



Application of sodium carbonate–hydrogen peroxide for PAHs degradation in real wastewater and evaluation of their toxicity TEQ value

Jolanta Kozak*, Maria Włodarczyk-Makuła

Department of Environmental Engineering, Faculty of Infrastructure and Environment, Czestochowa University of Technology, 69 Dabrowskiego Str. 42-201 Czestochowa, Poland, emails: j.kozak@is.pcz.pl (J. Kozak), mwm@is.pczest.pl (M. Włodarczyk-Makuła)

Received 4 November 2019; Accepted 3 May 2020

ABSTRACT

The aim of the research was determination the changes in the polycyclic aromatic hydrocarbons (PAHs) concentration in wastewater during the photo-Fenton process and the changes in chemical oxygen demand (COD) value. Moreover, the estimation of toxicity changes based on the toxic equivalency factor model was evaluated. Industrial wastewater (effluent) from the wastewater treatment plant in the autumn season was collected. According to the literature recommendation, the value of pH was getting to the level of about 3.5–3.8. As the oxidant sodium carbonate–hydrogen peroxide (v/v 2/3) in the doses from 1.2 to 8.0 g/L were used. As the source of iron $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ iron sulfate in a constant dose of 1.0 g/L was added. The reaction time was 20 min. Next, the samples were exposed to ultraviolet rays for 360 s. Sodium carbonate as a solid was used. Before and after the process of oxidation the PAHs concentration and COD value have been determined. Preparation of samples for the PAHs determination was carried out by the liquid–liquid phase extraction. Quantitative and qualitative analysis of PAHs using gas chromatography-mass spectrometry was performed. The effectiveness of the removal of PAHs was in the range of 89.1%–96.6%, and the value of COD decreased in the range of 9%–29%. The initial level of total equivalent concentration was 9.01×10^{-3} mg/L and after the oxidation process decreased to 0.055×10^{-3} mg/L.

Keywords: PAHs; photo-Fenton; AOPs; sodium carbonate–hydrogen peroxide (v/v 2/3); hydroxyl radicals; TEQ; coke wastewater

1. Introduction

Nowadays, the development of industry generates the formation of new types of toxic compounds, often with an unknown impact on living organisms. The source of toxic compounds is mainly industries such as pharmaceutical, wood, food, coal processing as well as oil refining. Polycyclic aromatic hydrocarbons (PAHs) belong to group of persistent organic pollutants. PAHs presence in coke wastewater has been confirmed in many scientific research [1–8]. The methods of wastewater management in coke plant installations depend on the size of the coke plant and the technological solutions used. Wastewater produced on-site can be subjected to a multi-stage treatment process, or

after pre-treatment, can be reused. Next, that wastewater are used to wet quenching of coke and become a potential source of air pollution with high volatile hydrocarbons. In some plants, effluents may also be discharged into surface waters or sewage systems. Currently, coking plants are required by best available technique (BAT) guidelines to modernize existing coking installations and equipment. BAT requirements specify the allowable concentration of PAHs in treated coke wastewater at a level below 0.05 mg/L [9].

PAHs are widely widespread in the environment, there are found in all ecosystems. All PAHs can be classified into two categories: low molecular weights (LM-PAHs, containing 2–3 benzene rings PAHs), and high molecular

* Corresponding author.

weights (HM-PAHs, containing 4–6 benzene and pentene rings PAHs) [10]. The negative effect is related to the number of rings in the molecule. For example with increasing molecular weight, aqueous solubility decreases, and melting point, boiling point, and the $\log K_{ow}$ (octanol/water partition coefficient) increases [11]. Moreover, due to their high lipophilicity can accumulate in fat tissue (bioaccumulation) and move along food chains (biomagnification). PAHs are present in every element of the environment. Due to the above-mentioned properties, they are hardly biodegradable. Also, they easily adsorb onto solid surfaces. Even their low concentrations are dangerous. Toxicity depends on the structure of PAHs and other associated factors. Depending on the type of organism, they show acute to moderate toxicity. It results in tumor formation, effects on development, reproduction, and the immune system [11–16].

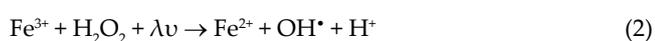
To the PAHs group belongs several hundred compounds. The US Environmental Protection Agency listed 16 of them as being particularly toxic and recommended monitoring them in the environment [16]. Assessment of toxicity and risk associated with the PAHs mixture was made on the assumption that all PAHs in the mixture can be divided into two groups: cancerogenic and non-cancerogenic PAHs. All carcinogenic PAHs have given the toxic equivalency coefficient 1 and for non-carcinogenic PAHs 0. However, it is known that some PAHs are less carcinogenic than BaP, so to avoid errors Nisbet and LaGoy have developed and introduced an updated list of the toxicity equivalency factor (TEF), which seems to better reflect the strength of individual PAHs [17,18].

Due to their bad influence on health and living organisms, the removal of PAHs from wastewater is an important issue. According to the current state of knowledge, technic or methods are not able to complete removal of this kind of pollutant from wastewater, so biological and chemical processes used in water treatment plant are often insufficient. The advanced oxidation process (AOP) methods seem to be promising as demonstrated in numerous research.

One of them is, discovered in the XIX century Fenton process. In this reaction, mixtures of iron salt, and hydrogen peroxide, called Fenton's reagent, are used ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) in an acidic environment. The generation of hydroxyl radicals is a multi-step process. A combination of Fenton reagents and UV radiation is called the photo-Fenton process. UV radiation cause better effectiveness of the process. In simple terms, the Fenton process carry out according to reaction (1) [19–22].



The photo-Fenton process carry out according to reactions (2) and (3) [16–19]:



The use of UV radiation increases the efficiency of removing pollutants, extends reaction time, and reduces costs.

Hydroxyl radicals react with almost all types of organic contaminants, they also cause the destruction of compounds resistant to biodegradation and toxic compounds for example cosmetic ingredients, dyes, pharmaceuticals, endocrine active compounds. Moreover caused destruction toxic compounds present in wastewater from the textile, paper and wood industries, food, and from coal processing and refining of crude oil [23–26].

The novelty of process is used as an alternative source of hydroxyl radicals in the photo-Fenton process to PAHs degradation presence in coke wastewater. Hydrogen peroxide is a typical and widely tested source of hydroxyl radicals. The use of sodium carbonate–hydrogen peroxide is novelty. The search for new sources of hydroxyl radicals is interesting because of the economics and better control over the oxidation process. In addition, the reagent in the form of powder improves the safety of the reaction. Moreover the authors were the first, which proposes a study effectiveness of sodium carbonate–hydrogen peroxide in the photo-Fenton process to degrade PAHs present in coke wastewater. Based on a literature review [27,28] and the results of use e.g. metal peroxides as a source of H_2O_2 in the Fenton reaction, the authors have decided to examine the efficiency of PAHs degradation present in coke wastewater using sodium carbonate – hydrogen peroxide. In earlier research of authors, the calcium peroxide as a source of hydroxyl radicals was used [29,30], the efficiency of the removal of four-ring PAHs reached almost 98%. The search for others sources of hydroxyl radicals is important for economic reasons, in addition, the convenience of use and storage, as well as control over the process are important. The research subject is also important due to the BAT recommendation. The BAT requirements concern the search for the best available methods of eliminating pollutants forming in coke plants [9].

The aim of the research was to determine the changes in the PAHs concentration in real wastewater. The changes of total equivalent concentration (TEQ) for all tested polycyclic aromatic hydrocarbons (PAHs) presence in coke wastewater, during the modified Fenton process, was also investigated.

2. Experimental procedure

2.1. Material

The examined material was coke wastewater, collected from the outflow of wastewater treatment plant located in the coke plant. The composition of the wastewater is not subject to high variable due to the season, because the plant operates continuously throughout the year with the same load. Any changes may be due to temperature differences. Wastewater has been collected once, during the autumn season, in October. In other published studies of authors, wastewater has been collected many times during the year and the level of the initial concentration of PAHs was similar.

The coke wastewater are biologically treatment with the use of activated sludge. The scheme of the wastewater treatment process are shown in Fig. 1. The wastewater was characterized by determining the initial concentration of the studied hydrocarbons and the initial value of chemical oxygen demand (COD).

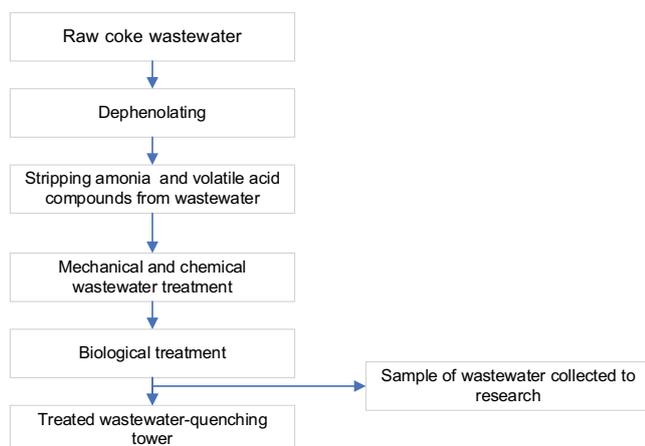


Fig. 1. Steps of coke wastewater treatment in Coke treatment plant.

2.2. Methodology

The experiment has been conducted in a laboratory scale. Initially the wastewater samples were acidified to pH 3.5–3.8. Nitric acid (HNO₃) has been used for this purpose. The oxidant used in the study was sodium carbonate–hydrogen peroxide (2/3). The addition of oxidants affects the slight change of pH of a solution. This oxidant is widely used in industry and has no toxic effect on living organisms. The pH range was chosen based on literature data. Low pH is required to achieve the high efficiency of the Fenton method. In the first steps, sodium carbonate–hydrogen peroxide (2/3), was introduced into the wastewater in the following doses: 1.2, 1.5, 2.0, 2.8, 4.0, 4.4, 7.0, and 8.0 g/L, then FeSO₄·7H₂O iron sulfate in constant dose 1.0 g/L was added [24]. The reaction time was 20 min. Next the samples were exposed to ultraviolet rays for 360 s. Sodium carbonate–hydrogen peroxide was used as a solid. The irradiation was carried out using a lamps emitting UV-C light with a wavelength $\lambda = 265$ nm. Two lamps with power 40 W were used. UV lamps have been placed above the level of wastewater. The irradiation was carried out in a plastic cuvette. The height of the irradiated wastewater layer was 2 mm. After technological research samples of wastewater were analyzed. Each time, analyzes COD values and concentration of PAHs were carried out.

The statistical *t*-student's test was used to statistical evaluation of obtained results. Test was chosen on the basic following parameters sample size ($n < 30$), degrees of freedom ($n - 1 = 2$), significance level $\alpha = 0.05$. The critical value obtained for the test was $t = 4.303$. For individual hydrocarbons and oxidants dose, different values of the computer significance level p were obtained.

2.3. PAHs analysis

Qualitative and quantitative identification of PAHs was carried out before and after the oxidation processes. The preparation of samples for the PAHs determination has been carried out by the liquid–liquid phase extraction. The extraction has been carried out at temperature about

22°C, the extraction time was 60 min. Organic solvents (cyclohexane and dichloromethane) as extractant was used. After that, samples were being shaken for 60 min in an automatic shaker and has been separated on laboratory separator. Then, samples were subjected to concentration and purification using SPE columns and vacuum conditions. For this purpose, Bakerbond C18 columns of a capacity 75 mL were used. Subsequently the eluates were then concentrated to 2 mL using an evaporator under a gentle stream of pure nitrogen. Then 2 mL of the extract was transferred into a well-labeled vial and stored in the fridge at 4°C prior to gas chromatography mass spectrometry (GC-MS) analysis. Model Fisons GC 800/MS 800 (Italy). Analyses of PAHs were performed using GC-MS. The assay consists of manual injection using a microsyringe 2 μ L of the extract on the DB-5 column using helium as the carrier gas [26]. The temperature program was 40°C/min and the final temperature was 280°C for 60 min. The following compounds were tested in the extract: two-rings of PAHs (naphthalene Nap) three-rings of PAHs (acenaphthene Ac, acenaphthylene Acyl, fluorene Flu, phenanthrene Phen) four-ring of PAHs (fluoranthene Fl, pyrene Pyr, benzo (a) anthracene BaA, chrysene Ch). All studied PAHs were selected according to the US EPA list [31].

3. Toxicity equivalency factor

TEF is used to more accurately estimate the carcinogenic properties of mixtures of chemical compounds. Determines the toxicity and risk associated with the presence of mixtures of chemical compounds with similar structures and similar mechanisms of interaction. In the case of cancerogenic PAHs (c-PAHs) to estimate the risk associated with a mixture of cPAHs is also used the individual compounds potency equivalency factor (PEF). The reference compound is benzo (a) pyrene. PEF was developed to evaluate the toxicity of compounds to reference substances. The PEF calculation rules are often changed because of environmental conditions. The use of PEFs values for cPAHs was adopted by the California Environmental Protection Agency to characterize the toxicity of these mixtures [32–36]. PEF is synonymous to TEF and may are used interchangeably. TEF for individual hydrocarbons are listed in Table 1. To assess Toxicity Equivalent Concentrations is used the mathematical expression which is provided below:

$$TEQ = \sum (C_i \text{ TEF}_i) \quad (4)$$

where TEQ is the total toxicity equivalent concentration; C_i is the concentration of the individual congener or cPAH in the mixture; TEF_i is the toxic equivalency factor of the individual congener or cPAH associated with its respective mixture.

4. Results

4.1. Changes of COD value

At the adopted oxidation time, changes in the concentration of organic pollutants expressed by COD have been examined. The average initial value of COD was 538 mg/L,

after the photo-Fenton process the value of COD decrease in the range of 9%–29% (from 380 to 489 mg/L). Other non-easily degradable contaminants haven't been degraded.

4.2. Removal of two and three-ring PAHs during the photo-Fenton process

In this study, the total PAH concentration in wastewater before oxidation was 0.53 mg/L. The initial concentration of naphthalene and three ring PAHs is shown in Fig. 2. Research revealed that higher molecular weight PAHs were more concentrated in coke wastewater than light.

The initial concentration of hydrocarbons containing two and three rings (LM-PAHs) was on average 88 $\mu\text{g/L}$ (16.8% of the total concentration). Naphthalene was dominant, with an initial concentration of 38 $\mu\text{g/L}$ (Fig. 1). After use the oxidant at dose 1.5 g/L the concentration decreased to 3.3 $\mu\text{g/L}$ (Fig. 3). In the case of acenaphthylene, acenaphthene, (Figs. 4 and 5) the highest decrease of concentration was for a dose of sodium carbonate–hydrogen peroxide 1.5 or 2 g/L, for fluorene 2.8 g/L (Fig. 6), and for phenanthrene 8 g/L (Fig. 7). For most of the tested hydrocarbons, in the beginning a decrease in concentration was observed. But next an increase in concentration with an increase in the dose of oxidant was observed. The reason for this could have been the formation of other compounds with similar structure, on account of the fragmentation of molecules with a more complex structure. Additional research is needed to determine the cause. Taking into account the sum of concentration of LM-PAHs, for all doses of sodium carbonate–hydrogen peroxide (2/3), concentration drops were noticed. The most effective in removing light hydrocarbons was the application sodium carbonate–hydrogen peroxide at dose 2 g/L (Fig. 8). No linear relationship between the increase of dose and decrease of concentration of LM-PAHs has been observed.

4.3. Removal of four rings PAHs during the photo-Fenton process

In the case of four ring PAHs (which belongs to HM-PAHs) concentration in wastewater before oxidation was average 435 $\mu\text{g/L}$ which was over 83% of total concentration (Fig. 9). Fluoranthene was the dominant with an initial concentration

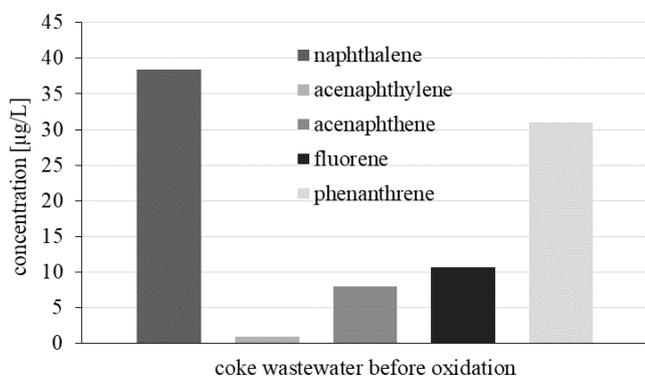


Fig. 2. Concentration of LM-PAHs in coke wastewater before oxidation process.

of 161 $\mu\text{g/L}$. After use oxidant at dose 8 g/L, the concentration decreases to 2.3 $\mu\text{g/L}$ (Fig. 10).

In case of pyrene, benzo(a)anthracene the highest decrease in concentration was reached after use dose of oxidant at 2 g/L (1.12 and 0.29 $\mu\text{g/L}$, respectively) (Figs. 11 and 12), increasing the dose did not increase the removal efficiency. For chrysene at dose 4.4 g/L, caused a decrease in concentration by over 99% (0.68 $\mu\text{g/L}$) (Fig. 13).

4.4. Statistical evaluation

In the Statistica program, the statistical significance of the obtained results was calculated for the assumed parameters

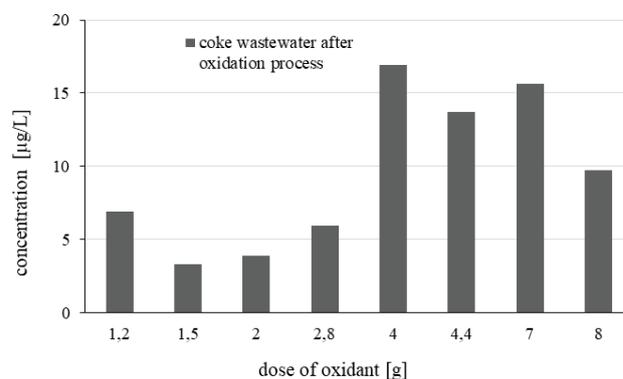


Fig. 3. Changes of the concentration of naphthalene.

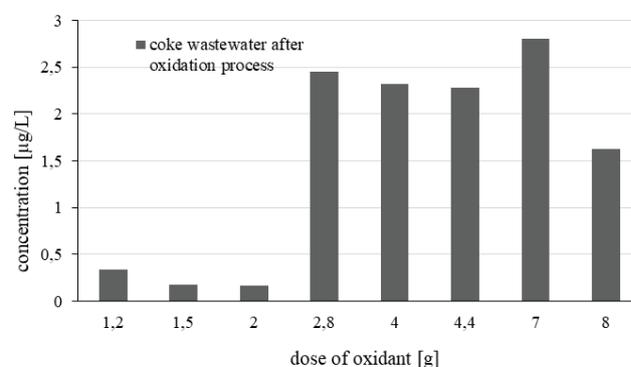


Fig. 4. Changes of the concentration of acenaphthylene.

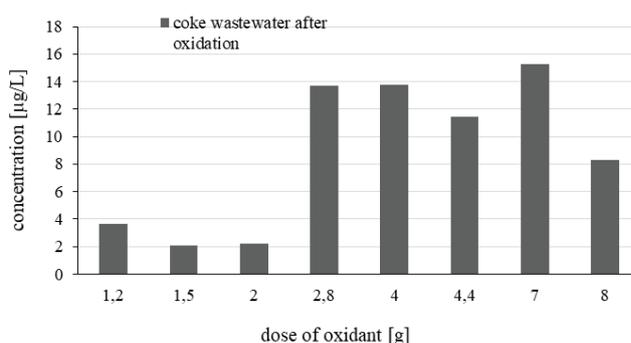


Fig. 5. Changes of the concentration of acenaphthene.

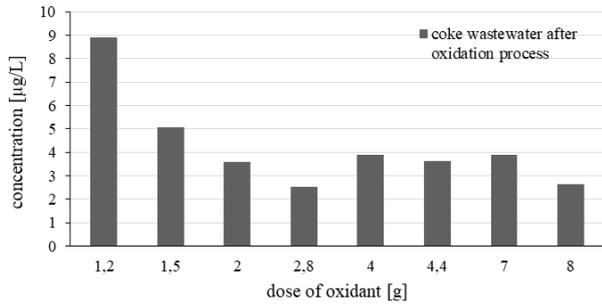


Fig. 6. Changes of the concentration of fluorene.

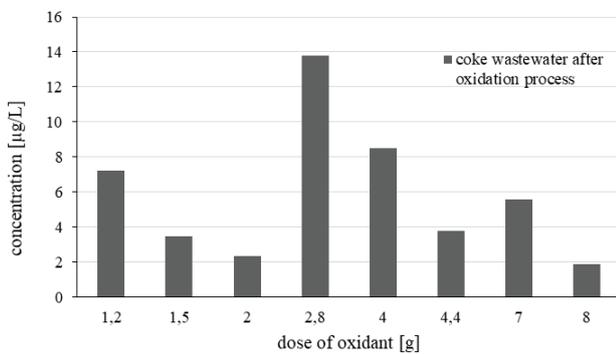


Fig. 7. Changes of the concentration of phenanthrene.

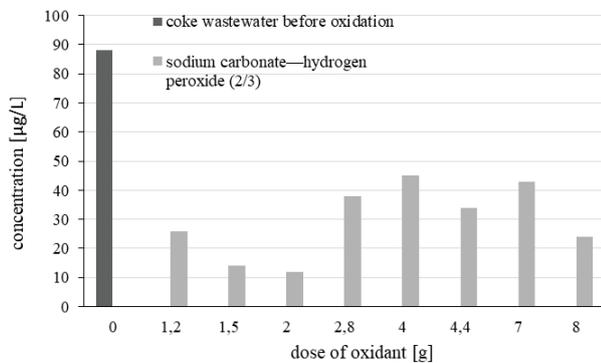


Fig. 8. Changes of the sum of the concentration of light molecular weights PAHs (LM-PAHs).

(statistical level of significance $\alpha = 0.05$. The \pm symbol was used to indicate the significance level, which means a statistically significant and statistically insignificant result, respectively. The results are shown in Table 2.

4.5. Evaluation of TEQ value

To assess the changes in the toxicity the total equivalency concentration was determined. The results are shown in Tables 3–5. The initial TEQ in coke wastewater was 9.01×10^{-3} mg/L (according to Nisbet and LaCoy) and 0.157 mg/L (according to United States Environmental Protection Agency (USEPA)) (Table 3). After the photo-Fenton

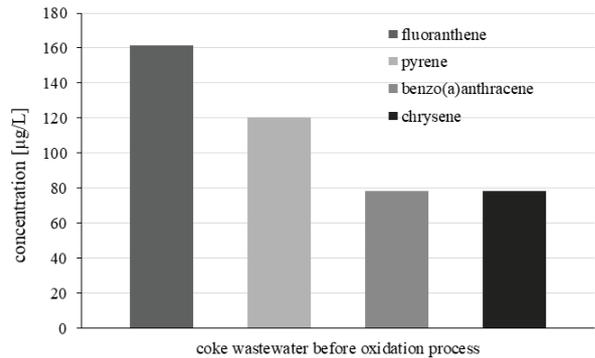


Fig. 9. Concentration of four rings PAHs in coke wastewater before oxidation process.

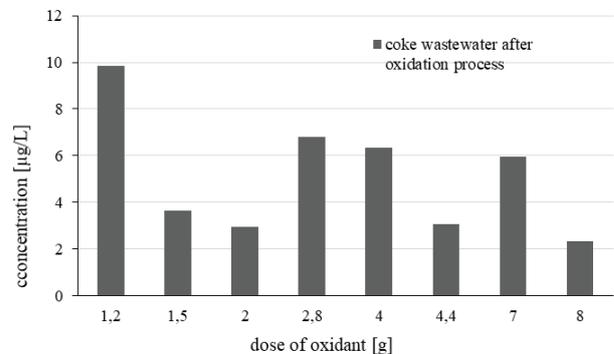


Fig. 10. Changes of the concentration of fluoranthene.

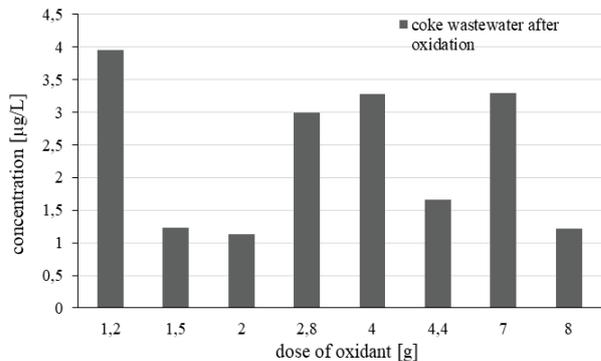


Fig. 11. Changes of the concentration of pyrene.

process TEQ value decreased after use all doses of oxidant. The lowest value 0.055×10^{-3} mg/L (according to Nisbet and LaCoy) was reached after used sodium carbonate–hydrogen peroxide at dose 2 g/L (Table 4). The TEQ index calculated according to USEPA data was the lowest (1.24×10^{-3} mg/L) for the dose 8 g/L (Table 5). The TEQ estimation for the PAHs mixture often requires more detailed knowledge of the composition of the mixture and the biological activity of all its components. It seems that the risk assessment associated with the determination of TEQ is more accurate in the case of mixtures containing only parent hydrocarbons.

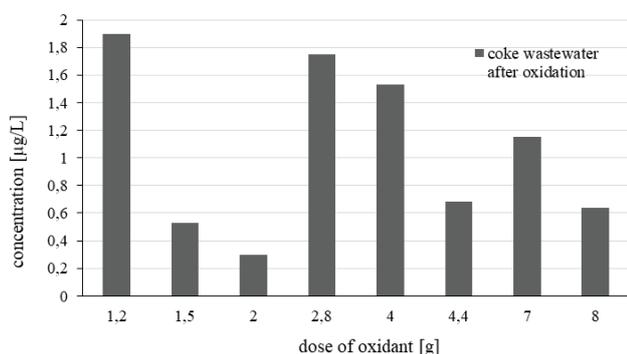


Fig. 12. Changes of the concentration of benzo(a)anthracene.

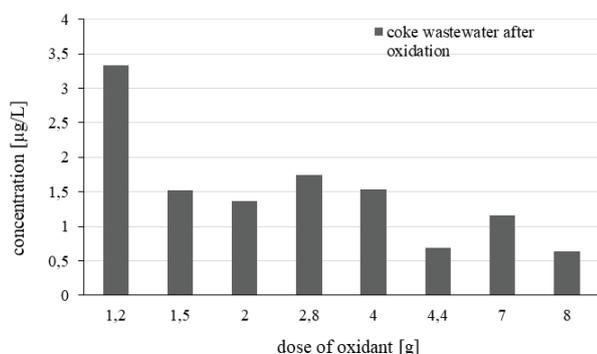


Fig. 13. Changes of the concentration of chrysene.

Table 1
Proposed TEFs for individual PAHs [17,34]

Compounds	USEPA	Nisbet and LaCoy
Naphthalene	0	0.001
Acenaphthylene	0	0.001
Acenaphthene	0	0.001
Fluorene	0	0.001
Phenanthrene	0	0.001
Anthracene	0	0.01
Fluoranthene	0	0.001
Pyrene	0	0.001
Benzo(a)anthracene	1	0.1
Chrysene	1	0.01

The assessment of the PAHs mixture and other by-products is difficult and often incorrect [34–36]. This is due to the lack of data on the potency of these compounds, so the results obtained may differ from those obtained by the toxicity test.

5. Discussion

The subject of the research was to determine changes in the concentration of all tested PAHs base on changes of concentration before and after the oxidation process. For all doses of oxidant, a significant decrease in concentration

Table 2
Statistical evaluation of results (according to *t*-student's test), for selected doses

	Doses of Na ₂ CO ₃ 1.5H ₂ O ₂ (g)		
	1.2	1.5	2.0
Naphthylene	+	+	+
Acenaphthylene	+	+	+
Acenaphthene	+	+	+
Fluorene	+	+	+
Fenanthrene	+	+	+
Fluoranthene	+	+	+
Pyrene	+	+	+
Benzo(a)anthracene	+	+	+
Chrysene	+	+	+

below the initial value was obtained. In the wastewater after the oxidation process, the total concentration of all tested hydrocarbons met the requirements set out in the BAT recommendation, which lists, among others, the permissible concentration of PAHs below 0.05 mg/L and COD below 220 mg/L [9]. In previous research by authors with use sodium carbonate–hydrogen peroxide at a similar dose of oxidant but longer time of radiation, the effectiveness of removal was in the range of 94%–97.7% [37] thus, it can be concluded that the extension of the exposure time did not increase the efficiency of PAHs removal. Another oxidant that could be a source of hydroxyl radicals was calcium peroxide [29,30]. Also in this research the material was coke wastewater previously pretreated and the photo-Fenton process was used. The effectiveness of removal for 4–6 ring PAHs was in the range of 89%–98%. LM-PAHs were less effective removal than HM-PAHs, both after the use of sodium carbonate–hydrogen peroxide and calcium peroxide under the same process conditions. In other studies with use magnesium peroxide in the Fenton process, in order to remove outdated pesticides, a removal efficiency of 96% was achieved [38].

The obtained results are consistent with the data present in the literature [39–41]. Da Rocha et al. [42] showed that the effectiveness of degradation of 16 PAHs in petrochemical wastewater in the photo-Fenton process reached 96%. In this study, the solar light was used, also obtaining a reduction in the toxicity of the sample by about 50%. The AOP processes are also used to remove other non-easily degradation and toxic compounds, for example, cosmetic ingredients, dyes, pharmaceuticals, endocrine active compounds, as well as those present in wastewater from the textile, paper, wood, and food and coal processing industries [43–48]. Unfortunately during the oxidation process new compounds with different toxicity may be formed, therefore, in order to comprehensively confirm the toxicity of wastewater after the oxidation process, it is necessary to perform a toxicity assessment using test organisms.

Advanced oxidation processes are indicated as promising techniques especially in relation to the removal of organic pollutants, however, many factors such as the reaction environment, temperature, reagents concentration, and

Table 3
Value of TEQ (mg/L) of PAHs in wastewater before oxidation process (based on Nisbet and LaCoy and USEPA)

Compounds	Individual PAHs concentration in wastewater before oxidation process, average [mg/L]	TEQ in wastewater before oxidation process [mg/L] (according to Nisbet and LaCoy)	TEQ in wastewater before oxidation process [mg/L] (according to USEPA)
Naphthalene	0.0384	3.84×10^{-5}	0
Acenaphthylene	0.0009	9×10^{-7}	0
Acenaphthene	0.0079	7.9×10^{-6}	0
Fluorene	0.0106	1.06×10^{-5}	0
Phenanthrene	0.0311	3.11×10^{-5}	0
Anthracene	–	–	0
Fluoranthene	0.1617	1.62×10^{-4}	0
Pyrene	0.1205	1.21×10^{-4}	0
Benzo(a)anthracene	0.0785	7.85×10^{-3}	0.0785
Chrysene	0.0785	7.85×10^{-4}	0.0785
Total	0.5278	$TEQ = 0.901 \times 10^{-2}$	TEQ = 0,157

Table 4
Value of TEQ (mg/L) of PAHs in wastewater after photo-Fenton process (according to Nisbet and LaCoy)

PAHs	TEQ in wastewater after photo-oxidation process, 10^{-3} [mg/L] The doses of $Na_2CO_3 \cdot 1.5 H_2O_2$ [g/L]							
	1.2	1.5	2	2.8	4	4.4	7	8
Naphthalene	0.007	0.003	0.004	0.006	0.013	0.016	0.015	0.009
Acenaphthylene	0.0003	0.0002	0.0002	0.002	0.002	0.002	0.002	0.001
Acenaphthene	0.004	0.002	0.002	0.013	0.013	0.011	0.015	0.008
Fluorene	0.009	0.005	0.003	0.002	0.004	0.004	0.004	0.003
Phenanthrene	0.007	0.003	0.002	0.013	0.009	0.004	0.006	0.002
Fluoranthene	0.01	0.004	0.003	0.007	0.006	0.003	0.006	0.002
Pyrene	0.004	0.001	0.001	0.003	0.003	0.002	0.003	0.001
Benzo(b)anthracene	0.19	0.05	0.03	0.17	0.15	0.07	0.11	0.06
Chrysene	0.03	0.02	0.01	0.02	0.02	0.007	0.011	0.006
Total	0.261	0.088	0.055	0.236	0.22	0.119	0.172	0.092

Table 5
Calculated TEQ (mg/L) of PAHs in wastewater after photo-Fenton process (according to USEPA)

PAHs	TEQ in wastewater after photo-oxidation process, 10^{-3} [mg/L] The doses of $Na_2CO_3 \cdot 1.5 H_2O_2$ [g/L]							
	1.2	1.5	2	2.8	4	4.4	7	8
Naphthalene	0	0	0	0	0	0	0	0
Acenaphthylene	0	0	0	0	0	0	0	0
Acenaphthene	0	0	0	0	0	0	0	0
Fluorene	0	0	0	0	0	0	0	0
Phenanthrene	0	0	0	0	0	0	0	0
Fluoranthene	0	0	0	0	0	0	0	0
Pyrene	0	0	0	0	0	0	0	0
Benzo(b)anthracene	1.9	0.5	0.3	1.74	1.5	0.7	1.1	0.6
Chrysene	3.33	1.51	1.36	1.74	1.53	0.68	1.15	0.64
Total	5.23	2.01	1.66	3.48	3.03	1.38	2.25	1.24

initial concentration of pollutants or presence of coloring substances as like PAHs molecule structure have an influence on the effectiveness of process [49]. The results obtained

in the study are difficult to compare with the data available in the literature. Although the Fenton process and its modifications are currently of interest to researchers, available

results often refer to different reaction conditions or other research material, hence the difficulty in making a comparative assessment.

6. Conclusion

The aim of the research was determination the changes in the concentration of PAHs during the photo-Fenton process and changes of COD value. In the process sodium carbonate–hydrogen peroxide has been used as an oxidant. Moreover, a constant dose of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ iron sulfate and a constant time exposure to ultraviolet radiation have been applied. In the research, the real wastewater has been used. The initial content of the tested PAHs was 0.53 mg/L and the COD value was 538 mg/L. Moreover the changes of TEQ for all tested polycyclic aromatic hydrocarbons (PAHs) presence in coke wastewater, during the modified Fenton process have been calculated. These calculations have been made based on Nisbet and LaCoy and US EPA data. The application of the oxidation process allowed to reduce the concentration of PAHs and organic pollutants. The decrease in the COD value was not greater than 30%, which indicates that only easily degradable organic compounds could be degraded under the accepted conditions of the experiment. The effectiveness of removal was depended on doses of oxidant and was in the range of 89.1–96.6%. The obtained degradation efficiency was better in the case of four-ring hydrocarbons than in the case of LM PAHs and reached even 99%. The results obtained in this experiment do not differ from the results of earlier studies. In other studies using calcium peroxide as a source of hydroxyl radicals, the efficiency of PAH degradation did not exceed 96%. TEQ value after the photo-Fenton process decrease from 9.01×10^{-3} to 0.055×10^{-3} mg/L (according to Nisbet and LaCoy), so by over 99% and to 1.24×10^{-3} mg/L (86% according to USEPA). However, it should be emphasized that other hardly degradable compounds are present in coke wastewater, which may also affect wastewater toxicity. Further ecotoxicological tests using test organisms are required. The results obtained in this study indicate that the modified photo-Fenton process, consisting of the use of sodium carbonate–hydrogen peroxide (v/v 2/3) can be used for post-treatment of industrial wastewater, which are heavily loaded by PAHs, for example, coke wastewater. The results obtained are corresponding with the BAT requirements for coke oven installations therefore the modified photo-Fenton process can be used as the final step of wastewater treatment (after biological processes) before discharged to the sewage system or to reuse for other industrial purposes.

Acknowledgments

The research was funded both by the project BS/MN-400-301/19 and by the scientific subvention of Czestochowa University of Technology.

References

- [1] E.E. Chang, H.S. Hsing, P.C. Chiang, M.Y. Chen, J.Y. Shyngrn, The chemical and biological characteristics of coke-oven wastewater by ozonation, *J. Hazard. Mater.*, 156 (2008) 560–567.
- [2] M. Smol, M. Włodarczyk-Makula, The effectiveness in the removal of PAHs from aqueous solutions in physical and chemical processes: a review, *Polycyclic Aromat. Compd.*, 37 (2017) 292–313.
- [3] K. Mielczarek, J. Bohdziewicz, A. Kwarcia-Kozłowska, Coking plant wastewater treatment in integrated system combining volume coagulation and advanced oxidation with pressure membrane techniques, *Civ. Environ. Eng. Rep.*, 7 (2011) 83–98.
- [4] M. Włodarczyk-Makula, Changes of PAHs content in wastewater during oxidation process, *Rocz. Ochr. Srod.*, 13 (2011) 1093–1104.
- [5] M. Włodarczyk-Makula, Simultaneous oxidation and adsorption of PAHs in effluents from industrial treatment plant, *Desal. Water Treat.*, 117 (2018) 329–339.
- [6] M. Włodarczyk-Makula, E. Wiśniowska, A. Turek, A. Obstój, Removal of PAHs from coking wastewater during photo-degradation process, *Desal. Water Treat.*, 57 (2016) 1262–1272.
- [7] A. Turek, M. Włodarczyk-Makula, W.M. Bajdur, Effect of catalytic oxidation for removal of PAHs from aqueous solution, *Desal. Water Treat.*, 57 (2016) 1286–1296.
- [8] L. Chu, J. Wang, J. Dong, H. Liu, X. Sun, Treatment of coking wastewater by an advanced Fenton oxidation process using iron powder and hydrogen peroxide, *Chemosphere*, 86 (2012) 409–414.
- [9] IPPC, Best Available Techniques Reference Document on the Production of Iron and Steel December, Integrated Pollution Prevention and Control, 2001.
- [10] A.J. Forsgren, Occurrence and Fate Polycyclic Aromatic Hydrocarbons (PAHs), Taylor & Francis, Boca Raton, FL, 2015.
- [11] A.T. Lawal, Polycyclic aromatic hydrocarbons. A review, *Cogent. Environ. Sci.*, 3 (2017) 1–89.
- [12] D.M. Pampanin, M.O. Sydnes, Petrogenic Polycyclic Aromatic Hydrocarbons in the Aquatic Environment Analysis, Synthesis, Toxicity, Environmental Impact, Beckham Book, UAE, 2017.
- [13] IARC, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Vol. 92, Some N-heterocyclic Polycyclic Aromatic Hydrocarbons and Related Exposures, International Agency for Research on Cancer, Lyon, France, 2010.
- [14] H.I. Abdel-Shafy, M.S.M. Mansour, A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation, *Egypt. J. Pet.*, 25 (2016) 107–123.
- [15] J.H. Sun, G.L. Wang, Y. Chai, G. Zhang, J. Li, J. Feng, Distribution of polycyclic aromatic hydrocarbons (PAHs) in Henan Reach of the Yellow River, Middle China, *Ecotoxicol. Environ. Saf.*, 72 (2008) 1614–1624.
- [16] USEPA, Code of Federal Regulations, 40 CFR 423, Appendix A, US Environmental Protection Agency, 1982.
- [17] C. Nisbet, P. LaGoy, Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs), *Regul. Toxicol. Pharmacol.*, 16 (1992) 290–300.
- [18] T. Petry, P. Schmid, C. Schlatter, The use of toxic equivalency factors in assessing occupational and environmental health risk associated with exposure to airborne mixtures of polycyclic aromatic hydrocarbons (PAHs), *Chemosphere*, 32 (1996) 639–648.
- [19] R. Munter, Advanced oxidation processes – current status and prospects, *Proc. Est. Acad. Sci. Chem.*, 50 (2001) 59–80.
- [20] M. Cheng, G. Zeng, D. Huang, C. Lai, P. Xu, C. Zhang, Y. Liu, Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds – a review, *Chem. Eng. J.*, 284 (2016) 582–598.
- [21] R.G. Zepp, B.C. Faust, J. Hoigne, Hydroxyl radical formation in aqueous reactions (pH 3–8) of iron(II) with hydrogen peroxide: the photo-Fenton reaction, *Environ. Sci. Technol.*, 26 (1992) 313–319.
- [22] M. Litter, N. Quici, Photochemical advanced oxidation processes for water and wastewater treatment, *Recent Patents Eng.*, 4 (2010) 217–241.
- [23] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, *Catal. Today*, 53 (1999) 51–59.

- [24] M.A. Oturan, J.J. Aaron, Advanced oxidation processes in water/wastewater treatment: principles and applications. A review, *Crit. Rev. Environ. Sci. Technol.*, 44 (2014) 2577–2641.
- [25] M.C. Pereira, L.C.A. Oliveira, E. Murad, Iron oxide catalysts: Fenton and Fenton like reactions - a review, *Clay Miner.*, 47 (2012) 285–302.
- [26] A. Machulek Jr., S.C. Oliveira, M.E. Osugi, V.S. Ferreira, F.H. Quina, R.F. Dantas, S.L. Oliveira, G.A. Casagrande, F.J. Anaissi, V.O. Silva, R.P. Cavalcante, F. Gozzi, D.D. Ramos, A.P.P. da Rosa, A.P.F. Santos, D.C. de Castro, J.A. Nogueira, Application of Different Advanced Oxidation Processes for the Degradation of Organic Pollutants, M. Nageeb Rashed, ed., *Organic Pollutants -Monitoring, Risk and Treatment*, InTech, Croatia, 2013, pp. 142–166.
- [27] A. Northup, D.J. Cassidy, Calcium peroxide CaO_2 for use in modified Fenton Chemistry, *J. Hazard. Mater.*, 152 (2008) 1164–1170.
- [28] K. Barbusiński, J. Główkowska, K. Tomys, Coke plant wastewater treatment by Fenton reagent, *Arch. Environ. Prot.*, 30 (2006) 21–28.
- [29] J. Kozak, M. Włodarczyk-Makula, Photo-oxidation of PAHs with calcium peroxide as a source of the hydroxyl radicals, *E3S Web Conf.*, 30 (2018), doi: 10.1051/e3sconf/20183002009.
- [30] J. Kozak, M. Włodarczyk-Makula, Comparison of the PAHs degradation effectiveness using CaO_2 or H_2O_2 under photo-Fenton reaction, *Desal. Water Treat.*, 134 (2018) 57–65.
- [31] US-EPA, Polycyclic Aromatic Hydrocarbons (PAHs), Office of Solid Waste, Washington, DC, 2008.
- [32] G.N. Liwuoha, J. Nwigoo, M.C. Lonojake, Determination of total potency equivalent concentration (Tpec) of carcinogenic polycyclic aromatic hydrocarbons (cPAHs) in soils of Bodo-city, *J. Appl. Sci. Environ. Manage.*, 19 (2015) 495–499.
- [33] USEPA, Health Effect Assessment for Polycyclic Aromatic Hydrocarbon (PAH), EPA 549/1–86–013, Environmental Criteria and Assessment Office, Cincinnati, OH, 1984.
- [34] E.B. Balcioglu, Potential effects of polycyclic aromatic hydrocarbons (PAHs) in marine foods on human health: a critical review, *Toxin Rev.*, 35 (2016) 1–9.
- [35] D. Delistraty, Toxic equivalency factor approach for risk assessment of polycyclic aromatic hydrocarbons, *Toxicol. Environ. Chem.*, 64 (1997) 81–108.
- [36] S.H. Safe, Hazard and risk assessment of chemical mixtures using the toxic equivalency factor approach, *Environ. Health Perspect.*, 106 (1998) 1051–1058.
- [37] J. Kozak, M. Włodarczyk-Makula, The use of sodium percarbonate in the Fenton reaction for the PAHs Oxidation, *Civ. Environ. Eng. Res.*, 28 (2018) 124–139.
- [38] I. Skoczko, Rozkład pestycydów metodą Fentona z wykorzystaniem MgO_2 , *Rocz. Ochr. Srod.*, 15 (2013) 1460–1473 (in Polish)
- [39] C. Lin, W. Zhang, M. Yuan, C. Feng, Y. Ren, C. Wei, Degradation of polycyclic aromatic hydrocarbons in a coking wastewater treatment plant residual by an O_3 /ultraviolet fluidized bed reactor, *Environ. Sci. Pollut. Res. Int.*, 21 (2014) 10329–10338.
- [40] L. Xiaoyong, W. Zeying, L. You, L. Junpeng, S. Chunming, Enhanced degradation of polycyclic aromatic hydrocarbons by indigenous microbes combined with chemical oxidation, *Chemosphere*, 213 (2018) 551–558.
- [41] A. Rubio-Clemente, R.A. Torres-Palma, G.A. Penuela, Removal of polycyclic aromatic hydrocarbons in aqueous environment by chemical treatments: a review, *Sci. Total Environ.*, 478 (2014) 201–225.
- [42] O.R.S. Da Rocha, R.F. Danta, M. Bezerra, M. Lima, V. Lins, Solar photo-Fenton treatment of petroleum extraction wastewater, *Desal. Water Treat.*, 55 (2013) 5785–5791.
- [43] I. Kim, N. Yamashita, H. Tanaka, Photodegradation of pharmaceuticals and personal care products during UV and UV/ H_2O_2 treatments, *Chemosphere*, 77 (2009) 518–525.
- [44] M. Engwall, J.J. Pignatello, D. Grasso, Degradation and detoxification of the wood preservatives creosote and pentachlorophenol in water by the photo-Fenton reaction, *Water Res.*, 33 (1999) 1151–1158.
- [45] I.R. Bautitz, R.F.P. Nogueira, Photodegradation of lincomycin and diazepam in sewage treatment plant effluent by photo-Fenton process, *Catal. Today*, 151 (2010) 94–99.
- [46] N.C. Fernandes, L.B. Brito, G.G. Costa, S.F. Taveira, R.N. Marreto, Removal of azo dye using Fenton and Fenton-like processes: evaluation of process factors by Box-Behnken design and ecotoxicity tests, *Chem. Biol. Interact.*, 291 (2018) 47–54.
- [47] S.G. Cetinkaya, M.H. Morcali, S. Akarsu, C.A. Ziba, M. Dolaz, Comparison of classic Fenton with ultrasound Fenton processes on industrial textile wastewater, *Sustainable Environ. Res.*, 28 (2018) 165–170.
- [48] P.A. Carneiro, R.F.P. Nogueira, M.V. Zanoni, Homogeneous photodegradation of C.I. Reactive Blue 4 using a photo-Fenton process under artificial and solar irradiation, *Dyes Pigm.*, 74 (2007) 127–132.
- [49] K. Barbusiński, Modification of the Fenton Reaction Using Calcium and Magnesium Peroxides, Wydawnictwo GIG, Katowice, 2006 (in Polish)