

Proceedings



The Use of Sodium Carbonate – Hydrogen Peroxide (2/3) in the Modified Fenton Reaction to Degradation PAHs in Coke Wastewater ⁺

Jolanta Kozak * and Maria Włodarczyk-Makuła *

Department of Chemistry, Water and Wastewater Technology, Czestochowa University of Technology, 69 Dąbrowskiego Str., 42-200 Częstochowa, Poland

* Correspondence: j.kozak@is.pcz.pl (J.K.); mwm @is.pcz.czest.pl (M.W-M.); Tel.: +34-32-50-919 (M.W-M.)

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Abstract: The aim of the research was to determine the effectiveness of removing micro-organic pollutants, including PAHs, using the modified Fenton method. The tested material was pretreated coke wastewater, in which the initial chemical oxygen demand (COD) value and initial polycyclic aromatic hydrocarbons (PAHs) concentration were determined. The samples were then subjected to an oxidation procedure. Before the process, the pH was adjusted to 3.5–3.8. Next, the following doses of sodium carbonate—hydrogen peroxide (2/3): 1.2 g/L, 1.5 g/L and 2 g/L, and a constant dose of iron sulphate were added. The next step was exposing the samples to UV light for 6 min and separating the organic matrix from the samples of wastewater. After the tests, the final value of the COD and the final PAHs concentration were determined. The average content of organic pollutants in pretreated coke wastewater determined by the COD index was 538 mg/L, and after the oxidation process, the COD index decreased in the range from 9 to 29%. The efficiency of the degradation of the sum of 16 PAHs was varied and was in the range of 94–97.6%. The research results show that sodium carbonate—hydrogen peroxide (2/3) can be used for the degradation of organic pollutants, such as PAHs, in the modified Fenton process.

Keywords: PAHs; photo-Fenton process; sodium carbonate—hydrogen peroxide (2/3); hydroxyl radicals

1. Introduction

The main source of organic micro-pollution in water environment is industrial sewage, especially coke wastewater. A shortened description of raw and pretreated coke wastewater is presented in Table 1.

Table 1. Shortened description of coke wastewater, raw and after pretreated [1-3].

	Unit Val		Value
		Raw Coke Wastewater	Pretreated Coke Wastewater
pН	-	9.5–9.2	9.4–9.0
COD	mg O ₂ /dm ³	4500-2200	700–530
TOC	mg C/dm ³	1000–960	180–160
TC	mg C/dm ³	1200-1100	460
Phenol index	mg/dm ³	540	-

Polycyclic aromatic hydrocarbons (PAHs), together with other compound such as ethers, alcohols, glycols, aliphatic and aromatic amines and phenols, belong to the group of organic micropollutants. PAHs are toxic and mutagenic, easily adsorb on solid surfaces and bio accumulate in the tissues of living organisms. Due to high resistance to conventional degradation processes, they are classified as persistent organic pollutants [4]. For this reason, new techniques are being sought out to efficiently remove these compounds. The Fenton process belongs to the advanced oxidation process (AOP) [5].

The Fenton reaction mechanism involves many steps. In the first step, H_2O_2 is decomposed, which is initiated and catalyzed by Fe^{2+} ions in an acidic environment. Fe^{2+} ions are necessary for the release of hydroxyl radicals from hydrogen peroxide [6]. The support of the Fenton process with UV radiation is called photo-Fenton reaction (UV-Fenton).

In the classic Fenton process (Reaction 1), the Fe³⁺ ions are formed and collected, and after the Fe²⁺ ions are exhausted, the reaction practically stopped. In the UV-Fenton reaction, under the influence of UV light, photo reduction from Fe³⁺ ions to Fe²⁺ is run; moreover, the additional OH• radicals are formed (Reaction 2). The Fe²⁺ ions can further react with hydrogen peroxide according to the Fenton process, generating new OH• radicals, which leads to increased efficiency of the micropollutant removal [7,8].

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

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + OH^{\bullet} + H^+$$
(2)

The advantage of this method over the basic process is the extension of the time oxidation process and the production of additional hydroxyl radicals.

Modifications of the Fenton process can be included; for example, the use of alternative sources of hydrogen peroxide such as calcium peroxide, magnesium peroxide or sodium carbonate— hydrogen peroxide (2/3). In an acidic environment, these compounds are hydrolyzed and hydrogen peroxide, which is a source of hydroxyl radicals, is released. Furthermore, the process is run according to the classic Fenton reaction.

When PAHs are present in the test sample, hydroxyl radicals quickly react with them, causing their oxidation. In addition, UV light causes their direct photolysis [9].

- PAH + $\lambda v \rightarrow$ intermediate products
- $PAH + OH \rightarrow intermediate products$

2. Aim of the Research

The aim of the research was to determine the effectiveness of using sodium carbonate hydrogen peroxide (2/3) in the photo-Fenton reaction to the degradation of organic pollutants, including PAHs.

3. Materials and Methods

The material was pretreated coke wastewater collected from the outflow of a biological wastewater treatment plant. Before the oxidation process, the initial organic pollutants expressed by the COD parameter and the initial PAHs concentration were determined. The first step of oxidation was adding the following doses of sodium carbonate—hydrogen peroxide (2/3): 1, 2 g/L, 1, 5 g/L and 2 g/L. The acidic environment of reaction had a pH of 3, 5–3, and 8. Then, a constant dose of FeSO₄ · 7H₂O in an amount of 1 g/L was added. The reaction time was 20 min. The next step was to expose samples to UV rays for 6 min. The height of the irradiated layer was 2 mm. A 36 W UV lamp emitting UV-C light with a wavelength of λ -264 nm was used. The extraction of PAHs from coke wastewater was based on shaking samples in a liquid-liquid system with the mixture of cyclohexane and dichloromethane (5:1 v/v). The extracts were separated on a laboratory separator and purified on silica gel in a vacuum chamber. The obtained purified extract was concentrated under a stream of nitrogen and analyzed on a GC-MS kit. In the wastewater before and after the photo-Fenton process, the quantity and quality of 16 PAHs recommended by the US Environmental Protection Agency was

determined. The statistical Student's *t*-test was used to do a statistical evaluation of the obtained results. This test was chosen on the basic following parameters: sample size (n < 30), degrees of freedom (n-1 = 2) and significance level α = 0.05. The critical value obtained for the test was t ≈ 4.303.

4. Results

The results obtained under proposed research conditions allow us to draw the following conclusions. The average content of micro-organic pollutants in pretreated coke wastewater determined by the COD index was 538 mg/L, and after the oxidation process, the COD index decreased from 9 to 29%. The total concentration of analyzed hydrocarbons at the beginning of the experiment was 1084 μ g/L. In the case of 2 and 3 rings of PAHs, the degradation process was less effective than for the 4-6 rings of hydrocarbons. Low molecular weight hydrocarbons are characterized by a high value of vapor pressure, which results in their higher volatility. For the 2 and 3 rings hydrocarbons, the fluorene was the worst to remove, for which the percentage of removal efficiency was 11–64%, while phenanthrene was the most effectively removed, with a percentage of efficiency of about 76–92%. In the case of the 4–6 rings hydrocarbons, the efficiency of degradation was over 99%. In those cases, dibenzo(ah)anthracene was the most effectively removed from wastewater with efficiency in the range of 97–99.9%, while fluoranthene had the worst efficiency of removal, which was in the range of 94–98%. The efficiency of the degradation of the sum of 16 PAHs was varied and was in the range of 94–97.6%. The changes in the concentration for all analyzed PAHs are shown on Figure 1. Also, the standard deviation for each result is marked on the graph. The removal efficiency for individual hydrocarbons was:

- naphtalene: 81–91%.
- 3 ring hydrocarbons: fluorene 11–64%, acenaphtylene 66–82%, acenaphtene 55–75% and phenanthrene 76–92%.
- 4 ring hydrocarbons: fluoranthene 94–98%, pyrene 96–99%, benzo(a)anthtacene 97–99%, chrysene 95–98.6%.
- 5 rings hydrocarbons: benzo(b)fluoranthene 96–99%, benzo(k)fluoranthene 98–99.5%, benzo(a)pyrene 97–99.2% and indeno(1,2,3-cd)pyrene 98–99.2%.
- 6 rings hydrocarbons: dibenzo(ah)anthracene 97–99.9% and benzo(ghi)perylene 94–99.3%.

In earlier studies, which used calcium peroxide, a decrease in PAHs concentration after the oxidation process was observed. The effectiveness of removal of selected hydrocarbons was in the ranged of 89–98%. The decrease of the level of organic pollutants expressed by COD index was 30–35%. The effectiveness of PAHs degradation was directly proportional to the calcium peroxide dose [10]. In the data described by Engwalla et al. [11], the authors showed that the 2 and 3 PAHs were more efficiently removed in the photo-Fenton process than the 4–6 rings PAHs. In the research of da Rocha et al. [12], the degradation efficiency of 16 PAHs in petrochemical wastewater in the photo-Fenton process reached 96%. However, comparing the obtained results with the literature data is difficult because of the difference in the process condition.

5. Conclusions

Studies have shown that PAHs can be removed from coke wastewater during a modified Fenton process. The research results show that sodium carbonate—hydrogen peroxide (2/3) can be used for the degradation of micro-organic pollutants, such as PAHs, in the photo-Fenton process. The effectiveness of PAH removal from wastewater in the modified photo-Fenton process was varied and depended on the oxidant dose. The effectiveness of PAHs degradation was directly proportional to the sodium carbonate—hydrogen peroxide (2/3) dose.



Figure 1. The changes in the concentration for the sum analyzed PAHs depending on dose level of oxidant. The standard deviation for each result is marked on the graph.

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Abbreviations

- TOC total organic carbon
- TC total carbon
- COD chemical oxygen demand

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