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CHEMICAL OXIDATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN WATER BY FERRATES(VI)

Abstract: Polycyclic aromatic hydrocarbons (PAHs) are a common part of the environment where they come from burning fossil fuels (through an incomplete combustion process). From a toxicological point of view, PAHs are considered to be carcinogens with a mutagenic and teratogenic effect. On the other hand, ferrates are generally believed to be the ideal chemical agent for water treatment due to their strong oxidation potential. Herein, the efficiency of degradation of PAHs (with the special emphasis on B[a]P) by ferrates under laboratory conditions was studied. The formation of degradation products was also considered. For this, two types of ferrates were used and both of them efficiently degraded B[a]P. When comparing ferrates that were bought from a Czech and USA company, no significant changes in terms of B[a]P degradability were observed. It was determined that the degradation efficiency of PAHs by ferrates was dependent on their molecular weight. Two and three cyclic PAHs have been completely degraded within 30 minutes, whereas five (and more) cyclic PAHs, only partially. The results obtained with ferrates were compared to the ones obtained with a classical oxidizing agent - KMnO_4 . In a qualitative test to detect degradation products of PAHs, two were identified, namely fluorene-9-one derived from fluorene and acenaphthylene, formed from acenaphthene.

Keywords: polycyclic aromatic hydrocarbons, benzo[a]pyrene, ferrate, degradability, spiked water, oxidizing agent

Introduction

There is a wide range of homocyclic and heterocyclic derivatives of PAHs that contain nitrogen, oxygen or sulphur atoms in their aromatic structure. This large group, together with PAHs, is referred to as polycyclic aromatic compounds (PACs) [1].

16 PAHs (EPA_{16}) with a star (*) and, according to the USEPA (Environmental Protection Agency), are included among the priority pollutants [2]. Dangerous compounds were selected by European Union (EU) for monitoring [3-5], fluoranthene, however, was recently removed [6].

A significant amount of PAHs arises from incomplete combustion of fossil fuels and other organic substances such as coal and wood combustion, the use of combustion engines, and the production of heat and electricity [7]. Motor vehicle emissions can contribute up to a 35 % increase in PAH intake in developing countries [8].

PAHs also arise when food, especially meat products and fish are baked, fried, toasted or grilled due to the incomplete combustion or thermal decomposition (pyrolysis) of

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organic material) [9]. High levels of PAHs may contain oil and coal extracts, including asphalt [10] and creosote [11], used as preservatives for wood. PAHs enter the environment as air pollutants and over time they get into water, soil, sediment and living organisms [12]. Forest fires, volcanic eruptions and soil metabolism (especially perylene) are the largest natural resources of them [13].

USEPA and the World Health Organization (WHO) have selected 16 “priority pollutants” from the PAH group (their structures are shown in Figure 1). The International Agency for Research on Cancer (IARC) has assessed the carcinogenic risk for 49 PAHs with regard to the results of epidemiological and animal studies. 3 PAHs of Class 2A were identified as likely carcinogens: benzo[a]anthracene, benzo[a]pyrene and dibenz[a,h]anthracene; another 12 PAHs were classified as potential carcinogens, class 2B: benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene and indeno[1,2,3-cd]pyrene. Other PAHs, which are the priority pollutants, were categorised as class 3, assigned to compounds that cannot be classified (tests were not sufficiently conclusive to exclude or demonstrate carcinogenicity) [12]. In Europe, legislation on air protection focuses primarily on the control of benzo[a]pyrene (annual target level of 1 ng/m^3), as this compound exhibits the highest toxic load from all airborne PAHs [14, 15].

Fig. 1. Structures of the 16 PAHs on the USEPA priority pollutant list

The physical properties of selected PAHs are shown in Table 1.

Table 1

Physical properties of selected PAHs [16, 17]

Substance	At 25 °C					log <i>K</i> _{ow}	log <i>K</i> _{oc}
	MW	MP	BP	VP	S		
	[g/mol]	[°C]	[°C]	[Pa]	[g m ⁻³]		
Naphthalene (NAP)	128	31	218	10.4	31	3.37	3.11
Acenaphthylene (ACE)	152	96	278	3 · 10 ⁻¹	38	3.92	3.79
Acenaphthene (ACY)	154	92	265	9 · 10 ⁻¹	16	4.00	3.83
Fluorene (FLU)	166	116	295	9 · 10 ⁻²	1.9	4.18	4.15
Anthracene (ANC)	178	216	340	1 · 10 ⁻³	0.045	4.54	4.41
Phenanthrene (PHN)	178	101	339	2 · 10 ⁻²	1.1	4.57	4.22
Pyrene (PYR)	202	111	375	1.2 · 10 ⁻³	0.26	5.22	4.74
Fluoranthene (FLA)	202	156	360	6 · 10 ⁻⁴	0.13	5.18	4.82
Benz[a]anthracene (B[a]A)	228	160	435	2.8 · 10 ⁻⁵	0.011	5.91	5.66
Chrysene (CHY)	228	255	448	5.7 · 10 ⁻⁷		1.65	5.37
Benzo[b]fluoranthene (B[b]F)	252	168	481	-	0.0015	5.80	5.89
Benzo[k]fluoranthene (B[k]F)	252	217	481	5.2 · 10 ⁻⁸	0.0008	6.00	5.89
Benzo[a]pyrene (B[a]P)	252	175	495	7.0 · 10 ⁻⁷	0.0038	6.04	5.71
Indeno[1,2,3- <i>cd</i>]pyrene (IND)	276	164	536	-	0.00019	6.58	6.14
Benzo[g,h,i]perylene (B[ghi]P)	276	277		-	0.00026	6.50	-
Dibenzo[a,h]anthracene (D[ah]A)	278	267	524	3.7 · 10 ⁻¹⁰	0.0006	6.75	5.97

MW - molecular weight, MP - melting point, BP - boiling point, VP - vapour pressure of the solid, S - water solubility, K_{ow} - octanol/water partition coefficient, K_{oc} - soil partition coefficient

The vapour pressure of PAHs decreases by more than 11 orders of magnitude with the increasing number of condensed benzene rings. Larger PAHs (with three and four rings) are distributed between the gaseous and solid phases in the environment. PAHs with five or more aromatic rings are found to be almost exclusively linked to a particle or solid phase [18]. The solubility of PAH in water with 2 to 6 rings decreases by 5 orders with the increase of their molecular weight. For this reason, two- and three-ring PAHs are likely to be found in the aqueous phase, in comparison to higher molecular weight PAHs that tend to associate with the dissolved organic matter (DOM) and solid phase such as soot [19]. The soil/water partition coefficient (K_{oc}) is the ability of the substance to pass from water to the organic constituent of the soil. The log K_{oc} value is relatively high for PAHs, indicating a strong tendency for PAHs to be trapped in soils and sediments, although originally most are scattered in the atmosphere [20]. Due to the low solubility of PAHs in water they usually can be found at extremely low concentrations. The typical groundwater interface is 10 to 50 ng/dm³, and for surface waters it is 50 to 250 ng/dm³ [21].

These compounds can occur in the gas phase and in conjunction with atmospheric particles, particularly in the fraction of submicron particles, which promotes their transport over long distances. Both gaseous and particulate PAHs are deposited in dry and terrestrial ecosystems by dry deposition processes (gas absorption, gravity deposition, swirling diffusion) and precipitation excretion, which include both droplet formation and cloud capture. Therefore, atmospheric deposition of PAH is a significant source of PAHs at local, regional and global scale, which is responsible for the presence of these compounds in remote areas and open oceans far from their emission sources [22].

Nitro- and oxy-PAHs are reaction products of PAHs and reactive components (e.g. oxides of nitrogen, ozone) in the combustion chamber and atmosphere [23]. It is known that many PAHs and nitro-PAHs found in the air have mutagenic and carcinogenic effects and may pose a risk to human health [24]. For example, while testing *Salmonella*

typhimurium (strain TA98) without the presence of exogenous metabolizing enzymes (i.e. hepatic S9 fraction) it was found that 1-nitropyrene, 1,3-dinitropyrene, 1,6-dinitropyrene and 1,8-dinitropyrene were 200, 6.3E4, 8.0E4 and 1.1E5 times more mutagenic than benzo[a]pyrene (+S9). This intense sensitivity of *S. typhimurium* to nitro-PAHs is attributed to the presence of native nitroreductase enzymes that initiate the metabolism of nitro-PAH to their final mutagenic metabolites - arylhydroxylamine [23, 25]. Mutagenic oxy-PAHs include quinones of pyrene and benzo[a]pyrene, some ketones and pyrene-3,4-dicarboxylic anhydride.

Laboratory-grown organisms kept in sediments from sites contaminated with PAH are subjected to photoactivated toxicity. Determined toxicity depends both on the intake of PAH (or other contaminants) and on UV exposure [26]. Photosensitive sediment toxicity was confirmed by Monson et al. [27] in *in situ* tests performed at sites where contaminated sediments were collected by Ankley et al. [28].

Iron salts are known only in the ferrous (Fe(II)) and the ferric forms (Fe(III)); the higher oxidized forms Fe(IV), Fe(V) and Fe(VI) give unstable compounds called ferrates. Ferrates are more stable at low temperatures and higher pH [29]. The ferrate(VI) ion has a formula FeO_4^{2-} and its aqueous solution has a typical red-violet colour [30]. Ion FeO_4^{2-} has a tetrahedral structure similar to its solid-state geometry and four covalent Fe-O bonds. Potassium ferrate is insoluble in common organic solvents. It can be suspended in ether, chloroform, benzene, alcohols (to 20 % water) and other solvents without rapid decomposition.

Since there is a continuous search for appropriate water treatment methods [31-36], ferrates emerged as a potential alternative for conventional processes due to several advantages. For example, they are strong oxidants throughout the whole pH range [37]. They have a higher oxidation-reduction potential than Mn(VII)/Mn(IV), Cr(VI)/Cr(III) (Table 2) or commonly used oxidants (e.g. ozone, hydrogen peroxide, chlorine, perchlorate, hypochlorite) and can be therefore applied for remediation of drinking and wastewater [38, 39]. Ferrates can be photoreduced to Fe(V) to produce an even stronger oxidant than Fe(VI) [40]. Ferrate(VI) is capable of quickly oxidizing many toxic pollutants including chemical weapons [37, 41] however, according to our knowledge, it was never used for oxidizing highly toxic PAHs.

Table 2

Reduction potential of Cr(VI), Mn(VII) and Fe(VI) in aqueous solutions [37]

Acidic medium	E^0 [V]	Basic medium	E^0 [V]
$\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$	1.33	$\text{CrO}_4^{2-}/\text{Cr}(\text{OH})_3$	-0.12
$\text{MnO}_4^-/\text{MnO}_2$	1.67	$\text{MnO}_4^-/\text{MnO}_2$	0.56
$\text{FeO}_4^{2-}/\text{Fe}^{3+}$	2.20	$\text{FeO}_4^{2-}/\text{Fe}(\text{OH})_3(\text{s})$	0.72

The SEKM (*in Czech*: system evidence kontaminovanych mist) system, managed by the Ministry of the Environment of the Czech Republic, records a total of 524 sites contaminated by PAHs in the Czech Republic, of which no corrective action has yet been taken on 117 sites [42]. This was the reason why PAHs (and in particular B[a]P) were chosen as model pollutants for testing the decontamination efficiency of ferrates.

In this study, ferrates were used for the removal of PAHs, including the most toxic B[a]P, from the spiked water. A highly pure ferrate purchased from Sigma-Aldrich has been tested but because it was removed from the market - we have conducted a search for

a suitable alternative to it (with the same or at least similar properties). For comparison, in addition to commercially obtained ferrate samples, the potassium permanganate was used. In addition, several reaction intermediates were found and reported herein.

Materials and methods

Chemicals

Highly pure potassium ferrate (> 90 % K_2FeO_4 , from Sigma-Aldrich (SA)) and potassium ferrate (> 55 % K_2FeO_4 , from Santa Cruz Biotechnology, Inc. (SCB)) were used in this study. Further, another ferrate (LAC 035; produced by Czech company LAC s.r.o.) was used. ICP/OES analysis of the used ferrates is shown in Table 3.

ICP/OES analysis of the used ferrates

Table 3

Concentration of elements in ferrate samples [mg/kg]	SA	SCB	LAC 035
Ag	< 2.0	< 2.0	< 2.0
Al	< 4.0	8.25	226
As	< 4.0	< 4.0	< 4.0
B	< 20.0	< 20.0	< 20.0
Ba	10.45	2.8	5.82
Be	4.71	1.32	3.03
Ca	14.37	35.8	233
Cd	< 2.0	< 2.0	< 2.0
Co	< 4.0	< 4.0	26.6
Cr	1190	35.7	222
Cu	< 4.0	< 4.0	6.42
Fe	323600	82230	276800
K	431300	480600	450900
Li	0.81	0.18	0.50
Mg	1.45	5.32	206
Mn	1830	5.05	55.2
Mo	< 4.0	< 4.0	< 4.0
Na	154	5015	638
Ni	< 2.0	< 2.0	237
Pb	< 10.0	< 10.0	< 10.0
Sb	< 4.0	< 4.0	< 4.0
Se	< 4.0	< 4.0	< 4.0
Si	180	1202	10
Sn	< 4.0	< 4.0	8.50
Sr	0.21	0.23	0.31
Ti	0.91	0.45	218
Tl	< 4.0	< 4.0	< 4.0
V	< 4.0	< 4.0	156
Zn	20.2	< 4.0	12.4

Content of Fe was determined by elementary analysis as 35.7 % (LAC 035). Atomic Absorption Spectrometry analysis specified content of selected heavy metals: 0.0389 % Cr and 0.034 % Ni (LAC 035).

Stock ferrate solution was prepared by dissolving different weights (depending on ferrate purity and required final FeO_4^{2-} concentrations) of the solid sample in cooled, tap

water. Ferrates are highly inhomogeneous and unstable, therefore, precise concentrations cannot be calculated in advance. Final concentrations of the Fe(VI) stock solutions were calculated retrospectively after spectrophotometric measurement. All Fe(VI) stock solutions were prepared just before the experiments (max. 10 minutes before).

Benzo[a]pyrene C₂₀H₁₂ (purity 99.5 %, 10 ng/mm³ in Acetonitrile) and PAH-Mix 9 (containing 16 PAHs of 98-99.6 % purity, 10 ng/mm³ in Acetonitrile) were purchased in Ehrenstorfer company.

Supelco PAH Kit 610-N (16 EPA individual PAHs: acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, dibenzo[a,h]anthracene, fluoranthene, fluorene, chrysene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene, pyrene).

The internal standard of four isotopically labelled PAHs (ISTD) was added: D8 - naphthalene 12.29 µg/mm³, D10 - phenanthrene 100 µg/cm³, D12 - chrysene 100 µg/cm³, D12 - perylene 100 µg/cm³. The ISTD stock solution was prepared by mixing 3 cm³ of Perylene, 1 cm³ of Chrysene, 1 cm³ of Phenanthrene, 3.3 mm³ of Naphthalene and 10 cm³ of Acetone (HPLC grade) in a 20 cm³ vial.

The other chemicals used in the experiments were purchased in the required analytical grade and were used without further purification. These include Na₂SO₃ anhydrous p.a., 95 % hexane for HPLC and absolute methanol for LACHNER HPLC, 95 % HPLC for Chromservis s.r.o. and Na₂SO₄ anhydrous p.a., KMnO₄ p.a. by PENTA; PAHs and benzo[a]pyrene were obtained from Dr. Ehrenstorfer GmbH.

Methods

Experiments with spiked water with B[a]P were carried out in 250 cm³ reactors. 200 cm³ of tap water, 20 mm³ of B[a]P, and the ferrate solution (dose 5 cm³, 10 cm³ or in several doses) were dispensed to continuously stirred reactors. The FeO₄²⁻ concentration was measured spectrophotometrically in each experiment. The concentration of B[a]P was 4 · 10⁻³ µM (equivalent to 1 µg/dm³). After a certain period, the reaction was stopped by the addition of 100 mm³ of 1 M Na₂SO₃ solution. The solutions were extracted with 4 cm³ of heptane and 2 cm³ of methanol (shaking for 60 min at horizontal shaker) the same day. One cm³ was taken from each extract and 10 mm³ of ISTD stock solution was added to the GC-MS/MS analysis. Each set of samples contained control and base samples. Control samples were processed in the same way as experimental samples, without the addition of B[a]P. The base samples contained the standing water tapped B[a]P without the addition of ferrate. Experiments were performed in triplicate at ambient temperature.

Experiments with water-doped PAHs were performed in 250-cm³ reactors. 200 cm³ of standing tap water, 20 mm³ of PAH-Mix 9 and finally the ferrate solution (5 cm³) were dispensed to the continuously stirred reactors. The concentrations of each PAH in each reactor were 4 · 10⁻³ µM (i.e., 1 µg/dm³). The FeO₄²⁻ concentration was measured spectrophotometrically in each experiment. The dose of KMnO₄ was chosen to suitably correspond to the added ferrate moles. After a certain period, the reaction was stopped by the addition of 100 mm³ of 1 M Na₂SO₃ solution. A mixture of 4 cm³ of hexane and 2 cm³ of methanol (shaking for 60 min at horizontal shaker) was used as the extraction agent. One cm³ was taken from each extract and 10 mm³ of ISTD stock solution was added to the GC-MS/MS analysis. Each set of samples contained control and base samples. The control, base and experimental samples were processed in the same way as mentioned in the previous section.

An experiment to determine degradation products of PAHs was performed in two sets of 17 vials of 20 cm³ volume with cap and PTFE coated septa. 10 cm³ of demi water was added to all 34 vials. Then several crystals of 16 individual PAHs were added into individual vials (approx. 1 mg). Samples were shaken for 1 hour on horizontal shaker. This was followed by addition of 5 cm³ of ferrate SA stock solution (ferrate set of vials) or 5 cm³ of demi water (control set of vials). The concentration of FeO₄²⁻ in the stock solution was measured spectrophotometrically and corresponded to 1.36 mM. The reaction time was 120 minutes. After this time, the individual filtrates were extracted with 5 cm³ of hexane (shaking for 30 min at a horizontal shaker). Moreover, one blank was also assigned - a sample without PAHs or ferrates. Extracts were measured by GC-MS (full scan mode of operation).

Analytical methods

Gas chromatography in conjunction with mass spectrometry is currently a common analytical method that combines the high capillary gas chromatographic separation capability with detection highly specific for the given analyte while allowing information on the structure of unknown substances. For measurements, a Thermo Trace 1310 gas chromatograph with a TSQ 8000 mass spectrometer with triple quadrupole (GC-MS/MS) was used. Automatic dosing of the prepared samples was performed with a 1 mm³ PAL LHX-xt autosampler. Fe(VI) concentrations were determined using a SHIMADZU UV-1601 UV/VIS absorption spectrometer with a molar absorbance of 1150 M⁻¹ cm⁻¹ at 505 nm [43].

Most PAHs show fluorescent properties after excitation at their characteristic wavelengths, allowing their selective detection in different environmental samples. Fluorescence measurements do not interact nor destroy samples, and by-products are not generated during measurement [44]. Herein we have compared GC analytical technique with the fluorescent one in order to check the reliability of the GC-MS/MS method (Fig. 2). The fluorescence wavelength at the measurement of the B[a]P concentration for excitation and emission was selected at 297 and 405 nm, respectively [45, 46]. The Tecan Spark Microplate Reader Spectrofluorimeter was used for measurement.

Fig. 2. Comparison of spectrofluorimetric and GC-MS/MS techniques with B[a]P (mean + standard deviation contaminated samples). Base (1-3) - no ferrate addition, only dose $4 \cdot 10^{-3}$ μ M of B[a]P

Comparison of two detection methods to determine the exact B[a]P concentration, spectrofluorimetric method and GC-MS/MS on 39 samples showed very good match in the results (Fig. 2) [44] and it could be therefore inferred that the GC-MS/MS method is highly reliable and can be used in this study for quantitative determination of PAHs.

Results and discussion

B[a]P reactivity with ferrate with spiked water

Several ferrate species at different doses were applied to a system containing a tap water with B[a]P. Based on several studies demonstrating the degradation effects of ferrates on organic pollutants, it was assumed that this substance should be completely removed from the reactor [37, 41, 47]. Complete B[a]P removal occurred only with the application of highly pure ferrate SA. For the other ferrates there was only a partial decrease of B[a]P concentration in the reactors (Figs. 3-5).

Fig. 3. Comparison of various ferrate SA doses for the removal of B[a]P (mean + standard deviation). Time 0 (base) - no ferrate addition, only dose $4 \cdot 10^{-3}$ µM B[a]P

When comparing ferrates SA and SCB at doses of about 30 µM, the B[a]P concentration dropped below the detection limit ($0.02 \mu\text{g}/\text{dm}^3$) in both ferrate treatments up to 120 hours. When the ferrate dose was increased two times, the complete degradation of B[a]P was observed already after 10 minutes of reaction. Ferrate SA in the concentration of 60 µM, was able to completely remove B[a]P after 10 minutes.

The cheaper, but equally good Czech ferrate alternative (LAC 035) achieved similar results in the degradation of B[a]P. Neither of the tested ferrate samples could degrade B[a]P to the USEPA [48] limit values. The best degradation attempt was achieved with a single dose of 60 µM ferrate, whereas LAC ferrate responded to degradation B[a]P better than SCB ferrate.

Furthermore, repeated additions of LAC 035 and SCB ferrates (5 times the same dose after 1 minute) did not cause better degradation of the contaminant (what was expected) but rather slightly inhibited the degradation of B[a]P in the reactor compared to single dose ferrate (Fig. 6).

Fig. 4. Comparison of various ferrate SCB doses for the removal of B[a]P (mean + standard deviation). Time 0 (base) - no ferrate addition, only dose $4 \cdot 10^{-3} \mu\text{M}$ B[a]P

Fig. 5. Removal efficiency of B[a]P by various doses of two different ferrates after 120 minutes

Fig. 6. Concentration B[a]P after 5 minutes of decontamination with different doses of two commercial ferrates (mean + standard deviation). Base - no ferrate addition, only dose $4 \cdot 10^{-3} \mu\text{M}$ B[a]P

PAHs reactivity with ferrate spiked water

Two types of ferrate were tested in a system containing tap water to degrade 16 PAHs (Fig. 7).

Fig. 7. Concentration of individual PAHs after addition of SA and SCB ferrates and KMnO_4 . Base - no ferrate addition, only dose of PAHs ($4 \cdot 10^{-3} \mu\text{M}$) corrected brackets in in the graph

Some studies on water oxidation showed that Fe(VI) could remove several organic pollutants (for example benzene, phenol, naphthalene, nitrilotriacetic acid) [49, 50]. For comparison, strong oxidizing agent, as a matter of fact, having several similar properties with ferrates - potassium permanganate, was also included.

PAHs with 2-3 aromatic rings were degraded by both ferrates within 30 minutes. Fluorene was found to be the most recalcitrant PAH and was completely removed only by using the KMnO_4 after 24 hours. Four circular PAHs, fluoranthene and pyrene were degraded by ferrate SA within 45 minutes and chrysene after 6 hours; The SCB removed these three PAHs after 180 minutes. The only PAH in this group that failed to be completely removed was B[a]A, the residual concentration of which remained in the reactors using both types of ferrates. For PAH with 5 or more cycles, only a partial decrease in concentration was observed, with B[b+k]F by 11.5 %; B[a]P - 8.7 %; IND - 15.1 %; B[g,h,i]P - 24.8 % and D[a,h]A by 27.3 % for SCB ferrate. These results correspond to the conclusions of several authors, which foreseen the increase of PAHs resistance to degradation with increase of the PAHs molecular weight [45, 46, 51, 52]. Better results have been achieved with the SA ferrate, where the complete degradation of the most toxic B[a]P occurred after 24 hours. For other PAHs with 5 aromatic rings, the concentration

decreased of B[b+k]F by 11.7 %; IND - 21.5 %; B[g,h,i]P - 41.8 % and D[a,h]A by 28.8 %. The use of the KMnO_4 oxidizing agent was effective after 24 hours and is more suitable for PAHs with a lower molecular weight i.e.: acenaphthylene, fluorene, anthracene, phenanthrene (3 cycles), pyrene, chrysene (4 cyclic). Concentration of PAHs in the reactors after 24 hours in presence of two types of ferrates and KMnO_4 is shown in Table 4.

Table 4
Concentrations of PAHs in the reactors after 24 hours in presence of two types of ferrates and KMnO_4
(control - 100 %)

Individual tested PAHs contained in the mixture	Initial concentration [%]		
	KMnO_4	SA	SCB
Naphthalene	11	< 1	< 1
Acenaphthylene	< 1	< 1	< 1
Acenaphthene	< 1	< 1	< 1
Fluorene	< 1	10	8
Anthracene	< 1	< 1	< 1
Phenanthrene	< 1	< 1	< 1
Fluoranthene	8	< 1	< 1
Pyrene	< 1	< 1	< 1
Benzo[a]anthracene	< 1	3	3
Chrysene	< 1	< 1	< 1
Benzo[a]pyrene	< 1	< 1	1
Benzo[b+k]fluoranthene	4	2	2
Benzo[g,h,i]perylene	4	6	4
Dibenzo[a,h]anthracene	2	4	4
Indeno[1,2,3-c,d]pyrene	1	3	2

Analysis of degradation products - qualitative experiment

It is known that some intermediates and by-products produced during the oxidation of PAHs, especially oxy-PAHs, have toxic and mutagenic effects. Some may be even more toxic than the original parent compound [53]. Therefore, it was necessary to find out what products are produced during the degradation of PAHs using ferrates.

Fig. 8. GC-MS full scan of the product of fluorene oxidation

As described for fluorene degradation [53], one of the major metabolites is 9H-fluoren-9-one. In our experiments, 9H-fluoren-9-one has been determined as the major and the most stable oxidation product (Fig. 8). Also, acenaphthylene was identified (GC-MS, NIST Library) as transformation product of acenaphthene.

Other PAH oxidation by-products included in the experiments were not detected by GC-MS/MS.

Conclusion

This paper summarizes the use of ferrates for removal of PAHs (especially B[a]P) in water phase. It has been shown that ferrates are able to degrade PAHs, as well as B[a]P itself, whereas the resistance of each PAHs increases with their molecular weight. The effectiveness of the degradation depends both on the quality of the ferrate and the way/quantity that it is dosed.

When comparing ferrates SA and SCB at a dose of 30 μM per reactor, the two ferrates were able to remove all B[a]P after 120 minutes. If the ferrate dose was increased twice, B[a]P was removed after 10 minutes.

Appropriate alternatives (Czech and foreign) for commonly used ferrates (that possess similar properties) have been found. The Czech Republic ferrate (LAC 035) degraded B[a]P better than ferrate SCB at single dose of 60 μM . Repeated additions of these ferrates did not improve degradation of B[a]P but slightly inhibited.

In the presence of ferrate SA, the residual concentration of PAHs after 24 hours was highest for fluorene and amounted to 10 % of the initial amount. Using the classic oxidant - KMnO_4 , the residual concentration of PAHs after 24 hours was highest for naphthalene, 11 % of the initial amount. Several oxidation products of PAHs were found i.e.: fluoren-9-one that was generated from fluorene, and acenaphthylene formed from acenaphthene.

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