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Simultaneous removal of PAHs and phenols from coking wastewater under anaerobic conditions

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ABSTRACT

The aim of the study was to evaluate concentration changes of selected polycyclic aromatic hydrocarbons (PAHs) and phenols during methane digestion of coke plant wastewater. Methane digestion was performed in a fixed bed one-stage reactor by complex microbial community. The temperature was held at 34℃ (mesophilic conditions); phenol load was equal to 0.13 kg/m^3 d. Concentration of phenols in influent was about 600 mg/L, whereas concentration of 16 PAHs total was up to over 600 ng/L. Up to 80% removal of phenols was observed; simultaneously, even 93% of PAHs were removed (60% in the case of carcinogenic compounds). Statistically significant, temporary increases in individual PAHs content in effluent were, however, observed. This indicates an important role of sorption/desorption processes on biomass in removal of PAHs from coking wastewater.

Keywords: Coke plant wastewater; Polycyclic aromatic hydrocarbons; Phenol; Methane digestion

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1. Introduction

Coking plant wastewater is generated mainly during coal coking and purification of a coal gas [1]. This type of wastewater is a serious environmental problem because it is a mixture of many organic and inorganic compounds such as phenols (they are main organic constituents, accounting for 80% of COD), cyanides, thiocyanides, ammonia, polycyclic aromatic hydrocarbons (PAHs), polycyclic nitrogen-containing aromatics, acyclic compounds, oxygen-containing heterocyclic and sulphur-containing heterocyclic compounds [1,2]. Coke wastewater also contains relatively high concentrations of oil and grease, as well as tar [3,4]. Chemical composition of coking plant wastewater varies between factories depending on the quality of raw coal, temperature of carbonation and technologies used in the factory [1]. The examples of coking wastewater physicochemical characteristics are listed in Table 1.

Contaminants such as phenols, cyanides and 16 PAHs (naphthalene, acenaphthene, fluoranthene, benzo(a)anthracene, benzo(a)pyrene, benoz(b)fluoranthene, benzo(k)fluoranthene, chrysene, acenaphthylene, anthracene, benzo(ghi)perylene, fluorene, phenanthrene,

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Table 1
Quality of coking treatment plant wastewater from various factories [2–6]

	Concentration, mg/L				
Parameter	Coke plant in China [2]	Coke plant in China [5]	Coke plant in USA [3]	Coke plant in Poland [4]	Selected coke plants in Poland [6]
Total phenols	80–120	No data	500	1,343	No data
Volatile phenols	No data	417–481	No data	No data	260–3,000
COD_{Cr}	900–2,000	2,489–4,111	4,500	5,374	No data
BOD_5	350–800	No data	No data	No data	No data
Free NH_3-N	150–420	315–430	2,600	120[a]	980–6,500[a]
Fixed NH_3-N			2,400		
pH[b]	No data	7.9–8.4	No data	9.1	7.5–9.5
Organic N	30–90	No data	No data	No data	No data
TKN	No data	No data	5,120	No data	No data
Cyanides	2–7	No data	200	67	10–100
Phosphates	No data	No data	No data	0.6	No data
Suspended solids	No data	No data	No data	331	No data

[a]As N–NH_4^+; [b]pH is abbreviation for potential of hydrogen.

dibenzo(g,h)anthracene, indeno(1,2,3-cd)pyrene, pyrene) are included by US EPA into a list of 126 priority pollutants [7]. PAHs may pose a serious environmental and health risk because they are toxic at low concentrations, have mutagenic and carcinogenic properties and tend to accumulate on solids (e.g. river sediments) and microorganisms to levels several orders of magnitude higher than above water concentration [5,8]. Coking plant wastewater is one of the most contaminated with PAHs industrial sewage. Zhang et al. stated that total concentrations of PAHs in coke plant wastewater were in the range from 98.5 ± 8.9 to 216 ± 20.2 μg/L, with dominant 3- and 4-ring compounds [9]. According to the results obtained by Włodarczyk-Makuła et al. the average concentration of total PAHs in coke plant effluent was equal to 188 μg/L with naphthalene as dominant compound [10]. Concentration of PAHs in coke plant wastewater is usually even 10–100 times higher than in municipal sewage. For example, the total PAHs in municipal WWTP in Sweden were stated to be in the range of <2 and 23.5 μg/L [11]. In Norway, concentration of 16 EPA-PAHs in municipal wastewater (average from 5 WWTP) was equal to 0.2–1.3 μg/L [12]. Data collected by Liu et al. indicate that in the sewage from domestic sources, the total concentration of 8 PAHs was on average 1.6 μg/L [13]. Also, the results obtained by Sánchez-Avila et al. (0.009–5.05 μg/L) confirm that concentrations of total PAHs in the municipal wastewater do not exceed several μg/L [14].

Coke plant industry in Poland annually generates over 9 mln tones of coke [15]. Production of one tone of coke, depending on the technology, results in generating from 0.35 to 0.45 m^3 of wastewater. Thus, annually over 4 mln m^3 of wastewater is generated [6]. It indicates that loads of PAHs that can be discharged into the environment may be even higher than 800 kg of PAHs a year.

Both biological and physicochemical processes are applied in the process of coking wastewater treatment. The main focus is put on removal of COD, phenols and nitrogen compounds from this kind of wastewater. Conventional processes for high-strength coke plant wastewater include caustic treatment and steam stripping followed by biological treatment [1]. Conventional aerobic activated sludge process is not very effective in coking plant wastewater treatment due to high concentration of refractory and toxic compounds [5]. Mainly, nitrification process is inhibited by them. It results in not satisfactory removal of nitrogen compounds. Experimental data indicate that in activated sludge process, free cyanides most seriously inhibit nitrification and in addition phenol compounds negatively affect this process. However, there is smaller possibility of inhibiting the process by phenol itself because of its biodegradation under anoxic and oxic conditions [1]. That is the reason why better results of coke wastewater treatment are achieved in anoxic–oxic or anaerobic–anoxic–oxic processes [5]. For example, Rong et al. [16] achieved over 94% removal of COD from coke plant wastewater using simultaneously nitrifying and denitrifying (SND) fixed film hybrid system (at hydraulic retention time 44 h). Contemporaneously total nitrogen removal higher than 94% was obtained. Zhao et al. [17] indicated that in laboratory conditions, treatment of coke plant wastewater in an anaerobic–anoxic–oxic membrane bioreactor (at total retention time 40 h) made it possible to obtain average COD removal 89.8 ± 1.2%.

Another problem concerning biological treatment is high variability of coke plant composition as well as no phosphorus compounds presence in them [4]. That leads both to using various chemical and physical pre-treatment processes and supplementation of P compounds during coke plant treatment. Yuan et al. [18] indicted that biodegradability of coke plant wastewater, measured as COD removal, could be improved with an extraction replacement-biodegradation coupling technique when n-octanol/cyclohexane mixture (in ratio 1:1) was used as an extractant. Pre-treatment of coke plant wastewater for 5 min using this method increased COD removal efficiency by 20%. Phenols can be effectively removed from coking plant wastewater using an anaerobic-anoxic-oxic membrane bioreactor system (>99.9%) [17]. Besides anaerobic processes are efficient in phenols’ removal. Studies by Janosz-Rajczyk et al. have indicated that reduction of 68–92% may be obtained [19].

PAHs are believed to be rather persistent in the environment. However, the results obtained by various researchers indicate that these compounds may undergo both biological and chemical degradation. For example, strong chemical oxidants are effective in PAHs removal. Studies by Zhao et al. showed that removal of PAHs during activated persulfate treatment may reach 92%, by modified Fenton’s reagent 80% [20]. Also, other physicochemical processes allow one to achieve high removal efficiency of PAHs from wastewater. Wu et al. using of 0.75 g/L of Ca^{2+}-montmorillonite in one-step process achieved more than 90% efficiency of PAHs removal (more than 99% in the case of benzo(a)pyrene) [5]. Smol and Włodarczyk-Makuła obtained the total PAHs removal from coking wastewater reaching 85% in series-connected filtration and ultrafiltration processes. During single ultrafiltration, almost 67% of the total PAHs were removed [21].

During activated sewage sludge treatment (with BNR removal) up to 70% removal of PAHs can be achieved [22]. Anaerobic biological pathways of PAHs degradation are distinct from aerobic transformations. Research works indicate that denitrifying and sulphate-reducing bacteria play the most important role in anaerobic transformations of these compounds [8,23,24]. However, degradation of PAHs was also confirmed under strict anaerobic conditions [8]. Christenesen et al. [25] showed that PAHs degradation under anaerobic conditions is possible in the presence of methanogens that consume hydrogen. Research work done by Yuan and Chang has indicated that the degradation rates of PAHs under anaerobic conditions are connected with redox potential and are as follows: sulphate-reducing conditions, methanogenic conditions and nitrate-reducing conditions. Some addition of electron donors (e.g. acetate, lactate, pyruvate) can enhance PAHs degradation both under methanogenic and sulphate-reducing conditions [24]. Biodegradation of PAHs could also be enhanced by ozonation pre-treatment making these compounds more available for microorganisms [26]. The results of the previous studies done worldwide indicate that degradation of PAHs is possible during methane fermentation and the efficiency and rate of this process is connected with the kind of microorganisms that are settled in the reactor and the kind of substrate. In the case of coke wastewater, PAHs removal is strictly connected with removal of tar from wastewater [4].

It must be emphasized that PAHs removal from coke plant wastewater is at present obligatory since BAT (best available techniques) and emission standards for the coke plant industry were defined. According to the BAT, the emission levels for PAHs that should be achieved during treatment of wastewater from coke plants are set at the level <0.05 mg/L. In the case of other coke plant wastewater contaminants, they are as follows: COD < 22 mg/L, BOD_5 < 20 mg/L, sulphides < 0.1 mg/L, thiocyanates < 4 mg/L, cyanides < 0.1 mg/L, phenols 0.5 mg/L and total nitrogen <15–50 mg/L [27].

The aim of the present study was to evaluate the possibility and effectiveness of simultaneous PAHs and phenols’ removal from coking wastewater during

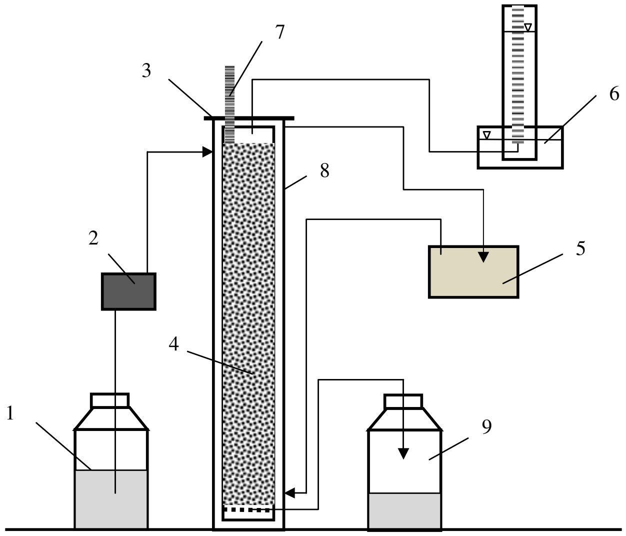

Fig. 1. The schematic diagram of the laboratory installation: 1—influent tank, 2—peristaltic pump, 3—fixed film bioreactor, 4—supporting medium, 5—ultra thermostat, 6—device for measuring the amount of biogas generated during fermentation, 7—thermometer, 8—heating jacket, 9—effluent tank.

methane fermentation in a fixed bed one-stage reactor by complex microbial community.

2. Materials and methods

2.1. Laboratory installation

A fixed film reactor was used for methane digestion of coke plant wastewater. The laboratory set-up was operated in the system of continuous substrate feed (Fig. 1). The bioreactor unit was made of plexiglass; it had diameter and height of 0.12 and 1.30 m, respectively. Working volume of the bioreactor was equal to 6.2 L. It was equipped with a water jacket to maintain constant temperature (isothermal conditions of the process (34 ℃) were ensured by the circulation of water between water jacket of the bioreactor—double wall—and ultra thermostat). The feed of substrate was done from the top, while output of treated effluent from the bottom. Output of biogas was done from the top. The collected biogas was directed into the glass cylinder, filled with a saturated solution of NaCl, for measurement of its quantity. Reactor was filled with kermezite.

The microorganisms capable for methane digestion were planted into the bioreactor from the closed fermentation chamber of WWTP in southern Poland. They underwent prior adaptation to phenol at concentration up to about 600 mg/L. In order to adapt microorganisms for high concentrations of phenol, synthetic wastewater was used. The composition of the synthetic wastewater was as follows:

(1) Mineral component (A): 6.0 g K_2HPO_4/L of distilled water.
(2) Mineral component (B): 0.16 g $CaCl_2 \cdot 2H_2O$/L, 6.0 g KH_2PO_4/L, 2.6 g $MgSO_4 \cdot 7H_2O$/L, 12.0 g NaCl/L. The compounds were diluted in distilled water.
(3) Fifty milliliter of mineral component (A) and 50 mL of mineral component (B) were mixed with 5.0 g $NaHCO_3$, 0.002 g $FeSO_4 \cdot 7H_2O$, phenol (from 0.1 to 0.6 g/L) and 0.2 g of yeast extract. All compounds were diluted with tap water to obtain synthetic phenol wastewater.

Mineral components (A) and (B) were prepared according to the formula given by Buraczewski [28].

After adaptation period, the reactor was fed by raw wastewater (influent). It was prepared by mixing synthetic wastewater with ammonia liquid from coking plant. Ammonia liquor was taken before (stage I of research work) and after removal of tar and oils (stage II of research work). In both cases, it did not undergo dephenolization. Proportion of synthetic wastewater and ammonia liquor was picked to obtain concentration of phenol equal to about 600 mg/L in the influent. pH of influent was corrected to 7.6–7.7 with 1n NaOH if necessary. The phenol load was equal to 0.13 kg/m^3 d; the organic compounds load was equal to 0.33 kg COD/m^3 d. HRT was equal to 3.4 d. Working volume of the reactor was equal to 6.22 L.

2.2. Process control

The process was controlled using standard methods [29]: pH—by a potentiometric method; alkalinity—acidimetrically, COD—by a dichromatic method; phenol by a spectrophotometric method at wavelength 295.5 nm; volatile fatty acids—by a distillation method; methane in biogas by Orsat apparatus. Analyses of physicochemical properties of wastewater were done each day. The methane content in biogas was analysed once in three days. Average daily samples were used for analyses.

2.3. PAHs identification and quantification

PAHs were separated from average daily samples of wastewater using a periodic extraction method. Fifty milliliters of coke plant wastewater were mixed with cyclohexane. Extraction was conducted for 1 h, at 20℃, in a shaker. After extraction, the organic fraction was separated from the water phase in a laboratory separator. An organic phase was concentrated in

Table 2
Retention times for 16 EPA-PAHs in GC–MS qualification and quantification

PAH compound	Retention time, min
Naphthalene	9.95
Acenaphthylene	16.72
Acenaphthene	17.60
Fluorene	20.09
Phenanthrene	25.00
Anthracene	25.23
Fluoranthene	31.46
Pyrene	32.46
Benzo(a)anthracene	39.89
Chrysene	40.24
Benzo(a)pyrene	56.60
Benzo(b)fluoranthene	51.77
Benzo(k)fluoranthene	52.07
Indeno(1,2,3-cd)pyrene	80.89
Dibenzo(a,h)anthracene	81.90
Benzo(ghi)perylene	88.10

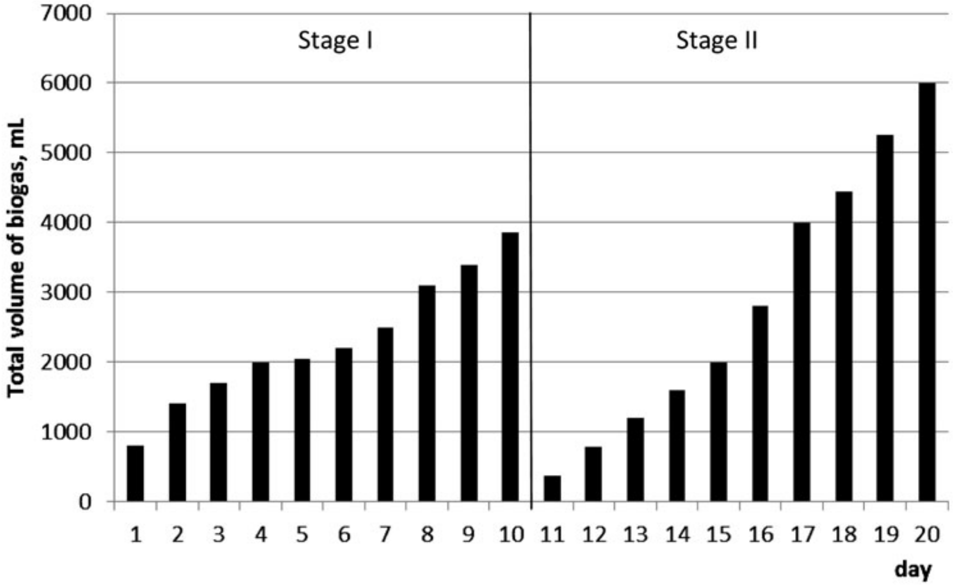

Fig. 2. Total biogas production during stage I and stage II of research.

water bath at 60°C to 2 mL, and then, it was purified using solid-phase extraction (at Bakerbond SPE PAH soil columns). The SPE columns were filled with 500 mg cyano and 1,000 mg of silica gel. The columns were conditioned with petroleum ether (3 × 3 mL). PAHs bounded into the packing of the columns were leached with 3 × 3 mL of acetonitrile/toluene mixture (3:1 v/v). The samples were extracted in triplicate. Eluates were analysed for 16 EPA-PAHs by gas chromatography-mass spectrometry (Fisons GC 8000/MS 800). Gas chromatographic separation was performed on DB-5 column (30 m length, 0.25 mm diameter and 1 μm film). Helium was used as a carrier gas. The flow rate of carrier gas was $0.5\,\mathrm{mL\,min^{-1}}$. The oven was kept at 40°C for 1 min, heated with 5°C for 1 min to 120°C and ultimately, the temperature 280°C was held for 60 min. Retention times for PAHs are listed in Table 2.

t-Student test (Microsoft Excel) was used to evaluate statistical significance of individual PAH compounds concentration changes. Analyses were done twice at each stage of research work.

3. Results and discussion

The study was conducted to check the possibilities and efficiency of simultaneous PAHs and phenols removal during methane fermentation of coke plant wastewater. Besides the changes in COD and VFA concentration were analysed. Methane digestion course was also evaluated based on biogas production changes (including methane analysis).

The total biogas production during methane fermentation of the wastewater is presented in Fig. 2. Based on that data, it could be stated that production of biogas was slightly higher during digestion of the influent containing coke wastewater after tar and oil removal. Daily production of biogas varied between less than 200 and 800 mL during the first stage of research and between about 400 and 1,200 mL during the second one. Variations of biogas production obtained in a fixed film bioreactor, however, should not be treated as a fully reliable indicator of methane digestion because in this type of reactor frequently biogas is held in the bed, and periodically loosened. Average contents of both methane and other gases in biogas are listed in Table 3. The methane content in biogas reaching 72–74% was high and gave evidence that methanogenesis was not inhibited by compounds present in coking wastewater. Methane production from 1 kg of COD removed was on average equal to $100\,\mathrm{L\,CH_4/kg}$ of removed COD and $125\,\mathrm{L\,CH_4/kg}$ of removed COD, for stage I and stage II, respectively.

Additional parameters of methane digestion effectiveness are the changes in COD, VFA and phenols concentration. For both stages, they are presented in Figs. 3–5. The process was performed at COD load of $0.33\,\mathrm{kg/m^{3}\cdot d}$ and the phenol load of $0.13\,\mathrm{kg/m^3\,d}$. Removal of phenols was comparable in both stages and varied between 55 and 80%. COD removal was slightly lower compared to the one obtained for phenols and varied between 54 and 71%. VFA weren't effectively removed during methane digestion. It indicates that further treatment or some change in technological parameters is necessary. It gave evidence that removal efficiency obtained in our study wasn't enough to achieve standards set by BAT for COD and phenols in treated coke plant wastewater either. The results of the previous study suggest that, for example, series-connected fixed film reactors make it possible to achieve higher COD, VFA and phenol removal [19].

The results showed that removal of oil and tar from coking wastewater didn't significantly affect removal of organic macro pollutants during methane fermentation process.

Alkalinity of influent was at above 900 mgCaCO$_3$/L. VFA/alkalinity ratio was lower than 0.3. It indicates that alkalinity of influent was enough to guarantee the proper course of methane digestion process.

The changes in PAHs concentration during anaerobic digestion of coking wastewater are presented in Figs. 6 and 7. The highest total concentration of 16 EPA-PAHs in raw wastewater observed during research work was equal up to 627 ng/L. The total concentration of carcinogenic PAHs was equal up to 66 ng/L. The concentration of PAHs total was lower than obtained by other authors for coke wastewater [9,10]. The total concentration of PAHs was about 20% higher in the influents containing wastewater without oil and tar removal. Even 93% of the total PAHs were removed from the wastewater during methane digestion; 60% removal of carcinogenic compounds was achieved simultaneously. Results of *t*-Student test indicate that removal was statistically significant. Statistically significant (in *t*-Student test), temporary increases in individual PAHs concentration in effluent were observed (Fig. 7) during stage II of research work. They concerned mainly PAH compounds of 4-, 5- and 6-ring structure. The results indicate that an important role, in higher molecular weight PAHs removal from wastewater during methane digestion, plays sorption on biomass. Higher molecular weight compounds are adsorbed into biomass, and occasionally desorbed into effluent.

Table 3
Composition and selected properties of biogas generated during stage I and stage II of research on methane digestion of coking wastewater

Compound	Range of concentration	
	Stage I	Stage II
CH$_4$, %	72	74
CO$_2$, %	7	6
N, %	19	17

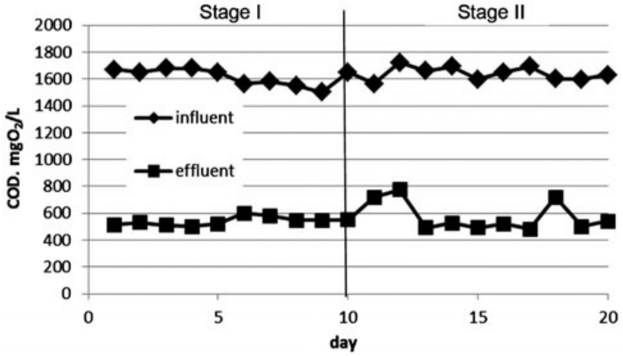

Fig. 3. COD changes during methane digestion of coke plant wastewater: stage I—wastewater without oil and tar removal, stage II—wastewater after oil and tar removal.

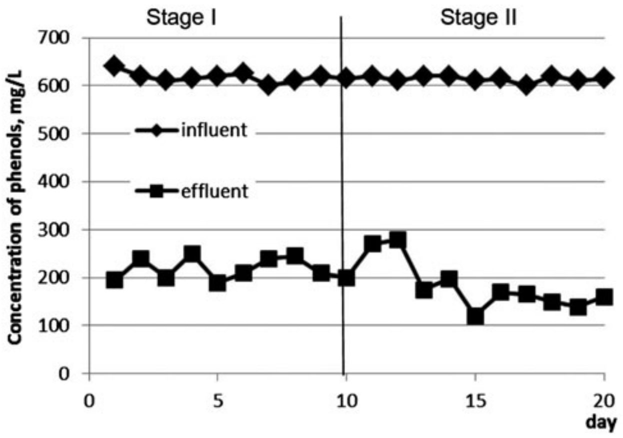

Fig. 4. Phenols concentration in influent and effluent: stage I—wastewater without oil and tar removal, stage II—wastewater after oil and tar removal.

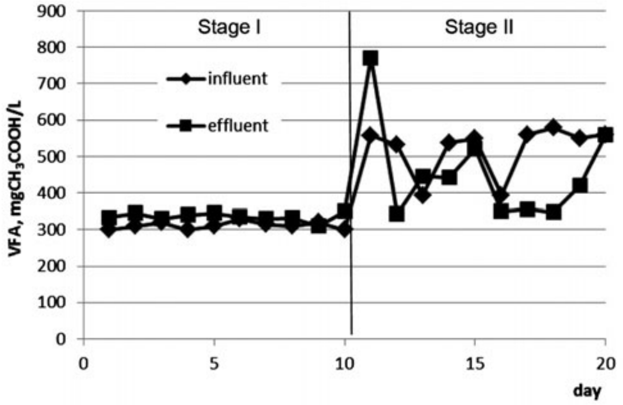

Fig. 5. VFA concentration in influent and effluent: stage I—wastewater without oil and tar removal, stage II—wastewater after oil and tar removal.

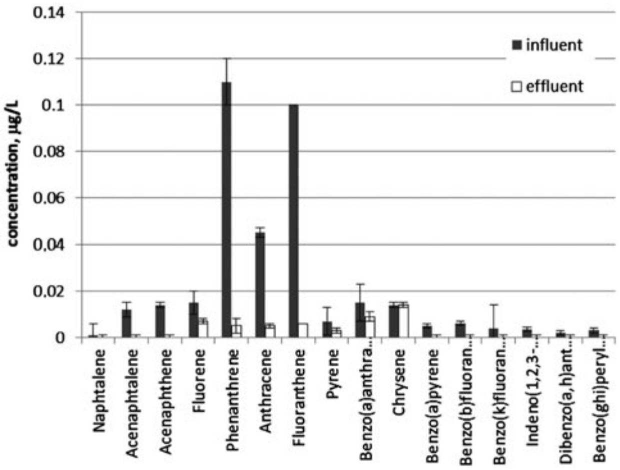

Fig. 6. Concentration changes of selected PAHs (as average concentration) during methane digestion of coking wastewater (stage I).

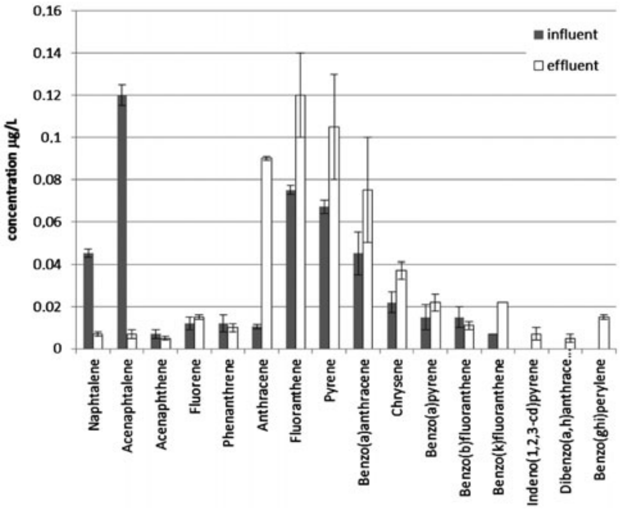

Fig. 7. Concentration changes of selected PAHs (as average concentration) during methane digestion of coking wastewater (stage II).

Lower molecular weight PAHs were probably degraded under conditions of anaerobic digestion; however, further studies on the mechanisms of this process are necessary, especially the explanation if biological, chemical or physical processes are of highest importance. There was no high correlation observed between concentration of PAHs in effluent and both K_{ow} coefficient and water solubility of individual PAHs. PAHs removal efficiency was enough to meet BAT emission standards; however, increases in PAHs concentration in effluent indicate that in the emergency physical or chemical processes (e.g. advanced oxidation processes) must be involved in treatment of coking wastewater.

4. Conclusions

The conclusions are as follows:

(1) Methane digestion of coke plant wastewater allowed one to remove up to 71% of COD and up to 80% of phenols.

(2) The highest concentration of PAHs in influent was equal up to 627 ng/L (the total concentration of 16 EPA-PAHs) . The highest total concentration of carcinogenic PAHs was equal up to 66 ng/L (about 10% of 16 EPA-PAHs total).

(3) Even 93% removal of the total 16 EPA-PAHs was observed during methane digestion (stage I). In the case of carcinogenic compounds, removal of about 60% was observed.

(4) Sorption/desorption processes may play an important role in PAHs removal from coking wastewater because a periodical increase in PAHs concentration in the treated effluent was observed.

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