Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22708

134 (2018) 57–64
December

Comparison of the PAHs degradation effectiveness using CaO_2 or H_2O_2 under the photo-Fenton reaction

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Received 29 March 2018; Accepted 19 June 2018

ABSTRACT

In this paper, the results of comparison of the polycyclic aromatic hydrocarbons (PAHs) degradation efficiency with using H_2O_2 or CaO_2 under the conditions of the photo-Fenton reaction have been presented. The research was conducted using the coke wastewater, pretreated in a biological, factory wastewater treatment plant. Despite of purification in biological treatment plant, coke wastewater should be subjected to an additional purification process. Purification was carried out with the use of advanced photochemical oxidation. Various doses of calcium peroxide or hydrogen peroxide and a constant dose of iron sulfate $FeSO_4{\cdot}7H_2O$ were added to the samples of wastewater. Next, the samples were exposed to UVC radiation, with a wavelength $\lambda = 264$ nm for 480s. The effectiveness of the oxidants was evaluated based on changes in the chemical oxygen demand and total organic carbon index values and changes in the concentrations of selected PAHs. The extraction of PAHs from the samples was carried out in a liquid–liquid system using a mixture of cyclohexane and dichloromethane. A qualitative and quantitative analysis of PAHs was carried out using a gas chromatograph with a mass spectrometer. After the chemical photooxidation process, the concentrations of total PAHs in coke wastewater decreased. While maintaining the same process conditions, the PAHs degradation efficiency using CaO_2 and $FeSO_4$ $7H_2O$ was 43%–97%, and with using H_2O_2 and $FeSO_4$ $7H_2O$ was 54%–96%. The removal efficiency of individual hydrocarbons was in the range of 0%–99.9%.

Keywords: PAHs; Photo-Fenton; AOPs; Hydrogen peroxide; Calcium peroxide; Hydroxyl radicals

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1. Introduction

As a result of coal pyrolysis, coke is obtained. During this process, coke wastewater is formed. Coke wastewater is characterized by high concentrations of toxic organic and inorganic compounds. Composition of coke wastewater depends on the type of raw coals and technology used in coking processes. The characteristics of raw and pretreated coke wastewater are presented in Table 1 [1–3]. Raw coking wastewater is purified in factory wastewater treatment plant using biological processes. Despite the high efficiency of removing organic compounds expressed by chemical oxygen demand (COD) and total organic carbon (TOC) indicators, purified coke wastewater contains large amounts of organic pollutants and polycyclic aromatic hydrocarbons (PAHs) [4,5]. Due to legal restrictions, it is not always possible to discharge this wastewater to the receiver or to use it for company purposes [6]. As shown by studies described in the literature, including earlier studies' authors [4,7], also biologically purified coke wastewater is heavily contaminated with PAHs. Because of their high toxicity, it is important to conducting research on limiting the load of these pollutants introduced into waters [8–10]. As described in the literature data, it has been repeatedly demonstrated that PAHs are carcinogenic, mutagenic, and

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Presented at the 13th Conference on Microcontaminants in Human Environment, 4–6 December 2017, Czestochowa, Poland.

Table 1
Characteristic of raw and pretreated coke wastewater [1–3]

Indicator	Raw coke wastewater Range	Treatment coke wastewater Range
pH	6–9	6–7
COD, mg O_2/L	930–3,120	537–720
TOC, mg C/L	600–700	180–320
Phenols, mg/L	11.6–533	–
CN^-, mg/L	6–9	–
Total iron, mg/L	2–7	–
N–NH_4^+, mg NH_4^+/L	490–2,200	160

genotoxic relative to indicator organisms [11–13]. Their presence in pretreated wastewater, used for industrial purposes in coking plants, is also important. Because that wastewater can be used in the process of wet quenching of coke in quenching towers, which causes the evaporation of significant amounts of PAHs and release them into the atmosphere.

Due to the number of rings, PAHs can be divided into small and large molecules. Each of these groups has different physical and chemical properties. The simplest PAHs composed of two or three aromatic rings are classified as low molecular weight hydrocarbons. Hydrocarbons containing four or more aromatic rings are classified as macromolecular [14]. The aromatic rings in the molecule may be variously connected, which may affect their susceptibility to the oxidation process. Heavy hydrocarbons are more stable, but also more toxic [13]. It is believed that the most toxic and best-studied PAH is benzo(a)pyrene, which is considered as an indicator of the entire PAH group [15,16]. However, among the group of 16 test compounds, there are also others with the same or comparable toxicity, such as dibenzo(a,h)anthracene or indeno(1,2,3-cd)pyrene [17].

Because the commonly used methods of wastewater treatment are not satisfactory, it is important to look for new methods and chemical compounds used to remove PAHs [18]. Advanced oxidation processes (AOPs) are proposed for the treatment of wastewater. The AOPs can be an important supplement to existing wastewater treatment plants. In AOPs different types of reaction are used, but all are based on the generation of radicals, in particular hydroxyl radicals. The hydroxyl radicals break down most organic molecules at constant rates, usually in the order of 10^6–10^9 mol/L·s [19,20], causing degradation of contaminants to simple compounds like CO_2 and H_2O and inorganic ions, such as Cl^-, NH_4^+, and SO_4 [21]. Among the various types of advanced oxidation processes, the photo-Fenton process should be distinguished. This method involves the degradation of organic compounds with the use of hydrogen peroxide and the source of iron (II) (Fenton reagent [Fe^{2+}/H_2O_2] in an acidic environment). In photo-Fenton process, hydrogen peroxide and the source of iron (II) (Fenton reagent [Fe^{2+}/H_2O_2] in acidic environment are used to degrade organic pollutants. Formation of hydroxyl radicals is supported by UV rays. In the basic Fenton reaction, the release of hydroxyl radicals from H_2O_2 proceeds according to reaction (1) [22].

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH\cdot + OH^- \tag{1}$$

In the photo-Fenton reaction, under the influence of UV radiation, the Fe^{2+} ions are regenerated and additional OH· radicals are produced. In the basic Fenton reaction, the Fe^{3+} ions are formed and deposited in the reaction (only a small amount is reduced from Fe^{3+} to Fe^{2+}). Fe^{2+} ions run out quickly and the reaction stops. In the photo-Fenton process comes photo reduction of Fe^{3+} to Fe^{2+} and more OH· radicals are formed Eq. (2) [23–26]. This leads to increased efficiency of pollutant degradation. The UV-Fenton reaction also causes the formation of hydroxyl radicals under the influence of light Eq. (3) [26].

$$Fe^{3+} + H_2O + \lambda\upsilon \rightarrow Fe^{2+} + OH\cdot + H^+ \tag{2}$$

$$H_2O_2 + \lambda\upsilon(UV) \rightarrow 2HO \tag{3}$$

In modifications of the Fenton reaction, alternative sources of hydrogen peroxide such as calcium peroxide or sodium carbonate are used. In the case of calcium peroxide, the initial step is hydrolysis of calcium peroxide according to reaction (4). Next, this process proceeds like the basic reaction of Fenton. According to a stoichiometric calculation, 1 g of CaO_2 calcium peroxide, in an aqueous medium and at an acidic environment, releases a maximum of 0.47 g H_2O_2 [27].

$$CaO_2 + 2H_2O \rightarrow H_2O_2 + Ca(OH)_2 \tag{4}$$

Literature reports indicate that CaO_2 has a number of advantages over H_2O_2. It is more stable, easy to store, and release of H_2O_2 depends on solubility in water and reaction environment, which makes the process easier to monitor and control [28]. In the literature, the use of calcium peroxide for the treatment of soil or groundwater is often described, where, as research shows, calcium peroxide works better than liquid H_2O_2 [29,30]. The efficiency of oxidation of organic pollutants including phenol in industrial wastewater was also investigated [31,32]. The use of the Fenton process as well as its modification in the degradation of organic pollutants of industrial wastewater has already been described in the literature [33–35]. However, there is lack of results about using a different source of hydroxyl radicals than hydrogen peroxide and a comparison of the effectiveness of both oxidants in the PAHs degradation. Therefore, the aim of the research was to compare the efficiency of PAHs degradation in coke wastewater under the photo-Fenton process using CaO_2 or H_2O_2.

2. Experimental procedure

2.1. Material

The tested material was pretreated coke wastewater taken from the factory wastewater treatment plant. Biological processes like nitrification and denitrification with the use of activated sludge are carried out in the wastewater treatment plant to remove organic pollutants. Samples were taken once from the outflow from the secondary settling tank. The initial stage of the preparation of wastewater for technological research was the filtration to remove impurities. Filtration was carried out on a porous filter paper with basis weight of 65 g/m². This wastewater has been characterized in terms of the content of organic compounds expressed by COD and TOC and the initial concentration of PAHs.

2.2. Experimental setup

Researches on the oxidation of organic compounds, including PAHs, in coke wastewater were conducted in laboratory scale. A total of 10 wastewater samples with averaged composition have been prepared. The research was conducted in two series. In the first series, calcium peroxide CaO_2 was introduced into the wastewater, then wastewaters were acidified and $FeSO_4·7H_2O$ iron sulfate was added. The reaction time was 20 min. Next the samples were exposed to ultraviolet rays. In the second series, a solution of hydrogen peroxide was introduced into the wastewater, then wastewaters were acidified and $FeSO_4·7H_2O$ iron sulfate was added. Next wastewaters were exposed to UV rays too. In the studies following values were adopted as constant:

- dose $FeSO_4·7H_2O$: 1g/L
- reaction time set at 20 min
- exposure time to ultraviolet radiation of 8 min
- the height of the irradiated wastewater layer was 2 mm
- pH value of wastewater 3.5–3.8.

Doses of chemical oxidants, that is, calcium peroxide CaO_2 or H_2O_2 hydrogen peroxide, were determined based on stoichiometric calculations (Eqs. (2) and (4) mentioned above). These doses were set so that the proportions of iron ions to the hydrogen peroxide released in the reaction were 0.5, 0.4, 0.3, 0.2, and 0.1. Calcium peroxide was used as a solid (typically 65%, powder), while hydrogen peroxide as a 30% solution. The irradiation was carried out using a lamp emitting UV-C light with a wavelength $\lambda = 264$ nm. The UV lamp has been placed above the level of wastewater. The irradiation was carried out in a plastic cuvette. After technological research involving photooxidation, samples of wastewater were analyzed. Each time, analyses of COD and TOC values and concentration of PAHs were carried out.

2.3. PAHs analysis

The preliminary stage was the extraction of organic substance from coking wastewater. For this purpose, cyclohexane and dichloromethane were added to the wastewater samples in a volume ratio 5/1(v/v). Then the samples were shaken on a laboratory shaker for about 60 min. After this time, the extracts were separated from the wastewater and cleaned on silica gel columns under vacuum conditions. The obtained purified extract was concentrated under a stream of nitrogen and analyzed by a gas chromatograph coupled with a mass spectrometer . The assay consists on injecting 2 μL of the extract on the DB-5 column using helium as the carrier gas. The temperature program was 40°C/min and the final temperature was 280°C for 60 min. In Table 2, limit of detection value and recovery rates of individual PAHs are presented. The recovery of PAHs was in the range of 52%–87%. The aim of the study was to determine the effect of photooxidation on the degradation of aromatic hydrocarbons having 4, 5, and 6 rings in the molecule, characterized by high stability and proven carcinogenicity. The following compounds were tested in the extract [36]: four rings of PAHs (fluoranthene, Fl; pyrene, Pyr; benzo(a)anthracene, BaA; chrysene, Ch), five rings of PAHs (benzo(b)fluoranthene, BbF; benzo(k)fluoranthene, BkF; benzo(a)pyrene, BaP; dibenzo(ah)anthracene, DahA), and containing six rings of PAHs (indeno(1,2,3-cd)pyrene, IP; benzo(g,h,i)perylene, BghiP). PAHs were selected according to the United States Environmental Protection Agency list [37]. In order to assess the statistical significance of the obtained results, a Student's *t*-test was carried out in the Statistica computer program. The test was selected based on the sample size ($n < 30$) for specific degrees of freedom ($n–1 = 2$), with the assumed significance level $\alpha = 0.05$, the critical value obtained for the *t*-test was $t \approx 4.303$.

Table 2
Limit of detection value and recovery of PAHs from coke wastewater

Compounds	Limit of detection (μg/L)	Recovery (%)
Fl	0.1	81
Pyr	0.1	73
BaA	0.1	65
Ch	0.1	65
BbF	0.5	61
BkF	0.1	87
BaP	0.15	77
DahA	0.2	52
IP	0.15	54
BghiP	0.1	68

3. Results

The concentration of TOC was on average 180 mg/L and COD was on average 538 mg/L. Oxidation with calcium peroxide reduced COD on average by 30%–35% and TOC on average by 46%–56%. Hydrogen peroxide reduced COD on average by 53%–56% and by 26%–43% TOC. In Table 3, the results regarding the evaluation of process effectiveness from a statistical point of view are presented. For this purpose, the Student's *t*-test was carried out in the Statistica computer program. Symbol "–" means that with the probability of 95% (statistical level of significance $\alpha = 0.05$), the obtained result does not differ statistically significantly from the value of the zero sample, while the symbol "+" means that the result is statistically significant. For individual hydrocarbons and oxidants, different values of the computer significance level *p* were obtained and on this basis the obtained results were interpreted. In Figs. 1–4, changes in PAHs concentrations containing four aromatic rings per molecule are shown. The total concentration of these compounds was 439 μg/L, which accounted for 44% of all PAHs. The degradation efficiency of individual hydrocarbons was varied and ranged from 15% to above 95% (concentration 3.3 μg/L for BaA) depending on the oxidant used. The most effective in the degradation of fluoranthene was hydrogen peroxide and iron sulfate in the proportion of 0.4, resulting in removal of this compound in 94.3% (9.1 μg/L). For chrysene, pyrene and benzo(a)anthracene, a ratio 0.2 resulted in the removal of these hydrocarbons above 95% which corresponded to the concentration of approximately 3.4 μg/L The concentration

Table 3
Statistical evaluation of results (according to parametrical *t*-Student's test)

	Fe^{2+}/H_2O_2 ratio									
	0.5		0.4		0.3		0.2		0.1	
	$CaO_2/Fe^{2+}/UV$	$H_2O_2/Fe^{2+}/UV$	$CaO_2/Fe^{2+}/UV$	$H_2O_2/Fe^{2+}/UV$	$CaO_2/Fe^{2+}/UV$	$H_2O_2/Fe^{2+}/UV$	$CaO_2/Fe^{2+}/UV$	$H_2O_2/Fe^{2+}/UV$	$CaO_2/Fe^{2+}/UV$	$H_2O_2/Fe^{2+}/UV$
Fluoranthene	–	+	+	+	–	+	+	+	+	+
Pyrene	+	+	+	+	+	+	+	+	+	+
Benzo(a)anthracene	+	+	+	+	+	+	+	+	+	+
Chrysene	–	+	+	+	+	+	+	+	+	+
Benzo(b)fluoanthene	+	+	+	+	+	+	+	+	+	+
Benzo(k)fluoranthene	+	+	+	+	+	+	+	+	+	+
Benzo(a)pyrene	+	+	+	–	+	+	+	+	+	+
Indeno(1,2,3,-cd)pyrene	+	+	+	–	+	+	+	+	+	+
Dibenzo(a,h)anthracene	–	+	+	–	+	+	+	+	+	+
Benzo(g,h,i)perylene	+	+	+	–	+	+	+	+	+	+

+/–, Significant/insignificant statistically result.

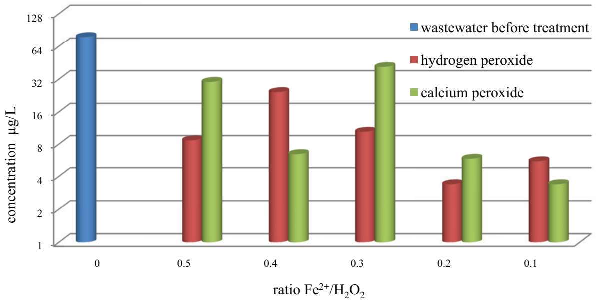

Fig. 1. Changes in the concentration of benzo(a)anthracene depending on a dose of oxidants.

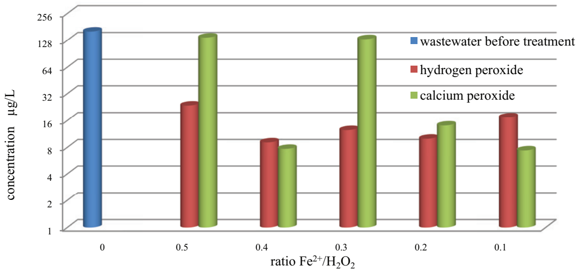

Fig. 3. Changes in the concentration of fluoranthene depending on a dose of oxidants.

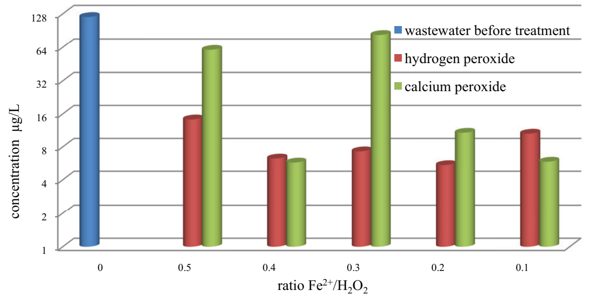

Fig. 2. Changes in the concentration of pyrene depending on a dose of oxidants.

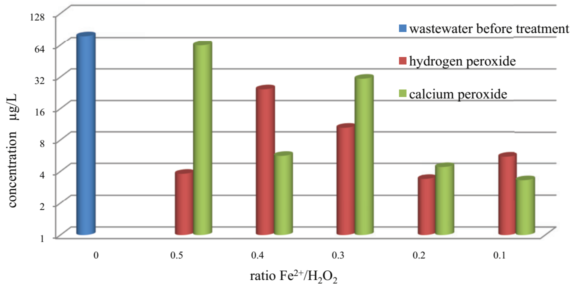

Fig. 4. Changes in the concentration of chrysene depending on a dose of oxidants.

decrease did not depend linearly on the increase in the oxidant dose. In the case of calcium peroxide, the concentration decrease was also not linear with the increase of the oxidant dose. The highest decrease in concentration for all four-ring hydrocarbons was observed for the highest dose of CaO_2 which corresponded to a ratio 0.1. In the case of pyrene also the ratio 0.4 caused degradation close to 96% and concentration 5.9 µg/L of this hydrocarbon. The average oxidation efficiency for the most effective ratio was around 96%.

The total concentration of five-ring hydrocarbons was 425.5 µg/L which accounted for 43% of the total PAHs tested. In Figs. 5–8, the changes in the concentration of five-ring hydrocarbons depending on oxidant dose level were presented. The use of hydrogen peroxide and iron sulfate allowed the removal of benzo(b)fluoranthene and benzo(k)fluorantene in over 97% (4.1 g/L). Fe^{2+}/H_2O_2 ratio 0.2 and 0.5 were the most effective.

For benzo(a)pyrene the highest degree of degradation over 96% (3.7 µg/L) was obtained for the Fe^{2+}/H_2O_2 0.2 ratio.

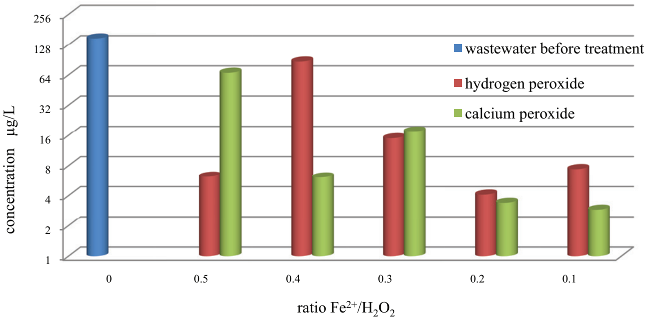

Fig. 5. Changes in the concentration of benzo(k)fluoranthene depending on a dose of oxidants.

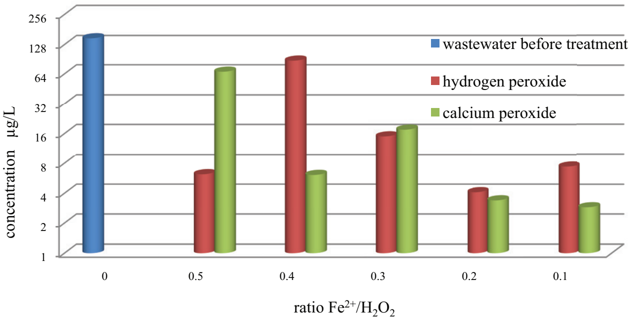

Fig. 6. Changes in the concentration of benzo (b)fluoranthene depending on a dose of oxidants.

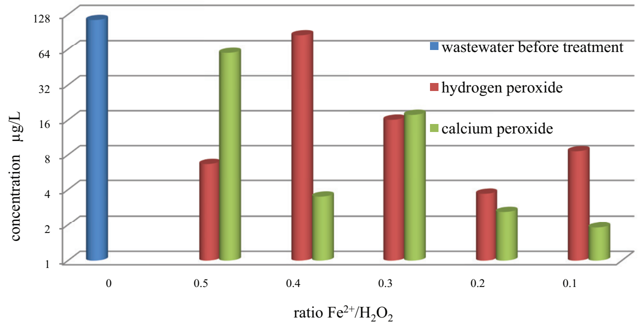

Fig. 7. Changes in the concentration of benzo(a)pyrene depending on a dose of oxidants.

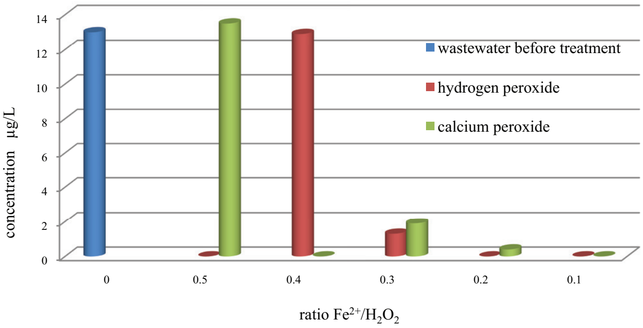

Fig. 8. Changes in the concentration of dibenzo(a,h)anthracene depending on a dose of oxidants.

Dibenzo(a,h)anthracene was removed almost entirely, reaching a concentration below the limit of quantification for the ratios of 0.5, 0.2, and 0.1. The decrease in the concentration for all hydrocarbons did not depend linearly on the oxidant dose level and was subject to fluctuations.

When the calcium peroxide and iron sulfate were used, the degradation efficiency of benzo(b)fluoranthene and benzo(k)fluoranthene was the same and was 98% for a ratio 0.1, which corresponded to the concentration 2.9 µg/L The decrease in concentration was subject to fluctuation. For benzo(a)pyrene, the highest degree of degradation was 98.3% (1.9 µg/L) for the Fe^{2+}/H_2O_2, 0.1 ratio. Concentration of dibenzo(a,h)anthracene was below the limit of quantification for the proportions 0.4 and 0.1. Because of high toxicity to living organisms, removal of this kind of pollutants from wastewater is a serious problem in the protection of the aquatic environment.

The total concentration of hydrocarbons containing six rings in the molecule was 130.8 µg/L which accounted for 13% of all PAHs tested. The efficiency of hydrogen peroxide and iron sulfate was the highest for the ratio 0.2 and 0.5 for indeno(1,2,3-cd)pyrene (Fig. 9), and degree of degradation for this hydrocarbon was more than 97% (2.3 and 1.9 µg/L)

Degree of degradation for benzo(g,h,i)perylene was 96.9% (1.4 µg/L) for a ratios 0.2 and 0.5 (Fig. 10). The use of calcium peroxide and iron sulfate in the proportions of 0.1 and 0.2 resulted in degradation of indeno(1,2,3-cd)pyrene in more than 98% (1.3 µg/L) and benzo (g,h,i)perylene in 98% (0.9 µg/L). Table 4 presents the percentage changes in the concentration of individual hydrocarbons in dependence on the oxidant used.

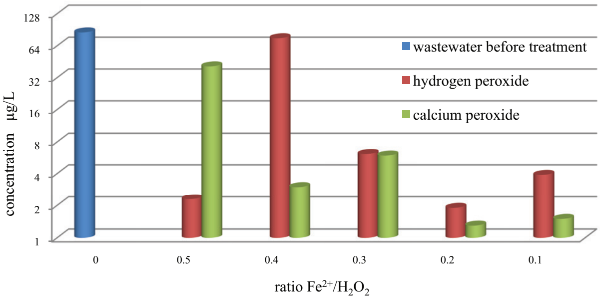

Fig. 9. Changes in the concentration of indeno(1,2,3-cd)pyrene depending on a dose of oxidants.

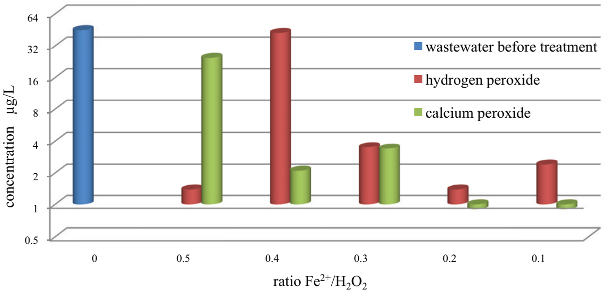

Fig. 10. Changes in the concentration of benzo(g,h,i)perylene depending on a dose of oxidants.

Table 4
Percentage changes in PAHs concentration depending on the oxidant used

Range of degradation (%)										
PAHs	0.5		0.4		0.3		0.2		0.1	
	CaO_2/ Fe^{2+}/UV	H_2O_2/ Fe^{2+}/UV	CaO_2/ Fe^{2+}/UV	H_2O_2/ Fe^{2+}/UV	CaO_2/ Fe^{2+}/UV	H_2O_2/ Fe^{2+}/UV	CaO_2/ Fe^{2+}/UV	H_2O_2/ Fe^{2+}/UV	CaO_2/ Fe^{2+}/UV	H_2O_2/ Fe^{2+}/UV
Fl	15	85.3	95	94.3	19	92.2	91	93.7	96	89.2
Pyr	49.5	88	95	94.7	31	93.9	91	95.4	95.8	91.2
BaA	61.6	88.9	91.3	69.4	47	86.7	92.5	95.7	95.6	92.9
Ch	19	95.1	92.7	69.4	61	86.7	94.4	95.7	95.8	92.9
BbF	55	95.7	95.9	41.3	88.2	89.9	97.7	97.2	98	95
BkF	55	95.7	95.9	41.3	88.2	89.9	97.7	97.2	98	95
BaP	48.1	94.2	96.9	25.8	84.6	86	97.7	96.8	98.3	92.3
IP	52.3	97.3	96.5	11.8	93.1	92.9	98.5	97.8	98.3	95.4
DahA	0	×	×	0.8	85.7	90	96.9	×	×	×
BghiP	45.9	96.9	95.3	5.9	92.5	92.2	98	96.9	98	94.7

×, Concentration below the limit of quantification.

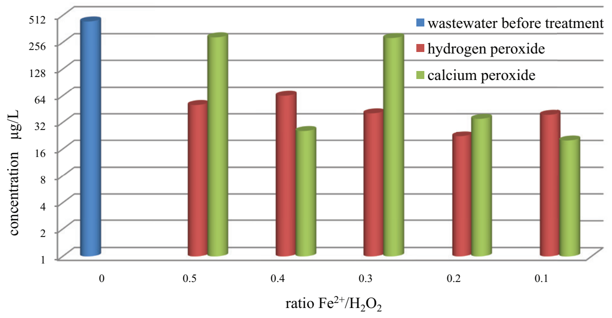

Fig. 11. Changes in the concentration of Σ 4 rings PAHs depending on a dose of oxidants.

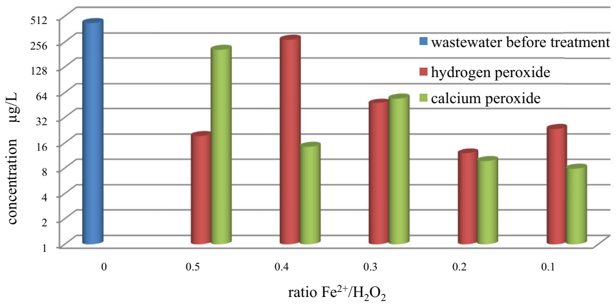

Fig. 12. Changes in the concentration of Σ 5 rings PAHs depending on a dose of oxidants.

Taking into consideration the degradation efficiency of the sum of hydrocarbons containing four rings per molecule (Fig. 11), five rings (Fig. 12), and six rings (Fig. 13), the most effective was the use of hydrogen peroxide under the photo-Fenton reaction conditions, in the proportion of 0.2. This resulted in the total removal of hydrocarbons in 94.9%, 97.2%, and 97.5%, respectively. In the case of calcium peroxide under the photo-Fenton reaction conditions, the best ratio was 0.1 for four- and five-ring hydrocarbons, causing their total removal in 95.4% and 98.1%, respectively. For six ring hydrocarbons, the best total degradation was achieved for the ratio 0.2 (98.2%).

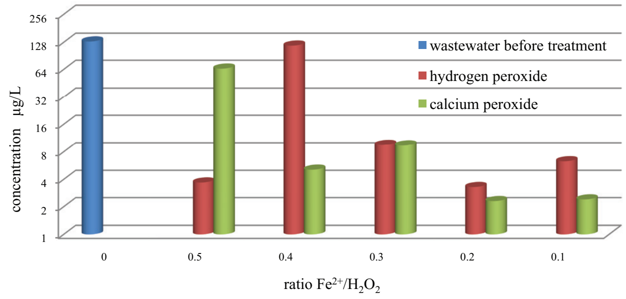

Fig. 13. Changes in the concentration of Σ 6 rings PAHs depending on a dose of oxidants.

In Fig. 14, changes in the concentration for total of 10 hydrocarbons tested depending on type and dose level oxidant are presented.

Under the same process conditions, the efficiency of PAHs degradation using CaO_2 and $FeSO_4\cdot7H_2O$ was 43%–97% and using H_2O_2 and $FeSO_4\cdot7H_2O$ was 54%–96%. The degradation mechanism of PAHs described in the literature is fragmentary. In the photo-Fenton process, PAHs are degraded by interaction of UV light and hydroxyl radicals. Light excites the molecule making it more susceptible to degradation, while hydroxyl radicals cause degradation of the benzene ring [35]. It is known that intermediate products are formed in the process, which can be more harmful than parent compounds. However, when the oxidation time is lengthened, they can transform until they are completely mineralized [27].

$$\text{PAHs} + \lambda\upsilon \rightarrow \text{intermediate products (aldehydes, phenols, epoxide compounds, carboxylic acids)} \quad (5)$$

$$\text{PAHs} + \text{OH}\cdot \rightarrow \text{intermediate products} \quad (6)$$

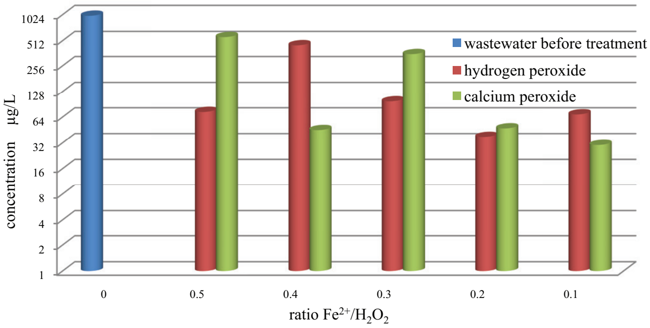

Fig. 14. Changes in the concentration of Σ 10 PAHs depending on a dose of oxidants.

The results obtained in the study can be compared with the data have been described in the literature. In the case of AOPs methods, which include various chemical and photochemical processes, the effectiveness is influenced by a number of factors such as reaction time, reaction pH, dose level of oxidant and catalyst, reaction temperature, the initial concentration of organic compounds, and the presence of color substances and sediments. It has been shown that naphthalene [38] anthracene and benzo(a)pyrene [39] undergo direct photolysis under the influence of UV light. However, combination of the oxidants and UV light results in better degradation of PAHs [40]. The use of UV/H_2O_2 resulted in the removal of benzo(a)pyrene and anthracene in 99% [41]. Combination of light and H_2O_2 resulted in an increase in the removal rate of phenanthrene and pyrene compared with UV or H_2O_2 alone [42]. The effect of the level dose of H_2O_2 on the efficiency of the benz(a)pyrene degradation process was also investigated. Studies have shown that increasing the level dose may result in reducing degree of degradation. Increasing the dose of H_2O_2 oxidant above 50 mg/L reduced the degree of degradation of benzo(a) pyrene from about 85% to 50% [16]. Another important factor is the pH value, whose optimum should be within 2.5–4 [43], and also temperature, which the increase, may have a positive effect on the hydrocarbon degradation process [16]. In addition to the abovementioned factors, the decomposition process is also affected by the chemical structure of hydrocarbons, and in particular, the presence of non-aromatic pentane rings, which degradation does not run according to the radical reaction [44]. Studies on PAHs photo degradation in municipal sewage showed that the degradation efficiency of 16 PAHs did not exceed 65% for real wastewater. When wastewater was enriched with the standard PAHs mixture, the effectiveness increased to 84% [7]. In the case of using calcium peroxide, the research concerned mainly the use of this oxidant to remove various contaminants from soil. It was shown that CaO_2 used for soil treatment removed 96% of petroleum hydrocarbons and liquid H_2O_2 74% [45]. In addition, it has been shown that CaO_2 work better than liquid H_2O_2 in the removal of PAHs from soil [30] and can also be used to decompose other organic pollutants, for example, 2,4,6-trinitrotoluene [29]. Comparison of the effectiveness of the use of various AOPs processes to the degradation of organic micro-contaminants including PAHs is not easy. Differences in process conditions as well as the use of various oxidants and various undergoing treatment medium have impact on the obtained results.

4. Conclusions

Based on the research and the results obtained, the following conclusions can be drawn. The total PAHs concentrations in coking wastewater before oxidation not exceed 1 mg/L (996.6 µg/L). During the experiment, it was found that it is possible to reduce the concentration of PAHs in coking wastewater as a result of the use of CaO_2 or H_2O_2 oxidants under the conditions of the photo-Fenton reaction. While maintaining the same process conditions, the efficiency of degradation of PAHs using CaO_2 under the conditions of the photo-Fenton reaction was 43%–97% and with the use of H_2O_2 under the conditions of the photo-Fenton reaction was 54%–96%. In the case of all tested hydrocarbons, the use of CaO_2 in the proportion Fe^{2+}/H_2O_2 0.4 was more effective than H_2O_2. Not all hydrocarbons were equally susceptible to oxidation. Specifically harmful hydrocarbons containing five and six rings per molecule were more susceptible to degradation than four-ring hydrocarbons. For individual hydrocarbons and used oxidants, the removal efficiency ranged from 0% to more than 99.9%.

The effectiveness of TOC removal using H_2O_2 under the conditions of the photo-Fenton reaction was 26%–43%, while the effectiveness of TOC removal using CaO_2 under the conditions of the photo-Fenton reaction was 46%–56%. The use of CaO_2 caused a more intensive decomposition of organic compounds (more effective decrease in TOC value) than H_2O_2. The degradation of organic compounds expressed as a decrease in COD value for the use of CaO_2 under the conditions of the photo-Fenton reaction was in the range of 30%–35%, and for H_2O_2 under the conditions of the Fenton reaction it was within 53%–56%.

Acknowledgment

The research was funded by the projects BS-MN-402-301/17 and BS-PB-402-301/11.

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