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ORIGINAL PAPER

Removal of organic and inorganic compounds from landfill leachate using reverse osmosis

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Abstract The main objective of this work was to evaluate an effectiveness of removing organic and inorganic pollutants from landfill leachate in a long-term reverse osmosis (RO) study. Investigations were carried out during the first year of RO exploitation since February till September 2013. Over 20 parameters were analysed both in leachate and permeate samples. In the first 1-year operation, the treatment performance was feasible for most of analysed leachate pollutants. The average removal rate of chemical oxygen demand (COD), electro-conductivity, ammonia nitrogen ($N\text{-}NH_4^+$), total inorganic nitrogen, cyanides (CN^-), iron (Fe) and chlorides (Cl^-) reached 97, 97.2, 98.7, 99, 93, 97.6 and 98 %, respectively. A smaller reduction rate—of 83 and 86 %—was obtained for sulphates (SO_4^{2-}) and sulphides (S^-), what is the result of sulphuric acid addition before treatment process in order to decline a pH to a value of 6.0–6.5. Boron was eliminated only by 81 % due to easy transportation through the membrane uncharged species of boric acid $B(OH)_3$, which predominate in leachate. Average reduction of nitrites (NO_2^-) and nitrates (NO_3^-) was 63.8 %, which is the result of inhibition NO_2^- oxidizers by nitrous acid and relatively low ratio of biochemical oxygen demand and COD (BOD/COD). The obtained permeate quality does not meet the Polish discharge standards for S^-. It is also foreseen that the concentration of $N\text{-}NH_4^+$ in maturate leachate will increase in the next years.

Keywords Landfill leachate · Pollutants · Reverse osmosis · Treatment

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Introduction

Sanitary landfilling is preferred over other waste management strategies such as incineration and composting owing to its economic advantages and minimum technology being practiced (Kamaruddin et al. 2013; Ahmed and Lan 2012). One of the main environmental problems arising from solid waste landfilling is generation of landfill leachate. They are the result of undergoing physicochemical and biological changes in landfill body, percolation of rainwater through the wastes and inherent moisture content in the waste (Theepharaksapan et al. 2011; Ahmed and Lan 2012). Landfill leachate is a complex mixture of inorganic and organic substances, which can be categorized into four groups: dissolved organic matter, inorganic macrocompounds, heavy metals and xenobiotic organic compounds (Ahmed and Lan 2012; Jemec et al. 2012; Kamaruddin et al. 2013). Organic content of leachate pollution is generally measured by chemical oxygen demand (COD) and biochemical oxygen demand (BOD). The ratio BOD/COD is commonly recognized to be the most representative of landfill leachate age because it is directly related to its biodegradability. As a measure of the inorganic compound content, an electroconductivity (EC) is used. Leachate is usually rich in ammonia ($N\text{-}NH_4^+$) and other inorganic components such as Fe^{2+}, Cl^- and SO_4^{2-}. Stabilized leachate is characterized by high concentration of $N\text{-}NH4^+$ and recalcitrant matter, which has profound implications to the effectiveness of different biological treatment technologies (Ahmed and Lan 2012). The concentration of heavy metals in leachate is variable (Szymański et al. 2011; Jemec et al. 2012). According to Dydo et al. (2005), Bulc (2006) and Kanga et al. (2008), other compounds, that may be harmful to environment, may be also found in leachate from landfills, such as: boron (B), sulphide (S^-) and cyanide (CN^-).

Landfill leachates contain a large number of compounds, of which 80–95 % correspond to inorganic material and between 5 and 20 % are of organic origin (Öman and Junestedt 2008).

As the treatability of landfill leachate depends on its composition and characteristics (Alvarez-Vazquez et al. 2004), different technologies including biological treatment, physicochemical treatment and membrane technologies have been developed in recent years (Kurniawan et al. 2006). Conventional biological process could be effective for the removal of organic substances, suspended solids and nutrients (Yahmed et al. 2009; Theepharaksapan et al. 2011). For the removal of recalcitrant compounds, advanced treatment processes such physicochemical of membrane technologies are required (Kurniawan et al. 2006; Theepharaksapan et al. 2011; Ahmed and Lan 2012). Among several membrane processes, the reverse osmosis (RO) seems to be one of the most promising and efficient method for landfill leachate treatment.

Several studies were performed to investigate the performances of RO system on the purification of landfill leachate (Robinson 2005; Wiszniowski et al. 2006; Li et al. 2009). The treatment of stabilized leachate from Kolenfeld (Germany) was carried out using RO. The maximum removal of COD and $N\text{-}NH_4^+$ with initial concentrations of 3,100 and 1,000 mg/l was found to be 98 and 93 %, respectively (Li et al. 2009). Reverse osmosis was also employed for the treatment of leachate from Wijsler landfill (The Netherlands). The reduction of COD and $N\text{-}NH_4^+$ was found to be 98 % with the initial concentrations of 335 and 140 mg/l, respectively (Kurniawan et al. 2006). The application of RO for treatment of stabilized leachate from Lipówka landfill (Poland) was also explored. With the initial concentration of 1,780 mg/l, RO gave for COD a 97 % removal efficiency (Kurniawan et al. 2006).

A review of the bibliography indicates that most investigations focused on changes of COD, BOD, $N\text{-}NH_4^+$ and heavy metals in a purification process with use of RO. However, there are no wider and systematic investigations on the effectiveness of the RO in removing other contaminations. The main objective of this work is to evaluate the removal efficiency of different (organic and inorganic) compounds from leachate during RO process. Following indicators were took into consideration: (a) general pollution parameters: electroconductivity (EC), pH; (b) inorganic anions: cyanide (CN^-), chloride (Cl^-), sulphates (SO_4^{2-}), sulphides (S^-), nitrites and nitrates ($N\text{-}NO_x^-$); (c) inorganic cations: nitrogen ammonia ($N\text{-}NH_4$), ferrous (Fe); (d) organic indicators: biochemical oxygen demand (BOD_5), chemical oxygen demand (COD); (e) additional parameters: total nitrogen (TN). The analysis/investigations were conducted during the first year of the RO system exploitation. The investigations were carried on since February till September 2013 in Siedliska Landfill (Poland).

Materials and methods

Field site

The leachate used in this study was collected from the municipal landfill in northern-eastern part of Poland, at the northern latitude 53°50′55″ and the eastern longitude 22°19′02″. The landfill covers an area of 25.5 ha and is operated since 1983 year. The site receives about 20,000 Mg of domestic waste yearly. The old part of landfill (Cell A)—which area of 7.7 ha was filled with 550,000 Mg of waste—was reclaimed and the new one (Cell B) with the area of 5.5 ha was built. The new cell has been estimated to contain about 280,000 Mg of waste.

The Cell A is sealed with a natural 31-m clay substrate functioning as a geological barrier. In order to protect the ground and water environment, a circumferential ditch to collect leachate was constructed. The Cell B is sealed at the bottom with a polyethylene membrane, which prevents to leachate infiltration into the soil–water environment. There is a leachate drainage system placed on the bottom of this cell. The leachate from both cells is directed to the first chamber of the two-chamber buffer tank and mixed there. The amount of leachate generated per day is about of 60–90 m^3. The second chamber of buffer tank is used for collecting technological wastewater from a composting installation placed at the landfill.

In order to solve the leachate problem, a RO system for leachate treatment was implemented at the end of 2012 year. Before entering into the RO membrane modules, the leachate was first fed into a sand filter, which was used to remove suspended particles larger than 50 µm in size. Then, a cartridge filter was employed for further removal of the suspended solids larger than 10 µm. In order to maintain the pH value of 6.0–6.5, sulphuric acid was dosed to the leachate before treatment process. The low value of the pH makes inorganic salts (such as calcium carbonates) more soluble. During the period of investigation, there was no any membrane cleaning process.

Table 1 Characteristic of CD9-RO module parameters

Items	RO
Configuration	Disc tube
Membrane type	Thin-film composite
Polymer type	Polyamide
Membrane area (m^2)	9
Package (m^2/m^3)	194
Rated operating pressure/bar	65
Module number	18
Operating temperature (°C)	0–45
Salt rejection	99 %
Water flux	Up to 50 $l/m^2/h$ at pressure of 70 Ba
Treatment capacity (m^3/d)	72
Recovery (%)	75

Pressurized leachate from both chambers of the buffer tank is fed into the ROCHEM CD9-RO disc-tube modules. The amount of leachate directed to the RO process is about 1,500 m^3 per month. The specifications of the CD9-RO module and operational parameters are listed in Table 1.

The permeate generated during the treatment process is stored temporary in a retention reservoir and next returned to individual installations of the plant (composting plant, crumbling yard). The permeate is recirculated onto a new storage yard (Cell B) to ensure proper humidity of the waste. A simplified flow diagram of the leachate treatment system is presented in Fig. 1.

Methods

The leachate and permeate samples used for chemical characterization were obtained directly from the site. The samples were collected six times, from February 2013 till September 2013. Each time, two samples—one of a raw mixed leachate from the Cell A and the Cell B, and second of permeate from a retention reservoir—were taken. During investigation period, 12 samples were taken. Collected samples were transported to the laboratory in 3l bottles and stored in dark at 4 °C to minimize biological and chemical changes. All analyses were made the same day as the sampling was taken according to the Standard Methods (Rice et al. 2012).

Leachate and permeate characterization included:

(a) General parameters: electroconductivity (EC), pH,
(b) Organic indicators: biochemical oxygen demand (BOD_5), chemical oxygen demand (COD),
(c) Inorganic cations: nitrogen ammonia ($N\text{-}NH_4^+$), ferrous (Fe),
(d) Inorganic anions: cyanide (CN^-), chloride (Cl^-), sulphates (SO_4^{2-}), sulphides (S^-), nitrites and nitrates ($N{-}NO_x^-$).
(e) Other: total nitrogen (TN), boron (B).

The electroconductivity and the pH were measured on-site by a conductivity and potentiometric method, respectively, using a portable pH metre (HACH HQ40).

The chemical oxygen demand was analysed using a colorimetric method with a HACH spectrophotometer (620 nm) after a 2-h reactor digestion ($K_2Cr_2O_7$ method) and the biochemical oxygen demand—using an OxiTop (WTW) measuring system based on a pressure measurement. Cyanide was determined colorimetrically by a pyridine-pyrazolone method. The results were measured with a HACH spectrophotometer at 612 nm. Chloride was analysed by an iron(III)-thiocyanate method (468 nm), sulphates—by a barium sulphate method (450 nm),

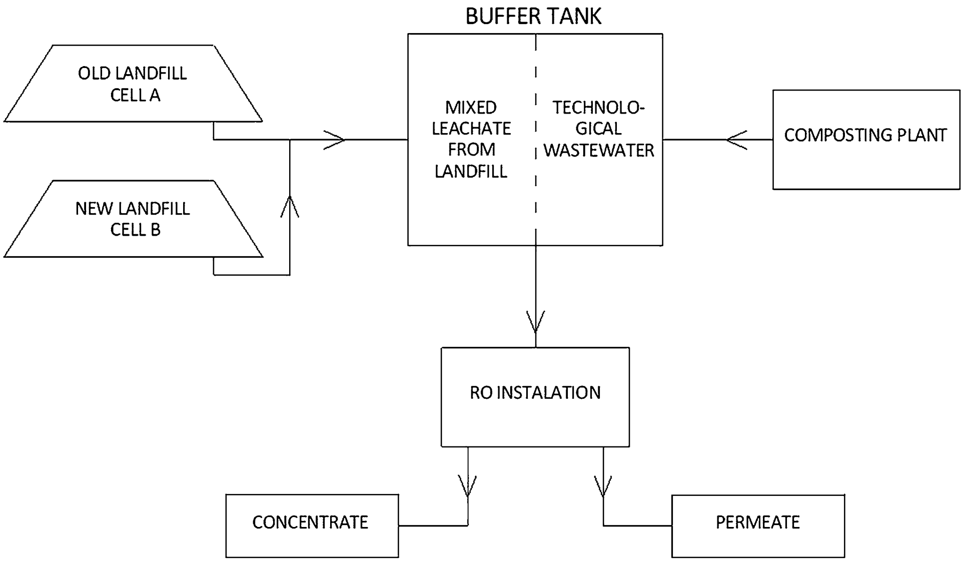


Fig. 1 Flow diagram of the leachate treatment system

Table 2 Chemical parameters used in this study and basic statistic

	N	Min	Max	Median	SD	Mean	Standard limits*
pH	6	7.21	7.90	7.39	0.256	7.45	6.5–9.0
EC	6	7,680.0	9,430.0	8,238.0	634.91	8,301.00	–
BOD	6	150.0	1,350.0	470.0	438.93	581.67	–
COD	6	285.0	2,250.0	1,286.7	629.40	1,266.42	–
$N\text{-}NH_4{}^+$	6	94.00	899.5	201.0	296.72	334.67	100
Fe	6	1.45	7.20	5.20	2.122	4.79	–
Cl^-	6	788.0	6,862.0	1,410.5	2,286.2	2,284.58	1,000
$SO_4{}^{2-}$	6	210.0	530.0	275.0	127.29	329.17	500
$N\text{-}NO_3$	6	0.00	1.40	0.00	0.571	0.33	–
$N\text{-}NO_2$	6	0.01	0.15	0.05	0.056	0.07	10
TN	6	260.0	1,450.0	415.0	455.33	567.50	–
TIN	6	94.15	899.63	201.3	296.55	335.06	–
$N\text{-}NO_x$		0.04	1.41	0.14	0.53	0.39	–
S	6	61.0	2,050.0	616.0	779.04	866.30	1
CN	6	0.07	0.18	0.11	0.039	0.12	0.5
B	6	3.20	6.10	4.70	0.999	4.78	10
BOD/COD	6	0.31	1.00	0.62	0.312	0.64	–
$COD/NH_4{}^+$	6	1.25	12.08	7.42	4.542	7.01	–
$BOD/NH_4{}^+$	6	0.28	8.51	3.85	3.360	3.97	–
Temperature	6	0.00	30.00	19.50	12.46	15.17	–
FA	6	0.62	2.89	2.59	0.875	2.18	–

All in mg/l except pH and EC (µS/cm)

* Standard limits according to Polish Minister of Building Regulation concerning the obligations of supplier of industrial wastewater and the conditions for discharging wastewater into sewerage system (Journal of Laws from 14.07.2006)

sulphides—by a methylene blue method (665 nm), all of them with use of colorimetric method with HACH spectrophotometer. Boron was measured by its reaction with carminic acid in the presence of sulphuric acid (605 nm) and ferrous by a phenanthroline method (510 nm), also with use of HACH spectrophotometer.

The nitrogen total was measured using N Tube Vials on the HACH spectrophotometer (410 nm) after a 0.5-h alkaline digestion (persulphate digestion method). Nitrogen ammonia, nitrite and nitrate were analysed with N Tube Vials on the HACH spectrophotometer (655, 507, 410 nm, respectively) using a salicylate method for $N\text{-}NH_4{}^+$, a diazotization method for $N\text{-}NO_2{}^-$ and a chromatropic acid method for $N\text{-}NO_3{}^-$. Basing on measured values of nitrogen compounds, the content of the total inorganic nitrogen (TIN) in the leachate was calculated from the following equation:

$$\mathrm{TIN} = C_{\mathrm{N-NO_2^-}} + C_{\mathrm{N-NO_3^-}} + C_{\mathrm{N-NH_4}} \tag{1}$$

where $C_{\mathrm{N-NO_2^-}}$, $C_{\mathrm{N-NO_3^-}}$, $C_{\mathrm{N-NH_4}}$ are the concentrations (mg/l) of nitrogen nitrite, nitrogen nitrate and nitrogen ammonia. The obtained results were the mean value of three determinations carried out simultaneously.

For data analysis, a Statistica software was used in this study. The basic statistic analysis included calculation of minimum, maximum, mean and median value. Measures of variability were reported in standard deviation. To asses the effectiveness of RO, a removal ratio was calculated for each contaminant in each period of sampling. For detailed analysis, an additional parameters were calculated such as BOD/COD ratio, $\mathrm{BOD/N{-}NH_4^+}$ ratio, $\mathrm{COD/N\text{-}NH_4^+}$ ratio and free ammonia (FA).

Results and discussion

Characteristics of the raw leachate

The results of the raw leachate characteristics are presented in Table 2.

The average pH of the raw leachate was 7.45 and varied between 7.21 and 7.90. According to Kurniawan et al. (2006), this value is typical for leachate at intermediate phase. This is due to degradation of the volatile fatty acids (VFAs) by methanogenic bacteria, what result in reduction in the organic strength of leachate leading to a pH higher than 7. Variation of the pH in leachate can influence the amount of sulphuric acid addition for the RO purification unit. The value of electrical conductivity usually fluctuates depending on the variation of precipitation and evaporation (Li et al. 2009). During the period of observation, the EC value varied from 7,680 to 9,430 µS/cm, with the mean value of 8,301 µS/cm. The BOD concentration of the raw leachate ranged from 150 to 1,350 mg/l, with the average value of 581.7 mg/l. The COD in leachate varied from 285 to 2,250 mg/l, with the average value of 1,266.4 mg/l. The calculated BOD/COD ratio was 0.64. Since the BOD decreases much faster than the COD (because the nondegradable portion of COD will largely stay unchanged in this process), the BOD/COD ratio in nonstabilized leachate is more than 0.1 ÷ 0.3 (Kurniawan et al. 2006; Ahmed and Lan 2012). Of toxic compounds, inorganic cations $\mathrm{N{-}NH_4^+}$ have been identified as one of the major toxicants to living organisms. The measured average $\mathrm{N{-}NH_4^+}$ concentration during the test period was 334.7 mg/l and ranged between 94 and 899.5 mg/l. The value of the second analysed inorganic cation—Fe varied from 1.45 to 7.2 mg/l, reaching the mean value of 5.2 mg/l. The average concentrations of $\mathrm{N{-}NO_x^-}$ in leachate were 0.39 mg/l (0.07 mg/l for $\mathrm{N\text{-}NO_2}$ and 0.33 mg/l for $\mathrm{N\text{-}NO_3}$, respectively). Concentration of total nitrogen ranged from 260 to 1,450 mg/l with mean value of 567.5 mg/l. The average concentrations for selected inorganic anions—$\mathrm{CN^-}$, $\mathrm{Cl^-}$, $\mathrm{SO_4^{2-}}$, $\mathrm{S^-}$, B were: 0.12 mg/l for $\mathrm{CN^-}$, 2,284.6 mg/l for $\mathrm{Cl^-}$, 329.2 mg/l for $\mathrm{SO_4^{2-}}$, 866.3 mg/l for $\mathrm{S^-}$, and 4.8 mg/l for B.

Overall, the leachate characteristics did not meet the standard limits specified by the Polish Minister of Building Regulation concerning the obligations of a supplier of industrial wastewater and the conditions for discharging wastewater into sewerage system (Journal of Laws of 14.07.2006). The limit values were exceeded in case of $\mathrm{N{-}NH_4^+}$, $\mathrm{Cl^-}$, $\mathrm{S^-}$ (Table 1).

Based on the observed pH, COD and BOD values, N-NH4 concentration and landfill age, the landfill leachate used in this research was at its intermediate phase. At this phase, the composition of leachate is characterized by moderate BOD values and BOD/COD ratio not <0.3. The BOD/COD ratio of analysed leachate—with the mean value of 0.64—shows that the leachate is biodegradable with a relatively high content of organic matter. The nitrogen ammonia content is not at a high level, and its mean value does not exceed 400 mg/l, what—according the Kurniawan et al. (2006)—indicates a not yet stabilized phase of leachate. For such a leachate composition, RO technology may be sufficient because it is recommendable to be applied both for poorly biodegradable and highly biodegradable leachate.

Removal of organic and inorganic compounds

The removal effect ratio (R_e) during purification with the RO system was calculated from the equation:

$$R_e = 1 - \frac{C_1}{C_0} \cdot 100\ \% \qquad (2)$$

where: C_1 is the pollutant concentration in permeate (mg/l) and C_0 is the concentration of pollutant in the raw leachate (mg/l). The reduction of major components in the leachate obtained during the study period from February 2013 till September 2013 is shown in Table 3.

The COD removal effect ranged from 92.3 to 99.9 %. The highest value of removal was obtained in March 2013, and then, this value started to decrease till the end of the study period, reaching its minimum in September 2013. The average BOD removal effect was 83.5 %. The highest value—97.8 % was obtained in May 2013, and then, it declined to 72.5 % in September. Such a removal efficiency of COD and BOD is in accordance with most leachate treatment with the use of RO. Liu et al. (2008) reported the COD removal efficiency of 99.5 ÷ 99.8 % and the BOD—98.2 %. Theepharaksapan et al. (2011) obtained during his investigation around 98 % of the COD removal and 89 % of the BOD removal. The results obtained during presented study are strongly correlated with the BOD/COD ratio of raw leachate. The highest value of BOD/COD ratio was observed in March (BOD/COD = 0.99) and May (BOD/COD = 1.0), in the time where the efficiency of COD removal was the highest. It suggests that removal efficiency of well-biodegradable leachate is higher. This is due to the fact that in this event, the purification efficiency results from two processes taking part at the same time: (a) a physical leachate treatment with the RO system and (b) a biodegradation of the organic matter, what in the end intensifies the final purification effect. Moreover, the biodegradable organic matter is also used as a carbon source for the denitrification of $\mathrm{N\text{-}NO_x^-}$. That is why, at the time when BOD/COD ratio of the raw leachate was the highest, the $\mathrm{N\text{-}NO_x^-}$ removal efficiency was also the highest and reached 97.7 % in March 2013 and 97.1 % in May 2013 (Fig. 2).

The removal efficiency of $\mathrm{N\text{-}NH_4{}^+}$ was high and ranged from 96.9 in July to 99.9 % in February 2013. The average rate of removal was 98.7 %. Because the $\mathrm{N\text{-}NO_x^-}$ concentration in leachate is low, the $\mathrm{N\text{-}NH_4{}^+}$ concentration is close to that of TIN. Thus, the TIN removal efficiency is

Table 3 Reduction rates of organic and inorganic components

Parameter	Feb-2013	Mar-2013	May-2013	June-2013	July-2013	Sep-2013	Average removal effect
pH*	5.21	5.59	6.52	6.55	5.97	6.16	6.00
EC	97.20	97.32	96.51	96.33	98.16	97.53	97.18
N-NH^4	99.98	99.43	98.96	98.07	96.93	98.98	98.72
Fe	98.89	93.10	98.43	97.32	99.35	98.62	97.62
Cl^-	96.18	99.13	97.28	98.18	99.13	97.86	97.96
SO_4^{2-}	78.40	92.08	60.82	92.27	96.67	78.33	83.09
COD	96.51	99.96	98.12	97.69	97.64	92.28	97.03
BOD	72.50	72.00	97.78	94.12	92.23	72.50	83.52
N-NO_3	–	–	100.00	100.00	100.00	100.00	66.67
N-NO_2	76.03	97.72	−645.45	−189.74	75.61	24.09	−93.63
TN	99.67	99.62	98.11	96.92	96.72	98.64	98.28
TIN	99.84	99.43	98.95	98.02	96.92	98.97	98.69
N-NO_x	7.53	97.72	97.08	80.81	75.61	24.09	63.81
S	99.80	99.12	98.65	95.32	62.30	63.80	86.50
CN	99.44	86.32	93.68	98.57	87.86	91.96	92.97
B	68.75	79.55	89.47	78.69	87.10	85.14	81.45

* pH value of permeate

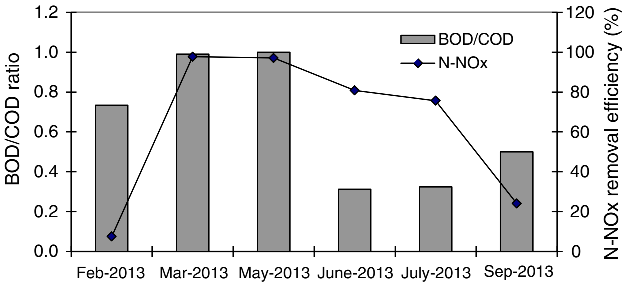


Fig. 2 N-NO_x^- removal effect depending on BOD/COD ratio value

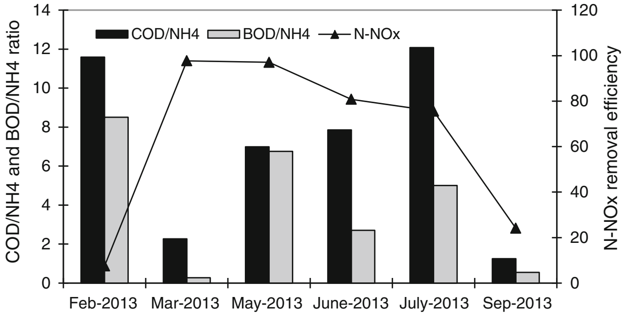


Fig. 3 Variation of COD/NH_4^+ and BOD/NH_4^+ and efficiency of N-NO_x^- removal

nearly equal to the N-NH_4^+ removal effect, with the same fluctuation trend. To achieve an effective nitrification, a supply of inorganic carbon is required as a carbon source for the nitrifying bacteria growth as shown in equation (Parkes et al. 2007):

$$NH_4^+ + 2O_2 + 2HCO_3^- \rightarrow NO_3^- + 3H_2O + 2CO_2 \qquad (3)$$

The concentration of inorganic carbon in the leachate treatment facility must be sufficiently large to sustain a nitrifying community capable of oxidizing all of N-NH_4^+. This can be difficult in facilities, where the influent N-NH_4^+ is quite high (Parkes et al. 2007). The leachate presented in this study is at its intermediate phase; thus, the NH_4^+ concentration is not high, and the concentration of inorganic carbon is sufficient to oxidize most of NH_4^+. Nevertheless, with time the N-NH_4^+ content increases causing that the amount of inorganic carbon becomes insufficient. Parkes et al. (2007) obtained less than 90 % NH_4^+ removal for an old leachate, pointing that a low concentration of inorganic carbon had limited N-NH_4^+ oxidation.

The ratio between biodegradable COD and N-NH_4^+ should be greater than four for the completion of the nitrate denitrification (Zhang et al. 2007). Variation of COD/N-NH_4^+ and BOD/N-NH_4^+ in the raw leachate during the study period is shown on Fig. 3.

When the ratio of feed COD to N-NH_4^+ ranged from 2.3 to 12, the N-NO_x^- removal efficiency was 75.6 ÷ 97.7 %. The low COD/N-NH_4^+ ratio in March 2013 did not disturb the nitrification since the dissolved oxygen content in the leachate was relatively high (4.9 mg/l). The lowest COD/N-NH_4^+ ratio and BOD/N-NH_4^+ ratio were observed in

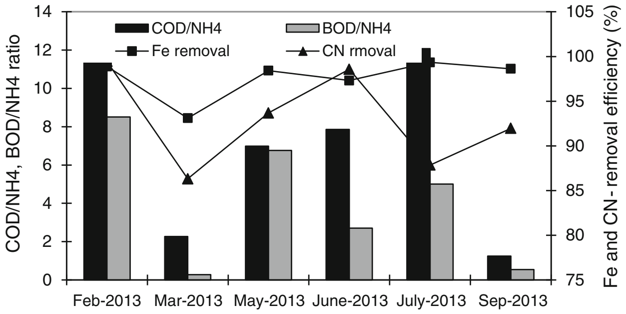


Fig. 4 COD/NH_4^+ and BOD/NH_4^+ ratio versus efficiency of Fe and CN^- removal

September 2013 (1.2 and 0.5, respectively) and resulted in a low N-NO_x^- removal efficiency which was 63.8 %. Parkes et al. (2007) reported that the N-NO_x^- accumulation can result from a free NH_3 and nitrous acid (HNO_2), which can inhibit the NO_2^- oxidation. Anthonisen et al. (1976) found out that the NH_3 concentration of 0.1 ÷ 1.0 mg/l can inhibit the NO_2^- oxidation, which is in agreement with Zhang et al. (2007). A free ammonia (FA) for the analysed leachate was calculated using the equation (Anthonisen et al. 1976):

$$C_{FA} = \frac{C_{\text{N-NH}_4} \cdot 10^{\text{pH}}}{\exp(6334/(273 + T) + 10^{\text{pH}})} \tag{4}$$

where $C_{\text{N-NH}_4}$ is the ammonia nitrogen concentration, *pH* is value of pH and *T* is the leachate temperature in °C. The results of calculations are presented in Table 2. The average value of FA was 2.2 mg/l; thus, it seems more likely that HNO_2 rather than free NH_3 is inhibiting the NO_2^- oxidizers and causing the NO_2^- to accumulate.

There was observed a correlation between COD/N-NH_4^+ ratio, BOD/N-NH_4^+ ratio and Fe, cyanide removal, what is shown on Fig. 4.

It was noted that the CN^- and Fe removal increases along with increase of COD (BOD)/N-NH_4^+ ratio. In the presence of cyanide ions, the iron salts immediately generate complex ions. The most stable of these is the $[Fe(CN)_6]_4$, and the logarithm of the stable complex value $[Fe(CN)_6]$ ($\log\beta_6$) is 24. Therefore, the content of cyanides and iron in the leachate is strongly correlated. At the same time, a concentrated H_2SO_4 can cause the compound to decompose with a parallel CO formation. Produced carbon compounds can be used by denitrifying bacteria as a carbon source (as an electron donor).

The average electric conductivity (EC) removal effect was 97.2 %. As the EC relates to the salt content in the leachate, the total ion concentration is a function of the EC, as shown in the equation below (Liu et al. 2008):

$$Y_{\text{TDS}} = k \cdot \delta_{25^\circ\text{C}} \tag{5}$$

where Y_{TDS} is the total dissolved solid (mg/l), $\delta_{25^\circ\text{C}}$ is the EC under 25 °C (µS/cm), *k* is the factor. At lower values of the EC, the concentrations have been close to those predicted by a more commonly applied linear conversion: $k = 0.75\delta$. The effectiveness of the EC removal in the RO process is very high and fluctuated from 96.3 % in June 2013 till 98.2 % in July 2013. It is in agreement with Liu et al. (2008), who reported a 90.5 % EC removal effect after the 1° RO and over 99 %—after the 2° RO. According to Li et al. (2009), investigation about 98 % removal effect of the EC was obtained both after the 1° RO and the 2° RO.

The EC removal efficiency is a result of the effectivity of removal of individual ions from contaminated leachate. Ions, which were analysed in leachate, were efficiently caught and removed by the RO. The average removal rate of Cl^- was—97.9 %, SO_4^{2-}—83.1 %, S—86.5 % and B—81.4 % (Fig. 5). Cl^- and SO_4^{2-} are the main ions generating the electroconductivity; thus, the fluctuation of Cl^- and SO_4^{2-} during study period was similar to of EC fluctuation.

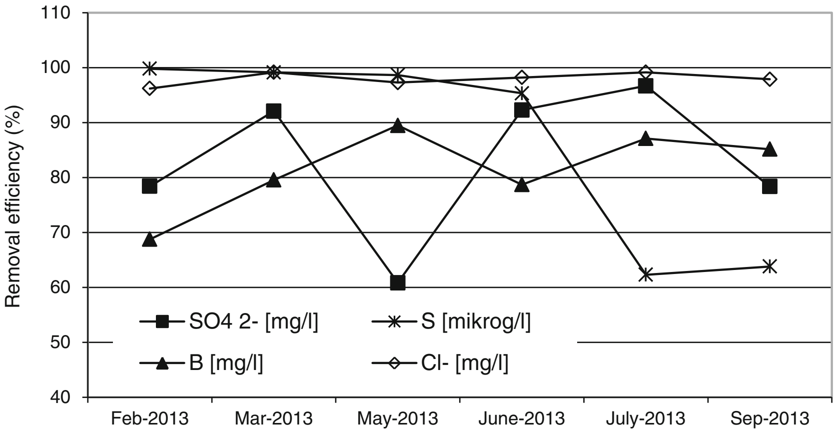
Nevertheless, the SO_4^{2-} rejection rate was smaller than the rejection rate of EC, and obtained removal efficiency for this compound was lower than reported in the literature. Renou et al. (2008) obtained more than 95 % efficiency in the removal of both Cl^- and SO_4^{2-}. The similar removal effect was achieved by Li et al. (2009). In both these studies, a two-stage (1° and 2°) RO system was employed, while the leachate analysed in our study was treated only with one-stage RO system. Besides, addition of sulphuric acid during RO process increases the sulphate ion level in the RO feed, in accordance with equation:

$$H_2SO_4 + 2H_2O \leftrightarrow 2H_3O^+ + SO_4^{2-} \tag{6}$$

which increases the concentration of sulphate in permeate. So, the reason for the lower removal rate of SO_4^{2-} is not lower membrane rejection for this compound but higher concentration of sulphate in the feed, which resulted in a higher SO_4^{2-} concentration in the permeate. Thus, during RO operation, the advantages provided by sulphuric acid dosign should be weighed against the risk of introducing excess sulphates into feed water.

The average S^{2-} removal effect was 86.5 %. The highest value—99.8 % was obtained in February 2013 and the lowest—62.3 % in July 2013. The form of sulphides contained in wastewater depends on the pH reaction. In the acid solution (at $pH < 6$ the), H_2S presence is prevailing, where at $pH \geq 8$ the main form is hydrosulphides (of a general formula: MeHS) and at

Fig. 5 Removal efficiency of Cl^-, SO_4^{2-}, B, and S during study period



pH: 6 ÷ 10 both forms of sulphides occur at the same time, in different percentage. As in case of sulphates, the lower—in comparison with other analysed parameters—removal efficiency of S^{2-} results from sulphuric acid (H_2SO_4) addition to leachate before the treatment process. In the presence of sulphuric acid, a certain part of sulphides present in leachate is converted into H_2S and SO_4^{2-}, according to equation:

$$S^{2-} + H_2SO_4 \rightarrow H_2S + SO_4^{2-} \tag{7}$$

Then, due to the reaction of metal ions with the hydrosulphide—resulting from the above reaction—sulphides are generated, according to exemplary reactions:

$$2Fe + 3H_2S \rightarrow Fe_2S_3 + 3H_2 \tag{8}$$

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O \tag{9}$$

$$2Fe(OH)_3 + 3H_2S \rightarrow Fe_2S_3 + 6H_2O \tag{10}$$

The result of above reactions is an increase of sulphide and sulphate's concentration in the obtained permeate, which results in their lower removal efficiency in analysed leachate. A drop in removal effect of sulphides was noted in July and September 2013 (Fig. 4). At the same time, the SO_4^{2-} removal efficiency increased, pointing to a possible oxidation of some portion of sulphides to sulphates. The average S^- concentration in permeate after the RO process was 42 mg/l. Due to a high concentration of sulphides, the permeate does not meet the standard limit for S^-, which is 1 mg/l (Table 2).

The rejection rate for B ranged from 68.7 % in February to 89.5 % in May 2013. In the studies conducted by Farhat et al. (2013), the B removal efficiency after the two stage of RO system was within the range 40–99 %. The B removal efficiency depends mostly on the pH. The dissociation of $B(OH)_3$ to the borate $[B(OH)_4^-]$ occurred at pKa = 9.27. This means that boron predominantly exists in aqueous solution as the uncharged $B(OH)_3$ below the pH of 9.27 and as the $B(OH)_4^-$ above the pH of 9.27, according to the equation by Richards et al. (2010):

$$H_2O + B(OH)_3 \leftrightarrow H^+ + B(OH)_4^- \quad (pK_a = 9.27) \tag{11}$$

No other forms of boron are predicted to be present in the solution. The neutral species of boron—$B(OH)_3$—is easily transported through the membrane due to both the lack of steric hindrance and lack of the charge repulsion. In addition, the $B(OH)_3$ has a trigonal planar structure [in contrast with the tetrahedral structure of the $B(OH)_4^-$], which enhances hydrogen bridges between the $B(OH)_3$ and the membrane functional groups, enabling the $B(OH)_3$ to permeate in a similar manner as carbonic acid or water via confection/diffusion (Richards et al. 2010). That is why it is generally difficult for the RO process to achieve an average boron rejection over 90 %. Improved rejection can be achieved by adding treatment stages or polishing steps. The use of the H_2SO_4 for leachate acidification before the RO treatment strongly influences on insufficient removal effect for boron. Boron element might be efficiently removed on RO membranes at a shifted pH, close to 11 (Dydo et al. 2005).

Conclusion

The landfill leachate used in this research was in intermediate phase, due to its BOD/COD ratio, value of pH, $N\text{-}NH_4^+$ concentration and landfill age. The leachate characteristics did not meet the Polish standard limits for discharging wastewater into sewage system in case of $N\text{-}NH_4^+$, Cl^- and S^-.

The RO treatment process was found to be acceptable for all parameters analysed in leachate. The highest removal performance was obtained for COD, EC, N-NH_4^+, TIN, CN^-, Fe, Cl^- and was 97, 97.2, 98.7, 99, 93, 97.6, 98 %, respectively. The BOD removal was within the range of 72–97.8 %. The average removal efficiency for SO_4^{2-}, S^- and B was 83, 86 and 81 %, respectively. The low $SO_4^{2-}$and S^- removal effect results from sulphuric acid dosage to the leachate before the treatment process. In the presence of H_2SO_4, a certain portion of sulphides is converted to SO_4^{2-} and H_2S. The advantages provided by sulphuric acid addition should be weighed against the risk of increasing sulphate and sulphide concentration in permeate. The smaller B removal efficiency results from the form it occurs in an aqueous solution, in which—at the $pH < 9.27$—an uncharged $B(OH)_3$ predominate. This neutral species is easy transported through the membrane, and for this reason, it is difficult for RO process to achieve a boron rejection over 90 %. The better boron removal efficiency would be possible at pH higher than 9.27. The lowest average removal effect was observed for N-NO_x^-, which was 63.8 %. The conducted analysis demonstrated that more likely, the HNO_2 is inhibiting the N-NO_2^- oxidizers, causing N-NO_x^- to accumulate. Besides, the low organic matter content, expressed as a BOD/COD, ratio can influence a decrease of the N-NO_2^- removal efficiency.

The quality of the permeate does not meet the discharge standard issued in Poland in case of S^-. Thus, a possibility of increasing the RO efficiency to removal of SO_4^{2-}, S^- and B should be considered, for instance, by selection and usage the proper and effective antiscalant instead of sulphuric acid addition. Besides, the leachate analysed in this study had the N-NH_4^+ concentration not high; thus, the concentration of inorganic carbon was sufficient to oxidize most of the nitrogen ammonia. With time, the N-NH_4^+ concentration in the leachate will increase, which will cause that the amount of an inorganic carbon can be insufficient. This suggests that in the next years, the treatment efficiency can be too low and an implementation of a leachate pretreatment should be taken into consideration.

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