*Desalination and Water Treatment*
www.deswater.com

doi: 10.1080/19443994.2015.1030107

57 (2016) 1286–1296
January

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# Effect of catalytic oxidation for removal of PAHs from aqueous solution

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Received 25 August 2014; Accepted 16 February 2015

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ABSTRACT

The aim of the study was to determine the removal efficiency of 16 polycyclic aromatic hydrocarbon (PAH) (Σ 3-, 4-, 5-, and 6-ring PAHs) from aqueous solution using dihydrogen dioxide in the presence of cobalt, platinum, and titanium catalysts. The research was based on the determination of the COD (Total Organic Carbon) in aqueous solution (distilled water with a standard mixture of 16 PAHs). On the basis of the determined value of COD, the oxidant dose—30% solution of dihydrogen dioxide—was calculated. Adequate amounts of dihydrogen dioxide and catalyst were added to the samples. The samples were mixed and left in laboratory conditions for 12 h. Then, PAHs were determined in duplicate. The analysis of PAHs included sample preparation and quantitative and qualitative chromatographic determination, which was performed using a gas chromatograph coupled to a mass spectrometer. The use of a cobalt catalyst resulted in the removal of 16 PAHs in 25%. A dose of an oxidant in the amount of 0.818 mL per liter of the analyzed sample was used. An increase in the amount of dihydrogen dioxide led to higher oxidation efficiency—31% and it gave the final concentration of 1,978 ng/L. Platinum catalyst caused the removal of 16 PAHs by 32%, reaching the final concentration of 1,940 ng/L. The best result for the removal of PAHs was achieved using a titanium catalyst. The amount of oxidant equal to 0.818 mL per liter of the analyzed sample caused a 91% decrease in the summary concentration of 16 PAHs.

*Keywords:* AOP; $H_2O_2$; GC–MS; PAHs; Platinum; Cobalt; Titanium oxide; Aqueous solutions

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of chemical compounds containing two or more fused aromatic rings. They have a different structure, in which benzene rings may occur in various mutual positions and the chemical activities [1]. PAHs are present in the air, soil, sewage, and surface waters. Due to their presence in nature, their carcinogenic and mutagenic properties should be eliminated from the environment. Toxicological studies have shown that

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*Presented at the 12th Scientific Conference on Microcontaminants in Human Environment*
*25–27 September 2014, Czestochowa, Poland*

the PAHs are carcinogenic. Carcinogenic properties also have their derivatives that occur in the environment or in a human organism as a result of metabolism [2]. PAHs derivatives may be formed by reacting with other components of the matrix (halogenation, nitration, sulfonation, alkylation, and acylation) [1]. Hydrocarbons are also subjected to oxidation reactions and photochemical degradation. The oxidation of hydrocarbons can provide products such as diols, quinones, and aldehydes, for example, benzo(a)pyrene can occur in the form of derivatives such as benzo(a) pyrene-1,6-dione and benzo(a)pyrene-3,6-dione [2,3]. In the literature, there is some available information for analyzing PAHs derivatives, which are formed during decomposition [4]. This is of importance because these derivatives have toxic effects on organisms once they are discharged into surface receivers. There is much literature data on PAHs removal in wastewater treatment plants. Some studies suggest that sampling at different times has a significant effect on the concentration of PAHs in raw wastewater [5,6].

Advanced oxidation methods of organic pollutants —AOP—are increasingly being used as treatment for industrial wastewater. These methods are based on the production of hydroxyl radical, which enables decomposition of organic compounds to $CO_2$ and $H_2O$. Some typical factors that cause the production of hydroxyl radicals are: dihydrogen dioxide, permanganate, ozone, UV radiation, and ultrasound [7]. The total decomposition of organic contaminants, without the use of chemicals, can be obtained using photocatalysis ($TiO_2$ + UV) [8]. In accordance with the IUPAC nomenclature, photocatalysis process is defined as the process of photocatalytic reaction of chemical transformation or initiating radiation or in the presence of a catalyst, which absorbs light and causes the chemical conversion of these compounds present in the sample. In addition to the chemical oxidant and ozone, dihydrogen dioxide can be used with the Fenton's reagent. It has been demonstrated that in the Fenton reaction ($Fe^{2+}/H_2O_2$), the efficiency of the process not only depends on: the dose of $Fe^{2+}$ and $H_2O_2$, pH, reaction time, and temperature, but also on the nature of the oxidized substance and the presence of other inorganic and organic compounds [9].

The conventional methods of wastewater treatment are not always effective and efficient, especially for the removal of compounds which are difficult to biodegrade (PAHs, phenols and their derivatives, and pesticides). Advanced oxidation methods are used to increase the effectiveness of removing hardly decomposable organic impurities. Currently, the whole range of oxidants used in enhanced oxidation processes that generate hydroxyl radicals are known. They exhibit a number of advantages allowing a lower dose of the primary oxidant, reducing the amount of toxic byproducts, and oxidizing organic substances in water and wastewater, leading to their complete mineralization. Not only the selection of a suitable oxidant is important, but also a catalyst for the contaminants present in the wastewater. Advanced oxidation method seems to be promising a method which enables cleaning of wastewater after biological treatment. Numerous experiments aiming at determining the mechanisms of transformation and PAHs removal from industrial wastewater are conducted both in the country and all over the world [10–14]. In order to accelerate the possibility of removing PAHs from coke wastewater, appropriate process parameters should be selected. It is considered that research on advanced oxidation of compounds present in the wastewater (biologically treated) using dihydrogen dioxide in the presence of a catalyst may demonstrate the ability to shorten the process for the removal of PAHs. Among 16 aromatic compounds from the list of US EPA (United States of Environmental Protection Agency), eight exhibit carcinogenic and/or mutagenic and teratogenic properties. Toxicity of these compounds depends primarily on the structure and environmental conditions. In Table 1, selected characteristics of 16 PAHs are presented [15].

The aim of the study was to determine the effectiveness of the removal of PAHs from water samples using dihydrogen dioxide in the presence of cobalt, platinum, and titanium catalysts.

## 2. Materials and methods

### 2.1. Experimental procedure

Reagents: reference mixture of 16 PAHs (produced by Ultra Scientific); 30% solution of pure dihydrogen dioxide (POCH, Poland); cobalt oxide (II, III), black (POCH, Poland); platinum catalyst (Schimadzu Ball Corporation); and titanium oxide (IV), pure (POCH, Poland).

Solvents: methanol for HPLC—purity 99.9% (POCH, Poland); dichloromethane for HPLC—purity 99.8% (POCH, Poland); and cyclohexane for HPL—purity 99.5% (POCH, Poland). Columns filled with silica gel (J.T. Baker). Reagents and solvents were obtained from the respective companies.

Laboratory research was carried out using distilled water with an addition of the standard mixture of 16 PAHs. To 1 L flask, 500 mL of distilled water and 0.5 mL of the standard mixture of 16 PAHs (200 ng/mL) were added. In the first control sample, COD was determined. On the basis of the calculated

Table 1
Selected properties of 16 PAHs [15]

| PAH | Molecular weight (g/mol) | The solubility in water at temp. 25°C (ng/L) | Carcinogenicity/mutagenicity* |
|---|---|---|---|
| Naphthalene | 128 | 37,100,000 | − |
| Acenaphthylene | 152 | 3,930,000 | − |
| Acenaphthen | 154 | 3,900,000 | − |
| Fluorene | 166 | 198,000 | − |
| Anthracene | 178 | 73,000 | − |
| Phenanthrene | 178 | 1,290,000 | − |
| Fluoranthene | 202 | 260,000 | −/+ |
| Pyrene | 202 | 135,000 | − |
| Benzo(a)anthracene | 228 | 14,000 | +/++ |
| Chrysene | 228 | 2,000 | +/++ |
| Benzo(b)fluoranthene | 252 | 1,200 | +++/++ |
| Benzo(k)fluoranthene | 252 | 550 | +/++ |
| Benzo(a)pyrene | 252 | 3,800 | ++++/+++ |
| Dibenzo(a,h) anthracene | 278 | 500 | ++/++ |
| Indeno(1,2,3,c,d) pyrene | 276 | 62,000 | +/+ |
| Benzo(g,h,i)perylene | 276 | 260 | +++/++ |

*−There was no activity; + poorly; ++ medium; +++ highly; and ++++ strongly.

Table 2
Preparation of test samples

| Sample | Type of sample | The amount of dihydrogen dioxide 30% (mL) | Dihydrogen dioxide dose (mg/L) | Catalyst |
|---|---|---|---|---|
| 1 | 500 mL $H_2O$ with standard mixture of PAHs | 0.0 | 0.0 | Without catalyst |
| 2 | | 0.409 | 586 | Cobalt |
| 3 | | 0.818 | 293 | catalyst |
| 4 | | 0.409 | 586 | Platinum |
| 5 | | 0.818 | 293 | catalyst |
| 6 | | 0.409 | 586 | Titanium |
| 7 | | 0.818 | 293 | catalyst |

COD value, the dose of the oxidant required for the oxidation of PAHs was calculated. Appropriate amounts of dihydrogen dioxide 30% (Table 2), and cobalt or platinum or titanium oxide catalyst were added to other samples (2–7). The sample was stirred for 30 min on a magnetic stirrer with a constant amplitude. The prepared sample was left for 12 h and then PAHs were determined.

### 2.2 Analytical methods of PAHs

The PAH analysis included initial sample preparation and chromatographic quantitative determination. The initial stage was the extraction of organic matter from wastewater. To 500 mL of water, methanol, cyclohexane, and dichloromethane, at a volume ratio of 20:5:1 were added. Then, the sample was subjected to shaking for 60 min maintaining constant amplitude. The extracts were separated from the water sample by centrifugation. Then, the extracts were purified in vacuum (SPE) using columns filled with silica gel (fill conditioning was performed with a mixture of dichloromethane and cyclohexane, v/v 1:5, 3 × 3 mL). The obtained extract was concentrated to a 2 mL volume under a nitrogen stream. The final step was to determine the quantitative and qualitative indication, which was carried out using a gas chromatography coupled with a mass spectrometer (GC–MS-QP2010 Plus SHIMADZU). The analysis was performed on a column ZB-5 ms, length of 30 m, and a diameter of 0.25 mm. Helium was used as a carrier gas (with flow rate 1.08 mL/min). The injection volume amounted 1 μL and split 1:5. The initial oven temperature was set at 140℃ and it was maintained for 1 min. Then, the temperature increased to 240℃ at a rate of 15℃/min, at 4℃/min to 275℃, and it was ultimately increased from 10℃/min to 320℃. The final temperature was maintained for 5 min. The resulting chromatograms were analyzed using the SIM. Qualitative and quantitative determinations were made on the basis of an external standard of 16 PAHs at a concentration of 200 ng/mL each. The changes in the concentration of PAHs were determined based on the analysis of samples before and after oxidation. Indications were performed in duplicate. To determine the significance of changes in the concentration of PAHs, Student's *t*-test was used. The confidence level 0.95 and a degree of freedom 2 were adopted. For the results performed in duplicate, $t_d$ theoretical value was equal 4.303 [16]. In Table 3, the recovery values of individual PAHs are shown. The reference value of each of the hydrocarbons was the same. The individual PAHs recoveries were in range of 7.5–168%. Recovery values were determined for a series of six repeated samples. On this basis, the average concentrations of individual PAHs were calculated. In further analysis, the obtained hydrocarbons concentration was taken as the initial one.

## 3. Results and discussion

The total concentration of 16 PAHs before oxidation amounted 2,869 ng/L—naphthalene concentration was a 15 ng/L, 3-ring compounds was 900 ng/L, 4-ring PAHs was 697 ng/L, 5-ring 943 ng/L, and 6-ring 313 ng/L, respectively. The effect of the cobalt catalyst with a suitable dose of dihydrogen dioxide, on the degree of oxidation of the selected group of the aromatic hydrocarbons was first studied. In Fig. 1, the changes in the concentrations of PAHs in water samples during the oxidation process using a cobalt catalyst and two doses of the oxidant are presented.

The use of the cobalt catalyst resulted in the removal of 16 PAHs in 25% using a 0.818 mL dose of oxidant $H_2O_2$ per liter of the analyzed sample. The increase in the amount of dihydrogen dioxide has contributed to higher oxidation efficiency—31%—which resulted in the final concentration of 1,978 ng/L. Chemical reactivity of individual hydrocarbons depends on the structural composition and therefore considering the oxidation process, PAHs were divided according to the number of rings in the molecule. Three-ring hydrocarbons include: acenaphthylene (Acyl), acenaphthene (Ac), fluorene (Flu), phenanthrene (Phe), and anthracene (Antr). Compounds belonging to this group have been oxidized in 28% at a lower dose oxidant yield, the final concentration at the level of 651 ng/L. Four-ring hydrocarbon group included: fluoranthene (Fl), pyrene (P), benzo(a)anthracene (B(a)A), and chrysene (Ch). The use of a cobalt catalyst at the lower dose of dihydrogen

Table 3
The reference values and recoveries of PAHs

| WWA | Number of rings | The reference value (ng/L) | The value indicated (ng/L) | Recovery (%) |
|---|---|---|---|---|
| Naphthalene | 2 | 200 | 15 | 7.5 |
| Acenaphthylene | 3 | 200 | 48 | 24 |
| Acenaphthene | 3 | 200 | 203 | 102 |
| Fluorene | 3 | 200 | 143 | 72 |
| Anthracene | 3 | 200 | 182 | 91 |
| Phenanthrene | 3 | 200 | 106 | 53 |
| Fluoranthene | 4 | 200 | 219 | 109 |
| Pyrene | 4 | 200 | 258 | 129 |
| Benzo(a)anthracene | 4 | 200 | 237 | 118 |
| Chrysene | 4 | 200 | 201 | 100 |
| Benzo(b)fluoranthene | 5 | 200 | 336 | 168 |
| Benzo (k)fluoranthene | 5 | 200 | 246 | 122 |
| Benzo (a)pyrene | 5 | 200 | 179 | 89 |
| Dibenzo(a,h)anthracene | 5 | 200 | 183 | 92 |
| Indeno(1,2,3,c,d)pyrene | 6 | 200 | 152 | 76 |
| Benzo(g,h,i)perylene | 6 | 200 | 162 | 81 |
| ∑ 16 PAHs | | 3,200 | 2,869 | 90 |

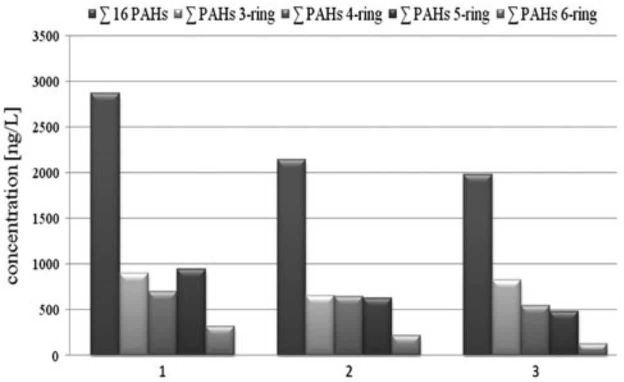

Fig. 1. Changes in the concentrations of PAHs using a cobalt catalyst.
Notes: 1—distilled water + st. 16 PAHs; 2—distilled water + st. 16 PAHs + 0.818 mL$H_2O_2$/L + cobalt catalyst; and 3—distilled water + st. 16 PAHs + 1.64 mL$H_2O_2$/L + cobalt catalyst.

dioxide resulted in the removal of these hydrocarbons only in the 7.8%, while an increase of the oxidant to 1.64 mL/L reduced the compounds by 22%. Five-ring hydrocarbons (benzo(b)fluoranthene (B(b)F), benzo(k) fluoranthene (B(k)F), benzo(a)pyrene (B(a)P), dibenzo (a,h), and natracen (D(a,h)a) have been removed in 33% using a lower dose of an oxidant. The increase in dihydrogen dioxide amount to 1.64 mL increased removal efficiency of these compounds to 50%, reaching the final concentration equal to 475 ng/L. The removal degree of 6-ring PAHs with an increased amount of oxidizer was 61%. From the first series of studies, it can be concluded that some higher chemical reactivity was observed at a dose of 1.64 mL of the oxidant $H_2O_2$ per liter of the analyzed sample. A study may suggest that the reactivity of examined hydrocarbons using a cobalt catalyst decreased in the series: 6-ring PAHs > 5-ring PAHs > 4-ring PAHs > 3-ring PAHs.

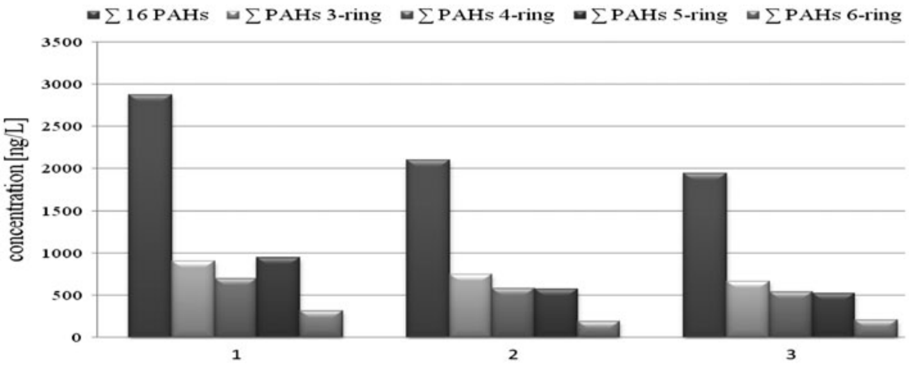

Fig. 2. Changes in the concentrations of PAHs using a platinum catalyst.
Notes: 1—distilled water + st. 16 PAHs; 2—distilled water + st. 16 PAHs + 0.818 mL$H_2O_2$/L + platinum catalyst; and 3—distilled water + st. 16 PAHs + 1.64 mL$H_2O_2$/L + platinum catalyst.

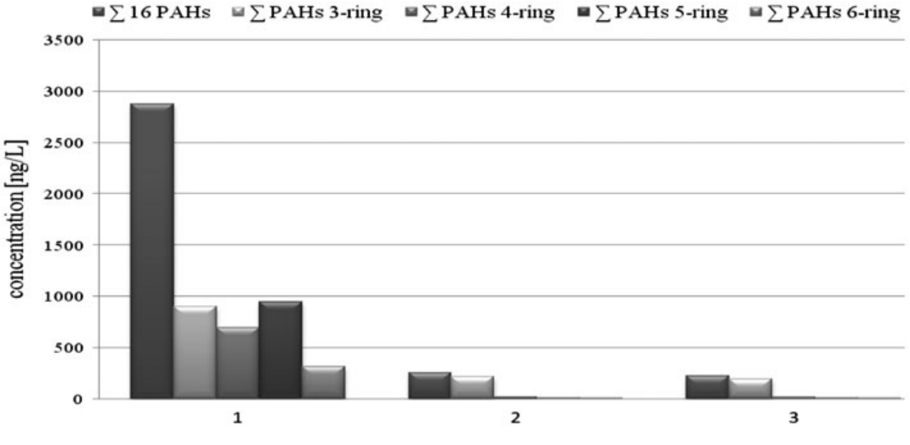

Fig. 3. Changes in the concentrations of PAHs using a titanium catalyst.
Notes: 1—distilled water + st. 16 PAHs; 2—distilled water + st. 16 PAHs + 0.818 mL$H_2O_2$/L + titanium catalyst; and 3—distilled water + st. 16 PAHs + 1.64 mL$H_2O_2$/L + titanium catalyst.

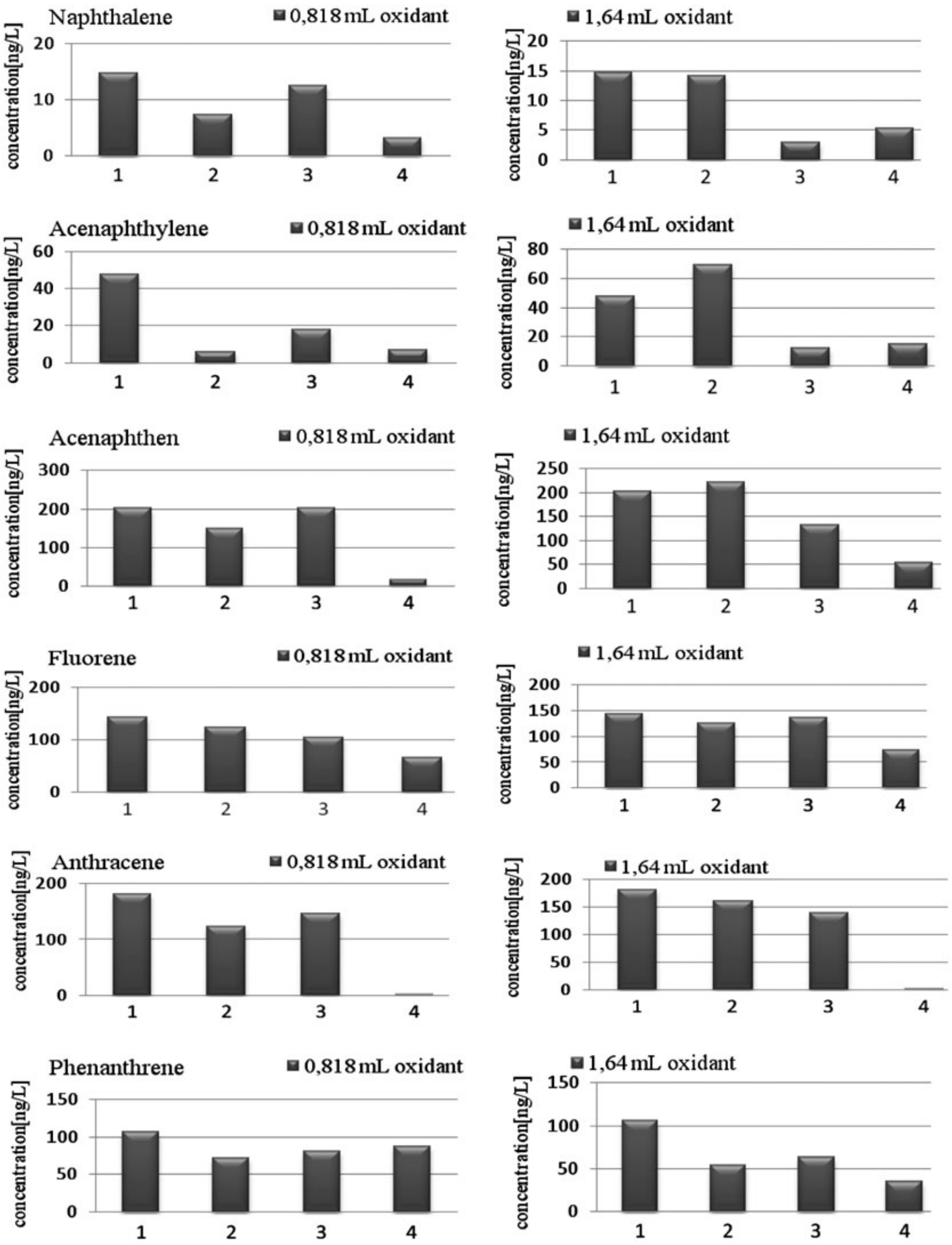

Fig. 4. Changes in the concentration of naphthalene and 3-ring PAHs according to the type of catalyst and oxidant dose. Notes: 1—initial concentration; 2—cobalt catalyst; 3—platinum catalyst; and 4—titanium catalyst.

The next stage of the study included the use of a platinum catalyst in the oxidation process of hydrocarbons in the presence of two doses a 30% solution dihydrogen dioxide. In Fig. 2, the changes in concentration of PAHs in the water samples during the oxidation process using a platinum catalyst are shown.

The average summary concentration of 16 PAHs in the examined samples after oxidation amounted to

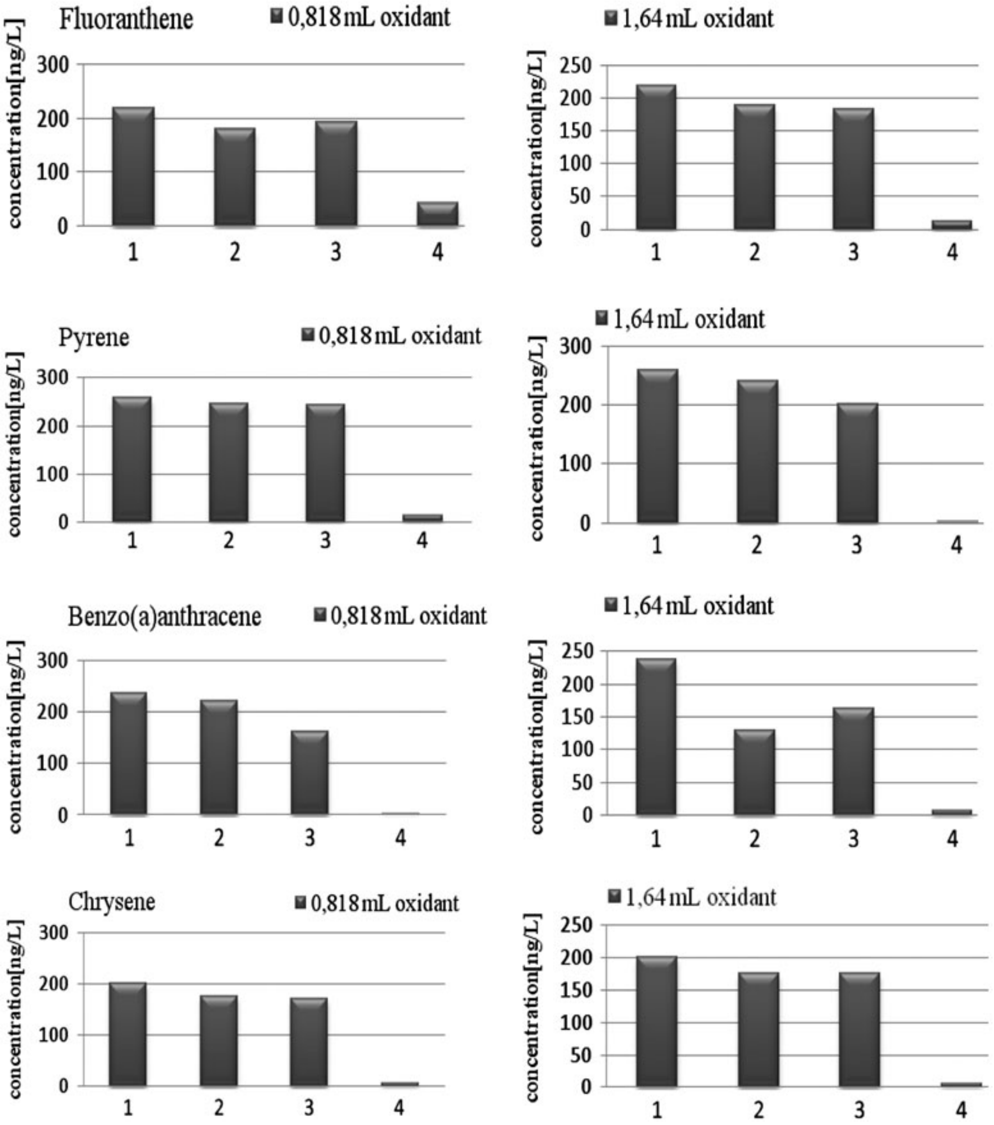

Fig. 5. Changes in the concentration of 4-ring PAHs according to the type of catalyst and oxidant dose.
Notes: 1—initial concentration; 2—cobalt catalyst; 3—platinum catalyst; and 4—titanium catalyst.

2,095 ng/L at a lower oxidant dose. An increased amount of dihydrogen dioxide resulted in the removal of total concentration of analyzed PAHs by 32% to obtain the final concentration of 1,940 ng/L. The greatest reduction degree of the analyzed hydrocarbons was recorded for 5- and 6-ring compounds. Five-ring hydrocarbons were removed in 39–45%. With increasing volumes of an added oxidant higher reduction resulted. The concentration of these compounds after oxidation amounted to 522 ng/L. The concentration of 6-ring hydrocarbons was reduced in 40% (188 ng/L) with a lower dose of an oxidant. Increasing the amount of dihydrogen dioxide did not improve the oxidation process. In the examined aqueous samples, in the process of catalytic oxidation, the concentration of 3- and 4-ring hydrocarbons has been reduced by 17% at a dose of 0.818 mL of oxidant per liter of the analyzed sample. Increasing the amount of that oxidant improved the reduction degree of hydrocarbons. For the total 3-ring hydrocarbons concentration, the final concentration of 666 ng/L (reduction by 26%) was obtained and for the 4-ring, 541 ng/L (reduction by 22%). In the second series of studies it can be concluded that the higher chemical reactivity was observed at 1.64 mL dose of oxidant $H_2O_2$ per liter of the analyzed sample. A study suggests that the

Table 4
Percentage removal of PAHs depending on the oxidant dose and catalyst type [%]

| PAH | Catalyst |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  | Cobalt |  | Platinum |  | Titanium |  |
|  | 0.818 mL $H_2O_2$/L | 1.64 mL $H_2O_2$/L | 0.818 mL $H_2O_2$/L | 1.64 mL $H_2O_2$/L | 0.818 mL $H_2O_2$/L | 1.64 mL $H_2O_2$/L |
| Naphthalene | 50 | 3.3 | 15 | 80 | 77 | 63 |
| Acenaphthylene | 88 | +45 | 63 | 74 | 84 | 68 |
| Acenaphthene | 27 | +10 | 0,2 | 34 | 92 | 74 |
| Fluorene | 14 | 13 | 27 | 6 | 55 | 50 |
| Anthracene | 32 | 11 | 20 | 23 | 99.7 | 99.6 |
| Phenanthrene | 33 | 49 | 24 | 41 | 19 | 67 |
| Fluoranthene | 18 | 14 | 12 | 16 | 80 | 94 |
| Piren | 5 | 7 | 5 | 22 | 95 | 99.8 |
| Benzo(a)anthracene | 7 | 46 | 32 | 31 | 99.9 | 97 |
| Chrysene | 12 | 12 | 14 | 12 | 96 | 97 |
| Benzo(b)fluoranthene | 31 | 34 | 10 | 25 | 98 | 98 |
| Benzo(k)fluoranthene | 18 | 34 | 50 | 52 | 99 | 99 |
| Benzo(a)pyrene | 37 | 78 | 60 | 62 | 99.6 | 99.5 |
| Dibenzo(a,h) anthracene | 55 | 73 | 59 | 53 | 99.6 | 99.6 |
| Indeno(1,2,3,c,d) pyrene | 37 | 78 | 38 | 37 | 99 | 99 |
| Benzo(g,h,i)perylene | 29 | 45 | 42 | 31 | 99 | 99 |

reactivity of examined hydrocarbons using a platinum catalyst decreases in the series: 5-ringed PAHs > 6-ring PAHs > 3-ring PAHs > 4-ring PAHs.

The last stage of the research included the process of using a titanium catalyst in the presence of a dihydrogen dioxide oxidant. Changes in the concentration of PAHs in the water samples during the oxidation process using a titanium catalyst are presented in Fig. 3.

The best results in removal of PAHs were obtained using a titanium catalyst. The amount of the oxidant 0.818 mL per liter of the analyzed sample resulted in reduction of the sum of 16 PAHs in 91%. Dihydrogen dioxide added to the water samples in the amount of 1.64 mL/L resulted in a decrease in 16 PAHs by 92% and the final concentration did not exceed 220 ng/L. Five- and six-ring hydrocarbons were removed at two doses of the oxidant in 99%. The final concentration after the process amounted to 2.4 and 7.4 ng/L, respectively. More than 97% removal of these four-ring hydrocarbons was obtained after a reduced amount of chemical oxidant. An increase in the dose of dihydrogen dioxide resulted in the reduction of the sum of these compounds by 98% and the final concentration was 15 ng/L. Three-ring hydrocarbons were reduced in the slightest degree, of at 76–79%. An increase in the dose of the oxidant has no significant effect on the catalytic oxidation. The final concentration of these compounds was 190 ng/L. After the third series of studies, one can conclude that the higher chemical reactivity was observed at a 0.818 mL dose of the oxidant $H_2O_2$ per liter of the analyzed sample. A study suggests that the reactivity of examined hydrocarbons using a titanium catalyst decreases in the series: 6-ring PAHs = 5-ring PAHs > 4-ring PAHs > 3-ring PAHs. From preliminary studies it can be concluded that the difference in the reduction of each group of hydrocarbon with the two doses of the oxidant was not as great since it only made up a few percent for the 3-ring hydrocarbon (3%) and for the 4-ring hydrocarbons (1%). For the other groups of hydrocarbons, increase in the amount of the oxidant did not improve the oxidation of hydrocarbons. Therefore, 0.818 mL dose of the oxidant was adopted as the optimal dose for this process.

Changes in the concentration of naphthalene and 3-ring hydrocarbons under the influence of different catalysts and two doses of an oxidant has been shown in Fig. 4. Naphthalene is a compound that is difficult to determine due to its high volatility. In this study, the largest multiplication factor was used for the recovery of this compound. It was removed at 80% using a platinum catalyst and an increased dose of the oxidant. For acenaphthylene, the most preferred catalyst is titanium

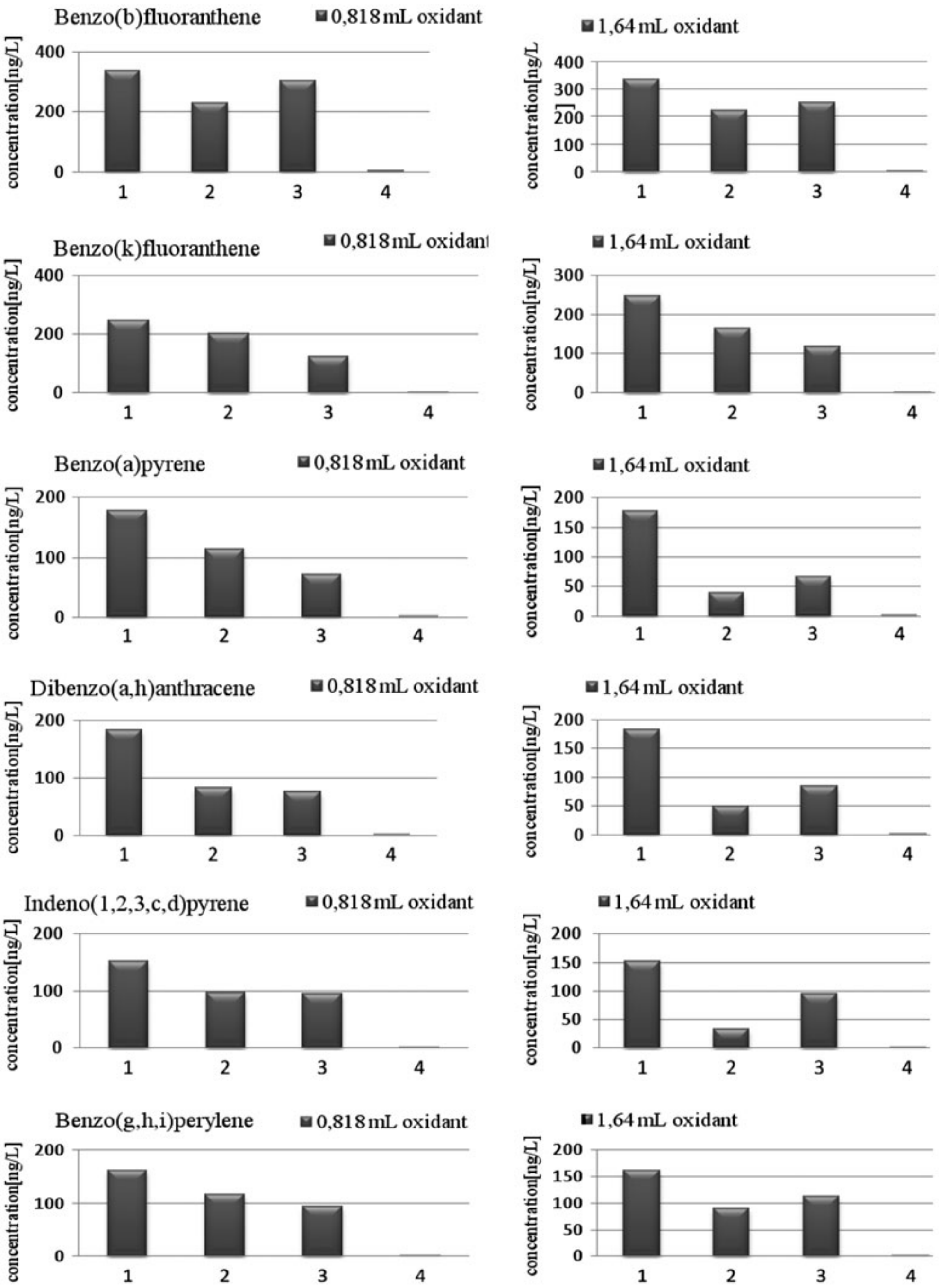

Fig. 6. Changes in the concentration of 5- and 6-ring PAHs according to the type of catalyst and oxidant dose.
Notes: 1—initial concentration; 2—cobalt catalyst; 3—platinum catalyst; and 4—titanium catalyst.

and a lower dose of an oxidant. The use of a cobalt catalyst and a reduced amount of dihydrogen dioxide resulted in the removal of the hydrocarbon in 88%. Acenaphthene after using cobalt and platinum catalyst was removed to a small extent. The application of the titanium catalyst resulted in a reduction from 74 to 92%. The removal degree of these two hydrocarbons (acenaphthylene and acenaphthene) may depend on the structural composition of the molecule. Acenaphthylene has, in its molecule, 6 unstable $\pi$ bindings. Fluorene has been removed in the slightest degree (6–55%) among the 3-ring compounds. Application of the

Table 5
The values of Student *t* distribution ($t_d = 4.303$) for groups of PAHs

| | The amount of oxidant (mL/L) | | | | | |
|---|---|---|---|---|---|---|
| | Cobalt catalyst | | Platinum catalyst | | Titanium catalyst | |
| PAH | 0.818 | 1.64 | 0.818 | 1.64 | 0.818 | 1.64 |
| ∑ 16 PAHs | 10 | 6.6 | 7.9 | 8.3 | 8.7 | 9.2 |
| 3-ring | 57 | 11 | 45 | 32 | 18 | 22 |
| 4-ring | 11 | 9 | 9.6 | 11 | 13 | 13 |
| 5-ring | 6.7 | 6.3 | 5.4 | 5.8 | 6.4 | 6.4 |
| 6-ring | 4.5 | 4.4 | 4.6 | 4.5 | 4.5 | 4.5 |

titanium catalyst gave the best removal effect. For other catalysts, no significant changes in the removal of the hydrocarbon were observed. The use of cobalt and platinum catalyst in the process of chemical oxidation resulted in a reduction of anthracene from 12 to 49%. The highest reduction of over 99% was obtained for the titanium catalyst. In Fig. 5, changes in concentrations of 4-ring hydrocarbons depending on the type of catalyst and oxidant dose are presented. The greatest effect of removing compounds belonging to this group was obtained after using an titanium catalyst. The percentage changes in the concentration of individual 4-ring hydrocarbons are presented in Table 4. The removal degree of fluoranthene for cobalt and platinum catalyst was in the range of 12–18%. The last group consisted of 5- and 6-ring hydrocarbons (Fig. 6). As can be seen in Fig. 6, the highest degree of reduction of individual hydrocarbons was also obtained after using a titanium catalyst. Benzo(b)fluoranthene was removed in 31–34%, when a cobalt catalyst has been used. Platinum catalyst did not improve reduction of this compound and the percentage of removal was in the range of 10–25%. The use of a platinum catalyst and the oxidant in two doses resulted in reduction of more than 50% of benzo(k)fluoranthene. For other hydrocarbons, except the titanium catalyst, cobalt catalyst at an increased dose of the oxidant has been proved to be preferred. The removal degree of the individual hydrocarbons amounted to 78% for benzo(a)pyrene, 73% for dibenzo(a,h)anthracene, 78% for indeno(1,2,3,c,d)pyrene, and 45% for benzo(g,h,i)perylene.

In order to better illustrate the changes in reaction systems using various catalysts, individual aromatic hydrocarbons and their reduction ratio are presented (Table 4).

Naphthalene was removed in 77%. At a lower amount of the oxidant, an increase in the chemical reagent did not improve the reduction of the compound. From the group of 3-ring hydrocarbons, phenanthrene was removed only in the 19%. However, an increase in the oxidant dose resulted in the reduction of this PAH in 67%. Also, less—55%—reduction was obtained for fluorene. Acenaphthylene was effectively removed (84%) at a dose of 0.818 mL of the oxidant per liter of the analyzed sample. Over 90% reduction was obtained for acenaphthene and anthracene. Among the 4-ring hydrocarbons, fluoranthene was reduced in 80%, but an increase in the oxidant dose resulted in the reduction of 94%. For other compounds belonging to the group—(P, B(a)A, Ch), 95–99% reduction of these compounds was obtained. Compounds belonging to the 5- and 6-ring hydrocarbons were removed in greater than 99%. Only benzo(b)fluoranthene was removed in 98%. The optimal dose of the oxidant to these hydrocarbons seems to be an 0.818 mL/L dose. To determine the significance of changes in the concentration of PAHs Student's *t*-test was used (Table 5).

The statistical calculations indicated that the changes in the summary concentration of 16 PAHs were significant in the case of using a cobalt *t*, platinum, and titanium catalysts at the two doses of the examined oxidant (the calculated $t_d$ value was greater than the critical value). The statistics showed that the application of cobalt, platinum, and titanium catalysts in the two doses was significant for 3-, 4-, 5-, and 6-ring hydrocarbons

## 4. Conclusions

(1) For the cobalt catalyst, the highest reduction of 16 PAHs was obtained at 1.64 mL/L dose of the oxidant. Chemical reactivity of considered hydrocarbons decreased in the series: 6-ring PAHs (61% reduction) > 5-ring PAHs (50% reduction) > 4-ring PAHs (22% reduction) > 3-ring PAHs (9% reduction).

(2) For the platinum catalyst, the greatest reduction of 16 PAHs was obtained at 1.64 mL/L dose of the oxidant. Chemical reactivity of examined hydrocarbons decreased in the series: 5-ring PAHs (45% reduction) > 6-ring PAHs (34% reduction) > 3-ring PAHs (26% reduction) > 4-ring PAHs (22% reduction).

(3) For the titanium catalyst, the highest reduction of 16 PAHs was obtained at 0.818 mL/L dose of the oxidant. Chemical reactivity of selected hydrocarbons decreases in the series: 6-ring PAHs = 5-ring PAHs (99% reduction) > 4-ring PAHs (98% reduction) > 3-ring PAHs (79% reduction).

## Acknowledgment

The research was funded by the projects BS/MN-402-303/12 and BS-PB-402-301/11.

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