Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22590

134 (2018) 41–51
December

PAH removal effectiveness comparison from hydraulic fracturing model wastewater in SBR reactors with granular and flocked activated sludge

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Received 29 December 2017; Accepted 5 June 2018

ABSTRACT

The paper discusses changes in removal efficiency of 16 polycyclic aromatic hydrocarbons (PAHs) in individual unit phases of the sequential biological reactor (SBR) reactor. The experiments were carried out in model SBR reactors operating with aerobic granulated and flocculated activated sludge. The model wastewater was prepared on the basis of PN-72/C-04550.09 and adjusted to the parameters of actual effluents generated during hydraulic fracturing. The scope of analytical determinations included chemical oxygen demand, NH_4^+, NO_3^-, total N, PO_4^{3-}, total P, acenaphthalene, acenaphthene, anthracene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene, and pyrene. The work focused on the removal rates of the PAHs tested in the individual SBR processing phases. 16 PAH sum removal rate during mixing phase occurred in similar way in both reactors up to the PAHs dose of 1,800 µg/L. Above this level, PAHs were removed at higher rates in granular sludge reactor. Similar dependence was also observed in the aeration phase; however, more pronounced changes in the rates of PAHs removal in individual reactors were present above 2,200 µg/L. Laboratory work has shown that aerobic granular activated sludge allows the removal of PAHs with greater efficiency as compared with the flocculated sludge. Also granular activated sludge shows higher resistance to increase in the amount of supplied toxic agent as compared with flocculated sludge.

Keywords: Granular aerobic activated sludge; Polycyclic aromatic hydrocarbons; Hydraulical fracturing wastewater

1. Introduction

Since the 1980s, organic pollutants entering the sewage treatment plants have become increasingly problematic [1]. This fact is particularly important in the case of municipal and industrial wastewater mixture, which contains a number of organic compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-para-dioxins, polychlorinated biphenyls, or halogenated pesticides [2]. PAHs enter a sewage treatment plant mainly as a result of rainwater runoff from transportation routes or with industrial wastewater flowing through the sewage system [3]. The industry supplying the largest amount of PAHs in wastewater includes processing of fossil fuels, along with coking and petrochemical wastewater [4,5]. A relatively new industry producing sewage, in which PAHs are present, is shale gas extraction by means of hydraulic fracturing.

The wastewater generated during hydraulic fracturing can be divided into two types. They are produced in different stages of gas extraction. In the beginning, they are the so-called flowback waters, chemical and physical characteristics of which are similar to those used for fracturing. In addition, these wastewaters may be enriched with chemical compounds found in the rock formation, in which the mining took place [6]. The second type is the so-called produced water. These waters are shale gas carriers. Unlike the return waters, they are characterized by significant salinity and are produced

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Presented at the 13th Conference on Microcontaminants in Human Environment, 4–6 December 2017, Czestochowa, Poland.

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for the rest of the mining well exploitation period [7,8]. The amount of PAHs in the effluent from hydraulic fracturing depends primarily on the composition of the fracturing fluid, namely the type and nature of chemical additives used, chemical composition of the rock, in which the shale gas is trapped, and chemical composition of the extracted gas.

The possibility for biological treatment of saline wastewater has not been considered due to activated sludge sensitivity to this pollution. However, in the 90's of last century, the research on biological wastewater treatment focused around the aerobic granular activated sludge. Properties of the aerobic granular sludge contribute to the fact that this may be an emerging technology in biological wastewater treatment systems. Numerous laboratory studies have shown that aerobic granules exhibit significantly higher resistance to toxicity in the effluent with respect to flocculated activated sludge [9,10]. In addition to the application possibilities for wastewater with a significant load of organic pollutants [11–13], the literature extensively describes the use of granulated sludge for the treatment of wastewater from various industries. So far, the effects of using the aerobic granules to treat wastewater containing organic compounds in the form of phenol [14], residues of pharmaceuticals [15], saline media [16], and wastewater containing heavy metals or pigments, have been described. However, the issue of removing the 16 PAH sum with aerobic granular activated sludge was not investigated.

The purpose of this work was to determine the removal rate of PAHs expressed as a total concentration in the presence of dissolved salts at a concentration of 4,000 mg/L and increasing concentration of PAHs in wastewater entering the sequential biological reactor (SBR) reactor in unit phases and operating with aerobic granular and flocculated activated sludge. The purpose of conducting experiment in parallel in reactors with flocked and granular sludge was to compare two forms of activated sludge in terms of efficiency and rate of PAHs removal.

2. Methods

The research was conducted in laboratory conditions in the model SBR reactor system. The reactors were made of reinforced polyethylene, and their parameters are given in Table 1. The studies were carried out for 132 d (264 cycles of reactor operation) in parallel in two reactors working with various types of activated sludge. Both reactors maintained the same aerobic conditions and 12-h operation cycle. The purpose of maintaining identical technological parameters in both reactors was to enable comparison of obtained results in both reactors. Technological parameters of the aerobic granular sludge and flocculated activated sludge, performance of the single aerator and duration of the unit phases of the reactor are presented in Table 1, while Fig. 1 shows mineral–organic structure of both types of activated sludge. Each of the reactors was filled manually. Duration of filling, mixing, aeration, sedimentation, and decantation of the SBR reactor, as well as air pump and agitator operation (Table 1) were coordinated by the programmable controller SIMENS, model LOGO!, type 230RC.

The model wastewater was prepared on the basis of PN-72/C-04550.09 and adjusted to the parameters of actual effluents generated during hydraulic fracturing, as reported by Granops et al. [17] and Jefimova et al. [18]. To basic composition of model sewage, casein peptone (0.152 ÷ 0.608 g/L), enriched dry broth (0.226 ÷ 0.904 g/L), ammonium chloride (0.020 ÷ 0.080 g/L), sodium chloride (0.007 ÷ 0.028 g/L), calcium chloride (0.008 ÷ 0.030 g/L), magnesium sulfate (0.002 ÷ 0.008 g/L), monobasic potassium (0.016 ÷ 0.064 g/L), and dibasic potassium phosphate (0.040 ÷ 0.160 g/L), were added. Model sewage was made using tap water, which was left to stand for 24 h in a laboratory room. PAHs were added to the model wastewater in the form of a solution based on distilled water of Grade I (in accordance with EN 3696:1999) and a PAH stock solution made from unleaded gasoline 95, burned truck oil, and diesel oil. Petroleum products were mixed successively in 60%, 30%, and 10% of the total mixture amount. Wastewater was added with PAHs to verify to what concentrations of these compounds, microorganisms will be able to adapt. The model wastewater characteristics are shown in Table 2.

The scope of analytical determinations included the following parameters: chemical oxygen demand (COD), NH_4^+, NO_3^-, total N, PO_4^{3-}, total P, acenaphthalene, acenaphthalene, anthracene, benzo[a]anthracene, benzo[b]

Table 1
Technological parameters of activated sludge in model SBR reactors

Technological parameter	Value in the reactor with aerated granular sludge	Value in the reactor with flocculated activated sludge
Total capacity of reactors	16 L	16 L
Actual capacity of reactors	15 L	15 L
Quantity of sewage supplied in a single cycle	5 L	5 L
Aerator performance	550 L/h	550 L/h
Volume exchange factor	0.33	0.33
Dry mass of activated sludge	4.0 g/m^3	4.0 g/m^3
Duration of filling phase	30 min	30 min
Duration of mixing phase	90 min	90 min
Duration of aeration phase	540 min	540 min
Duration of sedimentation phase	30 min	30 min
Duration of decantation phase	30 min	30 min

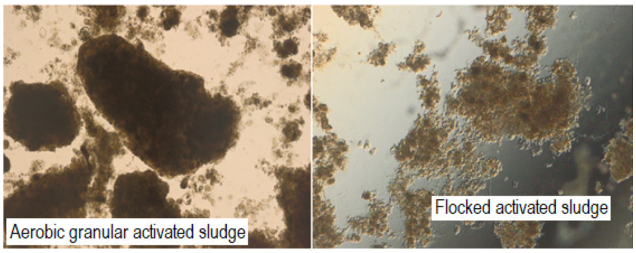

Fig. 1. Structure of studied types of activated sludge.

Table 2
Quality characteristics of model wastewater

Parameter	Range
COD (mg/L)	350.00 ÷ 872.00 ± 176.74
NH_4^+ (mg/L)	8.23 ÷ 8.98 ± 0.10
NO_3^- (mg/L)	38.05 ÷ 38.78 ± 0.09
Total N (mg/L)	46.54 ÷ 48.83 ± 0.17
PO_4^{3-} (mg/L)	35.47 ÷ 39.65 ± 0.31
Total P (mg/L)	11.34 ÷ 12.97 ± 0.12
Cl^- (mg/L)	4,000.00
Σ16 PAHs (μg/L)	25.00 ÷ 3,600.00

fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indene[1,2,3-cd]pyrene, naphthalene, phenanthrene and pyrene. Concentrations of 16 listed PAHs were analyzed in this work as their sum and determined by means of chromatography using a gas chromatography coupled with mass spectrometer coupled to a DB-5MS column. The stationary phase of the column was polydimethylsiloxane with 5% phenyl groups. Chromatograph parameters and method validation are given in Annex 1. COD value and concentrations of NH_4^+, NO_3^-, total N, PO_4^{3-}, and total P were determined in raw and treated wastewater accordingly to methods provided by Merck company (Merck Sp. z o.o., Warsaw, Poland). Sum of 16 PAH was analyzed in raw wastewater and wastewater after filling, mixing, aeration, and sedimentation phase.

Statistical calculations and analyzes were performed on the basis of licensed STATISTICA software ver. 13.1 running on the Windows 10 platform. The scope of statistical analyzes consisted of Pearson's correlation coefficients and regression equations developed using the multiple step regression method. The variables used for the analysis were characterized by normal distribution according to the Shapiro–Wilk test; therefore, correlations in the study results were expressed as Pearson's linear ones. The kinetics of removal equations for 16 PAHs sum was developed for the mixing phase and the aeration phase.

The limit of steps used to compute the equations was assumed to be 1,000. This amount guaranteed a formula with satisfactory coefficients of determination. The tolerance value was automatically selected by the program and was equal to 0.0001. The obtained numerical values for individual elements of the equation were not corrected by other statistical methods due to the use of increased precision calculations in the original algorithm.

3. Results and discussion

The COD removal effect (Figs. 2 and 3) during wastewater treatment was high in both reactors. In the case of a reactor working with granular sludge, there was no apparent relationship between the dose and the removal effect of this parameter. By day 67 of the experiment (up to a dose of 1,400 μg/L), the effect of COD removal remained above 90% and was highly stable irrespective of the PAHs dose. After 67 d, the effect slightly decreased. Over 1,800 μg/L PAHs dosed into the reactor (starting from 75 d), the effect of the PAHs dose on the removal effect of the COD was observed, which was associated with the time of microbial adaptation to higher hydrocarbon concentrations supplied to the reactor. The adaptation time was increased with increasing PAHs dose, which resulted in less effective removal of COD in this period. In the case of a flocculated sludge reactor, a significant deterioration of the COD removal effect was observed at almost every dose increase. By the 63 d of the experiment (up to 1,200 μg/L), a change in the COD removal effect was observed in the range of 65% to 90%. However, from 64 to 115 d of study (PAHs dose ranging from 1,200 to 3,200 μg/L), the effect of COD removal ranged from 50% to about 80%.

The efficiency of removal of individual nitrogen forms (Figs. 2 and 3) was similar in both reactors. In the case of NO_3^-, the most obvious differences in the removal efficiency in both reactors were observed. In the case of a reactor operating with granulated sludge, the NO_3^- removal effect changed from about 50% to almost 100% and did not show any dependence on an increase in PAHs dose. In the case of flocculated sludge, deterioration of the NO_3^- removal effect was observed at each PAH dose increase, while the removal effect itself ranged from about 0% to almost 100%, with the mean removal effect observed in the study period being around 50%. The changes recorded in total N removal in both reactors were similar and varied between about 20% to over 90%. In both reactors, a decrease in total N removal efficiency was observed, which was dependent on the amount of PAHs supplied to the reactor. The difference in the work of both reactors was the period of microorganisms adaptation to ever larger PAHs doses. In the case of granular sludge, the adaptation period was necessary after 71 d of testing (above 1,600 μg/L), but in the case of flocculated sludge—at each increase of the hydrocarbons dose. Similar correlations were observed with NH_4^+, except that after 85 d of study (above 2,000 μg/L), a significant deterioration of the compound removal effect was observed in the granular sludge reactor, which lasted up to 93 d of experiment (up to 2,400 μg/L).

The effects of total P and PO_4^{3-} removal (Figs. 2 and 3) in both reactors were similar. In the case of total P, the maximum removal efficiency was close to 90% in both reactors. For a flocculated sludge reactor, a high removal effect was recorded within the first 35 d (up to the dose of 240 μg/L), which averaged about 70%. After 35 d (above 320 μg/L), a significant deterioration in total P removal effect was observed, which was approximately 40%. In the case of a granular sludge reactor, in the first 65 d (to a dose of 1,200 μg/L), total P was removed with an efficiency between 50% and 90%. After 65 d, there was a deterioration of this compound removal effect, and a clear relationship was observed between the effectiveness of total P removal and the PAHs dose. On the other hand, for PO_4^{3-}, the average removal effect varied between 40% and 60% and did not show a clear dependence on the amount of hydrocarbons supplied to the reactors.

The first of the processing phases was the filling of model SBR reactors. No sewage treatment processes involving microorganisms occurred during this phase, and the observed changes in ΣPAHs concentrations were caused by dilution of wastewater supplied to the reactor as a result of their mixing with wastewater remaining in the reactor after the previous cycle. This phenomenon was caused by relatively slow reactor filling, which did not cause activated sludge to agitate after sedimentation phase in both reactors.

Up to a dose of 360 µg/L (49 d of experiment), the dilution effect of ΣPAHs in the granulated sludge reactor was stable and remained at the level of 40%–60%. There was a gradual decrease in the dilution level of the raw sewage after the filling phase, and at a dose of 2,200 µg/L (87 d of testing) in the wastewater after filling the reactor, a higher concentration of ΣPAHs was observed than that in the raw sewage. Then the dilution rate increased to about 40% and gradually decreased to 103 d of testing (2,800 µg/L). The dilution effect was then markedly differentiated by the end of the study period. In contrast, reactor working with flocculated sludge, in the first 49 d (PAHs dose from 25 to 360 µg/L), was characterized by a lack of dilution stability that ranged from 0% to about 65%. In the dose range of 360 to 1,800 µg/L (from day 49 to 77), a stable downward dilution effect reaching 0% on day 77, was observed. By the end of the study cycle, the dilution rate of the wastewater was observed, which showed a smaller quantitative change as compared with the granular sludge.

During mixing phase studied PAHs were removed from treated wastewater in anaerobic conditions. Efficiency of ΣPAHs removal during the mixing phase changed within the range of 0% to 60% depending on the PAHs dose in reactor with granular sludge. The greatest effect was recorded after 25 d of study (PAHs dose of 150 µg/L), while the lowest effect of removal of this group of compounds was observed

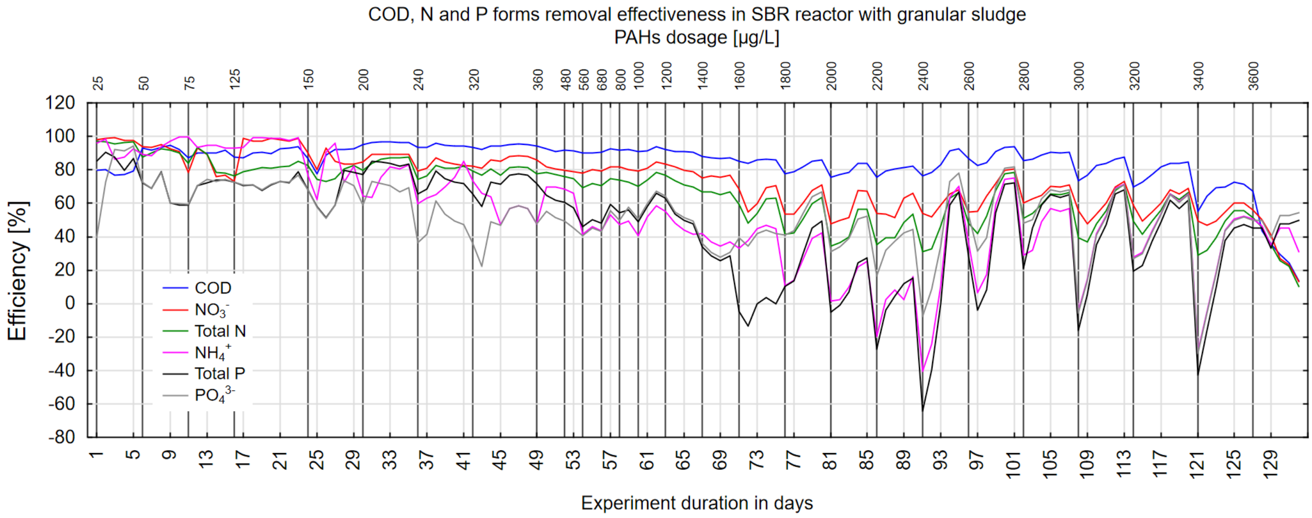

Fig. 2. Efficiency of COD removal, form of N and P in granular sludge reactor.

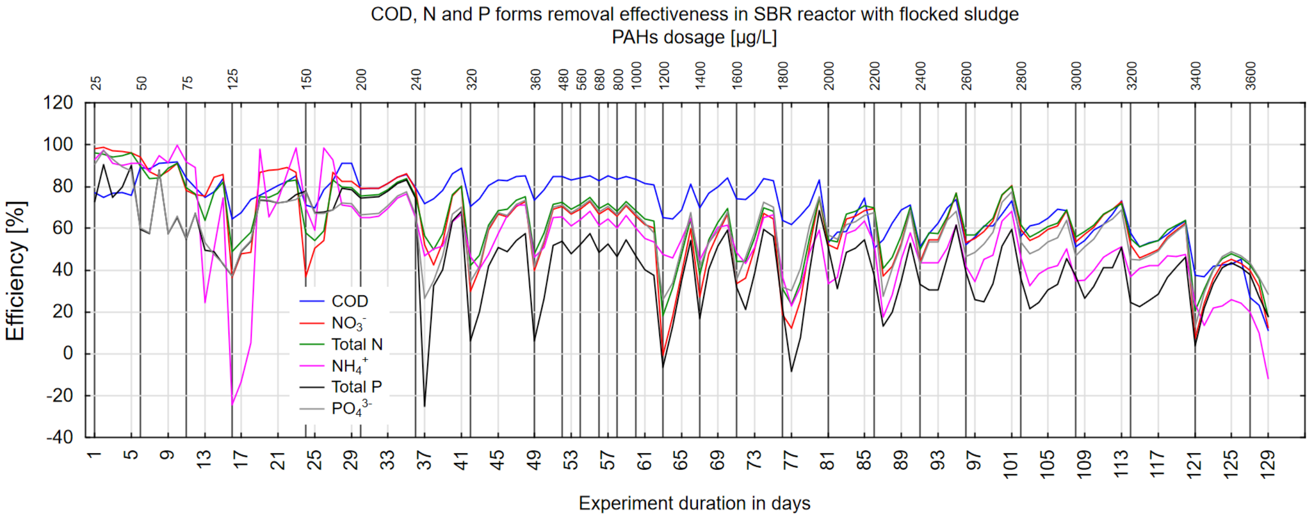

Fig. 3. Efficiency of COD removal, form of N and P in flocked sludge reactor.

in the final stage of the experiment. In the case of flocculated sludge, the efficiency of the process varied between 0% and 30% during the entire test cycle in the mixing phase. The highest mean effect was found between day 47 and day 71 (PAHs dose between 320 and 1,600 μg/L). During this period, the removal effect was very stable and varied between 15% and 25%. The efficiency of removing the PAHs after the aeration phase varied from about 10% to over 60%. The granular sludge reactor was more efficient than the flocculated sludge one. However, at the highest PAHs levels, the removal effect of the tested hydrocarbons was similar in both reactors and varied between about 10% and 40%.

The total PAHs in the whole wastewater treatment process, in the case of a granular sludge reactor, were removed with efficiencies ranging from approximately 80% to almost 100% for the first 57 d of the experiment (up to 680 μg/L). There was a gradual decrease in the tested hydrocarbons removal efficiency. At the highest doses of PAHs, their washout was observed. In the case of a flocculated sludge reactor, the removal efficiency for ΣPAHs in the first 57 d of the test varied from about 35% to 80%. After 57 d of study (over 800 μg/L), a gradual decrease in the effect of removal of individual groups of compounds was recorded. In the final phase of the study, ΣPAHs were removed with efficiencies ranging from 0% to about 60%, and the elution of these compounds from activated sludge was observed (Figs. 4 and 5).

The ΣPAHs removal rate (Fig. 6) in both reactors was similar, and the maximum removal rate was about 105.0 μg/g_{sdm}·h. Both granular sludge and flocculated sludge revealed similar rates recorded at day 69 (PAHs dose 1,400 μg/L). After this period, the rate of removal of individual groups of compounds was more varied and mainly dependent on the PAHs dose.

The rate of ΣPAHs removal (Fig. 7) during aeration phase by 69 d (up to 1,400 μg/L) was subject to similar oscillations in both reactors. Within that period, ΣPAHs were removed not faster than 7.94 μg/g_{sdm}·h. After 69 d, a clear and gradual

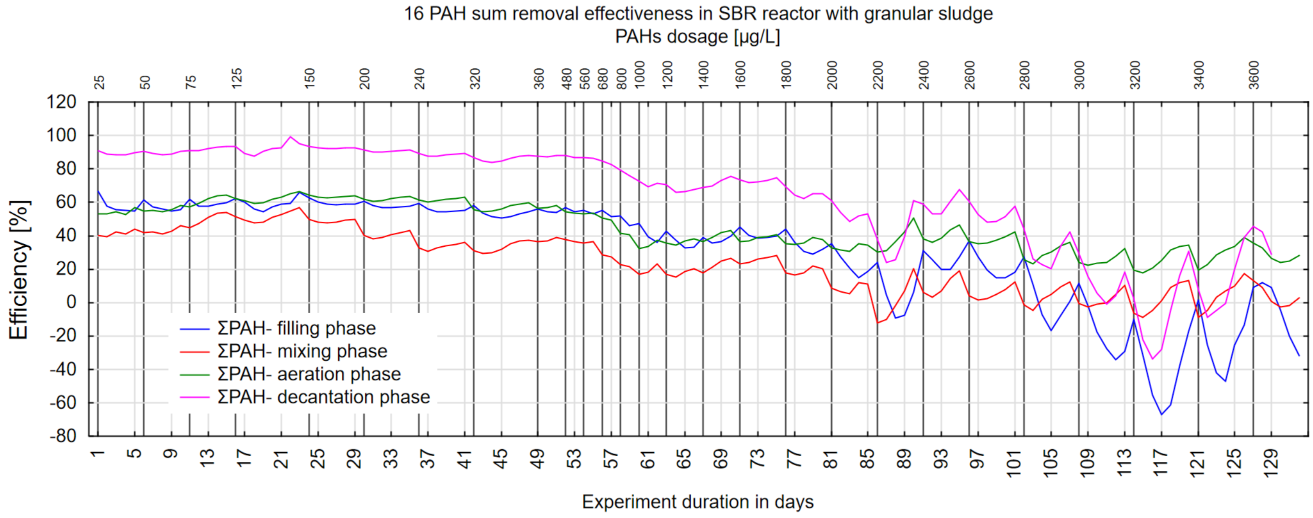

Fig. 4. Efficiency of ΣPAHs removal in individual processing phases in granular sludge reactor.

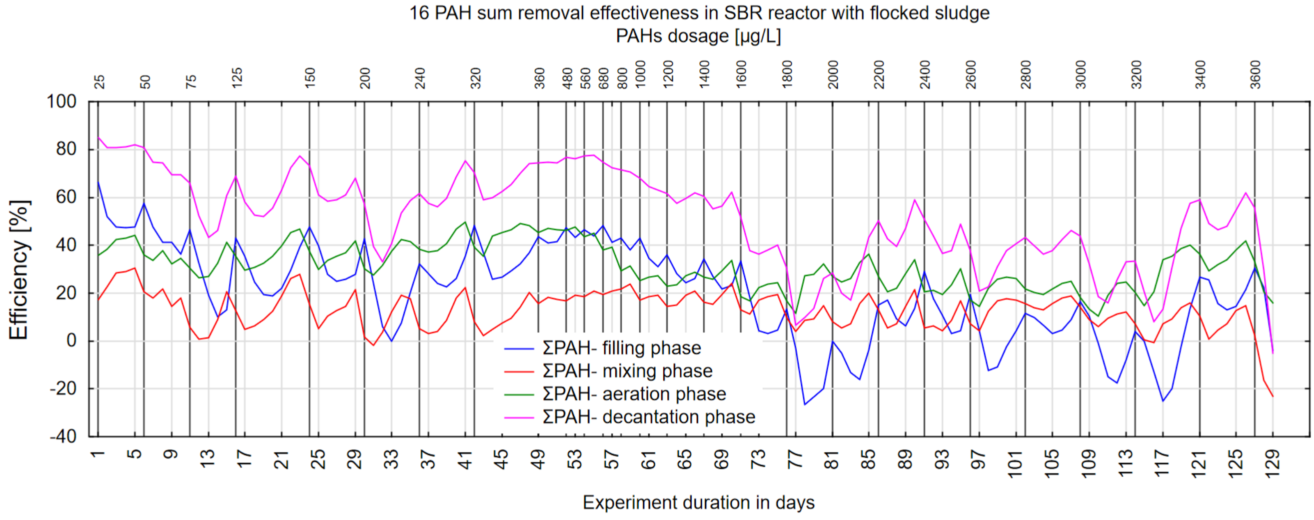

Fig. 5. Efficiency of ΣPAHs removal in individual processing phases in flocked sludge reactor.

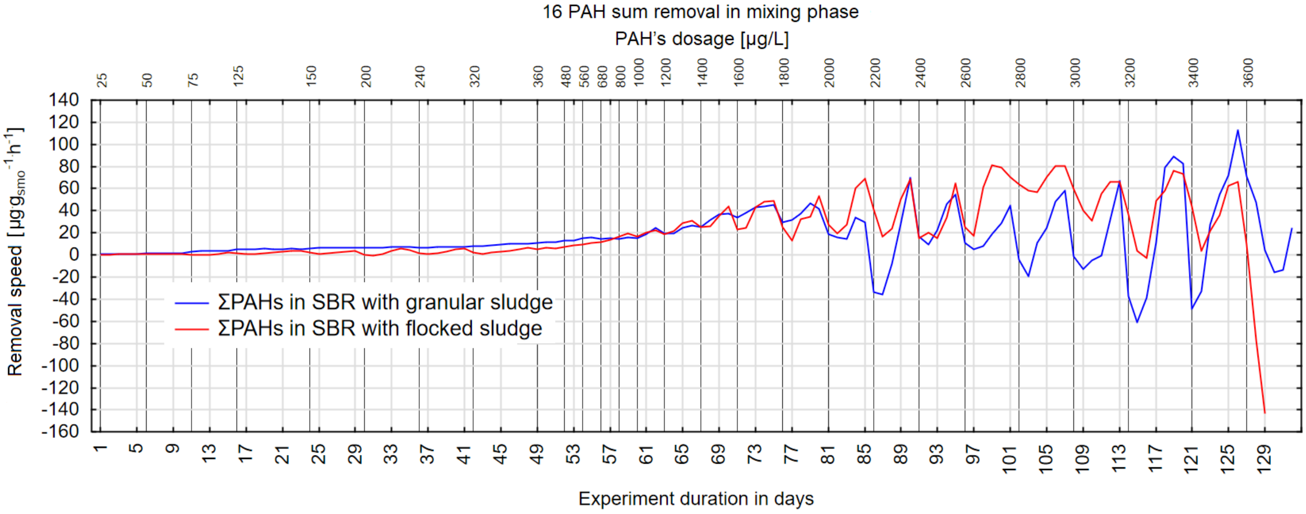

Fig. 6. Rate of ΣPAHs removal during mixing phase in reactor with granular and flocked sludge.

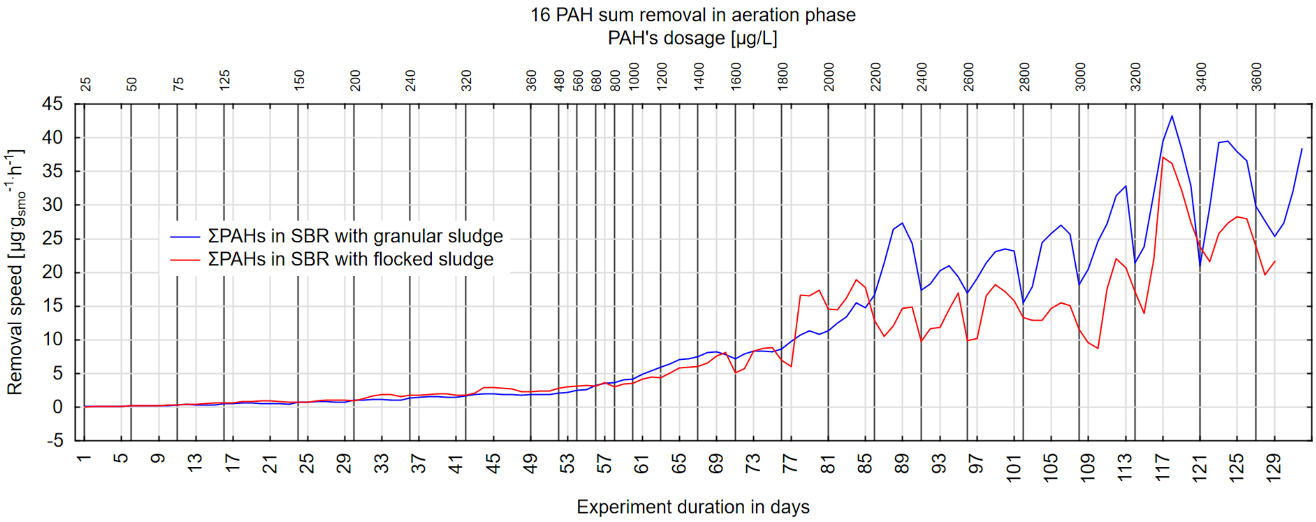

Fig. 7. Rate of ΣPAHs removal during aeration phase in reactor with granular and flocked sludge.

increase in the hydrocarbons sum removal was recorded, which amounted to about 42.88 and 36.52 µg/g$_{\text{sdm}}$·h, respectively, in granular and flocculated sludge reactors.

The equation describing the rate of PAHs sum removal during the mixing phase in reactor with granular sludge (Eq. (1)) at increasing PAHs concentration included five parameters, of which four (ln(ΣPAH), $(NH_4)^2$, log(ΣPAH), ΣPAH) were statistically significant. The estimated values were to the highest extent affected by ln(ΣPAH) and log(ΣPAH). The equation was characterized by R^2 coefficient equal to about 0.54 (Fig. 8) and estimation error of 0.98848. Equation describing the rate of PAHs sum removal (Eq. (2)) during mixing phase in reactor with flocculated sludge took into account six parameters including four statistically significant (ΣPAH, ln(ΣPAH), COD^3, and total P^3). Obtained determination coefficient (R^2) was about 0.61 (Fig. 9) and estimation error amounted to 1.0308. Variable that largely affected the estimated values was ln(ΣPAH). The PAHs sum removal rate during the phase of aeration in reactor with granular sludge at arising PAHs concentration (Eq.(3)) was described by five parameters, including two (ΣPAH, ln(ΣPAH)) statistically significant. Achieved equation was distinguished by determination coefficient R^2 equal to about 0.84 (Fig. 10) and estimation error on the level of 0.30677. Meanwhile, equation that described the rate of PAHs sum decomposition rate in reactor with flocculated sludge consisted of seven parameters, of which two (ΣPAH and ln(ΣPAH)) were statistically significant. The developed equation was characterized by R^2 of about 0.72 (Fig. 11) and estimation error of 0.29340, while variable mostly affecting the estimated values was ln(ΣPAH).

$$\begin{aligned} S_{\sum \mathrm{PAH}} &= 2.46\cdot 10^{-1}\cdot \ln\left(\sum \mathrm{PAH}\right) - 1.43\cdot 10^{-2}\cdot \left(\mathrm{NH}_4\right)^2 \\ &+ 5.66\cdot 10^{-1}\cdot \log\left(\sum \mathrm{PAH}\right) + 3.24\cdot 10^{-4}\cdot \sum \mathrm{PAH} \\ &- 1.09\cdot 10^{-11}\cdot \sum \mathrm{PAH}^3 - 7.68\cdot 10^{-1} \end{aligned} \tag{1}$$

$$S_{\sum \mathrm{PAH}} = 7.81\cdot10^{-4}\cdot\sum\mathrm{PAH} + 4.61\cdot10^{-1}\cdot\ln\left(\sum\mathrm{PAH}\right) - 4.41\cdot10^{-9}\cdot\mathrm{COD}^3 - 3.81\cdot10^{-4}\cdot\mathrm{Total}\,P^3 + 8.62\cdot\frac{1}{\sum\mathrm{PAH}} + 6.09\cdot10^{-1}\cdot\ln(\mathrm{COD}) - 4.83 \quad (2)$$

$$S_{\sum \mathrm{PAH}} = 3.25\cdot10^{-4}\cdot\sum\mathrm{PAH} + 1.14\cdot10^{-1}\cdot\ln\left(\sum\mathrm{PAH}\right) + 8.93\cdot10^{-2}\cdot\ln(\mathrm{COD}) - 3.18\cdot10^{-8}\cdot\sum\mathrm{PAH}^2 - 5.40\cdot10^{-12}\cdot\sum\mathrm{PAH}^3 - 5.63\cdot10^{-1} \quad (3)$$

$$S_{\sum \mathrm{PAH}} = 2.21\cdot10^{-4}\cdot\sum\mathrm{PAH} + 1.17\cdot10^{-1}\cdot\ln\left(\mathrm{COD}\right) + 8.16\cdot10^{-2}\cdot\ln(\sum\mathrm{PAH}) + 7.70\cdot10^{-4}\cdot\mathrm{COD} - 1.07.10^{-2}\cdot\mathrm{NO}_3 - 9.73\cdot10^{-12}\cdot\sum\mathrm{PAH}^3 + 6.37\cdot10^{-7}\cdot\mathrm{COD}^2 - 7.13\cdot10^{-1} \quad (4)$$

Quantitative changes in individual compounds, observed after the filling phase, were the consequence of the efficiency the process of wastewater treatment occurred. The COD and nitrogen and phosphorus forms in reactors, where the influence of PAHs dose after mixing phase was tested, were not higher than concentrations of these compounds in raw sewage. However, the weaker effect of wastewater dilution was observed with time. These changes were more obvious in reactor operating with flocculated sludge, while in that working with granular sludge, a gradual decrease in individual compounds dilution was recorded, which clearly depended on the PAHs dose.

The total efficiency of wastewater treatment in reactors, where PAHs doses were increased, was similar in terms of nitrogen and phosphorus forms. Slightly greater differences were found for COD removal effect, which was removed at definitely higher efficiency in reactor with granular sludge. The difference between reactors operating with different types of activated sludge consisted in larger stability of wastewater treatment effects in granular sludge reactor. The overall effect of individual PAHs and their sum removal up to 2,600 µg/L dose was higher in reactor with granular sludge. Above that dose, the PAHs removal efficiency in granular sludge reactor was lower as compared with the flocculated sludge. Such phenomenon is associated with storing the pollutants within granules of activated sludge that subsequently migrate into the layer of microorganisms

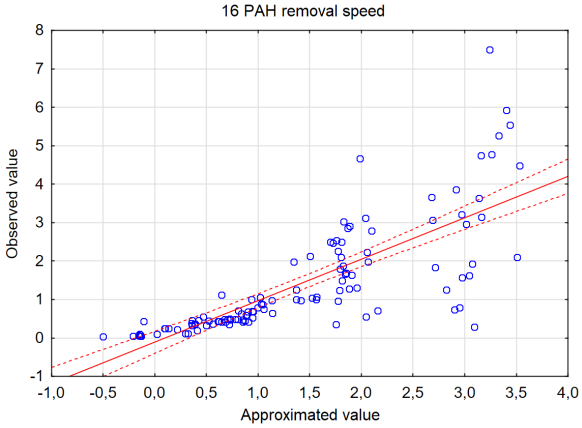

Fig. 8. Eq. (1) matches with observed values.

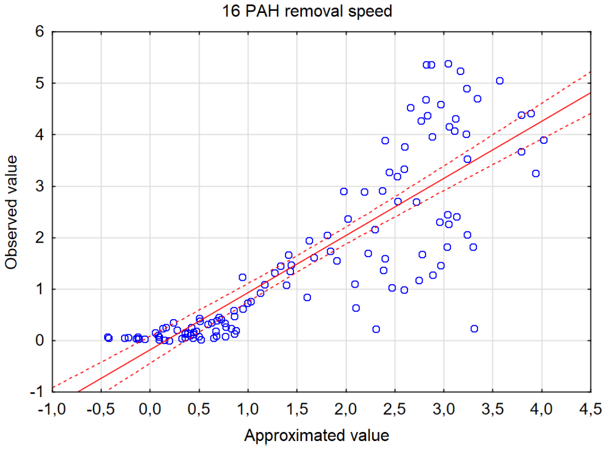

Fig. 9. Eq. (2) matches with observed values.

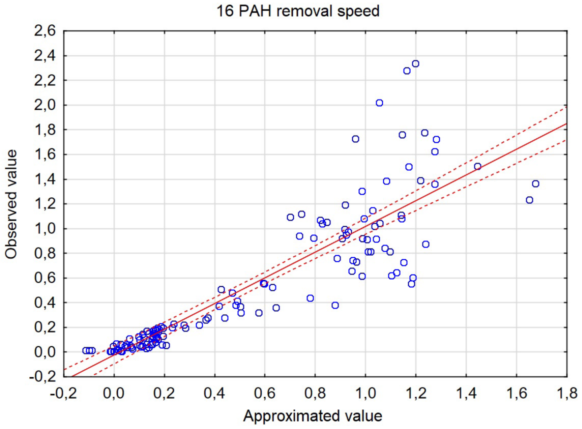

Fig. 10. Eq. (3) matches with observed values.

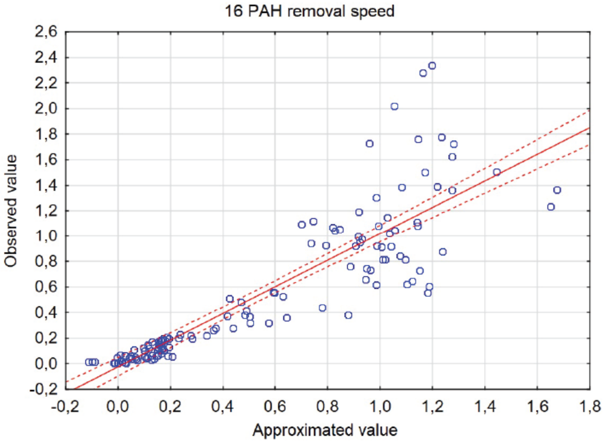

Fig. 11. Eq. (4) matches with observed values.

and are subject to biodegradation. Therefore, a single granule can be considered a grain of a filtration bed characterized by a specific sorption capacity. In the case when all granule micropores are filled, the sorption process does not occur, and microorganisms decompose pollutants stored within the granule structure [19,20]. Flocculated sludge, due to its structure, does not store pollutant to such extent as granular sludge. Therefore, at higher PAHs doses, microorganisms could have better access to PAHs contained in treated wastewater.

It should be emphasized that in literature devoted to the biological wastewater treatment, the PAHs removal subject is not often discussed, and the process itself is not fully understood. Tian et al. [2] in the mechanical–biological wastewater treatment plant, based on active sludge technology, located in China, observed 16 PAHs removal effectiveness varying from 72.4% to 100%. In turn, Qiao et al. [21] observed 16 PAHs sum removal effectiveness ranging from 29% to 34% in wastewater treatment plant located in China treating urban sewage. Man et al. [22] presented a comparison of naphthalene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and the sum of 16 PAHs removal effects in two wastewater treatment plants located in Hong Kong. The authors observed naphthalene removal varying from 79.3% to 93.9%, benzo[a]pyrene from 88.0% to 96.4%, indeno[1,2,3-cd]pyrene from 96.8% to 97, 8%, and total 16 PAHs from 79.2% to 94.4%. Similar research was conducted by Wang et al. [23]. The authors in the study considered the effectiveness of PAH removal in wastewater treatment plant located in Hefei (China) and for naphthalene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and 16 PAHs sum authors achieved removal effects equal to 35.7%, 72.5%, 84.7%, and 61.1%, respectively. On the other hand, Fatone et al. [24] observed 16 PAHs sum removal at the level of 90.7% in wastewater treatment plant located in Italy.

Analysis of the extent and PAHs removal process itself was carried out by many researchers. It should be emphasized that those studies were mainly performed in laboratory conditions. Pugazhendi et al. [25] reported that halothermophilic bacteria consortium at salinity from 4% to 30% decomposed PAHs with the number of rings not larger than four in 90% at concentration of 1,500 mg/L. The authors underlined that PAHs of high molecular weight (HMW) group were decomposed at salinity at the level of 4%. Efficiency of PAHs removal observed in here performed study was lower. The lower HMW group removal efficiency could have been caused by the dissolved salts addition and difference in research methodology itself, whose fundamental difference from a technical point was the cyclic PAH containing medium change.

Xie et al. [26] reported that *Sphingobium* bacteria are capable of decomposing phenanthrene at concentration reaching 102.0 mg/L in 51.1% in 72 h after exposure. In the presence of humic acid during the same period, the authors observed almost complete biodegradation of phenanthrene. Darma et al. [27] used *Enterobacter* strain and obtained phenanthrene degradation of about 80.2% at the concentration of 500 mg/L, while pyrene of 59.7% at initial concentration of 250 mg/L. Deng et al. [28] found that microorganisms present in microbiocapsules formed from chitosan are able to decompose pyrene in 95% during 3 d at initial concentration of 10.0 mg/L. Peng et al. [29] observed almost 70% degradation of benzo[a]pyrene at initial concentration of this compound at the level of 1.0 mg/L after 5 d. The authors used *Arthrobacter oxydans* species microorganisms. Krivobok et al. [30] studied ability to decompose anthracene applying 39 microfungal species. These authors reported that anthracene concentrations from 1.0 to 100.0 mg/L have not showed toxic properties toward tested microorganisms, while biodegradation of this compound at the initial concentration of 10.0 mg/L, in the case of 19 strains, occurred at efficiency above 50%. The most efficient group of microorganisms in anthracene decomposition was zygomycota that degraded this compound at average efficiency equal to 81%. Sanches et al. [31] in study upon PAHs removal by microorganisms with great sorption capacity (mainly *Diaphorobacter* and *Paracoccus*) recorded rates of acenaphthene and phenanthrene removal of, respectively, 0.086 1/h and 0.1561/h; the tests were carried out in anaerobic conditions. The authors underline that achieved rates of PAHs removal were very high.

The obtained efficiency and removal rate of 16 PAHs sum were lower than that presented in subject literature, which was mainly due to the researchers' different approach to PAH degradation in aqueous solutions. Most of the research presented in the literature is devoted to the analysis of selected microorganisms species and their ability to decompose a given compound without a cyclical purified medium change. Thanks to this approach, it is possible to better adapt microorganisms to toxic properties of considered compound. This results in ability to decompose much larger than considered PAH concentrations in conducted studies. The issue considered in conducted research was based on the best reflection of activated sludge process in SBR reactor in saline wastewater treatment containing PAHs, where there is a cyclic exchange of the treated medium. This limits the possibility of microorganisms adaptation to higher doses of PAH and, as a result, lower concentration of these compounds removal, to which activated sludge can adapt and allow effective wastewater treatment.

4. Conclusions

- According to conducted experiments, granular activated sludge usage might be considered in wastewater treatment plants where PAHs concentration in raw wastewater is causing problems with treated wastewater quality.
- The PAHs removal rates during mixing phase occurred in similar way in both reactors up to the PAHs dose of 1,800 µg/L. Above this level, PAHs were removed at higher rates in granular sludge reactor. Similar dependence was also observed in the aeration phase; however, more pronounced changes in the rates of PAHs removal in individual reactors were present above 2,200 µg/L.
- Overall efficiency of wastewater treatment in reactors in a view of nitrogen and phosphorus forms was similar. Slightly higher differences were observed in the case of COD removal effects, which was higher in reactor with granular sludge.
- Sum of tested hydrocarbons was removed at higher efficiency in reactor with granular sludge as compared with effects observed in reactor with flocculated sludge.

- Granular activated sludge shows higher resistance to increase in the amount of supplied toxic agent as compared with flocculated sludge. Increasing the dose of PAHs did not lead to deterioration in COD, nitrates, ammonia, total nitrogen, orthophosphates, and total phosphorus removal efficiency in such extent as in the case of flocculated sludge.

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Annex 1

Gas chromatograph working conditions:

- Carrier gas: Helium—purity 6.0
- Carrier gas flow rate—1 mL/min (splitless)
- Injected sample volume—1 μL
- Dispenser temperature—260°C
- Ion source temperature—230°C
- Transfer line temperature—300°C
- Scanning mode—single ion monitoring

Temperature program:

- Initial furnace temperature 60°C, isotherm 2 min
- Temperature increase of 30°C/min to 120°C—from 120°C temperature increase of 5°C/min to 300°C
- Final furnace temperature 300°C, isotherm 15 min

Table A1
Gas chromatography method validation results

Substance	Jon	LOD ng/L	LOQ μg/L	RSD	R^2 n = 5	Recovery %	16 PAHs concentration range μg/L
Naphthalene	128	0.21	0.1340	0.04	0.995	96	0 ÷ 1,000
				0.05	0.997	98	1,000 ÷ 2,000
				0.03	0.998	97	2,000 ÷ 3,000
				0.02	0.993	98	3,000 ÷ 4,000
Acenaphthalene	152	0.11	0.1340	0.02	0.999	95	0 ÷ 1,000
				0.03	0.997	98	1,000 ÷ 2,000
				0.01	0.996	97	2,000 ÷ 3,000
				0.02	0.998	93	3,000 ÷ 4,000
Acenaphthene	154	0.15	0.5120	0.03	0.993	95	0 ÷ 1,000
				0.02	0.995	94	1,000 ÷ 2,000
				0.04	0.997	92	2,000 ÷ 3,000
				0.03	0.995	97	3,000 ÷ 4,000
Fluorene	166	0.12	0.0530	0.02	0.993	93	0 ÷ 1,000
				0.01	0.998	95	1,000 ÷ 2,000
				0.01	0.999	94	2,000 ÷ 3,000
				0.03	0.997	96	3,000 ÷ 4,000
Phenanthrene	178	0.10	0.1900	0.02	0.993	92	0 ÷ 1,000
				0.02	0.994	90	1,000 ÷ 2,000
				0.01	0.998	91	2,000 ÷ 3,000
				0.03	0.993	93	3,000 ÷ 4,000
Anthracene	178	0.13	0.1210	0.04	0.997	97	0 ÷ 1,000
				0.02	0.993	89	1,000 ÷ 2,000
				0.03	0.995	97	2,000 ÷ 3,000
				0.02	0.997	95	3,000 ÷ 4,000
Fluoranthene	166	0.16	0.1300	0.02	0.996	94	0 ÷ 1,000
				0.03	0.996	93	1,000 ÷ 2,000
				0.02	0.997	91	2,000 ÷ 3,000
				0.02	0.992	98	3,000 ÷ 4,000

(Continued)

Table A1 *(Continued)*

Substance	Jon	LOD ng/L	LOQ µg/L	RSD	R^2 n = 5	Recovery %	16 PAHs concentration range µg/L
Pyrene	202	0.17	0.1290	0.01	0.991	92	0 ÷ 1,000
				0.03	0.993	94	1,000 ÷ 2,000
				0.02	0.997	95	2,000 ÷ 3,000
				0.02	0.996	93	3,000 ÷ 4,000
Benzo[a]anthracene	228	0.15	0.1100	0.01	0.993	97	0 ÷ 1,000
				0.02	0.992	98	1,000 ÷ 2,000
				0.03	0.994	99	2,000 ÷ 3,000
				0.01	0.998	95	3,000 ÷ 4,000
Chrysene	228	0.10	0.1040	0.04	0.997	94	0 ÷ 1,000
				0.05	0.997	93	1,000 ÷ 2,000
				0.03	0.996	97	2,000 ÷ 3,000
				0.04	0.994	95	3,000 ÷ 4,000
Benzo[b]fluoranthene	252	0.36	0.3130	0.03	0.997	97	0 ÷ 1,000
				0.02	0.992	97	1,000 ÷ 2,000
				0.03	0.997	97	2,000 ÷ 3,000
				0.03	0.992	96	3,000 ÷ 4,000
Benzo[k]fluoranthene	252	0.09	0.4630	0.04	0.995	94	0 ÷ 1,000
				0.03	0.995	96	1,000 ÷ 2,000
				0.02	0.996	95	2,000 ÷ 3,000
				0.05	0.997	92	3,000 ÷ 4,000
Benzo[a]pyrene	252	0.08	0.1000	0.03	0.992	97	0 ÷ 1,000
				0.02	0.993	93	1,000 ÷ 2,000
				0.03	0.994	94	2,000 ÷ 3,000
				0.04	0.992	96	3,000 ÷ 4,000
Indeno[1,2,3-cd]pyrene	276	0.09	0.0530	0.03	0.997	96	0 ÷ 1,000
				0.02	0.998	96	1,000 ÷ 2,000
				0.03	0.993	98	2,000 ÷ 3,000
				0.05	0.997	92	3,000 ÷ 4,000
Dibenzo[a,h]anthracene	278	0.08	0.0290	0.03	0.995	96	0 ÷ 1,000
				0.02	0.995	93	1,000 ÷ 2,000
				0.04	0.994	97	2,000 ÷ 3,000
				0.03	0.999	92	3,000 ÷ 4,000
Benzo[ghi]perylene	276	0.07	0.0280	0.03	0.997	97	0 ÷ 1,000
				0.04	0.995	93	1,000 ÷ 2,000
				0.03	0.997	95	2,000 ÷ 3,000
				0.04	0.993	94	3,000 ÷ 4,000
ΣPAH		2.17	2.60	–	–	95.13	0 ÷ 1,000
						94.38	1,000 ÷ 2,000
						95.38	2,000 ÷ 3,000
						94.69	3,000 ÷ 4,000

LOD, limit of detection; LOQ, limit of quantitation; RSD, relative standard deviation; PAHs, polycyclic aromatic hydrocarbons.