Multivariate analysis of a biologically activated carbon (BAC) system and its efficiency for removing PAHs and aliphatic hydrocarbons from wastewater polluted with petroleum products

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ABSTRACT

The efficiency of a biologically activated carbon system for treating wastewater polluted with petroleum products was examined and the effects of process parameters on its efficacy were evaluated. In each experiment 17 alkylated and 19 non-alkylated polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPHs, C_{10}–C_{40}) were extracted using semipermeable membrane devices from wastewater before and after treatment. The acquired data during experiments were analyzed using principal component analysis (PCA). The treatment system robustly removed dissolved PAHs across the studied ranges of the process parameters, providing overall removal efficiencies of 96.9–99.7% for the sum of 36 PAHs. However, the major contributor to their removal was sorption rather than biodegradation, and despite the general efficiency of the process there was up to a 9-fold range in the sums of quantified PAHs in the effluents between experiments. Combinations of long process contact time (24 h) with high temperature (24 °C) and moderate oxygen concentration (6–7 mg O_2 L^{-1}) resulted in good removal of bioavailable PAHs. The removal of TPHs was more dependent on biological activities during the wastewater treatment, and consequently more dependent on the process parameters. In addition, small but significant proportions of PAHs were volatilized and released during the wastewater treatment.

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1. Introduction

Aquatic environments receive waters containing wide ranges of organic micropollutants of both natural and anthropogenic origins. Some of the most ecotoxicologically relevant pollutants that originate in large part from human activities are petroleum products [1], which can be released from ship ballast waters, accidental oil spills, petrochemical and municipal wastewater discharges, urban runoff, and vehicle washing wastewaters [2,3]. Diesel, petrol and other crude oil distillation products are complex chemical mixtures, containing hundreds of chemical substances, which can be mainly divided into aliphatic and aromatic hydrocarbons with small amounts of additives [1,4]. Petroleum products contain varying percentages of hydrocarbons, depending on the distillation process used to generate them, and alkylated and non-alkylated aromatic hydrocarbons containing two or three aromatic rings are generally present in aqueous phases polluted by these products [5]. Polycyclic aromatic hydrocarbons (PAHs; two or more rings) raise substantial concerns because of their widely known toxic potential, including mutagenic, teratogenic, carcinogenic, photo-induced toxicity and endocrine-disrupting activities [1,6–9].

Advanced wastewater treatment processes are currently being developed to remove not only readily biodegradable compounds, such as several petroleum hydrocarbons, but also pollutants that are resistant to biodegradation. A conventional biological wastewater treatment involving activated sludge (AS) typically has several drawbacks, such as the formation of excess sludge and scum/foam formation, poor sludge settling, and sensitivity to high loads of pollution [10]. However, use of biologically activated carbon (BAC) systems can overcome many of the problems associated with AS systems. A BAC contains a sorbent and an AS mixture. The activated carbon used in BAC preparations has been shown to have high capacities to adsorb PAHs from marine sediments and soil [11,12], and BAC systems can remove a wide range of pollutants through a combination of the sorption of specific pollutants and biodegradation of less persistent compounds. The sorption

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and biodegradation processes are complementary and their combination provides several important advantages, including: low investment and operating costs; low excess sludge production; stable, robust performance during periods with shock loads of pollutants [13,14]; and automatic regeneration by the microorganisms attached to the carbon, which maintains the system's sorption capacity.

The aim of the study was to characterize a pilot-scale BAC system in terms of its capacity to remove dissolved PAHs and petroleum hydrocarbons from synthetic wastewater. Five process parameters (dissolved oxygen, salinity, temperature, process contact time and load of petroleum products) were varied according to a rational experimental design. In wastewater contaminated with petroleum product single ring aromatics (benzene, toluene, ethyl benzene, etc.) are found in relatively high levels, however this paper focus on alkylated and non-alkylated bioavailable two to six ring polycyclic aromatic hydrocarbons. The bioavailable fraction was measured by using semipermeable membrane devices (SPMDs). The behaviour of in total 36 individual dissolved phase/bioavailable alkylated and non-alkylated PAHs and dibenzothiophenes was studied in relation to process settings using multivariate data analysis.

2. Materials and methods

2.1. Synthetic wastewater preparation

The synthetic wastewater used in the experiments was prepared by diluting 1 L of synthetic medium [15] with tap water to 100 L, then adding 0.88, 1.53 and 2.19 mL portions of a 1:1 (v/v) diesel:petrol mixture to 350 L of diluted medium to preparation tank, yielding solutions with pollution loads of petroleum products of 2, 3.5 and 5 mg L^{-1}, respectively.

2.2. Laboratory set-up and operating conditions

A pilot-scale BAC system was used, consisting of a 500 L synthetic wastewater preparation tank with a stirrer, two 150 L BAC reservoirs (designated biosorbers BS1 and BS2), and two 100 L treated wastewater effluent vessels. The system was produced by Dinaitas AB (Kaunas, Lithuania) and is shown in Fig. 1. In order to minimize the number of experiments, two identical biosorbers operated in parallel during the study. The biosorber reservoirs were loaded with 8 L of the BAC, which was prepared and stabilized before use. The adaptation period required to form biofilms on the activated carbon surfaces was 1.5 months [16]. To reduce washout of the carbon particles during the operation of the process, drainage layers (three 9 cm thick gravel layers with gravel diameters, from the bottom, of 10 mm, 5 mm, and 2 mm) were installed at the bottom of each BAC reservoir.

The treatment process was studied under aerobic conditions, maintained by supplying air to the system from the bottom of the biosorbers via disk diffusers situated just above the drainage layers. The biosorbers were operated under batch conditions, as follows. Batches (300 L) of synthetic wastewater were pumped from the wastewater preparation tank by a feeding pump, equally distributed between the two biosorbers and continuously mixed with the suspended BAC layers in the biosorbers by the turbulence created by the air flow. After retention for a pre-decided process contact time with the BAC (according to the experimental design), the reservoirs were refilled with fresh portions of contaminated synthetic wastewater and the treated wastewater effluents were transferred to the effluent vessels, where they were sampled by passive water samplers (see below).

The dissolved oxygen concentrations were monitored by oxygen sensors (WTW, Germany). To maintain the wastewater temperature
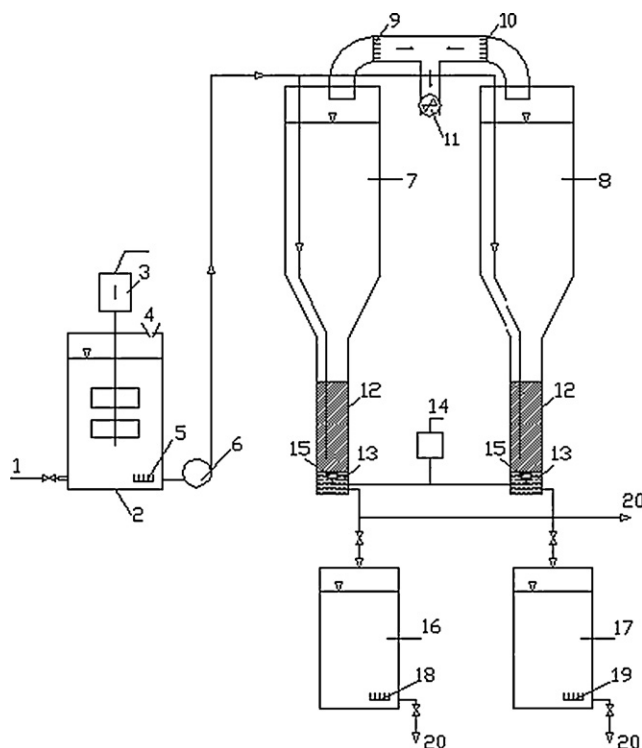

Fig. 1. Schematic diagram of the pilot-scale wastewater treatment system: (1) tap water supply; (2) simulated wastewater preparation tank; (3) stirrer, (4) diesel:petrol mixture feeding funnel; (5) SPMD (semipermeable membrane device) sampler for the wastewater influent; (6) feeding pump; (7) biosorber 1 (BS1) reservoir; (8) biosorber 2 (BS2) reservoir; (9) SPMD sampler for exhaust air from BS1; (10) SPMD sampler for exhaust air from BS2; (11) air vent; (12) biologically activated carbon (BAC); (13) drainage layers; (14) air compressor; (15) air diffusers; (16) treated wastewater effluent vessel from BS1; (17) treated wastewater effluent vessel from BS2; (18) SPMD sampler for treated wastewater effluent from BS1; (19) SPMD for treated wastewater effluent from BS2; (20) treated wastewater outlets to drainage.

at the highest tested temperature (25 °C), additional heating sheets were placed around the biosorbers.

2.3. Experimental schedule

In order to assess the effects of the examined variables efficiently, the study was performed according to a "two level fractional factorial" experimental design (Table 1) designed by MODDE 7 (Umetrics, Umeå, Sweden). Five process factors were systematically changed from selected minimum to maximum values within 19 independent experiments, 16 experiments plus triplicate centre point (S9, S10 and S19 in BS1, BS1 and BS2, respectively), to evaluate the variation in the experimental set-up.

Adaptation periods were applied to allow the system to equilibrate following changes in specific process factors, and (equally importantly) to allow potential "memory effects" from previous experiments with different biosorber settings to dissipate. The temperature of the biosorbers was maintained to within ±2 °C of the designed values. However, we had difficulties in maintaining the oxygen concentration (a highly influential parameter) at the designed levels; they ranged in practice from 1.4 to 11.5 mg L^{-1}, and thus we only used measured values during the result evaluation and modelling.

During each experiment composite samples of wastewater, suspended sludge, BAC and semipermeable membrane devices (SPMDs) were collected according to the Table 2. Five SPMDs were exposed to the exhaust air from the biosorbers during the S1, S10,

Table 1
Experimental design matrix generated by the software MODDE 7 and adaptation periods.

Date	Biosorber	Experimental week	Sample designations	Process factors				
				Oxyg (mgO$_2$ L^{-1}) (2; 5)	DSC (g L^{-1}) (0; 20)	Temp (°C) (15; 25)	Oil (mg L^{-1}) (2; 5)	Time (h) (12; 24)
Adaptation period 05.01. (27–07)[c]								
05.02. (07–14)	BS1	1	S1, Air1	2 (9.2)[b]	0	15 (13)[b]	2	24
	BS2		S11	5 (10.8)	20	15 (12)	2	24
05.02. (14–21)	BS1	2	S2	5 (10.8)	0	15 (13)	2	12
	BS2		S12	2 (11.5)	20	15 (13)	2	12
Adaptation period (temperature, salt)[a] 05.02. (22–15)								
05.03. (15–22)	BS1	3	S3	5 (7.2)	0	25 (24)	2	24
	BS2		S13, Air13	2 (5.5)	10	25 (23)	2	24
05.04. (04–11)	BS1	4	S4	2 (3.0)	0	25 (23)	2	12
	BS2		S14	5 (6.8)	10	25 (24)	2	12
Adaptation period (oil)[a] 05.04. (12–19)								
05.04. (19–26)	BS1	5	S5	2 (6.7)	0	25 (24)	5	24
	BS2		S15	5 (4.3)	10	25 (25)	5	24
05.04. (26–03)	BS1	6	S6	5 (1.4)	0	25 (25)	5	12
	BS2		S16	2 (7.6)	10	25 (25)	5	12
Adaptation period (temperature)[a] 05.05. (04–10)								
05.05. (10–17)	BS1	7	S7	5 (3.5)	0	15 (15)	5	24
	BS2		S17, Air17	2 (5.9)	10	15 (15)	5	24
05.05 (17–24)	BS1	8	S8	2 (1.8)	0	15 (15)	5	12
	BS2		S18, Air18	5 (6.8)	10	15 (15)	5	12
Adaptation period (temperature, salt, oil)[a] 05.05. (25–30)								
05.05. (30–06)	BS1	9	S9	3.5 (4.2)	5	20 (19)	3.5	18
	BS2		S19	3.5 (4.5)	5	20 (19)	3.5	18
Adaptation period (temperature, salt, oil)[a] 05.06. (07–14)								
05.06. (14–21)	BS1	10	S10, Air10	3.5 (3.6)	5	20 (19)	3.5	18

Process input factors: dissolved oxygen concentration (Oxyg, mg O$_2$ L^{-1}); dissolved salt, NaCl, concentration (DSC, g L^{-1}); temperature (Temp, °C); load of petroleum products, diesel:petrol mixture, 1:1 (v/v) (Oil, mg L^{-1}); process contact time (Time, hours) and designations for SPMD samples of the wastewater effluents (S1-S19) and the exhaust air (Air1, Air10, Air13, Air17, Air18) in each of the experiments.

[a] Adaptation period provided to allow the system to equilibrate following changes in the specified process parameters.
[b] Values in brackets indicate values measured during the experiments.
[c] Year.month. (days of the month).

S13, S17 and S18 experiments. The samples obtained from these SPMDs were designated Air1, Air10, Air13, Air17 and Air18, respectively (Table 1).

2.4. BAC quality parameters

The biomass concentrations in the samples were determined by the European sludge characterization method [17] at the Environ-mental Engineering Department, Kaunas University of Technology, Lithuania.

Indications of sorption capacities for organic substances in the wastewater were rapidly and conveniently obtained using red for-mazan adsorption method earlier described in Augulyte et al. [18].

Dehydrogenase enzyme activity (DHA) assays provide indica-tions of the viable (active) biomass in biological treatment systems and are widely used for determining the influence of pollutants

Table 2
Sampling occasions, sample matrices and final sample volumes.

Response parameter	Number of occasions per experimental week	Matrix	Final sample volume
Total petroleum hydrocarbons (TPH)	3	Wastewater (influent & effluent)	1 L[c]
Biochemical oxygen demand (BOD)	1	Wastewater (influent & effluent)	1 L
Chemical oxygen demand (COD)	1	Wastewater (influent & effluent)	1 L
Individual compounds[a]	1[b]	SPMDs (influent & effluent; exhaust air)	–[d]
Biomass concentration	1	Suspended sludge particles	50 mL[e]
Dehydrogenase enzyme activity (DHA)	2	Biologically activated carbon (BAC)	50 mL[e]
Sorption capacity	2	BAC	0.135 g w.w.[e]

[a] Thirty-six individual compounds, including alkylated and non-alkylated PAHs and dibenzothiophenes.
[b] Semipermeable membrane devices (SPMDs) were exposed continuously for 7 days during each experiment.
[c] Final sample volume pooled from number of sampling occasions during the experimental week.
[d] SPMD-extracted water volumes and air volumes for each individual compound used were from Huckins et al. (2004) and Bartkow et al. (2004).
[e] Amount collected per sampling occasion.

on microbial activity [19]. The assays measure the amounts of intensely red 1,3,5-triphenylformazan (TF) formed via the reduction of 2,3,5-triphenyltetrazolium chloride (which are proportional to the amounts of DHA present in the samples, and thus provide proxy indicators of bioactivity; [20]). For these tests, samples of BAC were taken from well-mixed reservoirs at the same time of day and analyzed according to the method described in Augulyte et al. [18].

2.5. Wastewater quality parameters

Total petroleum hydrocarbon (TPH) contents, i.e. contents of aliphatic hydrocarbons ranging from C_{10} to C_{40}, were determined according to the standard method [21] at the Environmental Engineering Department, Kaunas University of Technology, Lithuania. The extracts were analyzed according to Augulyte et al. [18].

Biochemical oxygen demand (BOD) and chemical oxygen demand (COD) were determined according to standard methods [22,23] at the JSC Kauno vandenys laboratory, Kaunas, Lithuania.

Analysis of dissolved phase alkylated and non-alkylated PAHs and dibenzothiophenes.

Passive $20\,cm \times 2.5$ sampling devices, SPMDs, supplied by ExposMeter AB (Tavelsjö, Sweden), were used to sequester dissolved and volatilized PAHs (and other organic pollutants) in the wastewater and exhaust air from the biosorbers, respectively. Triolein enclosed inside the membrane of these devices is capable of accumulating trace/ultra-trace levels of hydrophobic organic compounds during the exposure period, and the amounts accumulated are related to the time-weighted average concentrations of the pollutants in the sampled phase [24].

After their exposure, SPMDs were collected, stored, extracted and the accumulated compounds were analyzed as described by Söderström and Bergqvist [25], with further modifications by Augulyte et al. [18]. Mixtures of the ^{2}H-labelled PAHs and dibenzofuran-d8 in toluene obtained from Promochem (Kungsbacka, Sweden) were used as internal standards (ISs) and recovery standard, respectively, to evaluate losses during the preparation of samples and gas chromatography-mass spectrometry (GC–MS) analysis. Laboratory blanks (LBs), containing the solvents and clean-up material used during the preparation of the samples were used for each batch of samples. The concentrations of analyzed compounds, except naphthalene, in the LBs were ≤10% of their respective concentrations in the samples. The PAHs analyzed and their abbreviations are listed in Table 3.

To provide field controls (FC) for SPMD exposure during the deployments, single SPMDs were exposed to air during each deployment week and retrieved in the same manner as the other SPMDs. Possible contamination during handling was checked by comparing the analytical results obtained from each of the samples and the appropriate FC. The method limit of detection was calculated as the quantity of the pollutant that gave a response three times higher than the baseline noise. Recoveries for the surrogate ISs were 75–112%.

Dissolved PAH_{36} concentrations in the wastewater ($ng\,L^{-1}$) and gas-phase ($ng\,m^{-3}$) were calculated from the amounts of the compounds sequestered by the SPMD ($ng\,SPMD^{-1}$) [24]. The sampling rates used in the concentration calculations were obtained from Huckins et al. [26] and Bartkow et al. [27] (Table S1, Supplementary Material).

2.6. Removal efficiencies

The removal efficiencies of TPH, BOD, COD, sum of the 36 PAHs (sum PAH_{36}) and individual compounds were estimated from their respective influent and effluent concentrations in $mg\,L^{-1}$ or $ng\,L^{-1}$ [28]. The removal efficiencies of compounds with concentrations that were lower than their respective

Table 3
Abbreviations used for the analyzed polycyclic aromatic hydrocarbons (PAHs).

Naphthalene (Na)
2-Methylnaphthalene (2-mNa)
1-Methylnaphthalene (1-mNa)
Acenaphthylene (AcNapthy)
Biphenyl (Bi)
Acenaphthene (AcNapthe)
1,3-Dimethylnaphthalene (1,3-dmNa)
1,4-Dimethylnaphthalene (1,4-dmNa)
1,5-Dimethylnaphthalene (1,5-dmNa)
1,6-Dimethylnaphthalene (1,6-dmNa)
1,7-Dimethylnaphthalene (1,7-dmNa)
Fluorene (Fl)
2,3,5-Trimethylnaphthalene (2,3,5-tmNa)
Phenanthrene (Phe)
Anthracene (Ant)
Dibenzothiophene (Dit)
1-Methylphenanthrene + 1-methylanthracene (1-mPhe + 1-mAnt)*
2-Methylphenanthrene (2-mPhe)
3-Methylphenanthrene (3-mPhe)
9-Methylphenanthrene (9-mPhe)
1-Methyldibenzothiophene (1-mDit)
2-Methyldibenzothiophene (2-mDit)
4-Methyldibenzothiophene (4-mDit)
Fluoranthene (Fluo)
Pyrene (Py)
3,6-Dimethylphenanthrene (3,6-dmPhe)
1-Methylpyrene (1-mPy)
Benzo[a]anthracene (BaA)
Chrysene (Chr)
Benzo[b]fluoranthene (BbF)
Benzo[k]fluoranthene (BkF)
Benzo[e]pyrene (BeP)
Benzo[a]pyrene (BaP)
Perylene (Pe)
Dibenzo[a,h]anthracene (DahA)
Indeno[1,2,3-cd]pyrene (IcdP)
Benzo[ghi]perylene (BghiP)

* Unresolved peak.

detection limits in the wastewater effluents were regarded as 100%.

2.7. Multivariate data analysis methods

The multivariate method principal component analysis (PCA) was run using SIMCA-P +11 program (Umetrics AB, Umeå, Sweden). Data was auto-scaled and mean-centred. The significance of the acquired models was assessed by R^2 and Q^2 values (percentage and cross-validated percentage of the variation explained by the models, respectively) [29]. PCA enables visual inspection of the results by score and loading plots, where the condensed normalized values are plotted. The score plot shows the variation in objects where similar objects are found close to each other, whereas the loading plot shows the significance of included variables on the variation between the objects. Principal components obtained from the PCA were considered significant if their eigenvalues were >1.5. Outliers in the models were defined as points lying outside the 95% Hotelling's T^2 confidence intervals and/or distance to the model in X space (DModX) plots.

3. Results and discussion

3.1. PAHs removal efficiencies and their distribution during the treatment process

The removal efficiencies of both alkylated and non-alkylated PAHs and dibenzothiophenes were high, regardless of the conditions of the wastewater treatment process. The levels of these compounds in the dissolved phase decreased from 19–46 $\mu g\,L^{-1}$

in the influents, to 0.1–1.5 µg L^{-1} in the effluents, and the overall removal efficiencies were 96.9–99.7% for the analyzed PAH$_{36}$, 97.7–99.8% for the 17 measured alkylated PAHs and 95.4–99.9% for the 15 most commonly analyzed, so-called US-EPA priority PAHs (PAH$_{15}$, naphthalene excluded). The PAH profile of the influents was dominated by alkylated species (which were collectively five times more abundant than the non-alkylated PAHs). However, the alkylated:non-alkylated PAH ratio generally declined following the treatment (after which it ranged between 1.9 and 5.6, depending on the process settings), indicating that alkylated PAHs were more readily eliminated than non-alkylated PAHs.

During the experimental period five SPMDs were used to quantify losses of PAHs from the system to air. The collected amounts of PAH$_{15}$ from the gas-phase varied from 0.67 (Air13) to 2.4 µg SPMD^{-1} day^{-1} (Air18), corresponding approximately to concentrations ranging from 0.20 to 0.62 µg m^{-3}. Overall, these findings indicate that approximately 1–3% of the incoming PAH$_{15}$ were volatilized to the gas-phase, while ca. 2.5–3.3% were left in the effluents, during the experiments in which volatilization was assessed. In addition, the levels in the gas phase were directly related to levels found in the wastewater during the corresponding experiments (Table 1), and the gas-phase contained almost equal proportions of alkylated and non-alkylated PAHs, with alkylated:non-alkylated PAH ratios ranging from 0.8 to 2.0.

3.1.1. PAH profiles according to the treatment process conditions

PAH profiles (normalized to the total PAH$_{36}$ contents) in the gas-phase, wastewater influent and effluents were examined using PCA. The calculated model explained 79.5% of the variation with five principal components (PCs). In this model experiments S11 and S12 were recognized as outliers according to their DModX values, probably due to the very high salt concentration (20 g L^{-1}) used in these experiments. It has been noted that high salt concentrations can affect the metabolism of microorganisms in AS [30] and may reduce their oxygen uptake rates [31]. A second model, in which S11 and S12 were excluded, explained 81.3% of the variation in PAH profiles with five PCs. Although more than 95% of all PAHs were removed from the wastewater subtle differences in composition were detected using PCA. In this analysis the influent wastewater was clearly separated from all of the effluent samples, except S1, S2 and S3 along the first PC (Fig. 2a).

The influent wastewater was dominated by alkylated 2-ring PAHs (1-mNa, 2-mNa, 1,6-dmNa, 2,3,5-tmNa, Bi, and etc.), which are located on the right side of the loading plot (Fig. 2b). The effluents from experiments S1, S2 and S3, located in the score plot near

the influent sample (IN), had similar PAH profiles after the wastewater treatment process. We believe that the biodegradation capacity in the BS1 biosorber was low during these experiments, as indicated by the low removal efficiencies (varied between 18–28%) of the readily biodegradable TPH during them. Consequently, the PAH profiles found in these experiments were very similar to those of the influents, i.e. dominated by alkylated 2-ringed PAHs. The removal of dissolved PAHs from these samples was mainly due to sorption. The effluent profiles from most experiments were dominated by the PAHs that can be found on the left side of the loading plot (Fig. 2b), such as 3- and 4-ringed alkylated PAHs and dibenzothiophenes (3,6-dmPhe, 9-mPhe, 2-mDit, and etc.), and pyrene (Py).

All five air samples are located in a relatively tight group, except for the Air1 sample. The air samples have low PC2 values, a component explaining 17% of the variation in the PAH$_{36}$ profiles. The three-ringed PAHs Fl, Phe and 2-mPhe were dominant in the gas-phase during the treatment process (Fig. 2b), corroborating the general rule proposed by Baek et al. [32] that two-and three-ringed PAHs mainly reside in the gas-phase.

3.2. Removal efficiencies of TPH, BOD, COD and other parameters

TPHs removal (with hydrocarbons ranging from C$_{10}$ to C$_{40}$) was more influenced by the process conditions than for PAHs. TPH removal rates varied from 18 to 89% and the wastewater influents contained 1.03–4.57 mg L^{-1} TPH, whereas the effluents contained between 0.37 and 1.6 mg L^{-1}. In addition to the chemical analyses, BOD and COD were measured as indicators of the treatment efficiency in terms of the degradation of oxidizable compounds. BOD and COD decreased by 67.5–98.6% (influents contained 52–88 mg L^{-1} BOD) and 25.3–85.0% (influents contained 91–114 mg L^{-1} COD), respectively, depending on the process conditions. The sorption capacity of the system was also monitored during the experiments, and the measurements showed that 40–68% of the capacity was available in the biosorbers, depending on the process parameters.

3.3. BAC process treatment efficiency dependent on the process conditions

Forty-six variables (the removal efficiencies of: individual PAHs, sum of PAH$_{36}$, sum of alkylated PAHs, sum of PAH$_{15}$, BOD, COD, TPH; the sorption capacity (Sorp), DHA, biomass, and ratios of alkylated to non-alkylated PAHs (Ratio)) were calculated for each of 19 experiments and analyzed by a second PCA model, in which
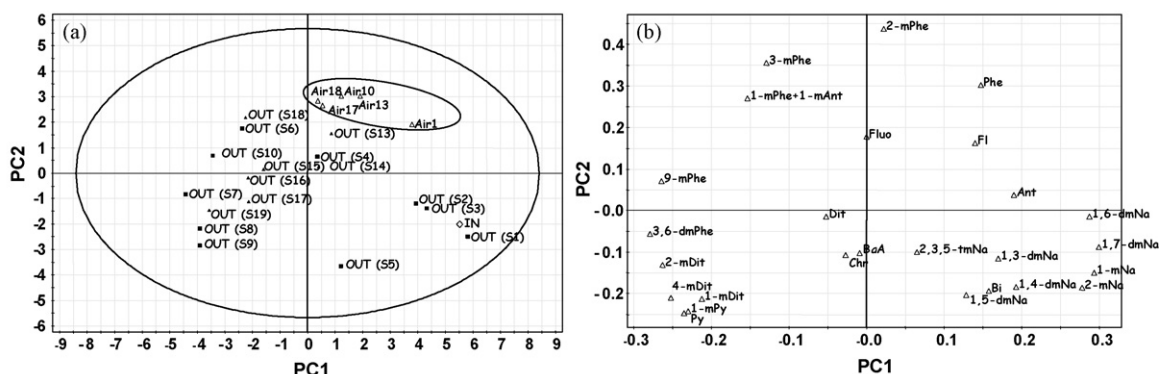

Fig. 2. Results of principal component analysis (PCA) of polycyclic aromatic hydrocarbon (PAH) profiles normalized to the sum of 36 PAHs (PAH$_{36}$) found in the wastewater and exhaust air semipermeable membrane device samples. PAHs accounting for <1% of the sum of PAH$_{36}$ contents were excluded from the model. (a) PC1/PC2, score plot, (b) PC1/PC2, loading plot. IN – influent wastewater (marked with open diamonds), OUT (S1, S2,. . ., S9, S10) – effluents during experiments S1, S2,. . ., S9, S10 from biosorber BS1, marked in black squares; OUT (S13, S14,. . ., S19) – effluents during experiments S13, S14,. . ., S19 from biosorber BS2, marked in black triangles. Air samples are marked with open triangles: Air1 – exhaust air from BS1 during experiment S1, Air10 – exhaust air from BS1 during experiment S10, Air13 – exhaust air from BS2 during experiment S13, Air17 – exhaust air from BS2 during experiment S17, Air18 – exhaust air from BS2 during experiment S18. The full names of the abbreviated PAHs are listed in Table 3.
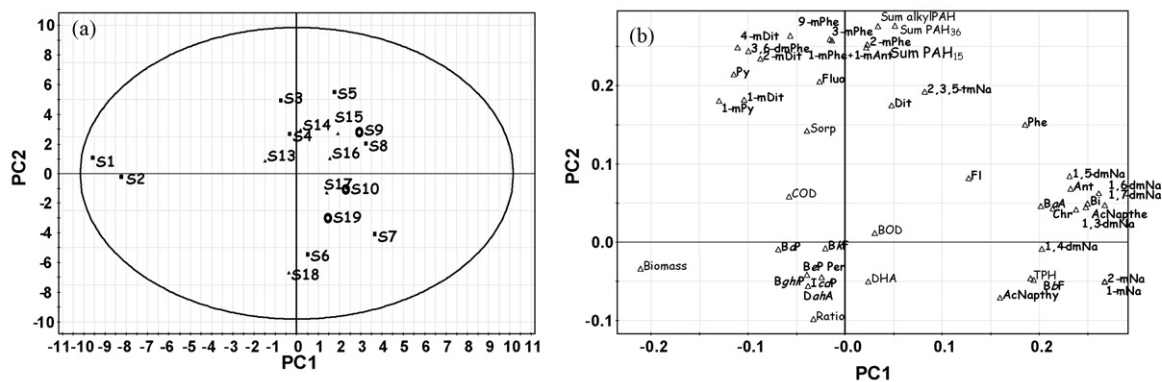
Fig. 3. (a) PC1 versus PC2 score plot obtained by principal component analysis of the data acquired in experiments performed with biosorbers 1 (BS1) and 2 (BS2), marked with black squares and black triangles, respectively. The triplicate samples (S9 and S10 samples from BS1 and the S19 sample from BS2) are marked with open black circles. The experimental settings are listed in Table 1. (b) Loading plot showing the dependency on the tested process parameters of the removal efficiencies of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total petroleum hydrocarbons (TPH), sum of 36 analyzed polycyclic aromatic hydrocarbons (PAHs) (Sum PAH$_{36}$), sum of alkylated PAHs (Sum alkylPAH), sum of 15 US-EPA priority PAHs (Sum PAH$_{15}$; naphthalene excluded) and individual PAHs (1-mNa, 2-mNa,....); and the sorption capacity (Sorp), dehydrogenase activity (DHA), biomass concentration (Biomass), and ratio of alkylated to non-alkylated PAHs (Ratio). Full names of the abbreviated PAHs are listed in Table 3.

the samples S11 and S12 were recognized as outliers (for reasons described in Section 3.1.1). The calculated PCA model had three significant PCs explaining 70.4% of the variation in the data. The first component explained 29% of the variation in the dataset and the second 27%. Three experiments with identical process settings (S9 and S10 in BS1 and S19 in BS2) were slightly spread in the PC1 versus PC2 score plot of the model (Fig. 3a), probably for several reasons, including the high variability of both biotic and abiotic aspects of the process that are difficult to control fully, and both sampling and analytical errors which may have caused the accuracy and precision of the large amounts of data generated during each experiment to vary slightly over time. Overall, the model revealed that variations in several process parameters had specific effects on treatment-related changes in the PAH contents of synthetic wastewater.

The score plot (Fig. 3a) indicates that there were no clear differences in the results of the experiments that could be attributed to differences between the two biosorbers BS1 and BS2. Except for the S1 and S2 samples (both from BS1), the samples representing the different experiments are well spread in the plot, regardless of which biosorber was used and there is no preponderance of either biosorber in any dimension of the plot. Biomass concentrations were highest in experiments S1 and S2, located on the left side of the score plot, probably at least partly because high amounts of oxygen were delivered to the biosorbers (measured values; 9.2 and 10.8 mg O$_2$ L^{-1}, respectively) in these experiments. Theoretically, the high rates of aeration should also have increased the removal efficiency of the readily degradable hydrocarbons. However this was not the case since the rates of TPH removal were poor (as mentioned earlier) in these two experiments, in which all of the examined process factors were the same except for the contact times (12 and 24 h, respectively). A possible explanation for this deviation from expectations is that the high rate of aeration may have caused heavy mixing of the BAC, which may have harmed the microorganisms and thus reduced the efficiency of the treatment of readily biodegradable hydrocarbons. The biomass concentration measurements we obtained provide no means of distinguishing between active and non-active biota during the treatment process and, hence, this possibility could not be verified. However, no indications of low bioactivity in these experiments were detected in the DHA measurements. In general the PAH$_{36}$ removal was less affected by the possible mixing effects since it is mostly dependent on sorption of the compounds and less on their biodegradation.

Generally, the calculated removal efficiencies of COD, BOD, TPH and the high molecular weight PAHs (BaP, BeP, Pe, DahA) and the DHA measurements varied little amongst the experiments (Fig. 3b). The removal efficiencies of alkylated PAHs, alkylated dibenzothiophenes and phenanthrenes, Fluo, Py and the sorption capacities of the biosorbers were closely correlated. These findings indicate that sorption was the major removal process during the treatment of PAHs in the wastewater, especially for the individual PAHs mentioned, whereas no clear correlation was found between the biomass concentration and removal of PAHs. The TPH removal efficiency was directly correlated with the removal efficiencies of the alkylated naphthalenes (representing easily biodegradable compounds).

The petroleum pollution load and oxygen level were almost identical (5 mg L^{-1} and 6.7 or 6.8 mg L^{-1}, respectively) in experiments S5 and S18, in which the PAH$_{36}$ removal efficiencies were the highest and lowest, respectively. In the score plot these experiments are separated in the second dimension (Fig. 3a). Increasing the process contact time (from 12 to 24 h), reducing the salt concentration (from 10 to 0 mg L^{-1}) and raising the temperature (from 15 to 24 °C) all appear to have contributed to the greater removal efficiency of dissolved phase PAHs in experiment S5 compared to experiment S18. The S18 experiment also yielded effluent with the highest alkylated:non-alkylated PAHs ratio, the most strongly negative loading value in the second dimension (Fig. 3b) and the lowest removal efficiencies for the sum of alkylated PAHs, alkylated phenanthrenes, etc.

3.4. PAHs profiles between two extreme process conditions

The specific PAH profiles of samples S18 and S5 that were detected in the PCA are shown in Fig. 4. Sample S18 has elevated concentrations of alkylated phenanthrenes, with concentrations ranging from 100 to 274 ng L^{-1}. In addition, the S18 effluent contained elevated levels of 1,6-dmNa, 2,3,5-tmNa, Phe and alkylated dibenzothiophenes, Fluo, Py, 3,6-dmPhe and 1-mPy. The low temperature (15 °C) and short process contact time (12 h) during S18 probably contributed to the relatively poor removal of these PAHs in this experiment. The differences in process settings between these extreme experiments resulted in up to 24-fold differences in the concentrations of individual PAHs in the effluents, a 9-fold higher sum of PAHs in the effluent from experiment S18, and overall PAH
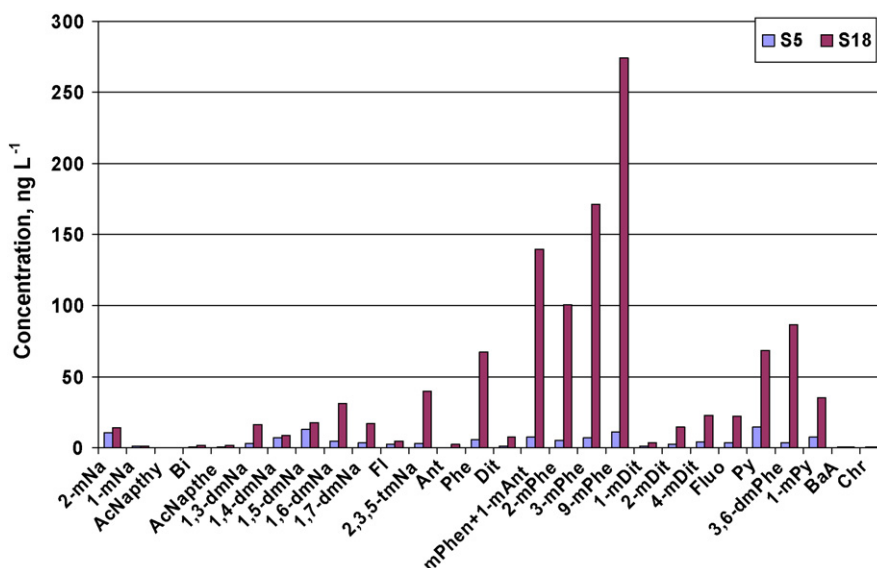
Fig. 4. Concentration profiles of the 28 quantified polycyclic aromatic hydrocarbons (PAHs) in the effluents from the experiments yielding the highest and lowest PAH removal efficiencies; S5 and S18, respectively. B*b*F, B*k*F, B*e*P, B*a*P, Pe, I*cd*P, B*ghi*P, D*ah*A were not detected in the effluents. The full names of the abbreviated PAHs are listed in Table S1, Supplementary Material.

removal efficiencies of 97.4% versus 99.7% in experiments S18 and S5, respectively.

A similar PAH profile, dominated by alkylated PAHs, to that obtained from the S18 sample (Fig. 4) was obtained from the S6 sample, which is located close to S18 in the score plot (Fig. 3a). S6 was run in the same biosorber the week after experiment S5, but with different process settings, including a shorter contact time (12 h vs. 24 h) and lower level of aeration (1.4 mg O_2 L^{-1} versus 6.7 mg O_2 L^{-1}), confirming that the process contact time and oxygen level are important process factors that influence the efficacy of the treatment process, in addition to unknown, uncontrolled process parameters.

4. Conclusions

The data presented here show that the investigated BAC system is capable of robustly removing PAHs from synthetic wastewater in conditions spanning wide ranges of process parameters, in large part due to its sufficient sorption capacity. Removal efficiencies of PAHs were consistently high. However, up to 9-fold differences in the sums of PAHs (and up to 24-fold differences for individual PAHs) in the effluents were found between experiments. Combinations of long contact time (24 h) and high temperature (24 °C) and moderate oxygen concentration (6–7 mg O_2 L^{-1}) resulted in relatively low concentrations of dissolved PAHs in the effluents. The efficiency of TPH removal was more strongly dependent on the process parameters and the biological activity during the wastewater treatments. The exhaust air, the wastewater before and after the treatment process were dominated by 3-ringed non-alkylated and alkylated PAHs, alkylated 2-ringed PAHs and 3- and 4-ringed alkylated and non-alkylated PAHs, respectively. Limited amounts of PAHs were released into the exhaust air from the biosorbers that were proportional to the amounts in the water effluent during the wastewater treatment process.

Further studies with real wastewater are needed to characterise the effects of the total organic carbon content on the BAC system's treatment process performance, and the influence of process contact time should be more rigorously examined by including tests with contact times shorter than 12 h. However, the presented study has indicated the BAC system to be a robust wastewater treat-

ment system with sufficient capacity for treating effluents from oil refineries and petrol stations.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.04.129.

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