CATALYTIC OXIDATION OF PAHs IN WASTEWATER

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Abstract
The aim of the investigations was to determine the effectiveness of the removal of 4, 5 -ring PAHs from coking wastewater using dihydrogen dioxide in the presence of a cobalt, platinum or titanium catalyst. A dose 7.4 mL of dihydrogen dioxide in the amount of and 14.8 mL/L of the analyzed sample were added to the samples. The samples were shaken and stored under laboratory conditions for 12 hours. The concentration of PAHs before and after the oxidation process were determined. The quantitative and qualitative chromatographic analysis was carried out using a gas chromatograph coupled with a mass spectrometer (GC-MS). The total concentration of 8 PAHs before oxidation reached the value of 9150 ng/L. The concentration of 4-ring compounds and 5-ring PAHs were equal to 6390 ng/L and 2760 ng/L, respectively. The highest decrease (93%) the sum of 8 hydrocarbons using a dose of oxidizer 7.4 mL/L and in the presence of titanium catalyst was achieved.

Keywords: oxidation, H$_2$O$_2$, GC-MS, coking wastewater, platinum catalyst, cobalt catalyst, titanium catalyst, PAHs

1. INTRODUCTION
Polycyclic aromatic hydrocarbons (PAHs) are a group of chemical compounds with two or more fused aromatic rings. They have a different structure, in which benzene rings may occur in various mutual positions and the chemical activity [1]. Toxicological studies shown that PAHs are carcinogenic compounds.

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Carcinogenic properties have PAH derivatives that occur in the environment or in human organisms as a result of metabolism have also carcinogenic properties [2]. PAH derivatives may be formed by reacting with other components of the matrix (halogenation, nitration, sulfonation, alklylation, acylation) [1]. The oxidation of hydrocarbons can provide products such as: diols, quinones and aldehydes, for example, benzo(a)pyrene can occur in the form of benzo(a)pyrene-1,6-dione and benzo(a)pyrene-3,6-dione, respectively [2,3]. In literature there is some information available about PAH derivatives formed during decomposition [4]. This is important due to toxicity of the derivatives to the organisms especially if sewage is discharged to surface receivers. There is not a lot of literature data on PAHs removal in wastewater treatment plants. Advanced oxidation methods of organic pollutants - AOP applied as treatment of industrial wastewater is of increasing importance. The following factors are responsible for the production of hydroxyl radicals: dihydrogen dioxide, permanganate, ozone, UV radiation and ultrasound [5]. The total decomposition of organic contaminants, without the use of chemicals can be obtained using photocatalysis (TiO₂ + UV) [6]. 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 (Fe²⁺/H₂O₂) the efficiency of the process depends on: the dose of Fe²⁺ and H₂O₂, pH, reaction time and temperature, respectively. The nature of the oxidized substance and the presence of other inorganic and organic compounds are significant factors as well [7]. The conventional methods of wastewater treatment are not always efficient, especially in the removal of compounds that are resistant to the biodegradation process (polycyclic aromatic hydrocarbons, phenols and their derivatives, pesticides). Advanced oxidation methods seem to be promising methods, which enable wastewater treatment after biological treatment. Numerous experiments aimed at determining the mechanisms of transformation and PAHs removal from industrial wastewater are conducted in Poland as well as in other countries [8-13]. Appropriate parameters and processes should be selected. In order to accelerate the possibility of removing polycyclic aromatic hydrocarbons from coke wastewater. The studies on advanced oxidation of compounds present in the wastewater (biologically treated) using dihydrogen dioxide in the presence of a catalyst may shorten the process of PAHs removal. The aim of the study was to determine the effectiveness of PAHs removal from wastewater using dihydrogen dioxide in the presence of cobalt, platinum or titanium catalyst.
2. MATERIALS AND METHODS

2.1. Materials
The study was conducted carried out coking wastewater, discharged from the biological treatment plant. The treatment plant consists of the following facilities: the denitrification reactor, the activated sewage reactor and nitrification reactor. Treated wastewater sample characterized by total organic compounds as COD and TOC. Fluoranthene, Pyrene, Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene and Dibenzo(ah)anthracene were determined in the treated wastewater as the initial concentration.

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

Solvents:
- methanol for HPLC—purity 99.9% (Avantor Performance Materials Poland S.A.);
- dichloromethane for HPLC—purity 99.8% (Avantor Performance Materials Poland S.A.);
- cyclohexane for HPLC—purity 99.5% (Avantor Performance Materials Poland S.A.).

2.2. Experimental procedure
The experiment was carried out using 1 liter of coking wastewater 7.4 ml or 14.8 ml of dihydrogen dioxide (30%) and an appropriate amount of cobalt catalyst, platinum or titanium. The dose of oxidant required for the oxidation of polycyclic aromatic hydrocarbons was calculated based on COD value calculation. Appropriate amounts of dihydrogen dioxide 30%, and cobalt or platinum or titanium oxide catalysts were added to samples. The sample was shaken on a magnetic stirrer (type MS 11 HS) with a constant amplitude (200 revolutions per minute) for 30 min. The reaction time was equal to 12 hours. Then, physico-chemical parameters and PAHs concentration in the effluent was determined. Changes in the PAHs concentration were determined before and after oxidation process.
2.3. PAHs analysis

The PAHs analysis included initial sample preparation and chromatographic quantitative determination. First, the extraction of organic matter from wastewater was carried out. Methanol, cyclohexane, and dichloromethane, at a volume ratio of 20:5:1 were added to 500 mL of wastewater, respectively. Then, the samples were shaken for 60 minutes while maintaining a constant amplitude of 20 mm and transverse 10 mm amplitude. The extracts were separated 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). Then the extracts were concentrated to a 2 mL volume under a nitrogen stream. The determination of the quantity and quality was carried out using a gas chromatography coupled with a mass spectrometer (GC-MS-QP2010 Plus SHIMADZU). The analysis was conducted on a column ZB-5 ms, with a 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 to 1 µL and split 1:5. The initial oven temperature was set to 140°C and it was maintained for 1 min. Then, the temperature increased to 240°C at a rate of 15°C/min, at 4°C/min. to 275°C, and it was ultimately increased from 10°C/min. to 320°C for 5 min. The obtained chromatograms were analyzed using the SIM. Qualitative and quantitative determinations were carried out using external standard of 16 PAHs at a concentration of 200 ng/L each of hydrocarbons. Samples were prepared in duplicate. In the Table 1 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 the range of 89% - 168%. Recovery values for series of 6 samples were also determined. Student’s t-test was used to determine the significance of changes in the concentration of PAHs. The confidence level 0.95 and a degree of freedom 2 were adopted. t_d theoretical value was equal to 4.303 for the samples prepared [14].

Table 1. The reference values and recoveries of PAHs

<table>
<thead>
<tr>
<th>PAH</th>
<th>Number of rings</th>
<th>The reference value [ng/L]</th>
<th>The value indicated [ng/L]</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoranthene</td>
<td>4</td>
<td>200</td>
<td>219</td>
<td>109</td>
</tr>
<tr>
<td>Pyrene</td>
<td>4</td>
<td>200</td>
<td>258</td>
<td>129</td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>4</td>
<td>200</td>
<td>237</td>
<td>118</td>
</tr>
<tr>
<td>Chrysene</td>
<td>4</td>
<td>200</td>
<td>201</td>
<td>100</td>
</tr>
<tr>
<td>∑ 4 ring PAHs</td>
<td></td>
<td>800</td>
<td>915</td>
<td>114</td>
</tr>
<tr>
<td>Benzo(b)fluoranthene</td>
<td>5</td>
<td>200</td>
<td>336</td>
<td>168</td>
</tr>
</tbody>
</table>
2.4. Correction value of COD indicator

The effect of residual dihydrogen dioxide with respect to the indicators of organic pollutants such as COD and TOC before and after the oxidation process should be considered. Available data [15÷17] suggest that the application of dihydrogen dioxide in the removal of organic compounds from wastewater, are experiencing fluctuations in the value of COD including the increase in the value of this indicator. In order to properly assess the effectiveness of the removal of organic pollutants TOC pointer should be taken into consideration. The value of this ratio does not depend on the dose of oxidant, and therefore control of the total organic carbon is a better indicator and determines the real contents of organic substances in wastewater. The amendment changes the TOC was determined in order to determine the effect of residual dihydrogen dioxide. The coefficient of determination of COD (\(f_i\)) was calculated according to the formula (1):

\[
f_i = \frac{(\text{COD}_0 - 0.011 \cdot R_i \cdot \text{COD}_0)}{\text{TOC}_i}
\]

where:

- \(\text{TOC}_i\) - concentration of total organic carbon in the sample and, mg/L
- \(\text{COD}_0\) - the initial value of the COD in the sample raw wastewater, mg/L
- \(R_i\) - the reduction of TOC in the sample, %.

3. RESULTS AND DISCUSSION

3.1 Calculation of COD value

In the studies, the calculation factor COD\(_{\text{experimental}}\) (\(f_i\)) for coking wastewater varied from 5.0 to 6.7. Using the formula (1) that is the product COD\(_{\text{calculation}}\) factor (\(f_i\)) and the value of TOC [mg /L] COD\(_{\text{calculation}}\) determined, and the results are shown in Figure 1. The obtained COD calculated values were lower than experimental COD for oxidation carried out in the presence of titanium catalyst. The optimal dose of dihydrogen dioxide was obtained using titanium catalyst. The removal of COD\(_{\text{calculation}}\) varied from 40 to 48%, respectively.
Changes in the PAHs concentration in wastewater during catalytic oxidation process

The total concentration of 8 PAHs before oxidation amounted to the value of 9150 ng/L. The concentration of 4-ring and 5-ring PAHs were equal to 6390 ng/L and 2760 ng/L, respectively. In the first step the effect of the cobalt catalyst with a suitably selected dose of dihydrogen dioxide on the degree of oxidation of selected group of the aromatic hydrocarbons was studied. In Figure 2 the changes in the concentration of PAHs in water samples during the oxidation process using a cobalt catalyst and two doses of the oxidant are presented, respectively. The application of the cobalt catalyst resulted in the removal of 8 PAHs of 79% using a 7.4 mL dose of oxidant H₂O₂ per liter of the analyzed sample. The increase in the amount of dihydrogen dioxide resulted in higher oxidation efficiency - 80% archiving the final concentration of 1884 ng/L. Chemical reactivity of individual hydrocarbons depends on the compounds structure and therefore the oxidation process PAHs according to the number of rings in the molecule were found. For 4-ring hydrocarbons (fluoranthene (Fl), pyrene (P), benzo(a)anthracene (B(a)A), chrysene (Ch)) have been oxidized in 80% at a lower dose oxidant yield. The final concentration of these PAHs reached the value of 1289 ng/L.
The application of a cobalt catalyst at the lower dose of dihydrogen dioxide resulted in the removal of 5-ring hydrocarbons of 79%, while an increase in oxidant to 14.8 mL/L reduced the compounds of 87%. A study may suggest that the reactivity of 5-ring hydrocarbons in the presence of a cobalt catalyst was higher than reactivity of 4-ring PAHs. In Figure 3 the changes in concentration of PAHs in the wastewater samples during the oxidation process using a platinum catalyst are shown. The average total concentration of 8 PAHs in the samples after oxidation amounted the value of 1370 ng/L in the presence of lower oxidant dose.

Increased amount of dihydrogen dioxide did not result in a decrease in the concentration of analyzed PAH. The concentration of 5-ring hydrocarbons was reduced by 83% (470 ng/L) with a lower dose of an oxidant. The increase of
the amount of dihydrogen dioxide did not improve the oxidation process. The concentration of 4-ring hydrocarbons was reduced by 86% at a dose of 7.4 mL of oxidant per liter of the analyzed sample. The final concentration of 900 ng/L for sum of 4-ring hydrocarbons concentration was obtained. It can be concluded that the higher chemical reactivity at a dose of 7.4 mL oxidant H$_2$O$_2$ per liter of the analyzed sample was observed. A study suggests that the reactivity of studied hydrocarbons using a platinum catalyst decreases as follows: 4-ring PAHs > 5-ring PAHs. In the last step of the studies the process using a titanium catalyst in the presence of dihydrogen dioxide oxidant was applied. Changes in the concentration of PAHs in the water samples during the oxidation process using a titanium catalyst are presented in Figure 4. It was found that the highest removal of polycyclic aromatic hydrocarbons was obtained using a titanium catalyst.

![TITANIUM CATALYST](image)

Fig. 4. Changes in the concentration of PAHs using a titanium catalyst,
1 - coking wastewater, 2 - coking wastewater + 7.4 mL H$_2$O$_2$/L + titanium catalyst,
3 - coking wastewater + 14.8 mLH$_2$O$_2$/L + titanium catalyst

The dose of the oxidant of 7.4 mL per liter of the analyzed sample resulted in the decrease of the sum of 8 PAHs of 93%. Dihydrogen dioxide added to the wastewater samples in the amount of 14.8 mL/L resulted in a decrease of 8 PAHs by 88% and the final concentration did not exceed the value of 1117 ng/L. Over 92% removal of 5-ring hydrocarbons using two doses of an oxidant, and the final concentration, equal to 200 ng/L were obtained. Four-ring hydrocarbons were removed of 94%, with a reduced dose of an oxidant. The final concentration of these compounds was equal to 407 ng/L. Increasing the dose of oxidant did not result the effect on catalytic oxidation significantly. After the third serie of studies one can conclude that the higher chemical reactivity was observed at a 7.4 mL dose of the oxidant H$_2$O$_2$ per liter of the analyzed sample. A study suggests that the reactivity of studied hydrocarbons using a titanium catalyst decreases as follows: 4-ring PAHs > 5-ring PAHs. The removal of individual aromatic hydrocarbons is presented in Table 2.
### Table 2. Percentage removal of PAHs with various oxidant dose and catalyst [%]

<table>
<thead>
<tr>
<th>PAH</th>
<th>cobalt catalyst</th>
<th>platinum catalyst</th>
<th>titanium catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7.4 mLH₂O₂/L</td>
<td>14.8 mLH₂O₂/L</td>
<td>7.4 mLH₂O₂/L</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>39</td>
<td>52</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Pyrene</td>
<td>87</td>
<td>78</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>69</td>
<td>69</td>
<td>69</td>
</tr>
<tr>
<td>Benzo (a) anthracene</td>
<td>48</td>
<td>79</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>78</td>
<td>78</td>
<td>78</td>
</tr>
<tr>
<td>Chrysene</td>
<td>93</td>
<td>86</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>77</td>
<td>77</td>
</tr>
<tr>
<td>Benzo (b) fluoranthene</td>
<td>82</td>
<td>89</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>86</td>
<td>86</td>
<td>86</td>
</tr>
<tr>
<td>Benzo (k) fluoranthene</td>
<td>91</td>
<td>97</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>99</td>
<td>99</td>
<td>99</td>
</tr>
<tr>
<td>Benzo (a) pyrene</td>
<td>18</td>
<td>34</td>
<td>8</td>
</tr>
<tr>
<td>Dibenzo (a, h) anthracene</td>
<td>40</td>
<td>74</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>74</td>
<td>74</td>
<td>74</td>
</tr>
</tbody>
</table>

Among the 4 - ring hydrocarbons fluoranthene was removed from 25 to 94%, respectively. The effectiveness of PAHs oxidation was the highest in the presence of titanium catalyst. Benzo(a)anthracene was removed from 48 to 79% using a cobalt catalyst and platinum. 83% removal of hydrocarbons was achieved with the catalyst titanium and a lower dose of dihydrogen. Chrysene removal efficiency reached varied from 96 to 97% using a titanium catalyst. The final concentration of chrysene varied from 54 to 72 ng/L. The initial concentration of benzo(b)fluoranthene before the oxidation process was equal to 1730 ng/L, and after the oxidation process decreased to the value of 190 ng/L, using the titanium catalyst. The losses of 5-ring of PAHs were 99% using the titanium catalyst and 7.4 ml/L of oxidant.

It was observed that with increasing doses of the chemical oxidant the COD concentration of the cobalt catalyst and platinum increases as well. Changes in the value of the generic organic compounds may result in a change in the form of PAHs. This confirms the loss of the concentration of individual PAHs and quantity of added oxidant cobalt catalyst, and platinum. The use of titanium catalyst resulted in the highest reduction of COD concentration. A similar dependence was observed in the changes of individual PAHs concentration. It can be concluded that under catalytic oxidation conditions the process of mineralization of organic compounds may occur.

### 4. CONCLUSIONS

The efficiency of 8 PAHs removal was in the range of 79-80% under catalytic (cobalt catalyst) oxidation conditions. Chemical reactivity of studied hydrocarbons decreased as follows: 5-ring PAHs (87% removal) > 4-ring PAHs (76% removal), respectively. The highest removal of PAHs at the dose of the oxidant equal to 7.4 mL/L for the platinum catalyst was obtained. Chemical
reactivity of the studied hydrocarbons decreased in the series: 4-ring PAHs (86% removal) > 5-ring PAHs (83% removal). The highest efficiency of PAHs removal was archived at 7.4 mL/L dose of the oxidant using titanium catalyst. Chemical reactivity of the selected hydrocarbons decreases in the series: 4-ring PAHs (94% removal) > 5-ring PAHs (93% removal).

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

REFERENCES

KATALITYCZNE UTLENIANIE WWA W ŚCIEKACH

Streszczenie

Celem badania było określenie skuteczności usuwania 4, 5- pierścieniowych WWA ze ścieków koksoniczych przy użyciu ditlenku dwiodoru w obecności katalizatora kobaltowego, platynowego i tytanowego. Do próbki dodawano odpowiednią ilość ditlenku dwiodoru i katalizatorów. Dawka utleniacza wynosiła 7,4 ml i 14,8 ml/l. Próbki
mieszano i pozostawiono w warunkach laboratoryjnych przez 12 godzin. Po tym czasie oznaczono stężenie WWA. Ilościową i jakościową analizę chromatograficzną przeprowadzono przy użyciu chromatografu gazowego sprzężonego ze spektrometrem masowym. Największy ubytek (93%) sumarycznej ilości ośmiu WWA osiągnięto przy zastosowaniu dawki utleniacza 7,4 ml/l analizowanych ścieków oraz katalizatora tytanowego.

Słowa kluczowe: utlenianie, H₂O₂, GC-MS, ścieki koksownicze, katalizator platynowy, katalizator kobaltowy, katalizator tytanowy, WWA

Editor received the manuscript: 17.08.2015