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PAHs removal from municipal landfill leachate using an integrated membrane system in aspect of legal regulations

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ABSTRACT

Among the many pollutants present in aqueous solutions, special attention is given to polycyclic aromatic hydrocarbons (PAHs). This is connected with their mutagenic, teratogenic and carcinogenic effects on organisms, confirmed by toxicological tests. Among the 16 PAHs identified by the US Environmental Protection Agency as being necessary to assess in environmental samples, nine showed toxic effects. In addition, in the Water Framework Directive PAHs are listed as priority substances for the aquatic environment. Therefore, there is a justified need to search for highly effective methods of removing these contaminants from water and wastewater. The purpose of this paper is to monitor changes in the concentrations of PAHs during integrated membrane treatment processes. The leachate used in this study originated from a local municipal waste landfill located in Southern Poland. In the first stage of research, leachate was filtrated on a sand bed (pre-filtration). After the pre-filtration, leachate was directed to the membrane module for the main filtration. One DK nanofiltration membrane manufactured from thin film polyamide (TF) was used during the investigation. 16 PAHs listed by the US EPA were analysed: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chryzene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3,c,d)pyrene and benzo(g,h,i)perylene.

The initial concentration of 16 PAHs in the landfill leachate was 9.86 µg/L. They proved very effective in removing PAHs from the leachate during the study. After filtration on a sand-bed, the concentration of PAHs decreased to 5.43 µg/L, and to 1.73 µg/L after nanofiltration. The value of the retention coefficient of the 16 PAHs in the nanofiltration process reached 69.2%. The highest retention coefficient ratio—99.2% was observed for benzo(g,h,i)perylene. For indeno(1,2,3,c,d)pyrene the retention coefficient was also high and reached 92.7%. The retention coefficient of the 5-ring compounds was 85.6%. The smallest retention coefficient (30.5%) was observed for fluorene. The concentration of the 3-ring compounds was reduced to 51.2% and the 4-ring to 66.2%. The concentration of naphthalene decreased to 47.1%. The average degree of 16 PAH removal from leachate in the integrated membrane process, including nanofiltration and filtration on a sand-bed, was 80.2%.

Keywords: Municipal landfill leachate; Waste management; Legal regulations; Membrane techniques; Pre-filtration; Sand bed; Nanofiltration (NF)

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1. Introduction

One of the primary objectives of the European Union (EU) related to waste management is to break the link between economic growth and the generation of waste [1]. In order to resolve this issue, the EU established a legal framework [2] for controlling the entire life cycle of waste from its production to disposal [3], focusing on recovery and recycling [4]. According to Eurostat data (2016), the amount of municipal waste generated per capita in EU couties has been systematically increasing in recent years. In 2014, municipal waste generation totals vary considerably between individual countries, ranging from 272 kg per capita in Poland to 759 kg per capita in Denmark. These variations are the consequence of differences in consumption patterns and economic wealth, but also the types of systems of waste collection and models for its management [5]. Differences are observed between countries regarding the degree to which waste from commerce, trade and administration is collected and managed together with waste from households [6]. The handling of municipal waste is a huge challenge in waste management at both a European and world scale [7]. The amount of waste generated at EU-28 level, including waste by treatment category—landfill, incineration, material recycling, composting and digestion, is shown in Fig. 1.

As a result of the introduction of EU legalisation, the rate of landfill compared with municipal waste generation dropped from 63.8% in 1995 to 27.5% in 2014 [6]. However, huge volumes of waste continue to be directed to municipal landfill. The problem with wastewater issues begins with the generation of leachate on refuse tips [8]. The leachate is defined as aqueous effluent formed as a consequence of rainwater percolation through wastes, biochemical processes in cells within the waste, and the inherent water content of wastes themselves [9]. The composition of leachate depends on many factors such as the topography of the area where the landfill is located, amount and variability of precipitation, humidity, evaporation rate, soil conditions, method of sealing the landfill, contact of deposits with surface water and groundwater, type of waste and degree of fragmentation, method of storage and waste compaction, humidity and water holding capacity, physical and biochemical transformations occurring within the waste (degradation phase), age of the tip, season, process of exploiting the structure, and type of vegetation growing on the landfill after reclamation [10–12]. Municipal leachate consists of a complex mixture of organic and inorganic components [13]. Organic contaminants present in the leachate are mainly organic nitrogen compounds, aliphatic and aromatic hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs), organic acids and other compounds. The mineral contaminants in the leachate are mainly heavy metal ions like Zn^{2+}, Mn^{7+}, Cr^{6+}, Pb^{2+}, Cu^{2+}, Ni^{+}, Hg^{2+}, anions like NO_3^-, NO_2^-, HCO_3^-, Cl^-, SO_4^{2-}, PO_4^{3-}, alkaline cations like Ca^{2+}, Mg^{2+}, and K^+ and the ammonium cation NH_4^+ [14–17]. A complete and detailed identification of all the chemical compounds in leachate is difficult even if the best analytical methods are applied.

More than 200 individual organic compounds have been identified in the landfill leachate, including mono- and bicyclic aromatic hydrocarbons. Some of the most toxic organic compounds present in the leachate are PAHs [18]. Only a few sources in the available literature are focused on the identification of PAHs in leachate from municipal landfill. The compounds present in leachate mainly come from the leaching of materials deposited in the landfill. Hydrocarbons are periodically released during the decomposition of organic matter contained in the waste. PAHs are characterised by poor solubility in water, however their solubility may increase in the presence of other organic compounds in water solution. The consequence of this is that relatively high concentrations of PAHs are noted in the leachate. Some of the most important factors affecting the level of the PAH content in leachate are the season and type of materials deposited in the landfill [19–20]. The concentration of PAHs in the municipal leachate is very variable, e.g. 0.06 –0.07 µg/L [21], 23.64–26.95 µg/L [18], 100 µg/L [22], 2218 µg/L [23], 7966 µg/L [24]. Among the 16 PAHs identified by the US Environmental Protection Agency (EPA) as necessary to measure in environmental samples, nine showed toxic effects. Therefore, there is a justified need to search for highly effective methods of removing these contaminants from wastewater, including leachate.

The paper presents the effectiveness of the integrated membrane treatment processes in the removal of PAHs from municipal leachate: filtration on a sand bed (prefiltration)—nanofiltration (NF) in relation to the legal regulations.

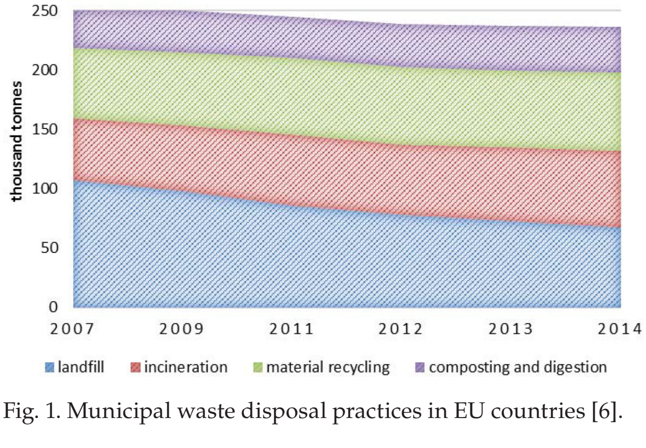

Fig. 1. Municipal waste disposal practices in EU countries [6].

2. Legal regulations concerning polycyclic aromatic hydrocarbons (PAHs) in the aquatic environment

In the Water Framework Directive (2013/39/UE) [25] PAHs are listed as priority substances for the aquatic environment. For the EU countries, including Poland [26], this means that it is necessary to monitor the PAH content in surface and underground waters. The original 16 PAHs considered as a priority are naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene [27].

According to the current Regulation of the Minister of the Environment on conditions of wastewater discharge to receivers, PAHs are indicated as substances that should be eliminated from the wastewater due to the carcinogenic, mutagenic and teratogenic properties. However, the permissible concentrations of PAHs in wastewater are not given (Journal of Laws 2014, item. 1800) [28]. The limit values of PAHs are listed in the regulations concerning the classification of surface and underground waters (Journal of Laws 2014 item. 1482) [29] and monitoring (Journal of Laws 2011, no. 258, item. 1550) [30]. For the assessment of groundwater, benzo(a)pyrene and the sum of PAHs are mentioned (without specifying what compounds should be analysed). The limit of the concentration of PAHs for the hydrogeochemical background is in the range of 0.000001–0.0001 mg/L, and the concentration limits for individual classes are as follows: 0.0001 mg/L – I class, 0.0002 mg/L – II class, 0.0003 mg/L – III class, 0.0004 mg/L – IV class and more than 0.0005 mg/L – V class (Journal of Laws 2008, no. 143, item. 896) [31]. According to the Regulation of the Minister of Housing, the limit value of PAH concentrations in wastewater entering the sewage system is given in terms of carbon content and is 0.2 mg C/L (Journal of Laws 2006, no. 136, item. 964) [32].

Moreover, according to the Minister of Health (Journal of Laws 2015, item. 1989) [33] in relation to water intended for human consumption, benzo(a)pyrene and 4 other hydrocarbons, benzo(b) fluoranthene, benzo(k fluoranthene, benzo(g,h,i)perylene, and indeno(1,2,3,c,d)pyrene have to be determined. In the current Regulation of the Minister of the Environment regarding the requirements to be met by water intended for human consumption (water quality categories A1, A2, A3), PAHs and their concentration limits are also indicated, but there is no information which hydrocarbons need to be analysed. An acceptable level of PAHs for categories A1, A2 is 0, 2 µg/L and for category A3 –1, 0 µg/L (Journal of Laws 2002, no. 204, item. 1728) [34].

Taking into account the toxic effect of PAHs on organisms, there is a justified need for highly effective removal of these compounds from wastewater before putting them into the environment. Therefore, the development of concepts and technological solutions to ensure the effective removal of PAHs is a topical issue and it was the subject of the present work.

PAHs have to be eliminated from aqueous solutions during treatment processes. In order to remove PAHs from leachate it is possible to use practically the same processes as for wastewater treatment or different combinations of these methods [35]. The major biological treatment processes comprise both aerobic and anaerobic, while physicochemical treatment processes include oxidation, coagulation-flocculation, chemical precipitation, adsorption on activated carbon, and membrane processes [36]. Currently, the most effective methods [37] of PAH removal include membrane techniques [38,39]. Due to the fact that the possibility of applying individual processes is limited by the size of the molecule retained on the membrane [40], the most important techniques applied in the removal of PAHs are nanofiltration (NF) [41] and reverse osmosis (RO) [42].

3. Materials and methods

3.1. Characteristic of leachate

The leachate from a municipal, non-hazardous and neutral waste landfill (Journal of Laws 2013, item. 523) [43] located close to an urban area in Southern Poland was used in this study. According to the Polish legislation (Journal of Laws 2011, no. 115, item. 1229) [44], leachate from landfill is considered an industrial effluent and must be purified before being discharged to the receivers (Journal of Laws 2014, item. 1800) [28]. An analysis of leachate discharged to a natural reservoir (Journal of Laws 2014 item.1800) [28] or sewers (Journal of Laws 2006 no. 136, item. 964) [32] shall be carried out in accordance with any of the methods contained in the publications as specified in the regulation on the landfills (Journal of Laws 2013, item. 523) [43]. Currently, the landfill is classified as an old one due it having been used for the deposit of waste since 1987. The landfill area is 128.4 ha plus a protection zone of 342 ha. A network of drains at the bottom of the landfill collects the leachate that flows through the decomposing waste (Journal of Laws 2001, no. 62, item. 628) [45]. The landfill leachates are accumulated in a special retention tank located at the plant with a capacity of 3,300 m^3. According to the technical and economic assumptions, the life of the landfill was determined at 34 years, with an inflow stream of 285,000 tonnes in 1987 increasing to 385,000 tonnes in 2020. By maintaining the current flow of waste and implementing a Waste Management Plan, the life of the landfill can be extended to approx. 50 years.

Leachate samples were taken from the retention tank and stored in 10 l containers at a temperature of 10°C. The concentration of the 16 polycyclic aromatic hydrocarbons listed by the U.S. Environmental Protection Agency, pH, temperature, ammonium nitrogen, nitrate nitrogen, chemical oxygen demand (COD), total organic carbon (TOC), total carbon (TC), suspended solids (SS) and turbidity were determined. Measurements of the indicators were performed in four replicates for raw and treated leachate. The leachate was analysed in accordance with the generally accepted methodologies [46] presented in Table 1.

The pH of the leachate collected from the plant was 8.2. The temperature of the leachate measured in the retention tank was 19°C. The concentration of ammonium nitrogen in raw leachate reached 347.2 mg $N–NH_4^+$/L, nitrate nitrogen –4.5 mg NO_3^-/L, COD –5,078.9 mg O_2/L, TOC –517.6 mg C/L , TC –364.9 mg C/L. The content of suspended solids was 65.1 mg /L and the turbidity value was 24.1 NTU.

A qualitative and quantitative analysis of PAHs was carried out on a THERMO Scientific HPLC device. The system includes a pump P4000, autosampler AS3000 and FLD detector. PAHs were separated on a Restek Pinnacle ® II PAH 4 µ m, 150 × 10 mm column using the gradient elution technique [47]. The following PAHs were analysed: 2-ring (naphthalene), 3-ring (acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene), 4-ring (fluoranthene, pyrene, benzo(a)anthracene, chrysene), 5-ring (benzo(a) pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene) and 6-ring hydrocarbons (indeno(1,2,3,c,d)pyrene, benzo(g,h,i)perylene). The concentration and percentage share of PAHs in raw landfill leachate is presented in Table 2.

3.2. Experimental Procedure

In the first stage of the research, leachate was filtrated on a sand bed (pre-filtration). After the pre-filtration, the leach-

Table 1
Indicators and methodologies used in study

Indicator	Methodology and equipment
16 PAHs (listed by US EPA), µg/L	High performance liquid chromatography HPLC with fluorescence detection (FL 3000)
pH	Cole Palmer pH-meter
Temperature, °C	*in situ* – lab thermometer
Ammonium nitrogen, mg N–NH_4^+/L	Cuvette tests of HACH LANGE on a spectrophotometer DR 2800th
Nitrate nitrogen, mg NO_3^-/L	
Chemical oxygen demand (COD), mg O_2/L	Test method with spectrophotometer HACH DR 4000th
Total organic carbon (TOC), mg C/L	High temperature catalytic oxidation – GC Multi N/C 2100 apparatus
Total carbon (TC), mg C/L	
Suspended solids (SS), mg/L	Gravimetric method
Turbidity, NTU	Nephelometric method – HACH 2100N IS Turbidimeter

Table 2
The concentration and percentage share of the selected PAHs in landfill leachate

PAHs		Average concentration (ng/L)	Standard deviation (σ)	Percentage share (%)
Naphthalene	Naph	258.99	24.1	2.6
Acenaphthylene	Acyl	34.21	3.3	0.3
Acenaphthene	Ac	45.99	3.0	0.5
Fuorene	Fl	1,231.09	131.6	12.5
Phenanthrene	Fen	10.33	4.3	0.1
Anthracene	Ant	90.00	4.0	0.9
Fluoranthene	Flu	3.00	0.9	0.0
Pyrene	Pir	13.07	4.0	0.1
Benzo(a)anthracene	BaA	3,568.32	753.1	36.2
Chryzene	Chr	789.05	76.1	8.0
Benzo(a)pyrene	BaP	785.09	110.1	8.0
Benzo(b)fluoranthene	BbF	980.07	39.2	9.9
Benzo(k)fluoranthene	BkF	1,234.98	120.4	12.5
Dibenzo(a,h)anthracene	DahA	342.09	22.2	3.5
Indeno(1,2,3,c,d)pyrene	IP	234.09	19,0	2.4
Benzo(g,h,i)perylene	BghiP	237.89	99.1	2.4
Total of all PAHs		9,858.29	88.4	–

ate was directed to a membrane module for the main filtration process – a high-pressure cross flow GE-Water SEPA CF Membrane Cell. The setting operated in a cross-flow closed system in which the retentive was recycled to the feed tank [18]. The flow diagram with the equipment used in the applied pressure filtration process is presented in Fig. 2.

One flat GE-Water DK nanofiltration membrane manufactured from thin film polyamide (TF) was used during the investigation. The pH range of the membrane operation is 2–10 with a maximum temperature of 50°C and a salt rejection rate for $MgSO_4$ of 98.0% [48]. The filtration area was 144 cm^2, the transmembrane pressure of the process remained at a value of 1.5 MPa, and the linear flow velocity over the membrane surface was 2 $m \cdot s^{-1}$.

3.3. *Effectivness of the membrane process*

The membrane process capacity was calculated through the determination of the volumetric permeate flux for deionised water – J_w and simulated solutions J_v [49]. The efficiency of the filtration was determined using the following formula (1):

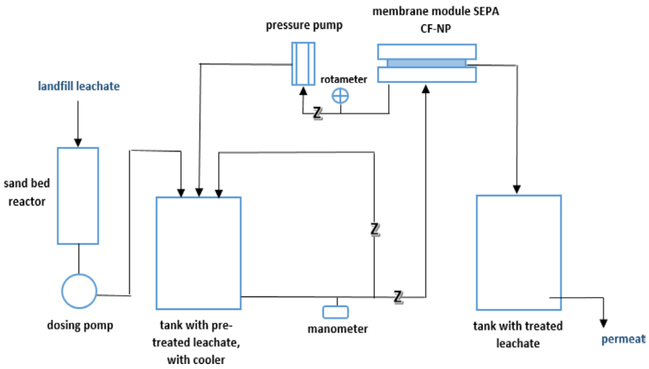

Fig. 2. Scheme of equipment for applied pressure filtration process (GE-Water) [17].

$$R = \frac{1 - C_p}{C_v} \cdot 100 \quad (1)$$

where R is the retention ratio, %; C_n is the concentration in the feed, mg/L; C_p is the concentration in the permeate, mg/L.

The test results of the selected indicators and the PAH concentrations in the leachate were analysed statistically using Pearson correlation coefficients.

4. Results and discussions

4.1. Changes in the permeate flux during the nanofiltration process

The transport properties of the DK membrane were determined on the basis of the dependence of the volumetric deionised water flux on the transmembrane pressure. The changes in the volumetric permeate flux with time in the nanofiltration process of municipal leachate is presented in Fig. 3. The filtration was conducted for a total time of 30 h.

For the initial 1.5 h (approximately), gradual reductions in the speed of permeate flux in an integrated system were observed. The permeate flux stabilised at a rate of $13.96 \cdot 10^{-6}$ $m^3/m^2 \cdot s$ after 140 min of nanofiltration. The reduction in permeate flux could be associated with fouling [50], which could be a consequence of the:

- characteristics of the feed water – a high concentration of organic matter and suspended solids,
- properties of the NF membrane – surface charge and roughness,
- hydrodynamic conditions – pressure, temperature, and crossflow velocity [51].
- The retentate was recirculated back to the feed reservoir.

In the Mariam and Nghiem [52] and Schoeman et al. [53] research, raw landfill leachate was tested without any pretreatment. Membrane fouling was particularly severe when no pretreatment was applied – it was not possible to use the membrane again. An improvement in properties could be observed when pre-treatment was used as an initial treatment.

4.2. PAH removal efficiency in an integrated membrane process

The initial concentration of 16 PAHs in municipal landfill leachate was equal to 9.86 µg/L (Table 3). The removal of selected PAHs during the investigation (both during pre-filtration and nanofiltration processes) was very effective.

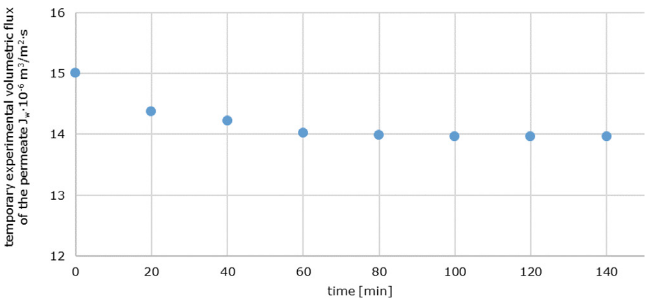

Fig. 3. Changes in permeate flux during NF.

Table 3
PAH removal efficiency in the pre-filtration and nanofiltration processes

PAHs	Proportion removed [%]	Retention coefficient, R [%]
	Pre-filtration	Nanofiltration (NF)
Naf	33.5	47.1
Acyl	38.4	61.5
Ac	27.5	57.3
Fl	41.4	30.5
Fen	11.7	41.5
Ant	47.7	69.3
Flu	–	82.5
Pir	42.2	60.4
BaA	46.5	66.9
Chr	40.7	55.1
BaP	50.0	76.6
BbF	50.0	83.7
BkF	38.0	92.8
DahA	53.1	89.4
IP	53.3	92.7
BghiP	49.9	99.2

4.2.1. Pre-filtration

After filtration on a sand-bed, the concentration of PAHs decreased to 5.43 µg/L. The highest concentration in the leachate resulting from the pre-filtration was determined for benzo(a)anthracene – 1.91 µg/L (35.2% of the total hydrocarbon content). The total share of 4-ring compounds after pre-filtration reached 44% (2.39 µg/L). The contribution of 5-ring compounds was also large and amounted to 33.3% (1.81 µg/L). The contribution of 3-ring compounds was 15.3% (0.83 µg/L), with fluorine acting as the dominant item in the content –13.3% (0.72 µg/L). The proportion of naphthalene was 3.2% (0.17 µg/L) and the share of 6-ring compounds was 4.2% (0.23 µg/L). The percentage share of PAHs in landfill leachate treated on a sand bed is presented in Fig. 4.

The average level of PAH removal in the process of filtration on a sand bed was 41.6%. The PAH removal efficiency in both processes, pre-filtration and nanofiltration, is presented in Table 3.

For the 6-ring compounds, the most effective removal of PAHs was observed after the pre-filtration, – 51.6%. The average efficiency of 5-ring compounds reached 47.8%, 4-ring – 43.1%, 3-ring – 33.3%, and naphthalene – 33.5%.

4.2.2. Nanofiltration

After nanofiltration, the concentration of PAHs decreased to 1.73 µg/L. The percentage share of PAHs in landfill leachate after nanofiltration is presented in Fig. 5. The largest share of PAHs in the treated leachate, reach-

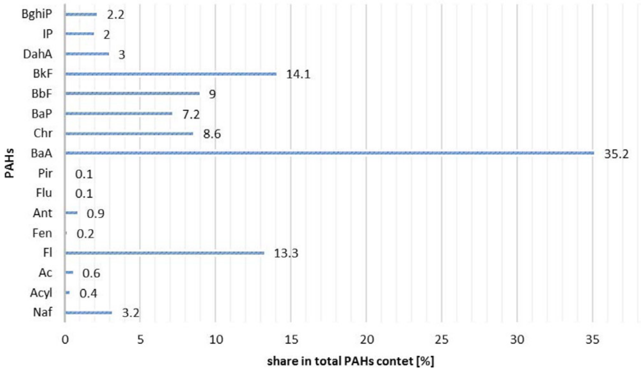

Fig. 4. The percentage share of PAHs in landfill leachate after pre-filtration.

Table 4
Correlation coefficients between the change in the content of PAHs and selected indicators in landfill leachate

PAHs	Indicator			
	COD	TOC	TC	SS
Naph	0.997	0.999	0.997	0.999
Acyl	0.998	0.998	0.996	1.000
Ac	0.998	0.983	0.978	0.995
Fl	0.959	0.988	0.992	0.972
Fen	0.974	0.937	0.927	0.962
Ant	0.990	1.000	1.000	0.996
Flu	0.877	0.808	0.792	0.853
Pir	0.993	1.000	0.999	0.998
BaA	0.991	1.000	1.000	0.996
Chr	0.992	1.000	0.999	0.997
BaP	0.991	1.000	1.000	0.996
BbF	0.994	1.000	0.999	0.998
BkF	0.998	0.983	0.977	0.995
DahA	0.992	1.000	1.000	0.997
IP	0.993	1.000	0.999	0,997
BghiP	0.998	0.998	0.996	1.000

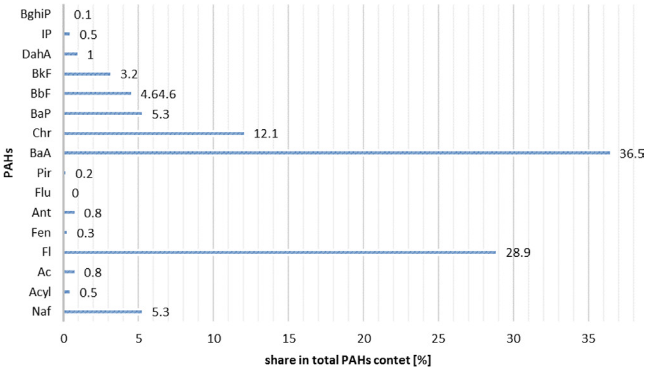

Fig. 5. The percentage share of PAHs in landfill leachate after nanofiltration.

ing almost 50%, was observed for 4-ring compounds (0.85 µg/L), with benzo(a)anthracene taking the dominant role – 36.5% (0.63 µg/L). The share of naphthalene after nanofiltration was 5.3%, and its concentration was at a level of 0.09 µg/L. The proportion of 3-ring PAHs was 31.3% (0.54 µg/L), with the highest content provided by fluorene –28.9% (0.5 µg/L). The percentage share of 5-ring hydrocarbons was 14.1% (0.24 µg/L), and 6-ring – 0.5% (0.09 µg/L).

The value of the retention coefficient of 16 PAHs in the nanofiltration process reached 69.2% (Table 3). The highest retention coefficient – 99.2% was observed for benzo(g,h,i) perylene. For indeno(1,2,3,c,d)pyrene, the retention coefficient was also high and reached 92.7% and for benzo(k) fluoranthene 92.8%. The retention coefficient of the 5-ring compounds was 85.6%. The lowest retention coefficient (30.5%) was observed for fluorene. The concentration of the 3-ring compounds was reduced by 51.2% and the 4-ring – 66.2%. The concentration of naphthalene decreased by 47.1%.

During the nanofiltration process, high retention coefficients were estimated for the hydrocarbons studied. A high degree of retention of low molecular weight PAHs may be related to the physical process of degassing which is taking place during filtration of the gas phase through a microporous membrane structure. The volatile organic contaminants (low molecular weight PAHs) dissolved in aqueous solutions flow through the membrane in a countercurrent to the gaseous phase, causing them to be released from the solution [54]. Taking into account the retention coefficient obtained for the individual hydrocarbons, it can be concluded that the degree of PAH removal depends on the molecular weight – the retention coefficients of macromolecules (5 and 6-rings) were higher than the low-molecules (2,3 and 4-rings). It was also shown that the degree of PAH removal increased with the value of the *octanol/water partition coefficient* (K_{ow}). The highest retention coefficients were estimated for hydrocarbons with a value of $K_{ow} > 5$. The results of other authors confirm this dependence [55,56]. The values of retention coefficients also depend on the cut-off used for the DK membrane which is adapted to retain compounds with a molecular weight of 150–300 g/mol, while the molecular weight of the PAHs analysed is in the range from 128.2 g/mol (naphthalene) to 278.4 g/mol (dibenz(a,h)anthracene). The hydrocarbons with a molecular weight of less than 150 Da were probably removed by adsorption onto the surface and in the nanofiltration membrane pores. This is a phenomenon known as fouling [57] – deposition on the membrane surface and/or pores of the substances contained in the filtered sample [58–60]. Due to their hydrophobic nature, PAHs are adsorbed on suspended solids, which have a significant impact on the fouling of the membrane analysed. This is supported by the decrease in the volume of the permeate flux over time.

4.2.3. An integrated process: pre-filtration – nanofiltration

The average degree of 16 PAH removal from leachate in the integrated membrane process, including nanofiltration and filtration on a sand-bed, totalled 80.2%. The removal efficiency for individual hydrocarbons was in the range of 48.8% for fenantrene to 99.6% for benzo(ghi)perylene. PAH removal efficiency in an integrated process is presented in Fig. 6.

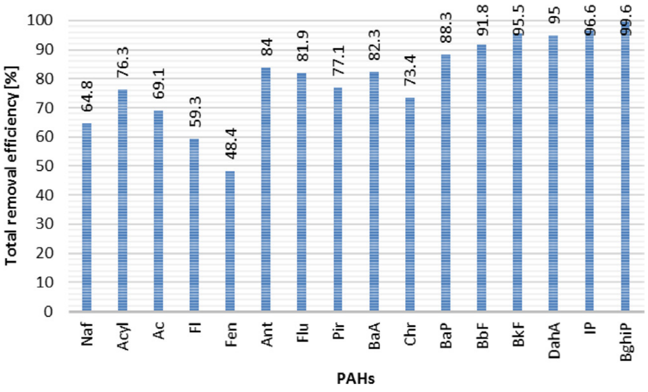

Fig. 6. Total PAH removal efficiency in an integrated treatment process: pre-filtration – nanofiltration.

The values of the correlation coefficients obtained in the research are presented in Table 4. High values of correlation coefficients during the treatment of leachate in the integrated system indicate a significant dependence of the concentration of hydrocarbons on the value of selected indicators: COD, TOC, TC and SS. For individual hydrocarbons, the correlation coefficients were above 0.8. Complete dependency (correlation coefficient = 1) was also observed for the hydrocarbons studied, mainly for TOC. The PAH concentration was reduced in parallel with a decrease in the indicators analysed.

4.3. Management aspect of leachate treatment

The study showed that there is a very efficient removal of toxic organic pollutants from landfill leachate in integrated membrane processes. The previous work of the authors confirms this conclusion [17,18,61]. Due to their toxicological properties and the unsatisfactory results obtained when removing polycyclic aromatic hydrocarbons in conventional processes, there is a justifiable need to seek highly effective methods for removing PAHs from leachate. In recent years there has been an increase in the introduction of the latest technology, including the modernisation of existing processes. This has resulted in the development of highly effective integrated methods of leachate management consisting of a combination of physical and chemical or biological methods with membrane processes [62]. It is assumed that membrane modules will be introduced to the technological line of existing and planned leachate treatment plants. The application areas of new membranes and the preparation technologies for them are developing very dynamically and this could have a positive effect on growth in the use of membrane processes. In addition to meeting the increasingly stringent environmental legislation, the membrane technologies analysed contribute to a decreased pollution load in wastewater which could allow the recovered water to be recycled [63]. By the introduction highly effective methods of leachate treatment, a significant improvement in environmental protection is possible through the use of the latest technology that meets the standards and requirements of the EU [64].

An analysis of the costs of membrane installations, especially in the initial phase of investment, operation and maintenance, has indicated that the costs are higher than those associated with commonly used biological methods. However, the current costs associated with the development of high-efficiency technologies are increasingly being incurred by the Management Entities [65]. This partially results from the possibility of obtaining support for projects aimed at environmental protection [66,67] under "Horizon 2020" and the instruments for its implementation (the European Institute of Innovation and Technology, the European Structural Funds and the investment action plan for eco-innovation, green plan measures for SMEs and the European programme for consumers) [68].

5. Conclusions

The integrated membrane process (pre-filtration-nanofiltration) was used for the removal of selected polycyclic aromatic hydrocarbons from the leachate arising from municipal landfill. Pre-filtration on a sand bed was used in order to protect the surface of the membrane and keep its hydraulic properties.

The initial concentration of 16 PAHs listed by EPA in raw stabilised leachate was 9.86 μg/dm^3. During the laboratory-scale experiments, a progressive decrease in the PAH content was observed. The concentration of PAHs decreased to:

- 5.43 μg/L after pre-filtration on a sand bed (average removal of the 16 PAHs investigated: 41.6%),
- 1.73 μg/L after nanofiltration (retention coefficient of 16 PAHs: 69.2%).

The total removal of 16 PAHs from leachate after the integrated treatment (pre-filtration on a sand bed and nanofiltration) was 80.2%. The total removal for individual hydrocarbons varied in the range from 48.8% for fenantrene to 99.6% for benzo(ghi)perylene.

The results of the study confirmed the high efficiency of membrane processes in the removal of organic compounds from the leachate arising from municipal landfill using membrane processes. Nanofiltration should be applied to the technological lines of leachate treatment plants.

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