammonium was reduced for 88.9, 88.1, and 37.1% for XLE, NF90, and NF270 membranes, respectively. Regardless of that, relatively high removal by XLE and NF90 membranes concentrations were still 12 times higher than MCLs and even 60 times higher for NF270.

If the treated water is discharged into surface water, TOC can be up to 30 mg L^{-1}. This limit was accomplished with NF90 and XLE membranes; whilst concentration for NF270 was 39.25 mg L^{-1} (removal

Table 4
Concentrations of the effluent and additional removal rates after membrane treatment

	NF270		NF90		XLE		MCLs
	Conc. (mg L^{-1})[a]	*R* (%)	Conc. (mg L^{-1})[a]	*R* (%)	Conc. (mg L^{-1})[a]	*R* (%)	(mg L^{-1})[a]
Color	No color	–	No color	–	No color	–	No color
COD (S.D.)	67 (2)	94.6	25 (3)	98.0	20 (4)	98.4	125
NH_4^+-N	664.5	37.1	126.1	88.1	117.4	88.9	10
Turbidity/NTU	0.14	99.1	0.08	99.5	0.15	99.0	–
pH	7.87	–	8.22	–	7.36	–	6.5–9.0
TC	207.30	76.9	35.42	96.0	35.06	96.1	–
IC	168.05	55.3	28.06	92.5	27.95	92.6	–
TOC	39.25	92.5	7.36	98.6	7.11	98.6	30
κ/μS cm^{-1}	11,050	25.5	1,428	90.4	876	94.1	–
Cl^-	3,228.37	14.8	368.89	90.3	188.36	95.0	–
F^-	0.93	61.4	0.02	99.2	0.47	80.5	10.0
NO_2^-	32.78	58.4	1.88	97.6	2.93	96.3	1.0
NO_3^-	0.44	79.4	0.11	94.9	0.05	97.7	2.0
SO_4^{2-}	0.31	94.4	0.25	95.5	0.15	97.3	250
Br^-	–	–	0.40	87.7	0.09	97.2	–
Ag	$<1.0\times10^{-7}$	–	1.0×10^{-7}	–	$<1.0\times10^{-7}$	–	0.1
Al	3.13×10^{-3}	93.0	4.24×10^{-3}	90.6	1.77×10^{-3}	96.1	3.0
As	6.08×10^{-3}	64.8	1.02×10^{-3}	94.1	7.00×10^{-3}	59.5	0.1
Au	1.25×10^{-2}	38.7	3.19×10^{-3}	84.4	1.26×10^{-2}	38.2	–
B	7.17	5.7	4.66	38.7	7.12	6.3	1.0
Bi	7.36×10^{-2}	83.9	5.30×10^{-2}	88.4	$<1.0\times10^{-7}$	>99.9	–
Ca	19.5	64.5	5.54×10^{-1}	99.0	26.0	52.7	–
Cd	2.79×10^{-5}	76.2	$5.55\times\cdot10^{-6}$	95.3	1.66×10^{-5}	85.8	0.1
Co	3.16×10^{-4}	99.3	2.58×10^{-5}	99.9	4.80×10^{-4}	99.0	1.0
Cr	5.51×10^{-3}	92.4	1.45×10^{-3}	98.0	5.71×10^{-3}	92.1	0.5
Cu	$6.37\times\cdot10^{-3}$	83.6	1.20×10^{-3}	96.9	5.29×10^{-3}	86.4	0.5
Fe	3.55×10^{-2}	92.9	6.73×10^{-3}	98.6	2.82×10^{-2}	94.3	2.0
Hg	$<1.0\times10^{-7}$	–	$<1.0\times10^{-7}$	–	$<1.0\times10^{-7}$	–	0.01
K	549	25.8	60.7	91.7	621	16.1	–
Mg	14.7	86.9	$<1.0\times10^{-7}$	>99.9	25.5	77.2	–
Mn	1.24	72.9	1.92×10^{-3}	99.9	1.76	61.5	2.0
Na	931	26.7	64.6	94.9	106	91.6	–
P	$<1.0\times10^{-7}$	–	$<1.0\times10^{-7}$	–	$<1.0\times10^{-7}$	–	–
Pb	5.40×10^{-2}	4.4	4.60×10^{-3}	91.9	–	–	0.5
Pt	7.35×10^{-5}	74.2	4.96×10^{-5}	82.6	6.78×10^{-5}	76.2	–
Rb	3.74×10^{-1}	25.8	3.98×10^{-2}	92.1	4.09×10^{-1}	18.8	–
Se	1.65×10^{-2}	20.7	2.30×10^{-3}	88.9	2.07×10^{-2}	0.48	0.02
Si	6.25	41.0	3.77×10^{-1}	96.4	7.28	31.3	–
Sn	2.21×10^{-4}	92.0	2.21×10^{-5}	99.2	2.23×10^{-6}	99.9	2.0
Sr	8.05×10^{-2}	73.9	8.90×10^{-4}	99.7	1.13×10^{-1}	93.4	–
Th	$<1.0\times10^{-7}$	–	$<1.0\times10^{-7}$	–	–	–	–
Ti	1.49×10^{-2}	71.3	2.68×10^{-4}	99.5	1.79×10^{-2}	65.5	–
U	$<1.0\times10^{-7}$	–	$<1.0\times10^{-7}$	–	–	–	–
V	2.15×10^{-2}	3.6	2.04×10^{-3}	90.8	2.22×10^{-2}	0.45	0.05
W	5.22×10^{-4}	84.3	2.18×10^{-4}	93.4	3.85×10^{-4}	88.4	–
Zn	8.96×10^{-3}	96.6	6.05×10^{-3}	97.7	5.29×10^{-3}	98.0	2.0

[a] Concentrations are in mg L^{-1} or otherwise written.

S.D. – Standard deviation.

was higher than 92.5%). The removal of TOC for used NF membranes was much higher than the removal (55–60% TOC) obtained by Linde and Jönsson [27]. Concentrations of TC and IC were the highest for NF270 membrane, while in the case of NF90 and XLE membranes, concentrations were similar.

The NF and RO membranes exhibit an anion rejection typical of charged membranes. They were removed with a high percentage (>80.5%) with XLE and NF90 membranes and >58.4% for NF270 (except 14.8% for Cl^-). It is obvious that divalent ions were better rejected than monovalent ions. Concentrations of all anions defined by law were below MCLs, except for nitrite. Its concentrations were 1.88 and 2.93 $mg\,L^{-1}$ for NF90 and XLE, respectively, and much higher (32 $mg\,L^{-1}$) for NF270.

The concentration and removal rates of the final effluents (31 metals) are presented in Table 4. The characteristics of raw leachate (Table 2) showed that only two metals (B and Fe) had concentrations higher than MCLs. Concentration of ferrum additionally decreased over 92.9% with concentration below $6.73 \times 10^{-3}\,mg\,L^{-1}$ in membrane effluent. The additional removal of boron was 5.7, 6.3, and 38.7% with NF270, XLE, and NF90 membranes, respectively. These small removal percentages were not enough to decrease concentrations of boron below MCLs. Other metals, with relatively small concentrations in raw leachate, were in majority of cases additionally decreased for over 70%. Also, previous studies showed high removal of heavy metals [27,28]. Linda and Jönsson [27] applied nanofiltration AFC-30 membrane for removal of heavy metals from stabilized leachate. Membrane removed over 88% metal cations (Pb^{2+}, Zn^{2+}, and Cd^{2+}). In a similar study, Urase et al. [28] used NTR-7,250 membrane and achieved more than 99% removal for Cr^{3+} and Cu^{2+}.

3.5. Membrane flux

The successful application of RO/NF processes requires efficient control of membrane fouling. Fouling of membranes is influenced by the composition and chemistry of feed water, hydrodynamic conditions, and membrane characteristics. In this study, CF was used as a pretreatment and membrane flux was monitored.

Loose nanofiltration NF270 membrane had highest average water flux (213.40 $L\,m^{-2}\,h^{-1}$) compared to XLE (104.23 $L\,m^{-2}\,h^{-1}$) and NF90 (86.19 $L\,m^{-2}\,h^{-1}$) membranes.

As shown in Fig. 3, flux decreased for all used membranes. The initial flux decline (after 30 min of treating landfill leachate) was 69.1, 70.9, and 77.3% for NF270, NF90, and XLE membranes, respectively. Landfill leachate was treated for 5 h in order to collect the sufficient amount of sample to analyze all parameters. It is interesting to notice that the flux exponentially decreased during 5 h treatment in the case of NF270 membrane, from 65.86 to 26.55 $L\,m^{-2}\,h^{-1}$, i.e. to 59.7%. For NF90 and XLE membranes, the decrease was linear and much smaller in amount of 16.2% and 24.6%, respectively. The flux decline is mainly due to concentration polarization, i.e. the accumulation of dissolved organic and inorganic substances as well as colloidal and suspended particles above the membrane surface (formation of cake layer onto the membrane surface) and within the pore structure.

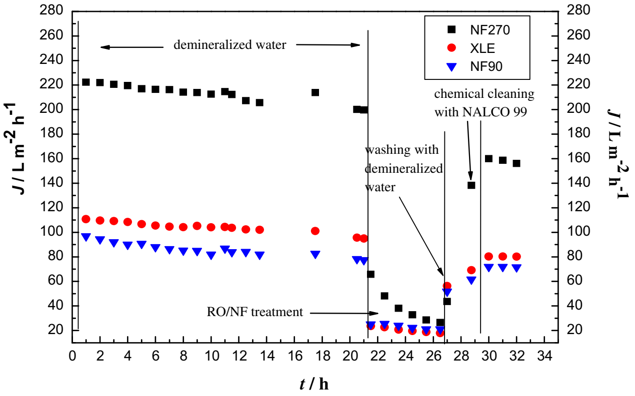

Fig. 3. Flux of demineralized water, flux during RO/NF treatment of landfill leachate, and flux after cleaning.

Fouling can be explained with few arguments. Firstly, if coagulation is carried out at alkaline pH, the effluent could foul RO and NF membranes by $CaCO_3$ scaling [1]. Also, an increase in pH (in the case of NF270 and NF90) may also increase the potential for scaling on the membrane surface due to $CaCO_3$ precipitation [9]. Moreover, if Fe^{3+} is used as a coagulant, the increased fouling could happen due to complex formation between iron and natural organic matter that may precipitate on the membrane surface or inside the pores [29]. Next and very important fact is the presence of organic compounds. Although coagulation is relatively effective for turbidity removal [3,13,14,22], it is ineffective for removal of organic compounds, especially these with low molecular weight that are present in landfill leachate and can cause severe membrane fouling [29,30]. As can be seen in Fig. 4, the normalized flux of all used membranes decreased. For NF270 membrane, the decrease was substantial and represents high degree of fouling. For NF90 and XLE membranes, the normalized flux decreased linearly, probable due to the apparatus configuration. Namely, experiments were operated in a batch circulation mode (concentrate streams circulated back to the feed tank). Therefore, the increase in osmotic pressure, which resulted from the accumulation of organic and inorganic compounds, has to be taken into account.

Membranes were washed with demineralized water and cleaned with the alkaline cleaning agent,

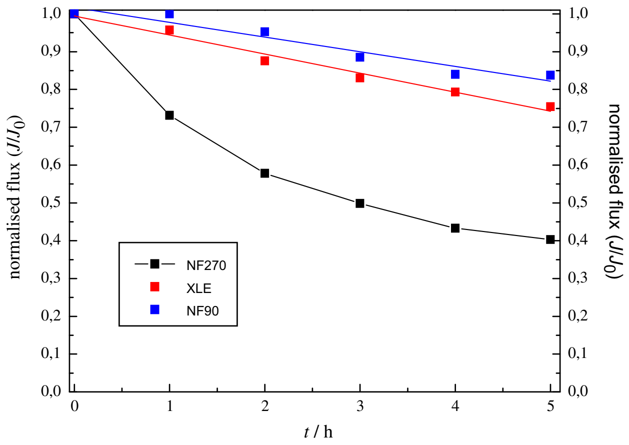

Fig. 4. Normalised flux for NF270, XLE, and NF90 membranes as a function of treatment time.

NALCO 99. The washing with demineralized water was not very effective, because the flux was recovered to 43.65, 56.26, and 41.64 $L\,m^{-2}\,h^{-1}$ for NF270, XLE, and NF90 membranes, respectively. These fluxes were below 50% of average flux before treatment of landfill leachate. Therefore, the chemical cleaning with alkaline agent was necessary. Since the effluent had high organic content (COD and TOC in Table 3) after the CF treatment, the alkaline agent was used. After this chemical cleaning, the membrane flux was recovered to 75.0, 77.0, and 83.4% of initial flux for NF270, XLE, and NF90 membranes, respectively.

Furthermore, membranes were tested with NaCl before the treatment of landfill leachate and cleaning as shown in Table 5. The highest increase of rejection, from 27.5 to 45.6%, was for NF270 membrane and 4.7% for NF90 membrane. There was no change in the case of RO XLE membrane.

According to these results, it can be concluded that the cake layer formed on the membrane surface, especially NF270 membrane, caused irreversible fouling, probably due to high values of turbidity (15.8), COD (1,240 $mg\,L^{-1}$), and TOC (521.4 $mg\,L^{-1}$).

The results presented in this study showed that CF of the landfill leachate were not efficient enough, since irreversible fouling occurred on NF270 membrane. Also, after the complete treatment, the concentration of ammonium, TOC (after NF270 membrane), nitrite, and boron was still higher than the MCLs range.

Table 5
Rejection of NaCl before and after landfill leachate treatment

	R_{before} (%)	R_{after} (%)
NF270	27.5	45.6
XLE	95.7	96.4
NF90	90.7	95.4

Such results bring it to the conclusion that ultrafiltration, for example, could be used between coagulation and RO/NF. Also, other steps could be involved after the membrane treatment.

In the future, CF and RO/NF treatment will be improved for the treatment of this kind of landfill leachate. The improvement of the treatment could help to accomplish MCLs values for ammonium, nitrite, and boron.

4. Conclusions

The leachate from Jakuševec landfill can be considered as the stabilized (old) leachate since pH was 8.05, and it also had relatively low COD value (1,720 $mg\,L^{-1}$).

Jar test showed that 1.0 g $Fe^{3+}\,L^{-1}$ was the optimal dose for the coagulation, as a method for pretreatment of leachate. The coagulation showed low removal of COD (27.9%) and ammonium (7.9%), and intermediate removal of TC, IC, and TOC. After the CF treatment, the values of COD, ammonium, TOC, nitrite, boron, and manganese were above the MCLs value.

The RO/NF treatment showed significant removal of almost all parameters. Still, concentrations of ammonium, nitrite, and boron were above MCLs. The significant flux decrease (69.1%–77.3%) was observed for all used membranes, while the cleaning process returned the flux to around 80% of initial values.

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