# Leaching of Organic and Inorganic Micropollutants from Chemically Stabilized Sewage Sludge—OFMSW Mixtures*

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Chemical oxidation of organic matrices is a promising alternative to biochemical and physical methods of waste treatment. In our study peroxyacetic acid and Fenton's reagent were used to oxidize mixture of sewage sludge and organic fraction of municipal solid waste (OFMSW). Before chemical stabilization the mixture was digested for 3 d at 37 °C. Chemical stabilization with $CH_3COOOH$, $H_2O_2$, and $FeSO_4 \cdot 7H_2O$ was performed in 1 $dm^3$ glass reactors for 24 to 72 h. Environmental effect of stabilized mixtures was evaluated using elution test according to the procedure given in PN-Z-15009/1997. In eluates selected organic (16 polycyclic aromatic hydrocarbons – PAHs) and inorganic (heavy metals) micropollutants were analyzed.
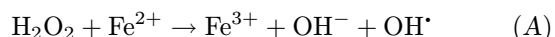
The most abundant congeners in supernatant were naphthalene (average concentration 2.84 $\mu$g $dm^{-3}$), chrysene (2.39 $\mu$g $dm^{-3}$), and benzo($b+k$)fluoranthene (4.54 $\mu$g $dm^{-3}$). The less abundant ones were acenaphthylene and acenaphthene. In water extracts the most abundant hydrocarbons were also naphthalene and selected 5- and 6-ring compounds. There was no correlation between individual PAH concentration and log $K_{ow}$ value. Individual PAHs concentration in eluted solution was lower than the corresponding solubilities of PAHs in water. Total concentration of heavy metals (Hg, Cu, Fe, Pb, Cd, Zn, Ni, Mn, Cr) reached 1900 $\mu$g $dm^{-3}$. The most abundant pollutants were Fe, Zn, and Mn. The lowest concentration was observed for Hg. Heavy metals concentration in the eluted solution was lower than level usually observed in landfill leachates.

The results of the tests indicate that peroxyacetic acid and Fenton's reagent chemical stabilization by-products should not be disposed on the landfills without further utilization; chemical stabilization is, however, the right way of the organic matter stabilization.

Strong oxidants (*e.g.* Fenton's reagent, peroxyacetic acid, $H_2O_2$) can be used to improve oxidation of volatile solids and dewatering of sewage sludge [1—4]. Chemical stabilization of organic matrices using selected oxidants has been performed both in laboratory ($H_2O_2$, Fenton's process, peroxyacetic acid) and on technical scale (SAPHYR$^{TM}$ Process) [1—5]. During SAPHYR process nitrites are used as oxidants for sewage sludge stabilization. The process is performed in acidic environment. At present two wastewater treatment plants worldwide use this process for sludge stabilization [5].

It was found that the use of such chemical agents might shorten the time of waste stabilization in comparison to conventional methods like anaerobic or aerobic digestion and composting. *Barbusiński* and *Filipek* [1, 3] have proved that chemical stabilization of excess activated sludge with Fenton's reagent reduced the content of volatile organic solids (VSS) by at least 38 % over 10 days [1]. *Flotron et al.* [6] observed that Fenton's reagent had no effect on the desorption of organic micropollutants from sewage sludge. The authors assumed that the hydroxyl radicals (OH$^\bullet$) formed in the Fenton reaction

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad (A)$$

oxidized only desorbed organic micropollutants.

Release of heavy metals from sewage sludge during treatment with Fenton's reagent is strongly dependent on the pH. Meanwhile, in acid environment heavy metals are released from the sludge, addition of basic agents, *e.g.* $Ca(OH)_2$, causes precipitation of some metals [7].

Due to the physicochemical diversity of the sludge, the results of the investigations on fates of organic and inorganic micropollutants during treatment of sewage sludge with chemical oxidants exhibit low repeatabil-

ity. Despite of this, careful evaluation of the effect of chemical oxidants on micropollutants fates is very important. Importance of investigations of micropollutants fates during chemical stabilization is mainly connected with toxicological properties of these compounds. They may disrupt biochemical processes in living organisms at very low concentrations (even less than $10^{-3} \mu g \ dm^{-3}$). For example, 4-, 5-, and 6-ring polycyclic aromatic hydrocarbons (PAHs) show carcinogenic and mutagenic properties. When stabilized sludge or municipal waste is amended with soil there is a danger that plants cultivation will transfer PAHs into the food chain [8].

In this study peroxyacetic acid and Fenton's reagent were used to oxidize co-fermented sewage sludge—OFMSW mixtures. Polycyclic aromatic hydrocarbons (PAHs) and heavy metals release from chemically stabilized matrix was studied.

## EXPERIMENTAL

Samples of the sludge were collected from the primary sedimentation tank and excess sludge densifier of a municipal sewage treatment plant. Samples of sludge were homogenized and mixed in a ratio 1 : 1 to obtain feed sludge for co-fermentation. Digested sludge was used as inoculum.

Physicochemical properties of sludge samples were estimated as follows. pH value was measured by a potentiometer (Microcomputer pH-meter CP-551, Elmetron). Total suspended solids (TSS) value was obtained as a residue after drying the waste sample at 105 °C to a constant weight. The amount of volatile suspended solids (VSS) corresponded to the mass of sludge burned at 550 °C parting from the dry residue. Volatile fatty acids (VFA) portion was deduced from the results of direct sludge distillation [9]. Analyses of the sludge composition and properties were performed on the day of sample collecting.

Composition of organic fraction of municipal solid waste (OFMSW) was based on the waste audit [10]. It was a mixture, which consisted of 55 % of potato starch, 35 % of food waste, 5 % of bread, and 5 % of others. Preferably, ready-made samples were used in this study. Remaining components were dried at 105 °C and then ground using a disc mill (MK-1, Zelmer). Prepared mixture of OFMSW was blended with distilled water to get a mixture comprising 60 % of TSS.

Feed sludge (6.1 dm³) was mixed with OFMSW (0.32 kg) and inoculum (1.6 dm³). Co-fermentation was conducted in a duplicate 10 dm³ flasks stirred manually once a day. The flasks were placed in the thermostat at a temperature of $(37 \pm 1)$ °C for 2 days.

Co-fermented sewage sludge—OFMSW mixtures were transferred into 1 dm³ glass reactors. The mixtures were chemically stabilized with peroxyacetic acid (15 vol. %, technical grade), $H_2O_2$ (30 vol. %), and

**Table 1.** Dosage of Reagents Added to the Co-Fermented Sewage Sludge—OFMSW Mixtures

| Reagent dose/(g $g_{d.m.}^{-1}$) | | |
|---|---|---|
| Peracetic acid | $H_2O_2$ | $FeSO_4 \cdot 7H_2O$ |
| 0.04 | 0.25 | 0.20 |

solid $FeSO_4 \cdot 7H_2O$. Doses of oxidants introduced into the reactors are listed in Table 1. Stabilization lasted for 24 h.

Chemically stabilized sewage sludge—OFMSW mixtures were centrifuged, transferred into 500 cm³ Erlenmeyer flasks, and diluted with distilled water (at a ratio of 1 : 10 by mass). These mixtures were shaken for 4 h using a shaker with horizontal motion (WU-4, Premed). After sedimentation for 16 h the mixtures were shaken for another 4 h. After sedimentation for 2 h the supernatant (water extract No. 1) was centrifuged and decanted. From supernatant, water extract No. 1 was obtained by filtration. The filtrate was stored in glass flasks for the further investigation. Solid phase was mixed with another portion of distilled water and the extraction procedure was repeated to obtain water extract No. 2. Water extract preparation was carried out according to the standard method [11].

In water extracts PAHs and heavy metals concentrations were analyzed. Moreover, content of these micropollutants was simultaneously analyzed in supernatant obtained after centrifugation of chemically stabilized sewage sludge—OFMSW mixture. Content of heavy metals (Hg, Cu, Fe, Pb, Cd, Zn, Ni, Mn, Cr) was measured using atomic spectrometric method according to Polish standard methods: PN-ISO8288: 2002 and SM-EN 1233: 2000 [12, 13]. Samples were mineralized using nitric acid solution. The mineralized samples were analyzed by atomic spectrometer Nova 400 (Analytik, Jena).

The amount of individual PAHs was estimated as follows. 0.5 dm³ of water extract or supernatant was extracted with 125 cm³ of methanol, 6 cm³ of dichloromethane, and 30 cm³ of cyclohexane. After the extraction, the samples were centrifuged. Supernatant was evaporated under nitrogen stream to 2 cm³ and purified in silica gel columns. The columns were conditioned in four cycles using each time 3 cm³ of cyclohexane—dichloromethane mixture ($\varphi_r = 1 : 5$). Collected leachate was concentrated to 2 cm³. All chemicals were of GC grade. The samples were extracted in triplicate. Purified extracts were analyzed for 16 EPA-PAHs by GC-MS (Fisons GC 8000/MS 8000). Gas chromatographic separation was performed using a DB-5 column (30 m length, 0.25 mm diameter, and 1 $\mu$m film) with He as a carrier gas. Carrier flow rate of 0.5 cm³ min⁻¹ was used during all experi-

**Table 2.** Recovery Data for PAHs Analysis in Supernatants

|  | Recovery/% | RSD[a]/% |
|---|---|---|
| Naphthalene | 21 | 3 |
| Acenaphthylene | 21 | 1 |
| Acenaphthene | 40 | 2 |
| Fluorene | 46 | 1 |
| Phenanthrene | 45 | 5 |
| Anthracene | 41 | 2 |
| Fluoranthene | 40 | 1 |
| Pyrene | 38 | 3 |
| Benzo($a$)anthracene | 43 | 2 |
| Chrysene | 45 | 3 |
| Benzo($a$)pyrene | 44 | 5 |
| Benzo($b$)fluoranthene | 45 | 4 |
| Benzo($k$)fluoranthene | 43 | 3 |
| Dibenzo($a,h$)anthracene | 41 | 1 |
| Benzo($ghi$)perylene | 40 | 2 |
| Indeno(1,2,3-$cd$)pyrene | 39 | 3 |
| Total PAHs | 44 | 4 |

a) RSD – relative standard deviation.

ments. Oven temperature of 40 °C was kept for 1 min, then the ramp started with the heating rate of 5 °C min$^{-1}$ up to a temperature of 120 °C. Finally, temperature of 280 °C was held for 60 min. The averaged PAHs recoveries ranged for water phases from 21 % to 46 % (Table 2).

In order to characterize environmental effect of the stabilized mixtures, toxicity of eluted solution was evaluated using Algaltoxkit F$^{TM}$ (*Selenastrum capricornutum*, 72 h acute), Ostracodtoxkit F (*Heterocypris incongruens,* 144 h chronic), Protoxkit F$^{TM}$ (*Tetrahymena thermophila*, 24 h acute) tests and the acute toxicity test with *Lebistes reticulatus* (96 h), as well. Toxicological tests were conducted according to the standard operational procedures and PN-90/C-04610/04 [14—17].

## RESULTS AND DISCUSSION

PAHs concentrations in water extract No. 1 and No. 2 as well as in supernatant are presented in Table 3. In supernatant separated from chemically stabilized sewage sludge—OFMSW mixture, the total PAHs concentration (20.35 $\mu$g dm$^{-3}$) was over 20 times higher than that measured in water extracts. The most abundant PAHs in supernatant were naphthalene (2.84 ± 2.77) $\mu$g dm$^{-3}$ and chrysene (2.39 ± 2.31) $\mu$g dm$^{-3}$. High concentration of 5-ring compounds – benzo($a$)pyrene and dibenzo($a,h$)anthracene was also observed. The less abundant PAHs were acenaphthene and acenaphthylene. Domination of PAHs with log $K_{ow}$ (from 5.91 to 7.6) was stated, however, correlation between individual PAHs concentration and log $K_{ow}$ value was low (log $K_{ow}$ estimates the log of octanol-water partition coefficient).

In water extract No. 1 the most abundant compounds were naphthalene and indeno(1,2,3-$cd$)pyrene. In water extract No. 2 the most abundant ones were 5- and 6-ring compounds. Like in supernatant only low correlation between individual PAHs and log $K_{ow}$ was observed in water extract No. 1. In the extract No. 2 moderate correlation was stated.

In water extracts concentrations of all analyzed PAHs were lower than their water solubility. In supernatant, concentration of some compounds (chrysene, benzo($b$)fluoranthene, benzo($k$)fluoranthene, benzo-

**Table 3.** PAHs Concentrations in Water Extracts from Chemically Stabilized Co-Fermented Sewage Sludge—OFMSW Mixtures Compared to these Micropollutants Content in Supernatant

| PAH concentration, $c/(\mu$g dm$^{-3}$) ± RSD[a] | Kind of matrix | | |
|---|---|---|---|
|  | Supernatant | Water extract No. 1 | Water extract No. 2 |
| Naphthalene | 2.84 ± 2.77 | 0.07 ± 0.01 | 0.07 ± 0.02 |
| Acenaphthylene | 0.03 ± 0.00 | 0.03 ± 0.00 | 0.03 ± 0.00 |
| Acenaphthene | 0.01 ± 0.01 | 0.01 ± 0.01 | 0.01 ± 0.01 |
| Fluorene | 0.07 ± 0.06 | 0.01 ± 0.01 | 0.01 ± 0.01 |
| Phenanthrene | 0.2 ± 0.18 | 0.01 ± 0.01 | 0.01 ± 0.01 |
| Anthracene | 0.49 ± 0.47 | 0.03 ± 0.01 | 0.02 ± 0.01 |
| Fluoranthene | 0.91 ± 0.87 | 0.02 ± 0.00 | 0.04 ± 0.02 |
| Pyrene | 0.40 ± 0.36 | 0.02 ± 0.00 | 0.04 ± 0.02 |
| Benzo($a$)anthracene | 0.96 ± 0.92 | 0.02 ± 0.01 | 0.05 ± 0.03 |
| Chrysene | 2.39 ± 2.31 | 0.03 ± 0.01 | 0.06 ± 0.04 |
| Benzo($a$)pyrene | 1.05 ± 0.79 | 0.02 ± 0.01 | 0.12 ± 0.03 |
| Benzo($b$)fluoranthene | 2.24 ± 2.18 | 0.04 ± 0.01 | 0.07 ± 0.04 |
| Benzo($k$)fluoranthene | 2.30 ± 2.24 | 0.03 ± 0.01 | 0.07 ± 0.04 |
| Dibenzo($a,h$)anthracene | 2.11 ± 2.05 | 0.04 ± 0.02 | 0.09 ± 0.05 |
| Benzo($ghi$)perylene | 2.27 ± 2.21 | 0.05 ± 0.02 | 0.16 ± 0.01 |
| Indeno(1,2,3-$cd$)pyrene | 2.08 ± 2.02 | 0.06 ± 0.03 | 0.10 ± 0.06 |
| Total PAHs | 20.35 | 0.49 | 0.95 |

a) RSD – relative standard deviation.

**Table 4.** PAHs Concentrations in Landfill Leachates

| PAH concentration, $c/(\mu g\ dm^{-3})$ | Ref. | | |
|---|---|---|---|
| | [18] | [19] | [20] |
| Naphthalene | 90.85 | n.d.[a]—0.708 | n.d.—2.70 |
| Acenaphthylene | 3.75 | 0.140—2.296 | n.d.—0.40 |
| Acenaphthene | 53.83 | n.d.—3.215 | n.q.[b] |
| Fluorene | 80.87 | 0.141—0.601 | n.d.—0.26 |
| Phenanthrene | 555.40 | n.d.—2.275 | n.d.—0.05 |
| Anthracene | 453.10 | 0.021—2.001 | n.d.—0.1 |
| Fluoranthene | 169.88 | 0.033—164.355 | n.d.—0.1 |
| Pyrene | 418.50 | n.d.—0.822 | n.d.—0.1 |
| Benzo(a)anthracene | 98.60 | 0.025—0.426 | n.q. |
| Chrysene | 110.00 | n.d.—0.731 | n.q. |
| Benzo(a)pyrene | 42.03 | n.d.—0.758 | n.q. |
| Benzo(b)fluoranthene | 60.70 | 0.006—1.758 | n.q. |
| Benzo(k)fluoranthene | 39.23 | n.d.—0.789 | n.q. |
| Dibenzo(a,h)anthracene | 18.03 | n.d.—1.176 | n.q. |
| Benzo(ghi)perylene | 18.20 | n.d.—3.837 | n.q. |
| Indeno(1,2,3-cd)pyrene | 4.95 | 0.060—3.677 | n.q. |
| Total PAHs | 2217.92 | 1.654—180.875 | 3.71 |

a) Not detected. b) Not quantified.

**Table 5.** Average Concentration of Heavy Metals in Supernatant and Water Extracts Compared to Landfill Leachates and Extracts from Municipal Waste and Sewage Sludge

| Metal | Concentration/$(\mu g\ dm^{-3})$ | | | | |
|---|---|---|---|---|---|
| | Supernatant | Water extract No. 1 | Water extract No. 2 | Landfill leachate [19, 21] | Water extract from municipal solid waste [22] |
| Hg | 3.4 | 1.4 | 0.5 | 2 | n.q.[b] |
| Cu | 33 | 33 | 19 | b.d.l.[a]—60 | 36.4 |
| Fe | 2060 | 1840 | 1480 | 464—44900 | 1465.8 |
| Pb | 29 | 15 | < 10 | < 10—200 | 44.1 |
| Cd | < 10 | < 10 | < 10 | < 10—20 | < 1.4 |
| Zn | 998 | 464 | 199 | 25—930 | 687.4 |
| Ni | 399 | 84 | 40 | 8—150 | 20 |
| Mn | 2450 | 285 | 120 | b.d.l.—4370 | 141.4 |
| Cr | 129 | 85 | 26 | < 10—100 | 7.7 |
| Sum | < 6111.4 | < 2817.4 | < 1904.5 | 50732 | 2404.2 |

a) Below detection limit. b) Not quantified.

(ghi)perylene, and indeno(1,2,3-cd)pyrene) was higher than their water solubility. Total PAHs concentration in water extract No. 1 was lower than in the extract No. 2. It means that PAHs in the environment do not desorb rapidly from solid phase. Based on the RSD values it can be stated that repeatability of the results was rather low. Similar low repeatability of PAHs analysis in supernatants was stated in the study of *Flotron et al.* [6].

Compared to the concentrations of PAHs observed in landfill leachate (Table 4), measured content of these micropollutants was rather low. However, PAHs concentrations in landfill leachates are very diverse (from not detected to even more than 500 $\mu g\ dm^{-3}$). It confirms the hypothesis of *Flotron et al.* [6] that chemical oxidation of sewage sludge may have no effect on desorption of PAHs from such matrix. On the

other hand, one should keep in mind that the PAHs behaviour during chemical oxidation of sewage sludge is most probably dependent on the doses of chemical oxidants and the duration of experiment.

Concentrations of heavy metals in supernatant and water extracts are summarized in Table 5. Similarly to the PAHs content, heavy metals concentration in supernatant was higher than that found in water extracts. The most abundant compounds in all samples were those of Fe and Mn, the less abundant ones were those of Hg and Cd. Contrary to PAHs fates during chemical stabilization heavy metals leaching from matrix was rapid. They were present in the highest concentrations in supernatant from chemically stabilized sludge and water extract No. 1. When extracted with water heavy metals content in extract decreased. Content of heavy metals in supernatant and water extract

**Table 6.** Toxicity of Water Extracts in %

| Test organism | Dilution, $\varphi_r$ | | | |
|---|---|---|---|---|
| | 1 : 0 | 1 : 2 | 1 : 10 | 1 : 100 |
| *Selenastrum capricornutum* | 20 | 12 | 0 | 0 |
| *Tetrahymena thermophila* | 30 | 22 | 15 | 0 |
| *Heterocypris incongruens* | 100 | – | – | – |
| *Lebistes reticulatus* | 100 | 24 | 0 | 0 |

No. 1 was comparable to the values observed in landfill leachates and water extract from municipal solid waste (see Table 5). Chemical oxidation of the sewage sludge—OFMSW mixtures did not increase the release of heavy metals from solid matrices.

Toxicological tests showed that the water extracts of chemically stabilized wastes were toxic for living organisms. In the case of invertebrates, *i.e. Heterocypris incongruens*, *Tetrahymena thermophila*, toxicity of water extracts varied. All mixtures showed strong toxicity for crustaceans (100 % mortality). Not diluted water extracts cause 20 % inhibition of *Selenastrum capricornutum* growth. Diluted with distilled water at a ratio of $\varphi_r = 1 : 10$, water extracts were nontoxic for algae and fish and only slightly toxic for *Tetrahymena thermophila* (see Table 6).

The physicochemical characteristic of sewage sludge after chemical stabilization indicated that VSS content in the sludge decreased to 34—37 % TSS (in mixture before stabilization it was equal to 60—70 %). Because of low content of organic solids in stabilized matrix it was stated that the mixture of sewage sludge and OFMSW after chemical stabilization was stable. The problem was, however, the high content of VFA in supernatant (reaching 7000 mg VFA dm$^{-3}$).

Based on the obtained results it can be stated that solid phase obtained after peroxyacetic acid and Fenton's reagent treatment was stable, however, supernatant separated from solid phase posed a risk for the environment. Further investigations are required to improve chemical stabilization method for sewage sludge and OFMSW treatment.

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