

REMOVAL OF PRIORITY PAHS FROM COKING WASTEWATER

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The purpose of these tests described in this study was to determine the effectiveness of removing eight aromatic compounds from the list of priority. Tests were carried out using coke produced during wastewater treatment of coke oven gas. The technology research was consisted in introducing into wastewater samples taken with 30% solution of hydrogen dioxide (50 mg/dm³, 100 mg/dm³, 300 mg/dm³, 600 mg/dm³, 900 mg/dm³, 1000 mg/dm³, 2000 mg/dm³). The PAHs analysis included: sample preparation, quantitative and qualitative chromatographic determination, it was also carried out using gas chromatography coupled with mass spectrometer. Total concentration of PAHs in the effluent eight coke before oxidation was 23 µg/dm³. The largest loss of hydrocarbons examined, reaching 62%, was noted at the dose of 50 mg/dm³ of the oxidant.

Keywords: oxidation, H₂O₂, PAHs, GC-MS, industrial wastewater

1. INTRODUCTION

Studies, reported in the literature has shown, that the wastewater from processing fuels like coke or petroleum is the most loaded organic micropollutants [2,16].

The presence of PAHs in coking wastewater were confirmed in literature reports and earlier research [9,11,12,13,15]. Bartkiewicz says that the content of organic compounds expressed as oxygen consumption may reach 1,000 mg/L. The concentration of total nitrogen and volatile phenols may be suitably in the range from 980 to 6500 and 260 to 3000 mg/dm³ [1].

The Directive of the European Parliament and the Council 2008/105/EC from the 16th of December 2008, provides environmental quality standards for priority substances and certain other pollutants [4]. In Polish legislation it is the

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ordinance of the Minister of the Environment from the 9th of November, 2011 [7]. Lists of priority substances on 8 PAH: naphthalene, anthracene, fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene.

With the above hydrocarbons, five exhibit carcinogenic, mutagenic or teratogenic effects that depend on the structure and environmental conditions.

Toxicological studies have shown that PAHs themselves are not carcinogenic, but only derivatives which occur in the environment, or in organisms as a result of metabolism [3]. PAH derivatives may be formed by reaction with other components of the matrix (halogenation, nitration, sulfonation, alkylation, acylation). [8]. Hydrocarbons are also oxidation reactions and photochemical degradation. The oxidation of hydrocarbons can give products such as diols, quinones and aldehydes, for example, benzo(a)pyrene can be in the form of derivatives such as benzo(a)pyrene-1,6-dione and benzo(a)pyrene-3,6-dione [3,6].

An advanced oxidation methods of organic pollutants – AOP are increasingly being used for a treatment of industrial wastewater. These methods rely from the generation of hydroxyl radical, which allows the decomposition of organic compounds to CO_2 and H_2O . The most common agents that cause the generation of hydroxyl radicals are hydrogen dioxide, permanganate, ozone, UV radiation and ultrasound [14].

The total degradation of organic contaminants, without using chemicals, can process photocatalysis ($\text{TiO}_2 + \text{UV}$) [5]. According to the IUPAC nomenclature, the process is referred as a photocatalytic reaction of chemical change, or initiation by radiation in the presence of a catalyst, which absorbs light and cause chemical conversion of the compounds present in the sample. In addition to chemical oxidation and ozone above, dihydrogen dioxide can be used in Fenton's reagent and permanganate. It has been shown, that in the Fenton reaction ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) efficiency of the process depends from the dose of Fe^{2+} and H_2O_2 , pH, reaction time and temperature, but also from the type of oxidized substances and the presence of other inorganic and organic compounds [10].

The purpose of these tests described in this study was to: determine the effectiveness of removing eight aromatic hydrocarbons from the coke wastewater.

2. MATERIALS AND METHODS

The tests were carried out using coke, produced during wastewater treatment of coke oven gas. In practice, the sewage is directed to a biological treatment works. Samples of water were taken as a temporary and pre-characterized, by

determining key indicators such as COD, TOC. Wastewater sample taken initially characterized by following the determination of such indicators as: COD with the American summary, TOC and N general - analyzer Multi N / C 2100, according to PN-EN 1484:1999. Concentrations of 16 PAHs compounds, including eight (Naf, Antr, Fl, BaP, BbF, BkF, BghiP, IP) were recognized as the original.

The technology research consisted introducing into water samples taken with 30% solution of hydrogen dioxide. The dose of the reagent was: 50 mg/dm³, 100 mg/dm³, 300 mg/dm³, 600 mg/dm³, 900 mg/dm³, 1000 mg/dm³, 2000 mg/dm³. The samples were mixed and left in the laboratory conditions a period of 60 minutes. After this time the PAHs were determined and the analysis of physico-chemical indicators in the effluent was repeated.

2.1. Analytical Methods of PAHs

PAH analysis included initial sample preparation and chromatographic quantitative determination. Initial stage was the extraction of organic matter from wastewater. To 500 ml of water were added solvents: methanol, cyclohexane, dichloromethane, at a volume ratio of 20:5:1. Then subjected of shaking for 60 minutes, where a constant amplitude was maintained. The extracts were separated from the water sample by centrifugation. Then the extracts were purified under vacuum (SPE) for the small columns filled with silica gel (fill conditioning was performed with a mixture of dichloromethane and cyclohexane, v/v 1:5, three times with 3 ml). Received extract was concentrated to a volume of 2 ml under a nitrogen stream. The final step was to determine the quantitative and qualitative indication, which was carried out using gas chromatography coupled with mass spectrometer (GC-MS-QP2010 Plus SHIMADZU). The analysis was performed on a ZB-5 ms length of 30 m and a diameter of 0.25 mm used as carrier gas helium, which was set at flow 1.08 ml/min. Injection volume was 1 µl, split 1:5. Initial oven temperature was set at 140°C and 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 increasing from 10°C/min. to 320°C. The final temperature was maintained for 5 min. Received chromatograms were analyzed using the SIM card. Qualitative and quantitative indications were based on external standard PAH 16 each at a concentration of 200 ng/cm³. The changes in the concentration of PAHs were determined on the basis of wastewater before and after oxidation. Samples were performed in duplicate.

3. RESULTS AND DISCUSSION

3.1 Preliminary studies

The initial stage of the study was to perform the basic signs of chemical indicators for coke plant before and after the oxidation process. Table 1 shows the values of the results.

Table 1. Characteristics of coke wastewater

Index	unit	Oxidant concentration (H ₂ O ₂) [mg/dm ³]							
		0	50	100	300	600	900	1000	2000
COD	mg/dm ³	770	676	732	878	846	786	808	846
TOC	mg/dm ³	119	113	129	150	112	109	114	128

With regard to the indicators of organic pollutants such as COD and TOC before and after the oxidation process, we can conclude that their values have been slightly altered. During the process of oxidation defects observed concentrations of the hydrocarbons, but they can create other compounds, because general indicators of organic pollutants (COD, TOC) may remain at a similar level.

3.2 Quantitative changes of PAHs

Initial concentration of 16 PAHs in coking wastewater was 38 mg /dm³. The concentration of eight main hydrocarbon was on average 23 µg/dm³, which composed 60% of the total amount of 16 PAHs. The concentration of benzo(a)pyrene was 14% of the total concentration of 16 PAHs, and 24% of the total amount of hydrocarbons on the of priority compounds list. As can be seen in the force of the Directive of the European Parliament on environmental quality standards for priority substances, downloaded coke wastewater does not meet the conditions for entry into the water and require a clean [4].

Introduction of the oxidant into the wastewater in an amount of 50 mg/dm³ caused significant changes in the removal of the analyzed hydrocarbons (8 PAH - 62%). If, however, the amount of hydrogen dioxide was 100, 900, 1000 mg/dm³ the 16 PAH removal was recorded at a level from 21% to 24%, and eight hydrocarbons at - 22%. Larger percentage reductions were achieved by adding an oxidant PAHs in an amount of 300 mg/dm³ and 2000 mg/dm³. Then the percentage removal of 16 PAHs and 8PAHs were respectively 60% and 57% , 47% and 43%. Analyzed changes in the concentration of hydrocarbons in coking wastewater depending on the dose of oxidant is shown in Figure 1.

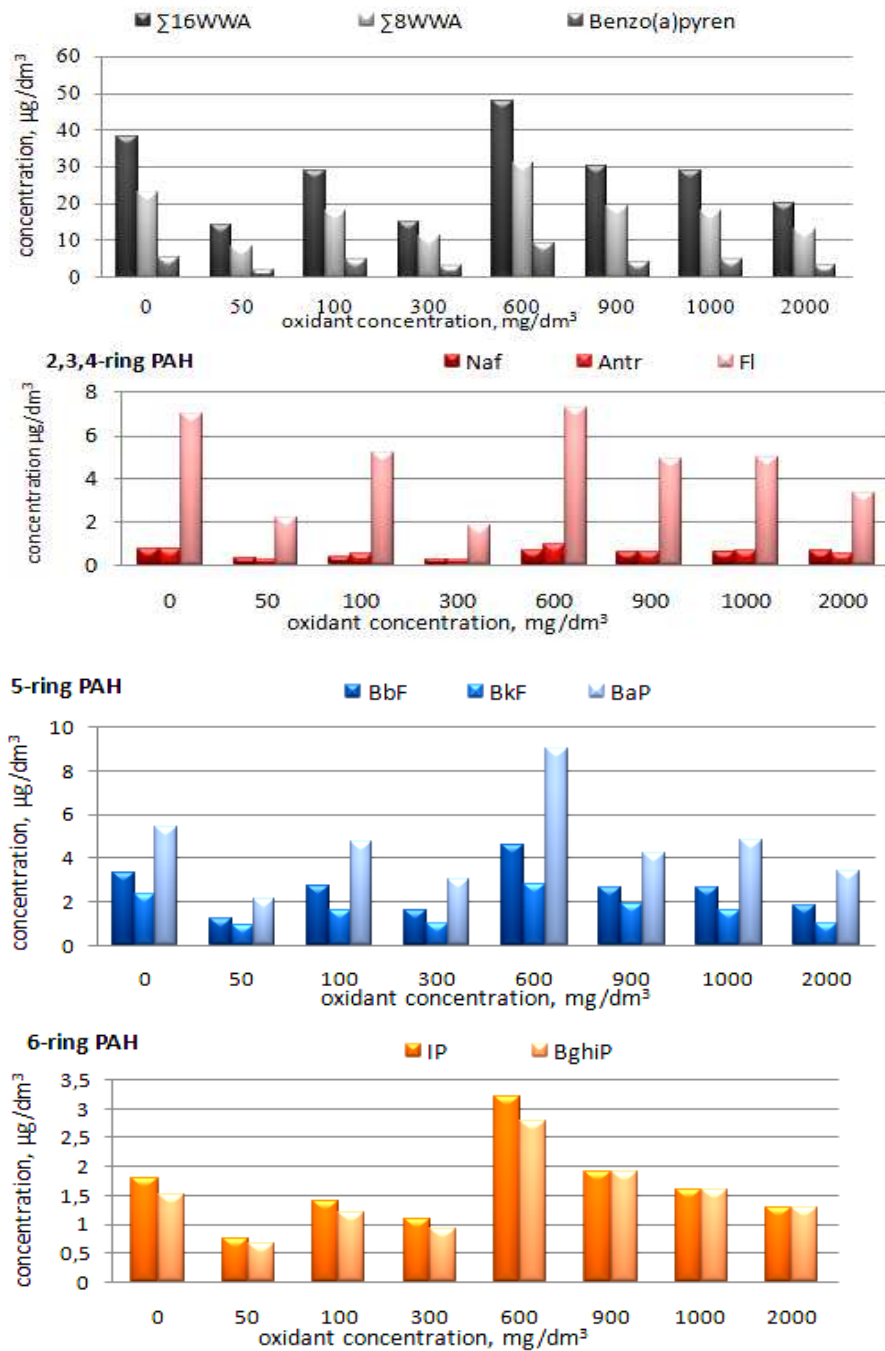


Fig. 1. Changes in the concentrations of PAHs in coking wastewater

In the process of oxidation, the wastewater prior to the parent compounds in the hydrocarbon group of eight, were: fluoranthene accounted for 31% ($7.0 \mu\text{g}/\text{dm}^3$), benzo(a)pyrene constituting 24% ($5.4 \mu\text{g}/\text{dm}^3$). Using suitable amounts of oxidant, the first one (Fig 1) remained at 18% -29%, and benzo(a)pyrene was vary from 23% to 30%. During the research process, the percentage of the remaining compounds in the mixture did not go under significant changes. The percentage of specific hydrocarbons are shown in Table 2, assuming Σ 8 PAH as 100%.

The highest tested concentration of PAHs losses to the sum of eight hydrocarbons were obtained using hydrogen dioxide in an amount of $50 \text{ mg}/\text{dm}^3$. Then, the efficiency of removal benzo(a)pyrene was respectively of 61% and the final concentration of the hydrocarbon did not exceed $2.1 \mu\text{g}/\text{dm}^3$. The highest 68% reduction was observed in the case of fluoranthene (table 2).

Table 2. The percentage and the percentage of removal of PAHs

		Concentration of H_2O_2 [mg/dm^3]								
		PAHs	0	50	100	300	600	900	1000	2000
Percentage %	Naf	3.0	4.0	2.2	3.0	2.0	3.2	3.4	4.8	
	Antr	3.0	3.0	3.2	2.3	3.0	3.2	3.8	3.8	
	Fl	31	26	29	18	23	26	27	25	
	B(a)P	24	25	26	30	29	23	26	26,7	
	B(b)F	14	14	15	16	15	14	14	13.6	
	B(k)F	10	11	9.2	10	9.0	10.2	8.6	7.5	
	I(1,2,3,c,d)P	8.0	9.0	8.2	11	10	10.2	8.6	9.8	
	B(g,h,i)P	7.0	8.0	7.2	9.7	9.0	10.2	8.6	9.8	
Percent removal %	Naf	0	57	51	65	8.0	20	16	14	
	Antr	0	67	33	72	-	24	10	32	
	Fl	0	68	26	74	-	30	29	53	
	B(a)P	0	61	13	44	-	22	11	37	
	B(b)F	0	64	18	52	-	21	21	45	
	B(k)F	0	59	30	56	-	17	30	56	
	I(1,2,3,c,d)P	0	58	22	39	-	-	11	28	
	B(g,h,i)P	0	55	20	38	-	-	-	13	

Amount of the eight PAHs, five of them have either carcinogenic, mutagenic or teratogenic (BaP, BbF, BkF, B(g,h,i)P, IP) properties. The content of these compounds in the wastewater before oxidation was $14 \mu\text{g}/\text{dm}^3$ representing 61% of 8 PAHs. Introduction of the oxidant into the wastewater in an amount of $600 \text{ mg}/\text{dm}^3$ did not result in any changes of the removal these compounds. If, however, the amount of hydrogen dioxide was $100 \text{ mg}/\text{dm}^3$, $900 \text{ mg}/\text{dm}^3$ or $1000 \text{ mg}/\text{dm}^3$ five PAHs removal was recorded in the range from 7% to 14%. A greater percentage reduction was achieved by adding an oxidant in an amount of $300 \text{ mg}/\text{dm}^3$ and $2000 \text{ mg}/\text{dm}^3$. Then the final concentration was $7.6 \mu\text{g}/\text{dm}^3$ and $8.8 \mu\text{g}/\text{dm}^3$, however the percentage PAHs removal rates reached

46% and 37%. The highest (59%) loss of the compounds was achieved at a dose of 50 mgH₂O₂/dm³, where the final concentration was 5.7 µg/dm³.

The use of an oxidant in doses 600, 900, 1000 mg/dm³ is not significantly reduced concentrations of the individual PAHs. Coking wastewater is rich organic material. In addition to the 8 analyzed polycyclic aromatic hydrocarbons during oxidation derivatives may be formed. The use of an oxidant in an amount of 50 mg/dm³ resulted in a reduction of 8 PAH in 62%. As the amount to be donated dihydrogen dioxide process to go with a smaller loss. This may be due to the transformation of complex aromatic hydrocarbons, compounds of the complex structure. Preliminary identification of water indicated the presence of coke indeno(2,1-c)pyridine, and dibenzopyrolu, indeno(1,2-b)pyridine. Unequivocal evidence of their presence requires further research and detailed interpretation received chromatogram.

4. CONCLUSIONS

Based on the study, the following conclusions can be drawn:

- High values of COD and TOC confirmed, that coke wastewater was highly loaded with organic compounds.
- The combined concentration of 8 PAHs in wastewater coke was 23 µg/dm³, with carcinogenic compounds accounted for 61% (14 µg/dm³).
- The percentage of the compounds in the mixture, did not go under significant changes during the testing process.
- The total amount of the eight PAHs removal efficiency was the highest (62%) when hydrogen dioxide was used at dose of 50 mgH₂O₂/dm³
- The effectiveness of removal PAHs from wastewater after the 50 mg/dm³ dihydrogen dioxide was: naphthalene - 57%, anthracene - 67%, fluoranthene - 68%, benzo(a)pyrene - 61%, benzo(b)fluoranthene - 64%; benzo(k)fluoranthene - 59%, indeno(1,2,3,c,d)pyrene - 58%, benzo(g,h,i)perylene - 55%.

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USUWANIE PRIORYTETOWYCH WWA ZE ŚCIEKÓW KOKSOWNICZYCH

Streszczenie

Celem badań opisanych w pracy było określenie skuteczności usuwania ze ścieków koksowniczych ośmiu węglowodorów aromatycznych z listy związków priorytetowych. Badania technologiczne polegały na wprowadzeniu do pobranych próbek ścieków przyjętych ilości 30% roztworu ditlenku wodoru (50 mg/dm³, 100 mg/dm³, 300 mg/dm³, 600 mg/dm³, 900 mg/dm³, 1000 mg/dm³, 2000 mg/dm³). Analiza WWA obejmowała przygotowanie próbek oraz ilościowe i jakościowe oznaczenie chromatograficzne, które prowadzono z wykorzystaniem chromatografu gazowego sprzężonego ze spektrometrem masowym. Sumaryczne stężenie ośmiu WWA w ściekach koksowniczych przed procesem utleniania wynosiło 23 µg/dm³. Największy ubytek badanych węglowodorów, sięgający 62%, odnotowano przy dawce utleniacza wynoszącej 50 mg/dm³.