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EFFECT OF CHEMICAL STABILISATION OF SEWAGE SLUDGE ON THE FATE OF PAHs

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Abstract: The results of investigations on PAHs concentration changes during chemical stabilisation of sewage sludge with Fenton's reagent (1 g of solid $FeSO_4 \cdot 7H_2O$ and 10 to 500 cm^3 of H_2O_2 (30%) per dm^3; for 2 hours at 20 ± 1°C) are presented. Raw and digested sewage sludge was chemically stabilised. Extraction of PAHs from the solid phase was performed using an ultrasonic method (with cyclohexane: dichloromethane mixture). To extract micropollutants from the supernatant cyclohexane: dichloromethane: methanol mixture was used). The results obtained suggest that PAH concentration changes in chemically stabilised sewage sludge are dependent not only on the chemical oxidant dose but also on the kind of sewage sludge (raw or digested) treated. However, no linear correlation was found between PAH concentrations and the dose of oxidant. A high correlation was observed between PAH concentrations in the supernatant and their water solubility.

Keywords: Polycyclic aromatic hydrocarbons; sewage sludge; Fenton's reagent

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are classified by the US Environmental Protection Agency as priority pollutants of environment due to their toxic and mutagenic properties. In the present work attention is focussed on the risk connected with the presence of these micropollutants in sewage sludge. In 2000, the European Union developed a draft working document on sludge which included limiting values for selected organic compounds, including PAHs in sewage sludge. The limit for the concentration of the sum of acenaphthene, phenenthrene, fluorene, fluoranthene, pyrene, benzo(b+j+k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene was established at 6 $mg \cdot kg_{d.m.}^{-1}$ (Working document on sludge, 2000). At present, the PAH concentrations in sewage sludge intended for agricultural application is limited only in France, Sweden and Denmark. Current French standards limit the concentration of fluoranthene (5.0 $mg \cdot kg_{d.m.}^{-1}$), benzo(b)fluoranthene (2.5 $mg \cdot kg_{d.m.}^{-1}$) and benzo(a)pyrene (2.0 $mg \cdot kg_{d.m.}^{-1}$). In Sweden and Denmark the total PAHs concentration is limited. The sum of these compounds must not exceed 3 $mg \cdot kg_{d.m.}^{-1}$ (Bernacka and Pawłowska, 2000).

Experimental data indicate that concentrations of PAHs in sewage are diversified and may reach even hundreds $mg \cdot kg_{d.m.}^{-1}$ (Stevens *at al.*, 2003; Bodzek and Janoszka, 1999). Because high concentrations of these micropollutants in sewage sludge pose a risk to the environment, a method enabling destruction or release of PAHs from this matrix is of great interest. It is well-known that PAHs can be degraded in both physico-chemical and biodegradation processes, as well as accumulated by microorganisms. Especially advanced chemical oxidation (e.g. Fenton's reagent use) is expected to be useful in PAHs degradation because of short reaction time, low costs and high effectiveness. During chemical stabilisation of sewage sludge with Fenton's reagent (mixture of Fe^{2+} salt and H_2O_2) PAHs oxidation may occur by way of very reactive hydroxyl radicals ($OH^{\bullet}$) formed by the following simplified scheme:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^{\bullet} + OH^-$$

Hydroxyl radicals can effectively react with almost all organic pollutants. Reaction rates with Fenton's reagent are limited by temperature (optimal was identified below 30°C), pH (optimal 3.0 ÷ 5.0), Fe^{2+}/H_2O_2 (selected experimentally), concentration of Cl^- and HCO_3^-, as well as the way of reagent introduction. (Barbusiński and Filipek, 2000). In sewage sludge technology, doses of Fe^{2+} and H_2O_2 used for conditioning and for stabilisation are 1 ÷ 6 g $Fe^{2+}\cdot L^{-1}$ and 0.3 ÷ 6 g $H_2O_2\cdot L^{-1}$ (Barbusiński and Filipek, 2000; Buykkamaci, 2004; Krzemieniewski *et al.*, 2003).
Investigations on the PAHs degradation by Fenton's reagent oxidation of sewage sludge are limited (Flotron *et al.*, 2003; Flotron *et al.*, 2005; Nam *et al.* 2001). The results obtained by. Flotron *et al.* (2003) indicate that Fenton's reagent did not cause desorption of the micropollutants from the solid phase. Therefore, removal of PAHs from sewage sludge should be preceded by their release from solid particles. Hydroxyl radicals rapidly react with PAHs present in the supernatant. Oxidation of PAHs adsorbed on sewage sludge was possible when high doses of H_2O_2 were used (Flotron *at al.*, 2005). The present study has been conducted to evaluate the fates of polycyclic aromatic hydrocarbons during chemical stabilisation of sewage sludge with Fenton's reagent.

MATERIALS AND METHODS

Sample collection.

Chemical stabilisation was performed using raw and digested sewage sludge. Samples of the raw sludge were collected from the primary sedimentation tank densifier of municipal sewage treatment plant in Częstochowa. Digested sludge was collected from closed digested tank (first stage of digestion, process parameters: temp. 35 ÷ 37°C, solids retention time 20 d) at the same plant. Sludge samples were homogenised before analysis and stabilisation.

Analysis of physicochemical properties of the sludge.

The following physicochemical properties of the sludge or supernatant were determined:

- total suspended solids (TSS) as dry residue obtained at 105°C,
- volatile suspended solids (VSS) as the mass of sludge volatilised from the mass of dry residue by combustion at 550°C,
- COD - using the dichromate method (Hermanowicz *at al.*, 1999),
- PAHs as described below.

Analyses were performed in triplicate on the same day as sample collection (before and after chemical treatment).

PAHs extraction from sewage sludge and supernatant.

$1\cdot10^{-4}$ kg of sewage sludge was weighed in glass 100 cm^3 Erlenmayer flasks and extracted with 25 cm^3 of cyclohexane/ dichloromethane (5:1, v/v) mixture. The extraction was conducted at 20°C in an ultrasonic bath (20 kHz) for 40 min. Supernatant (0.5 L) was extracted with 125 cm^3 of methanol, 6 cm^3 of dichloromethane and 30 cm^3 of cyclohexane. Additionally methanol was used as the agent for desorption of PAHs from solid particles present in supernatant (as recommended by the Polish standard on PAHs analysis in water with thin-layer chromatography). Extraction solvents were chosen based on earlier experiments). The extracts obtained were evaporated under a nitrogen stream to 2 cm^3 and than purified on silica gel columns. The columns were conditioned with 4 × 3 cm^3 of cyclohexane/ dichloromethane mixture (1:5 v/v). The collected leachate was concentrated to 2 cm^3 under a nitrogen stream.
All chemicals were of GC grade. The samples were extracted in triplicate. Purified extracts were analysed for 16 EPA-PAHs by gas chromatography-mass spectrometry (Fisons GC 8000/MS 8000). Gas chromatographic separation was performed on a DB-5 column (30 m length, 0.25 mm diameter and 1 μm film). Helium was used as a carrier gas. The flow rate was 0.5 $mL\cdot min^{-1}$. The oven was kept at 40 °C for 1 min., heated with 5 °C for 1 min. to 120 °C and finally temperature 280°C was held for 60 min. Detection limits and recovery data for PAHs are listed in Table 1.

Table 1 Recovery and detection limit data for matrices analysed in the experiment

Compound	Retention time [min]	Recovery [%]		Detection limits [$\mu g \cdot L^{-1}$]
		Sewage sludge	Supernatant	
Naphthalene	9.95	28.3	35.8	0.14
Acenaphtalene	16.72	52.5	60.2	0.31
Acenaphthene	17.60	31.2	40.5	0.43
Fluorene	20.09	43.5	45.5	0.46
Phenanthrene	25.00	23.5	35.4	0.59
Anthracene	25.23	40.4	48.8	0.54
Fluoranthene	31.46	62.5	70.2	0.30
Pyrene	32.46	60.2	75.5	0.22
Benzo(a)anthracene	39.89	62.4	68.4	0.28
Chrysene	40.24	45.6	60.0	0.28
Benzo(a)pyrene	56.60	55.5	65.5	0.21
Benzo(b)fluoranthene	51.77	46.6	54.2	0.28
Benzo(k)fluoranthene	52.07	40.6	52.4	0.27
Indeno(1,2,3-cd)pyrene	80.89	42.1	58.5	0.24
Dibenzo(a,h)anthracene	81.90	51.3	67.5	0.22
Benzo(ghi)perylene	88.10	52.2	75.5	0.20

Chemical stabilisation of sewage sludge.

Sewage sludge samples of 1 dm^3 were placed in 2 – dm^3 glass reactors and chemically stabilised with 1 g of solid $FeSO_4 \cdot 7H_2O$ and 10 to 500 cm^3 of H_2O_2 (30%) per dm^3. Stabilisation lasted for 2 hours at room temperature (20 ± 1°C). During stabilisation the samples stirred continuously using a magnetic stirrer (500 $rev \cdot min^{-1}$).

RESULTS AND DISCUSSION

Before chemical stabilisation all 16 PAHs analysed were present both in raw and digested sewage sludge - Figure 1.

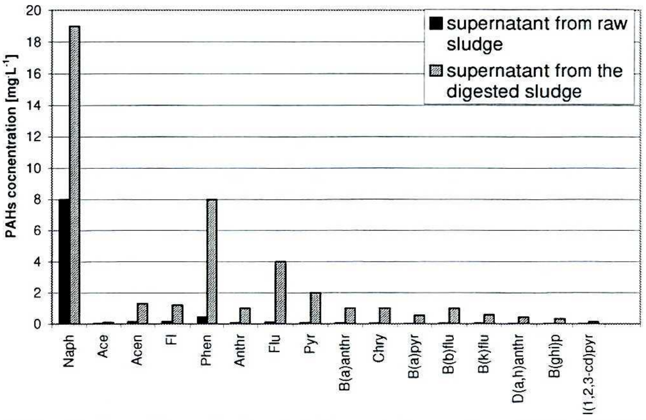

Fig. 1 Individual PAHs concentration in the solid phase of the sludge before chemical stabilisation with Fenton's reagent

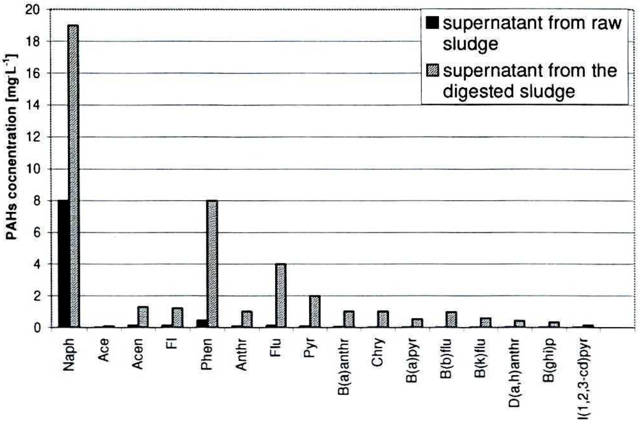

Fig. 2 Individual PAHs concentration in the supernatants before chemical stabilisation with Fenton's reagent

The most abundant compounds in the raw sludge were naphthalene and phenanthrene. In the digested sludge the most abundant were naphthalene and fluoranthene. The least abundant compound both in raw and digested sludge was acenaphtylene. The total concentration of PAHs before stabilisation was 17 and 56 mg$\cdot$kg$_{d.m.}$$^{-1}$ for raw and digested sludge, respectively.

In the supernatants separated from the raw sludge the total PAHs concentration was also lower than in those separated from the digested sludge and was 9 mg/dm^3. In supernatant separated from the digested sludge it was 41 mg/dm^3. Similarly to the sludge, in supernatants the most abundant compound was naphthalene - Figure 2.

In the raw sludge, the percentage content of PAHs based on the ring number was as follows: 2-ring compounds 36%; 3-ring compounds 34%, 4-ring compounds: 17%; 5-ring compounds 11%; 6-ring compounds1 %. In the supernatant separated from the raw sludge content of PAH groups was: 2-ring compounds 87%; 3-ring compounds 9%, 4-ring compounds: 2.7%; 5-ring compounds 0.6%; 6-ring compounds 0.7%. Clearly, in both the solid phase and supernatant 2- and 3-ring compounds were the most abundant. In the sludge higher contents of 4- and 5-ring compounds were observed compared to the supernatant. In the case of the solid phase of digested sludge the ranking was as follows: 2-ring compounds 52%; 3-ring compounds 13%, 4-ring compounds: 26%; 5-ring compounds 7%; 6-ring compounds 12 %. In supernatant separated from the digested sludge: 2-ring compounds 45%; 3-ring compounds 28%, 4-ring compounds: 19%; 5-ring compounds 6%; 6-ring compounds 2 %. In solid phase of the raw sludge the concentration of 2- and 3-ring compounds (about 65%) was similar to that observed in the digested sludge (about 70%), however a slightly higher concentration of naphthalene was noted in the digested sludge. Compared to the raw sludge, the digested one showed a high concentration of 6-ring compounds.

The sum of the concentrations of acenaphtene, phenanthrene, fluorene, fluoranthene, pyrene, benzo(b+k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene in samples of raw and digested sludge exceeded 6 mg$\cdot$kg$_{d.m.}$$^{-1}$ – the maximum value of the mentioned PAHs concentration in sewage sludge set by the European Union Draft Directive (Working document on sludge, 2000).

A good correlation (based on the correlation coefficient) between the content of individual PAH compounds in supernatants and their water solubility was found. Medium correlations were obtained between PAHs concentration in the supernatant and log K_{ow} values - Table 2. Similar results were observed for the solid phase of the sludge - Table 3. High correlation between water solubility and concentration of individual compounds in the supernatant was observed before stabilisation for both raw and digested sludge.

During chemical stabilization of the sewage sludge a decrease of the TSS and VSS content was observed both in raw and digested sewage sludge. In the raw sludge before stabilization the TSS content was 24 g/dm^3, VSS content was 15 g/dm^3 (62%). In the digested sludge the concentration of TSS was lower than in the digested one and was 15 g/dm^3 (VSS equal to 7 g/dm^3). After chemical treatment, the TSS in the raw sludge decreased as the dose of H_2O_2 increased – Figure 3. A similar effect was observed in the case of the digested sludge- Figure 3.

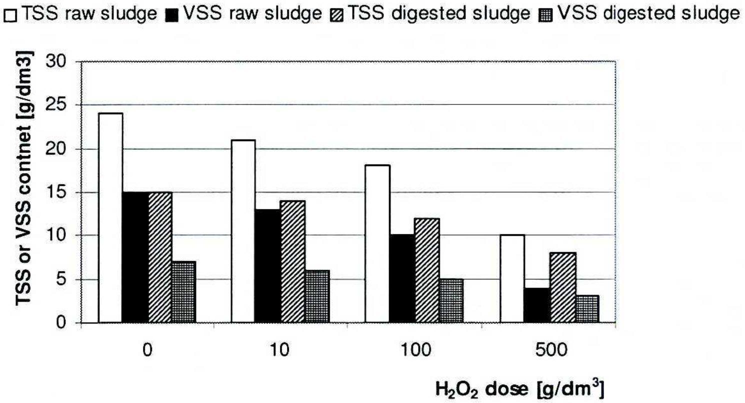

Fig. 3 TSS and VSS content changes in sewage sludge stabilised with various doses of Fenton's reagent

Table 2. Correlation between individual PAHs content in the supernatant and their water solubility or log K_{ow} (H – high correlation: correlation coefficient r > ± 0.7, M – medium correlation: correlation coefficient 0.4 < r ≤ 0.7)

Parameter	Before chemical stabilisation		After chemical stabilisation					
			raw			digested		
	Raw sludge	Digested sludge	1 g $FeSO_4 \cdot 7H_2O$ and 10 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 100 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 500 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 10 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 100 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 500 g H_2O_2
Log K_{ow}	r = -0.47 (M)	r = -0.54 (M)	r = -0.46 (M)	r = -0.46 (M)	r = -0.46 (M)	r = -0.49 (M)	r = -0.54 (M)	r = -0.46 (M)
solubility in water	r = 0.88 (H)	r = 0.77 (H)	r = 0.88 (H)	r = 0.88 (H)	r = 0.87 (H)	r = 0.86 (H)	r = 0.98 (H)	r = 0.87 (H)

Changes in the COD of supernatant were also observed during chemical stabilization of the sludge (data not shown). COD values increased up to 6450 mg O_2/dm^3 though no linear correlation was found between H_2O_2 dose and COD value of supernatants either for raw and or digested sludge.

The fates of PAHs in the solid phase during chemical stabilisation depended on the nature of the sludge. In the raw sludge an increase of PAHs concentration was observed in solid phase. The concentrations of these micropollutants increased as the dose of Fenton's reagent was increased (up to 62 mg·kg$_{d.m.}^{-1}$ in the sludge treated with 1 g $FeSO_4 \cdot 7H_2O$ and 500 g H_2O_2) - Table 3. The most abundant compound in the raw sludge treated with Fenton's reagent was naphthalene. Treatment of sewage sludge with 1 g $FeSO_4 \cdot 7H_2O$ and 100 g H_2O_2 significantly decreased concentration of 6 ring PAHs (indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene) as well as the 5 ring compound dibenzo(a,h)anthracene) in the solid phase.

Table 3 Correlation between individual PAHs content in the solid phase and their water solubility or log K_{ow} (H – high correlation, M – medium correlation)

	Before chemical stabilisation		Over chemical stabilisation					
			raw			digested		
Parameter	Raw sludge	Digested sludge	1 g $FeSO_4 \cdot 7H_2O$ and 10 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 100 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 500 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 10 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 100 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 500 g H_2O_2
Log K_{ow}	r = -0.47 (M)	r = -0.49 (M)	r = -0.46 (M)	r = -0.49 (M)	r = -0.46 (M)	r = -0.49 (M)	r = -0.43 (M)	r = -0.46 (M)
solubility in water	r = 0.68 (M)	r = 0.83 (H)	r = 0.87 (H)	r = 0.92 (H)	r = 0.87 (H)	r = 0.86 (H)	r = 0.86 (H)	r = 0.87 (H)

The most probable reason for the 5- and 6- ring PAHs concentration decrease was oxidation of these compounds with $OH^{\bullet}$ according to the formula proposed by Flotron *at al.* (Flotron *at al.*, 2003):

$$PAH + OH^{\bullet} \rightarrow PAH_{oxidised}$$

However in the case of 1 g $FeSO_4 \cdot 7H_2O$ and 100 g H_2O_2 no decrease of 5- and 6- ring compounds was observed. It confirms the idea of Flotron *at al.* that Fenton's experiments on PAHs often show low repeatability, especially in the solid phase of the sludge. According to these authors it is connected with the fact that Fenton's reagent has no influence on the desorption of PAHs from the sludge, but is effective in oxidation of desorbed compounds (Flotron *at al.* 2003). Therefore effective oxidation of PAHs in sewage sludge requires to steps: desorption of PAHs from the solid phase (as the first step) and then rapid oxidation with $OH^{\bullet}$ (Flotron *at al.* 2003).

During chemical stabilisation of digested sewage sludge there was also no observed correlation between Fenton's reagent dose and PAHs fates - Table 3. Decrease of total PAHs concentration in solid phase was observed when 10 and 100 g H_2O_2/dm^3 was applied. As the dose of hydrogen peroxide was increased to 500 g H_2O_2/dm^3 an increase in the total PAHs concentration in the solid phase was obtained. As well as before chemical stabilisation the most abundant compound in all samples was naphthalene.

After chemical stabilisation of the raw sludge an increase of the total PAH concentration in supernatant was observed - Table 4.

The concentration of total PAHs in supernatant increased as the dose of H_2O_2 increased. During stabilisation of digested sewage sludge the total PAHs concentration in supernatants from samples treated with 10 and 100 g/dm^3 of H_2O_2 decreased. In the sample treated with 500 g/dm^3 no significant changes of PAHs concentration was observed. The most abundant compound in all supernatants was naphthalene.

Chemical stabilisation of the raw sewage sludge with 1 g of Fe^{2+} and 100 cm^3 of H_2O_2 significantly decreased dibenzo(a,h)anthracene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene in supernatant. The same effect was observed in the solid phase of the sludge. The results of the experiment indicate that oxidation of PAHs in sewage sludge requires rather higher doses of strong oxidants to remove the compounds from the supernatant; however these doses of oxidant are not always suitable for desorption of PAHs from the solid matrix.

Table 4. PAHs concentration in raw and digested sewage sludge after chemical stabilisation

PAH	PAHs concentration, $mg \cdot kg_{d.m.}^{-1}$					
	Raw sludge stabilised with:			Digested sludge stabilised with		
	1 g $FeSO_4 \cdot 7H_2O$ and 10 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 100 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 500 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 10 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 100 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 500 g H_2O_2
Naph	13.9 ± 1.0	20.5 ± 2.3	53.5 ± 14.3	29.51 ± 3.2	7.99± 0.64	56.58 ± 8.79
Ace	0.03 ± 0.01	1.9 ± 2.6	0.04 ± 0.02	0.03 ± 0.01	0.01 ± 0.01	0.02 ± 0.01
Acen	0.22 ± 0.02	0.22 ± 0.01	0.36 ± 0.027	0.52 ± 0.06	0.09 ± 0.04	0.23 ± 0.15
Fl	0.13 ± 0.01	0.22 ± 0.03	0.57 ± 0.35	0.55 ± 0.06	0.08 ± 0.02	0.35 ± 0.25
Anthr	0.11 ± 0.01	0.10 ± 0.01	0.43 ± 0.20	0.63± 0.05	0.08 ± 0.01	0.35 ± 0.29
Phen	0.63 ± 0.09	0.78 ± 0.17	3.5 ± 1.9	5.31 ± 0.02	0.86 ± 0.12	3.19 ± 2.7
Flu	0.13 ± 0.02	0.21 ± 0.12	1.04 ± 1.17	1.16 ± 0.39	0.45 ± 0.33	1.44 ± 1.28
Pyr	0.07 ± 0.03	0.22 ± 0.04	0.81 ± 0.15	0.61 ± 0.17	0.23 ± 0.17	0.52 ± 0.42
B(a)anthr	0.04 ± 0.01	0.13 ± 0.10	0.48 ± 0.11	0.34 ± 0.09	0.03 ± 0.02	1.06 ± 0.52
Chry	0.02 ± 0.01	0.05 ± 0.01	0.29 ± 0.05	0.37 ± 0.25	0.23 ± 0.14	0.41 ± 0.29
B(b)flu	0.03 ± 0.01	0.03 ± 0.01	0.25 ± 0.16	0.29 ± 0.06	0.28 ± 0.21	0.57 ± 0.47
B(k)flu	0.03 ± 0.01	0.05 ± 0.04	0.25 ± 0.02	0.15 ± 0.02	0.16 ± 0.14	0.35 ± 0.29
B(a)pyr	0.02 ± 0.01	0.09 ± 0.04	0.14 ± 0.02	0.08 ± 0.04	0.16 ± 0.12	0.29 ± 0.26
D(a,h)anthr	0.02 ± 0.01	b.d.l.1)	0.21 ± 0.19	0.14 ± 0.03	0.61 ± 0.42	0.32 ± 0.25
B(g,h,i)p	0.02 ± 0.01	b.d.l.1)	0.13 ± 0.02	0.06 ± 0.01	0.15 ± 0.11	0.23 ± 0.14
I(1,2,3-cd)pyr	0.02 ± 0.01	b.d.l.1)	0.17 ± 0.01	0.14 ± 0.03	0.25 ± 0.21	0.17 ± 0.06
Σ PAHs	15.42	24.50	62.17	39.89	11.66	66.08

1) b.d.l. - below detection limit

Table 5 PAHs concentration in supernatant separated from raw and digested sewage sludge after chemical stabilisation

PAH	PAHs concentration, $mg \cdot L^{-1}$					
	Raw sludge stabilised with:			Digested sludge stabilised with		
	1 g $FeSO_4 \cdot 7H_2O$ and 10 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 100 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 500 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 10 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 100 g H_2O_2	1 g $FeSO_4 \cdot 7H_2O$ and 500 g H_2O_2
Naph	9.20 ± 0.69	13.00 ± 1.00	35.00 ± 9.00	19.00 ± 2.0	5.00 ± 0.43	37.72 ±12.00
Ace	0.02 ± 0.01	0.02 ± 0.00	0.03 ± 0.01	0.02 ± 0.01	b.d.l.$^{1)}$	0.02 ± 0.00
Acen	0.14 ± 0.01	0.15 ± 0.00	0.24 ± 0.18	0.35 ± 0.04	0.07 ± 0.03	0.15 ± 0.01
Fl	0.09 ± 0.00	0.15 ± 0.02	0.38 ± 0.24	0.36 ± 0.04	0.06 ± 0.01	0.23 ± 0.10
Anthr	0.07 ± 0.01	0.07 ± 0.00	0,29 ± 0,13	0.42 ± 0.04	0.05 ± 0.00	0.24 ± 0.10
Phen	0.42 ± 0.06	0.52 ± 0.11	2.34 ± 1.32	3.00 ± 0.02	0.57 ± 0.07	2.13 ± 0.00
Flu	0.08 ± 0.01	0.14 ± 0.08	0.93 ± 0.45	0.78 ± 0.26	0.30 ± 0.22	0.96 ± 0.80
Pyr	0.05± 0.02	0.14 ± 0.02	0.37 ± 0.14	0.40± 0.11	0.15 ± 0.11	0.35 ± 0.30
B(a)anthr	0.03 ± 0.00	0.08 ± 0.07	0.30± 0.11	0.23 ± 0.06	0.24 ± 0.21	0.70± 0.30
Chry	0.02 ± 0.00	0.03 ± 0.01	0.13 ± 0.05	0.24 ± 0.17	0.15 ± 0.17	0.27 ± 0.20
B(b)flu	0.02 ± 0.01	0.04 ± 0.02	0.21 ± 0.05	0.19 ± 0.04	0.19 ± 0.19	0.38 ± 0.30
B(k)flu	0.02 ± 0.00	0.03 ± 0.02	0.13 ± 0.05	0.10 ± 0.02	0.11 ± 0.11	0.24 ± 0.20
B(a)pyr	0.01 ± 0.00	0.05 ± 0.04	0.07 ± 0.02	0.05 ± 0.03	0.10 ± 0.10	0.19 ± 0.10
D(a,h)anthr	0.02 ± 0.00	b.d.l.	0.19 ± 0.06	0.10 ± 0.02	0.41 ± 0.52	0.22 ± 0.20
B(g,h,i)p	0.01 ± 0.00	b.d.l.	0.08± 0.02	0.04 ± 0.00	0.10 ± 0.11	0.16 ± 0.09
I(1,2,3-cd)pyr	0.02 ± 0.00	b.d.l.	0.11 ± 0.01	0.09 ± 0.02	0.17 ± 0.11	0.11 ± 0.01
Σ PAHs	10.24	14.42	40.80	25.82	7.67	44.07

CONCLUSIONS

The results obtained in the study suggest that fates of PAHs during chemical stabilisation of sewage sludge are dependent not only on chemical oxidant dose but also on the nature of the sludge. No linear correlation was found between the concentration of PAHs and the doses of oxidants. A good correlation was observed between the concentration of PAHs in the supernatant and their water solubility. Further studies on the mechanisms of this process are required.

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REFERENCES

[1] Barbusiński K., Filipek K. 2000. Aerobic Sludge Digestion in the Presence of Chemical Oxidising Agents. Part II. Fenton's Reagent. *Polish Journal of Environmental Studies* **9**(3): 145 - 149.

[2] Bernacka J., Pawłowska L. 2000. Potentially toxic substances in sludges from municipal treatment plants, Dział Wydawnictw IOŚ, Warszawa (in Polish).

[3] Bodzek D., Janoszka B. 1999. Comparison of Polycyclic Aromatic Hydrocarbons and Heavy Metals Contents in Sewage Sludge from Industrialised and Non-Industrialised Region. *Water, Air and Soil Pollution* **111**, 359 - 369.

[4] Buyukkamaci N. 2004. Biological Sludge Conditioning by Fenton's Reagent. *Process Biochemistry*. **39**, 1503 - 1506.

[5] Flotron V., Delteil C., Bermond A., Camel V. 2003. Remediation of Matrices Contaminated by Polycyclic Aromatic Hydrocarbons: Use of Fenton's Reagent. *Polycyclic Aromatic Compounds*. **23**, 353 -376.

[6] Flotron V., Delteil C., Bermond A., Camel V. 2005. Removal of Sorbed Polycyclic Aromatic Hydrocarbons from Soil, Sludge and Sediment Samples Using the Fenton's Reagent Process. *Chemosphere*. **59**(10),1427 - 1437.

[7] Hermanowicz W., Dojlido J., Dożańska W., Koziorowski B. Zerbe J., 1999. Physicochemical Characteristic of Water and Wastewater, Arkady, Warsaw (in Polish). 555pp.

[8] Krzemieniewski M., Janczukowicz W., Pesta J. Dębowski M., 2003. Effect of Fenton's Reagent and Phenomena Connected with Current Effect on Sewage Sludge Conditioning. *In* Proceedings of the Conference: Complex and Detailed Problems of Environmental Engineering, Koszalin, 195 -213 (in Polish).

[9] Nam K., Rodrigues W., Kukor J. 2001. Enhanced degradation of polycyclic aromatic hydrocarbons by biodegradation combined with modified Fenton reaction. *Chemosphere*. **45**(1),11 – 20.

[10] Stevens J.L., Northcott G.L., Stern G.A., Tomy G.T., Jones K.C., 2003. PAHs, PCBs, PCNs, Organochlorine pesticides, Synthetic Musks and Polychlorinated n-Alkanes in U.K. Sewage Sludge: Survey Results and Implications. *Environmental Science & Technology*. **37**, 462-467.

[11] Working Document on Sludge. 3rd Draft. EU Commission, Brussels, 27 April, 2000.

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