Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.26335

199 (2020) 441–450
September

Efficiency assessment of coke industry wastewater treatment during advanced oxidation process with biochar adsorption

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Received 20 November 2019; Accepted 10 July 2020

ABSTRACT

The aim of the study was to determine the treatment efficiency of coke industry wastewater during the application of integrated processes: advanced oxidation process and biochar (AOP-BC) adsorption. In the case of the AOP process, the focus was on the Fenton process in which the source of hydroxyl radicals was H_2O_2 (variant I) or sodium percarbonate (SPC) (variant II). An additional aim of the study was to assess the change in toxicity of coke industry wastewater treated in integrated systems. This stage was carried out using *Sinapis alba* and *Lepidium sativum*. It was found that while conducting the Fenton process as variant I (H_2O_2) at all reagent doses tested, the removal efficiency chemical oxygen demand and total organic carbon was 10% and 9% higher, respectively, compared to variant II. The most advantageous dose of regents was 2.5:1 and biochar – 4 g L^{-1}. It was observed that in the SPC + BC system the roots of *Lepidium sativum* and *Sinapis alba* were on average 10% and 12% longer compared to the H_2O_2 + BC system. Higher germination index of both tested plants, indicating lower wastewater toxicity, was recorded for the SPC + BC system.

Keywords: Coke industry wastewater; Fenton process; Sodium percarbonate (SPC); Biochar; Toxicity; Advanced oxidation process (AOP); *Lepidium sativum*; *Sinapis alba*

1. Introduction

Post-production wastewater generated during coal coking, gas purification and product recovery processes can be included in the group of industrial wastewaters particularly difficult to treat and biodegradation [1–3]. Their chemical composition depends, among others on technological parameters of coke production, coking process temperature, type of coal and methods to recover by-products [4–6]. The amount of process wastewater ranges from 0.15 to 0.35 m^3 t^{-1} coal, which, calculated per ton of coke, gives from 0.35 to 0.45 m^3 [2]. Coke industry wastewater is typical high-strength organic wastewater containing significant amounts of impurities such as cyanide, thiocyanate, phenols, sulfides, ammonia salts, polycyclic aromatic hydrocarbons and hexahydroxy N-containing heterocyclic compounds [6–9]. Most of these pollutions are toxic, carcinogenic, mutagenic and genotoxic to aquatic organisms. For this reason, coke wastewater can have long-term environmental and ecological effects [10–12]. Currently, most of the coking plants in Poland are modernizing the gas and wastewater treatment installations the use of best available techniques, which have the main goal to protect the environment [1]. Conventional treatment of coke industry wastewater includes solvent extraction of phenolic compounds, steam stripping of ammonia and biological treatment [9]. The biological treatment of coke wastewater is a very slow and sensitive process because the toxic compounds that are present can be harmful to the microorganisms involved [13]. In recent years, significant attention in wastewater or sludge technology has been

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Presented at the 14th Conference on Microcontaminants in Human Environment, 4–6 September 2019, Czestochowa, Poland

devoted to the so-called advanced oxidation process (AOP). AOP has been suggested for the partial or complete removal of pollutants from the wastewater or their transformation into less toxic and more biodegradable products [6,13,14]. The AOP has been also successfully used to degrade several food-processing wastewater (components such as gallic acid and protocatechuic acid) [15], landfill leachate [16] or textile wastewater [17].

The real advantage of AOP is the actual decomposition of individual pollutants contained in the wastewater, in contrast to many other physicochemical purification methods that only transfer pollutants from the wastewater phase to the sludge phase [2,14,18,19]. The oxidizing factor in AOP is free hydroxyl radicals characterized by the rapid and non-selective oxidation of many organic compounds to CO_2 and H_2O. Hydroxyl radicals have one of the highest oxidation potentials among all known oxidants (2.80 V) [9,18,20].

The Fenton's reaction was discovered by Fenton in 1894 [21]. In the Fenton process, the formation of hydroxyl radicals occurs as a result of the reduction of hydrogen peroxide using Fe^{2+} ions. Two mechanisms of hydrogen peroxide decomposition in the presence of iron(II) salts are given by the radical path (production of highly reactive OH^- radicals) and the non-radical path [22]. During the Fenton reaction, iron ions accumulate, and after complete oxidation, the hydroxyl radical production process stops. Hydroxyl radicals reacting with molecules of various organic substances (dissolved or suspended) lead to their chemical decay (oxidation or destabilization) as well as to the production of new compounds [17,23,24]. The main steps involved in the Fenton process are oxidation (1), neutralization (2), flocculation (3) and sedimentation (4). The effects of pollution degradation with Fenton's reagent depend on the dose of H_2O_2 in relation to iron ions, pH, temperature and reaction time. It is very important to select the appropriate dose of catalyst (Fe^{2+}) and H_2O_2, because the excess of hydrogen peroxide may react with OH^- instead of with pollutants (scavenging reaction) [25–27]. The acid reaction is necessary to produce a significant amount of hydroxyl radicals. It is most advantageous to carry out the Fenton reaction in the pH range from 3 to 5. At a higher pH, hydrogen peroxide decomposes rapidly on the flocs of $Fe(OH)_3$ that is formed, and at a lower pH, the formation of significant amounts of hydrogen ions, which in turn become scavengers of hydroxyl radicals [13,18]. The main advantages of Fenton's processes include simple and easy operations process, relatively inexpensive Fenton's reagent, short time of reaction, and no energy input is necessary to activate H_2O_2. A disadvantage of this process is mentioned a narrow pH range (pH 3–5) and iron ions are consumed more rapidly than they are regenerated. Iron ions may be deactivated due to complexion with some iron complexing reagents such as phosphate anions and intermediate oxidation products [18,28–30].

In order to increase efficiency as well as simplify the process, attempts are being made to modify the classic Fenton reaction. The conventional Fenton process is optimized by the heterogeneous system, electrochemical theory, photocatalytic principle, the synergistic reaction between Fe/Cu/air and Fenton or using alternative sources of H_2O_2 [31–37]. Calcium (CaO_2) and magnesium (MgO_2) peroxides as well as sodium percarbonate (SPC) Na_2CO_3 $1.5H_2O_2$ (SPC) may be such an alternative source SPC is also called dry hydrogen peroxide because it has the same advantages as liquid hydrogen peroxide. Compared with Fenton's reagent, SPC has many advantages:

- it is applicable in a wide pH range;
- environmentally friendly;
- non-corrosive;
- easy to transport and store;
- he ends products in SPC oxidizing organic compounds systems are usually carbon dioxide, water, and sodium carbonate, which occur naturally in groundwater;
- the decomposition products of SPC are non-toxic to microorganisms [38,39].

As a result of decomposition, SPC releases hydrogen peroxide and sodium carbonate. Eqs. (1)–(3) show the relevant reactions in such a Fenton-like process in the presence of ferrous iron [38–41]:

$$2\,Na_2CO_3 + 3H_2O_2 \rightarrow 2Na_2CO_3 + 3H_2O_2 \tag{1}$$

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

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \tag{3}$$

Numerous studies show the effectiveness of the sorption process for post-treatment industrial wastewater. Granulated activated carbon (GAC) is the most commonly used. However, an interesting alternative seems to be the use of biochar in the cleaning of pre-biologically or chemically treated wastewater. Biochar is often used directly with little post-treatment modification and is generally less resource, energy, and capital intensive to manufacture compared to highly refined GAC. It is assumed that the amount of energy needed to produce GAC from various sorbents ranges from 44 to 170 MJ kg^{-1}, while for producing biochar it requires up to 90% lower amounts energy (in the range from 1.1 to 16 MJ kg^{-1}) [42].

Biochar is a product prepared during biomass pyrolysis under limited oxygen content and at relatively low temperatures. The product properties, and especially its structure, can be modified through the choice of biomass (forest waste, agricultural waste, stones, fruit pomace, crop residues, forest waste, animal manure, food processing waste, paper waste, etc.) and parameters of biochar production technology (temperature, process speed, reactor shape). The method of preparing the raw material is also important for the physical properties of biochar drying, chemical activation, screening, etc. The listed parameters (process conditions and origin of the raw material) are factors determining the distribution of pore size and therefore the specific surface. During the thermal decomposition of biomass, weight loss occurs most often in the form of organic volatiles, leaving empty spaces that form an extensive network of pores [43]. Compared to other carbon materials, biochar is characterized by low production costs, high process efficiency due to the low pyrolysis temperature, low ash content. Porous biochar introduced into the ecosystem or used as a cleanser in water purification technologies can be a natural sorbent as a potential competitor of expensive activated carbon. Recently, biochar is considered as the main component of filters and absorbers, primarily due to its valuable application properties. The high permeability of biochar supports the removal of suspended solid particles, the presence of functional groups on the biochar surface through its modification, helps to absorb heavy metals and organic components, while the characteristic structure is responsible for the adsorption and/or degradation of biological pathogens and other impurities [44,45]. Biochar absorb hydrocarbons, other organic substances and some inorganic metal ions, showing the potential of water purification and soil improvement [46,47]. Biochar can replace carbon, coconut shells and wood-based activated carbons as a cheap sorbent for impurities and pathogens. Biochar can be used to remove impurities from water, while loading them with nutrients to be later used as soil corrections, ensuring long-term sorption capacity and constituting fertilizer [48].

Many toxic pollutions present in coke industry wastewater are refractive compounds that are not removed at individual stages of treatment or pre-treatment. Some of these pollutions have a very toxic effect even when their amount in the surface water is trace. This is due to their ability to accumulate in the environment. It is necessary to eliminate or significantly reduce the content of these impurities in the treatment plant inflow. This is due to compliance with the conditions that must be met by industrial wastewater discharged into the municipal sewage network. For this reason, there is a need to conduct research to determine the risk that refractory substances found in industrial wastewater can cause.

The research attempts to show whether and to what extent the replacement of H_2O_2 with SPC in the Fenton reaction affects the efficiency of deepened oxidation of organic compounds contained in coke wastewater. The assessment was also carried out as proposed in the coking wastewater treatment system (advanced oxidation – biochar adsorption) affects the change in wastewater phytotoxicity.

2. Material and method

2.1. Material

The research used post-production wastewater generated in the coke oven plant located in the Śląskie Voivodeship (Poland). The tested wastewater has already been mechanically pre-treated at the coking plant, as a result of which it has been removed, among other solid impurities, oils and tar substances. Post-production wastewater was characterized by phenolic odor and brown color. Their reaction was alkaline (pH 8.5). The chemical oxygen demand (COD) of wastewater generated in production processes averaged 7,350 mg L^{-1}, and the biochemical oxygen demand (BOD)/COD ratio was very low (0.014). High total organic carbon (TOC) concentrations (2,240 mg L^{-1}) have also been reported.

2.2. Biochar

The biochar used in the study was obtained in a 60 min autothermal biomass transformation process (Miscanthus) at 450°C. Technical biochar analysis was performed in accordance with PN-G-04560: 1998P (Table 1).

Nitrogen, carbon, hydrogen and sulfur content were carried out in the LECO elemental analyzer, (US). The heat of combustion was determined using an IKA Basic C 2000 calorimeter (Germany) (isoperibolic method). Scanning microscope Philips XL30/LaB6 (US) was used for structural analysis of biocarbon. Biochar porosity was determined using a PoreMaster 33 mercury porosimeter (with Quantachrome Instrumentals software, Quantachrome Corporation, US). Fig. 1 illustrates the structure of biochar. It can see a fibrous structure with open pores. The open porosity of biochar (BC) was estimated to 24.5% and specific surface area about 12.16 $m^2\ g^{-1}$ [42].

2.3. Research methodology

The research was carried out in three stages. In the first stage, organic compounds were oxidized in the Fenton process in which the source of H_2O_2 was 30% hydrogen peroxide (variant I) or SPC (variant II). Both reactions were carried out in laboratory reactors with a diameter of 8 cm and a capacity of 0.5 L. Coke industry wastewater were

Table 1
Proximate and elemental ultimate analysis of biochar sample (dry)

WT, %	7.9
VM_d, %	10.00
A_{d575}, %	15.80
FC, %	74.20
N_d	0.95
C_d	74.20
H_d	2.82
S_d	0.23
O_d	18.99

WT – total water; VM – total volatile fractions; *A* – ash content; FC – fixed carbon.

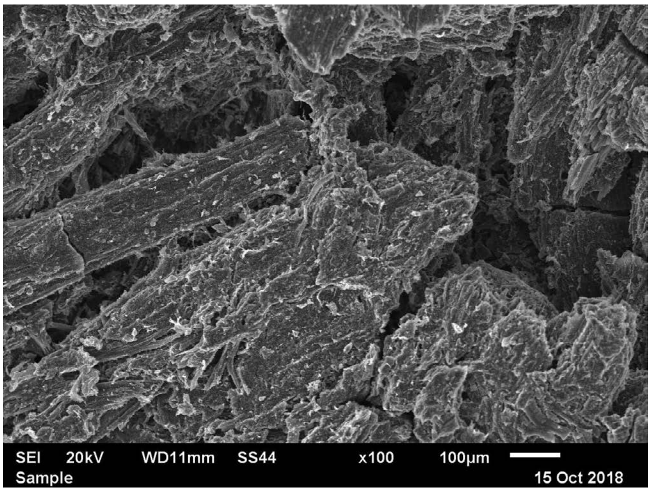

Fig. 1. The microstructure of biochar, magnification ×100.

subjected to pH correction to 3.5 (H_2SO_4 acid) before being directed to advanced oxidation with Fenton's reagent. Chemical reagents (hydrated iron(II) sulfate, 30% hydrogen peroxide solution and SPC) were dosed into the reactor once at the beginning of the cycle. The first to enter the reaction chamber was a 30% solution of H_2O_2 (variant I) or SPC (variant II) due to their strong alkalizing properties. After 10 min, the next wastewater pH correction was made to level 3.5 and iron ions in the form of $FeSO_4{\cdot}7H_2O$ were added. The time of quick mixing of wastewater and added reagents was a total of 20 min. The next stage of this process was a 60 min slow mixing of wastewater with Fenton's reagent, after which they were neutralized. The wastewater prepared in this way was left for 24 h for sedimentation. The variable parameter was the dose of hydrogen peroxide (variant I) and SPC (variant II) in relation to the constant proportion of iron(II) ions (4 g L^{-1}). The H_2O_2:Fe^{2+} ratio was 1.5:1, 2.5:1, 5:1, 10:1 and 20:1 [15,22]. Adsorption of impurities from preoxidized coke industry wastewater in the Fenton process (variants I and II) was carried out under static conditions. For samples with a volume of 250 cm^3, 0.5 g (dose-1 g L^{-1}), 1 g (dose-2 g L^{-1}) and 1.5 g (dose-6 g L^{-1}) of biochar were added respectively [42]. These biochar samples were shaken for 6h and next, they were left for 18 h of static contact. The mixing intensity was set at 200 rpm. Before the analysis of the treated coke industry wastewater, the samples were centrifuged (15 min) with a speed of 1,120 rpm and next filtered through a soft filter [49]. The effectiveness of the adsorption process at the assumed doses and contact time was assessed based on the degree of removal of pollutions designated as COD and TOC. The sorption capacity of the biochar used was calculated from the following relationship:

$$q = \frac{C_0 - C_t}{m} \tag{4}$$

where q is the adsorbent removal capacity of the given contaminant; "C_0" is the initial and "C_t" is the equilibrium concentration of the given contaminant (mg L^{-1}); "v" is the volume of solution (L) and "m" is the weight of the biochar (g) [42].

In the last step, raw and treated wastewater in the proposed systems were subjected to phytotoxic assessment. Fig. 2 presents a scheme of coke industry wastewater treatment in a system that associates the classic and modified Fenton process with the adsorption process on biocarbon, including the assessment of their phytotoxicity.

2.4. Physical and chemical analyses

Raw coke wastewater, coke wastewater after the Fenton process (variant I and variant II) and treated on biocarbon were subjected to analysis of COD, TOC and BOD values. COD was determined by the bichromate method using a HACH Dr/4000 spectrometer, (US) according to PN-85/C-04578/02 and BOD by the respirometric method, using the OxiTop WTW, (Germany). The TOC content in the tested samples was determined using the Kiper TOC 10C analyzer, (US) PX-120 carbon analyzer with AS40-Dione autosampler, (US). CP-401/CP-40 ph-meter was used to measure pH during the chemical oxidation process [2,18,24,25].

2.5. Phytotoxicity test

To assess the phytotoxicity of raw and treated coke wastewater, a test proposed by Walter et al. [50] was used in which two dicotyledonous plants were used: *Lepidium sativum* and *Sinapis alba*. The test consisted of placing a paper disc in a petri dish, adding 5 ml of the test solution and sowing ten seeds. Petri dishes with sown seeds were placed in an incubator at 25°C in the absence of light and incubated for 72 h. After this time, the number of germinated seeds and root length were determined. The obtained results allowed to determine the percentage ratio relative seed germination (RSG), relative root germination (RRG) and germination index (GI), which were calculated on the basis of the following formulas:

- the percentages of RSG

$$\text{RRG} = \left(\frac{R_E}{R_K}\right) \cdot 100\left[\%\right] \tag{5}$$

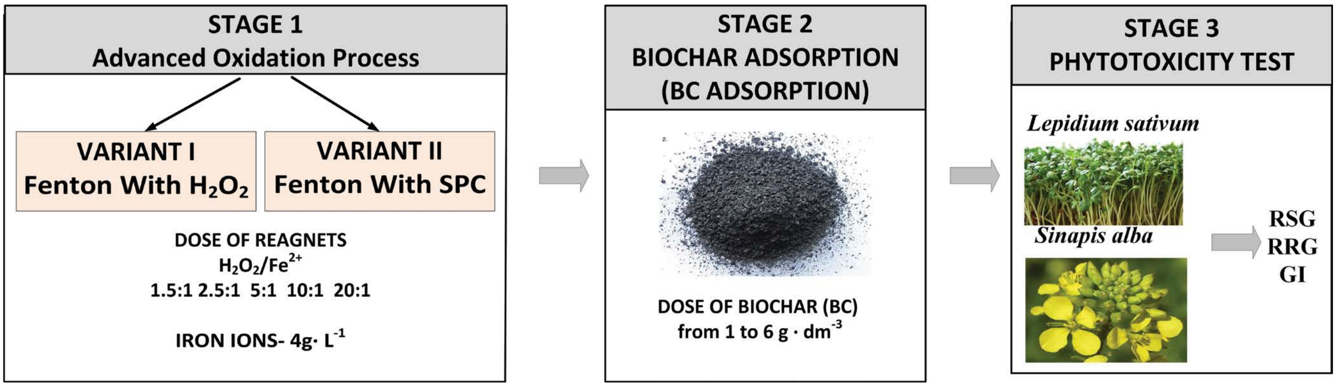

Fig. 2. Scheme of coke industry wastewater treatment by Fenton process (the option I and option II) associated with the biochar adsorption process.

where R_E is the root length on the tested sample and R_K is the sprout root length in distilled water,

- relative germination of seeds

$$\text{RSG} = \left(\frac{S_E}{S_K}\right) \cdot 100 \left[\%\right] \tag{6}$$

where S_E is the amount of seeds that have germinated on the sample tested and S_K is the amount of seeds that have germinated in distilled water.

- germination index

$$\text{GI} = \frac{\text{RSG} \times \text{RRG}}{100} \left[-\right] \tag{7}$$

The tests were carried out in ten replicates for each of the plants. The average of all ten replicates was given as the result [51].

3. Results and discussion

3.1. Comparison of the efficiency of the Fenton process with H_2O_2 and SPC in coke industry wastewater treatment

In this first stage of research, an attempt was made to use hydrogen peroxide (variant I) and SPC (variant II) to oxidize impurities contained in coke wastewater. An important factor when using this type of reagent is maintaining the correct pH (3.5–5–5). Lowering the pH of wastewater is associated with the necessity of later alkalizing. Alkalization must be carried out for both wastewaters discharged into the environment and wastewater subjected to post-treatment processes. Evaluation of the action of hydrogen peroxide on the organic substances contained in the wastewater, designated as COD, is associated with the elimination of the effect of residual hydrogen peroxide. Therefore, a relationship has been determined to allow the conversion of the quantity of TOC into COD. As the research shows, the size of the TOC indicator does not depend on the presence of residual H_2O_2 [52]. The value of the correlation coefficient *f*, determining the relationship between COD and TOC, was determined from the following relationship [52]:

$$f = \frac{\left(\text{COD}_0 - 0.01 \cdot \text{E f}_{\text{TOC}} \cdot \text{COD}_0\right)}{\text{TOC}_{\text{treat}}} \tag{8}$$

where $\text{TOC}_{\text{treat}}$, total organic carbon concentration in treated wastewater; COD_0 is the COD of raw coke industry wastewater; Ef_{TOC} is the TOC removal efficiency.

$\text{COD}_{\text{computing}}$ value in wastewater treated with hydrogen peroxide and SPC was calculated according to the relationship:

$$\text{COD}_{\text{computing}} = f \cdot \text{TOC} \tag{9}$$

The value of coefficient $f = 2.98$ was determined for the coke industry wastewater used for the study.

It was found that during the Fenton process as variant I at all tested doses of reagents, the removal efficiency of COD and TOC was 10% and 9% higher, respectively, compared to variant II. COD values with a reagent dose of 2.5:1 during the Fenton process using H_2O_2 and SPC were the lowest and amounted to 1,450 and 1,890 mg L^{-1}, respectively. At this dose, the TOC value from 2,240 mg L^{-1} (raw wastewater) decreased to 345 mg L^{-1} (variant I) and 548 mg L^{-1} (variant II). The highest COD values (2,680 mg L^{-1} – variant I and 3,240 mg L^{-1} – variant II) and TOC (950 mg L^{-1} – variant I and 701 mg L^{-1} – variant II) were observed when the reagent ratio H_2O_2/Fe^{2+} was 20:1. In variant I, the COD removal efficiency at the 20:1 dose of reagents was 63.5% and at the 2.5:1 dose, it increased up to 80.2%. During wastewater treatment with a 1.5:1 dose of reagents, higher COD and TOC values were observed compared to a 2.5:1 dose. The COD value after variant I and variant II was 1,970 and 2,340 mg L^{-1}, respectively. Increasing the dose of H_2O_2 or SPC oxidation did not contribute to a significant increase in the degree of wastewater oxidation. The discussed changes are presented in Figs. 3a and b.

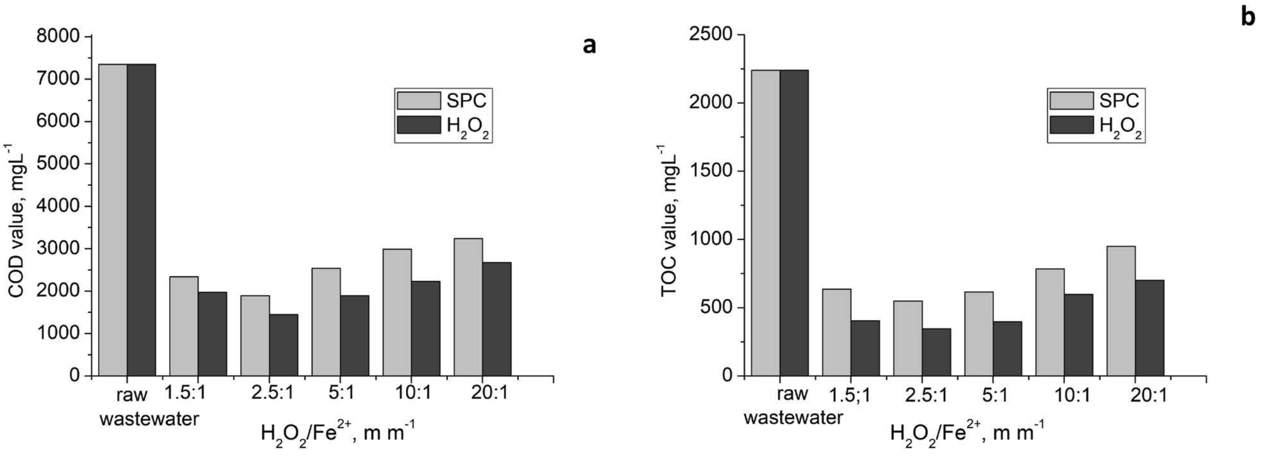

Fig. 3. The changes in COD (a) and TOC (b) values vs. the dose of reagents (H_2O_2 and SPC).

It was observed that the efficiency of coke wastewater treatment in both tested variants decreased along with the decrease in the share of Fe^{2+} ions in the reaction mixture. This is confirmed by the results of studies by Singh and Tan, who stated that as the amount of Fe^{2+} increases, the oxidation rate of organic substances increases [53]. This is also confirmed by research carried out by Rodrigues et al. [54] who showed that the rate of degradation increased with an increase in the concentration of the ferrous ion. However, it should be remembered that the excess of iron ions, just like the excess of hydrogen peroxide, acts as a scavenger of hydroxyl radicals and, consequently, leads to inhibition of the process [21]. As the Kozak and Włodarczyk-Makuła [32] studies show, the Fenton process is more effective in the presence of H_2O_2. During their tests, the degree of TOC removal from pre-biologically treated wastewater ranged from 10%–30% (SPC) to 26%–43% (H_2O_2) [10].

During coke industry wastewater treatment in modified Fenton (variant II) at the dose of reagents 2.5:1, the BOD index increased the highest from 105 mg L^{-1} (raw wastewater) to 235 mg L^{-1}. At the time when the process with this regent was conducted using H_2O_2, BOD also increased (to 215 mg L^{-1}). At this dose of reagents, the highest BOD/COD ratio was recorded from 0.014 (raw wastewater) to 0.029 (variant I) and 0.032 (variant II). It was found that in both variants at doses of 2.5:1, 5:1 and 10:1 to increase in BOD and BOD/COD ratio compared to raw wastewater (Fig. 4). When the dose of reagents was set at 20:1, the BOD decreased to 70 mg L^{-1} (variant I) and 85 mg L^{-1} (variant II). It was observed that the BOD reached higher values in option II at doses of 2.5:1, 10:1 and 20:1 on average by 15% compared to variant I.

As Rabelo et al. [55] during the chemical treatment, the organic matter present in the effluents was oxidized, rather than mineralized, higher percentage removals of COD and TOC, respectively, having been observed. For this reason, the photo-Fenton process increased BOD/COD ratio, but reduced BOD/TOC ratio. In his research, the BOD/COD ratio increased from 0.40 to 0.57. It was found that oxidized wastewater at a dose of reagents 2.5:1 would be directed to biochar post-treatment. It was connected with the best quality of obtained wastewater and the smallest amount of added oxidants.

3.2. Use of biochar in post-treatment coke industry wastewater after the oxidation process

In the second stage, pre-oxidized chemical wastewater in the Fenton reaction at the most advantageous dose of reagents (2.5:1) was cleaned in the biochar adsorption process. In the first step, in static conditions, the time for biochar sorption equilibrium was determined. It was found that sorption was most intense in the first 2 h. Already 0.5 h, the sorption process at a biochar dose of 2 g dm^{-3} resulted in an average of 8% (variant I) and 7% (variant II) of COD removal efficiency. The results obtained at this stage show that extending the contact time above 8 h slightly increases the efficiency of the sorption process. The discussed changes are presented in Figs. 5a and b.

It was observed that the best effects for both variants were noted for biochar dose at the level of 4 g L^{-1}. After 24 h of contact with biocarbon at this dose, the COD value from 1,890 mg L^{-1} (variant II) decreased to 1,228 mg L^{-1}. During the cleaning of wastewater from a variant I at a dose of 4 g L^{-1} it decreased to 1,029 mg L^{-1}. An increase to 6 g L^{-1} caused an increase in the COD value is treated wastewater (1,116.5 mg L^{-1} – variant I and 1,360.8 mg L^{-1} – variant II). After 24 h of running the process at the lowest dose of BC (2 g L^{-1}), the removal efficiency of COD ranged from 21% (variant I) to 26% (variant II). The discussed changes are presented in Fig. 6. Studies have shown that as the biochar dose was increased, sorption capacity decreased. The highest sorption capacity was recorded at the dose of 2 g L^{-1} which for variant I and variant II was 94.28 and 110.25 mg g^{-1}, respectively.

Better quality wastewater was obtained in variant I associated with biochar at its dose of 4 g L^{-1}. The removal efficiency of COD and TOC in the proposed system was 80.2% and 84.5%, respectively. It was found that despite the high degree of pollution removal during the treatment of the wastewater in the system associating the classic/modified Fenton process with the biochar adsorption process, it is not possible to discharge them to the natural receiver

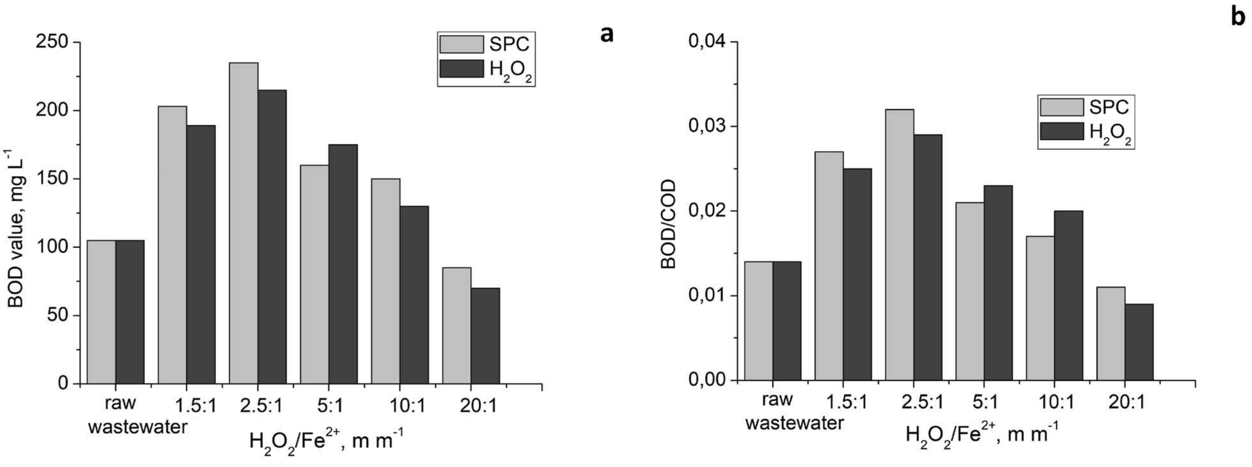

Fig. 4. The changes in BOD value (a) and BOD/COD index (b) vs. to the dose of reagents (H_2O_2 and SPC).

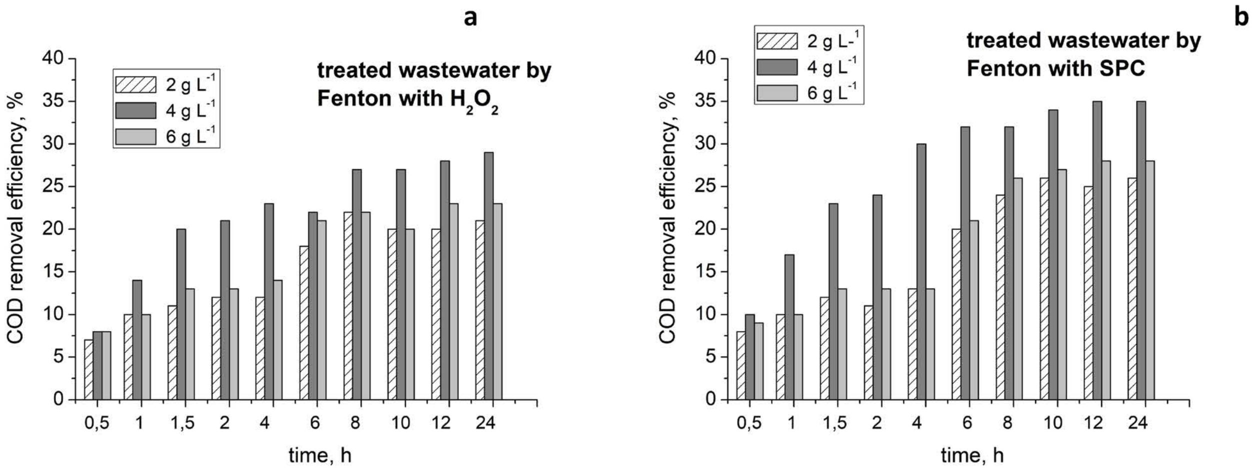

Fig. 5. Determination during biochar sorption equilibrium for H_2O_2 + BC (a) and SPC + BC (b).

(Table 2). In the future, it is planned to include the ozonation process in the proposed system or replace the adsorption process with a low-pressure membrane process, that is, ultrafiltration.

3.3. Assessment of phytotoxicity of the coke industry wastewater treated in the AOP associated with adsorption

In the last stage, treated wastewater was assessed for changes in their phytotoxicity. Two types of seeds were used in the toxicity test: *Lepidium sativum* and *Sinapis alba*. The average root length of control samples for *Lepidium sativum* and *Sinapis alba* was found to be 3.4 and 4.3 mm, respectively. For the control samples, the number of germinated was 10. Despite the high degree of removal of pollutions from coke industry wastewater for unsettled samples (100%), the number of germinated seeds for both plants was 0. After 2 seeds, the *Lepidium sativum* germinated at 50% wastewater dilution for variant I and variant II. It was found that in the RSG it reached the level of 100% in the case of *Sinapis alba* and *Lepidium sativum* with a dilution of

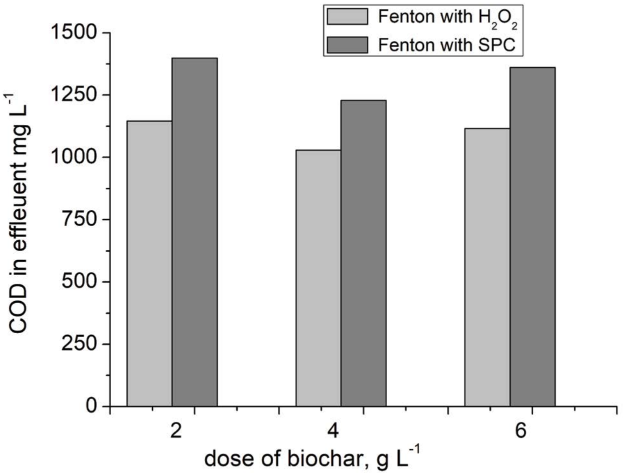

Fig. 6. Effect of biochar dose on COD in the effluent.

Table 2
Changes in the quality of coke industry wastewater treated in the AOP-BC system

Indicator	Raw wastewater	AOP H_2O_2/Fe^{2+} (2.5:1)		Adsorption Biochar dose 4 g L^{-1}		Indexes of wastewater pollution which is discharged to a natural receiver [7]*	Indexes of wastewater pollution which is directed to the system [7]**
		Fenton process with H_2O_2	Fenton process with SPC	H_2O_2 + BC	SPC + BC		
pH	8.5	7.10	7.14	7.98	8.09	6.5–9.5	6.5–9.5
COD, mg L^{-1}	7,350	1,450	1,890	1,029	1,228	125	†
TOC, mg L^{-1}	2,240	345	548	275	365	30	†
BOD, mg L^{-1}	105	215	235	n.s.	n.s.	25	†
BOD/COD	0.014	0.029	0.032	n.s.	n.s.	–	–

n.s. – not studies;
*Journal of law 2019 item. 1311;
**Journal of law 2006 no. 136. item.964;
†Values of indicators should be based on the permissible load of these pollutants for individual treatment plants.

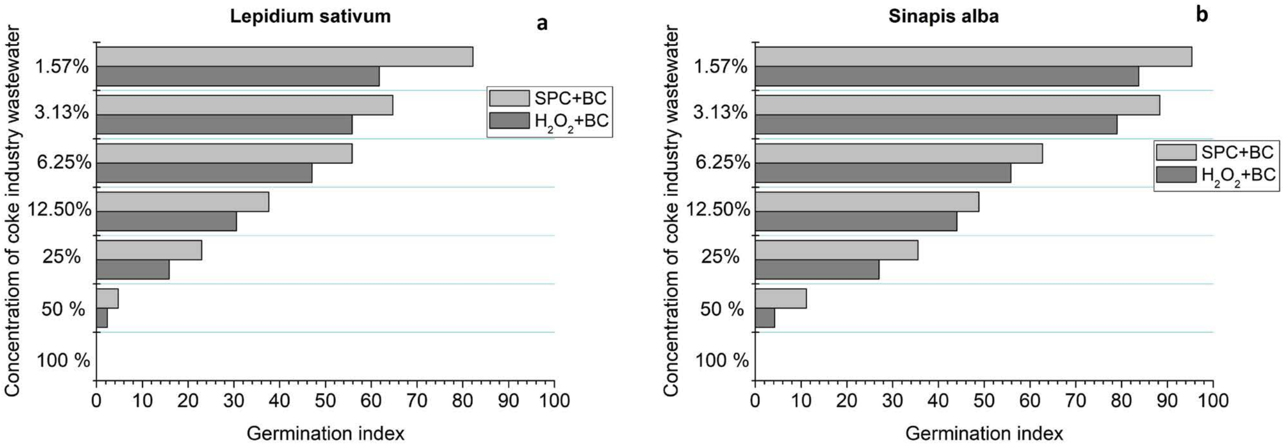

Fig. 7. Germination index size (GI) depending on wastewater dilution for *Lepidium sativum* (a) and *Sinapis alba* (b).

12.50% and 6.25% respectively. It was observed that in the case of the SPC + BC system, the roots of *Lepidium sativum* and *Sinapis alba* were on average 10% and 12% longer compared to the H_2O_2 + BC system. The discussed changes are presented in Table 3.

Higher GI of both tested plants, indicating lower wastewater toxicity, was noted for the SPC + BC system. Higher germination indexes were found for *Sinapis alba* and its highest value of 95.3 was recorded for the SPC + BC variant (concentration of coke industry wastewater – 1.57%). It was found that the index germination plant increased with increasing dilution of treated wastewater (Fig. 7).

The effect of wastewater on seed germination and plant growth has been the subject of research of numerous researchers [7,56,57]. The authors indicated that despite the fact that a reduction of TOC and COD of about 90% was noted in the treated coke wastewater, it still contains substances toxic. It was observed that with increasing concentration wastewater, germination inhibition also increases. And so, for a concentration of 60% germination inhibition ranged from 70%–80% and 30% of the concentration of treated wastewater from 70% to 80%. The inhibition increase for raw wastewater was 89% [57].

4. Conclusion

The results obtained in the study led to the following conclusions:

- during the Fenton process as variant I (H_2O_2) at all tested doses of reagents, the removal efficiency COD and TOC was 10% and 9% higher, respectively, compared to variant II;
- 2.5:1 turned out to be the best dose of reagents for both variants. COD values of wastewater treated in the Fenton process using H_2O_2 and SPC were the lowest and amounted to 1,450 and 1,890 mg L^{-1}, respectively;
- during coke industry wastewater treatment in modified Fenton (variant II) at the dose of reagents 2.5:1, the BOD index increased the highest from 105 mg L^{-1} (raw wastewater) to 235 mg L^{-1};

Table 3
Analysis of the phytotoxicity test for treated wastewater from coke industry wastewater

Concentration of coke industry wastewater	H_2O_2 + BC (H_2O_2/Fe^{2+} 2.5:1, BC – 4 g L^{-1})				SPC + BC (H_2O_2/Fe^{2+} 2.5:1, BC – 4 g L^{-1})			
	Lepidium sativum		*Sinapis alba*		*Lepidium sativum*		*Sinapis alba*	
	Average amount of seeds germinated	Average length of the root	Average amount of seeds germinated	Average length of the root	Average amount of seeds germinated	Average length of the root	Average amount of seeds germinated	Average length of the root
100%	0	0	0	0	0	0	0	0
50%	2	0.4	3	0.6	2	0.8	4	1.2
25%	6	0.9	9	1.3	6	1.3	9	1.7
12.50%	8	1.3	10	1.9	8	1.6	10	2.1
6.25%	10	1.6	10	2.4	10	1.9	10	2.7
3.13%	10	1.9	10	3.4	10	2.2	10	3.8
1.57%	10	2.1	10	3.6	10	2.8	10	4.1

- the best effects of wastewater post-treatment for both variants were noted for biochar dose at the level of 4 g L^{-1}. After 24 h of contact with biochar, the COD value from 1,890 mg L^{-1} (variant II) decreased to 1,228 mg L^{-1}. For variant II from level 1,430 mg L^{-1} it decreased to 1,029 mg L^{-1};
- it was observed that in the SPC + BC system the roots of *Lepidium sativum* and *Sinapis alba* were on average 10% and 12% longer compared to the H_2O_2 + BC system;
- higher GI of both tested plants, indicating lower wastewater toxicity, was recorded for the SPC + BC system.

Acknowledgment

The scientific research was funded by the statute subvention of Czestochowa University of Technology, Faculty of Infrastructure and Environment (BSPB–400–301/19).

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