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Advantages of continuous Fenton reaction over the traditional batch process in wastewater treatment in a single and two-step mode

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ABSTRACT

The article presents results of laboratory studies on the oxidation processes, by using Fenton's reagent for treatment of colourful and odour-emitting industrial wastewater characterized by high COD_{Cr} – 66 g O_2/L and TOC – 18 g/L values and pH below 1. Analyses were conducted for a continuous and cyclic process, divided into single- and two-step modes. Tests were performed for different initial mass ratios between COD_{Cr}:H_2O_2:Fe(II). It was found that the highest reduction of COD_{Cr} and TOC parameters, corresponding with a mass reduction efficiency equal to 75% and 65%, respectively, occurs for the two steps continuous Fenton process, at a mass ratio of COD_{Cr}:H_2O_2:Fe(II) equal to 1.0:2.5:1.25. The advantage of conducting the process in a continuous (flow) mode over a cyclic (batch) has been demonstrated and proven mostly by the stabilization of temperature and pH value of the reaction mixture, foaming limitation and decrease of the reaction time. It was also found that during a two-step continuous process COD_{Cr} removal efficiency increased even by 40% compared with the single-step process using the same amount of the reagents. Moreover, generation of solid wastes was reduced at 18.8% and other advantages such as increase of arsenic removal were also obtained in a two-step continuous Fenton reaction.

Keywords: Fenton reaction; Continuous mode; Wastewater treatment; Advanced oxidation processes; Process optimization

1. Introduction

One of the most important problems of modern environmental engineering is a constantly increasing amount of organic pollutants in industrial wastewater. It is mostly because of their toxicity, heterogeneous composition, resistance to the biodegradation process and last but not least, the ineffectiveness of the traditional treatment methods. That is why there is an urgent need to develop a new and more effective degradation and utilization methods for the mentioned organic pollutants or to modify the existing ones to improve their efficiency and effectiveness. In the case of wastewater containing a high level of hardly decomposable organic pollutants, one of the most common and effective methods of their degradation are the advanced oxidation processes (AOPs). By using AOPs, it is possible to oxidize many organic compounds directly to water and carbon dioxide or at least to transform them into simpler forms that can be removed by other common methods of wastewater treatment [1–3].

There are many different types of oxidizing agents that can be used in the wastewater treatment processes, such as chlorine, chlorine dioxide, oxygen, ozone, potassium permanganate and hydrogen peroxide. Moreover, it is also possible to increase the efficiency of the oxidation process by using a combination of the mentioned oxidizing agents and different process modification such as UV radiation or ultrasound to facilitate dispersion and increase

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the overall effectiveness of the processes [4]. Mentioned oxidation methods are a common choice, especially in the removal of the persistent organic pollutants, difficult to decompose or even completely resistant for biochemical decomposition processes. The efficiency of oxidation of inorganic pollutants is higher than that for the organic substances, which is related to the relatively high chemical stability of many compounds in this group. That is also one of the reasons why it is hard to make any theoretical estimation and predictions about the oxidation kinetics, for the mentioned organic substances, so it is done mostly based on the appropriate experimental analyses. The kinetics and efficiency of the oxidation process depend on the type, structure and concentration of the oxidizing agent, the dose of the oxidant, contact time, the presence of catalysts, temperature, and pH [5–10].

That is the reason of unflagging popularity of AOPs, which are methods of organic pollutants removal from water based on using highly reactive hydroxyl free radicals that are extremely effective oxidizing agents. Important features of hydroxyl radicals, besides the fact that they have the highest known oxidation potential, are their lack of selectivity and high reactivity towards many different organic compounds, especially in an acidic environment. There are many different methods of free radicals generation, such as chemical reactions (usually in systems: H_2O_2/O_3, O_3/OH^-, H_2O_2/Fe^{2+} or Fe^{3+}), photochemical reactions (by using H_2O_2/UV, O_3/UV), photocatalytic reactions (mostly based on TiO_2/UV systems), sonochemical and electrochemical reactions [3,5,11–13]. However, one of the most important and commonly studied methods of advanced oxidation is the Fenton reaction. It is a method widely used for oxidation of persistent and hardly biodegradable organic compounds, conducted in the acidic environment (in pH range 3–5) and leading to the generation of free radicals according to Eq. (1) [14]:

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

Despite the fact that the rate of the hydroxyl radical reactions with organic compounds can range from 10^7 to 10^{10} M^{-1} s^{-1}, the rate constant of the Fenton reaction is equal only 63 M^{-1} s^{-1} [2,14]. Thus, this is a limiting step of the whole wastewater treatment process and acceleration of that stage can significantly reduce the time needed for wastewater treatment. The oxidizing potential of the hydroxyl radicals generated in the reaction mentioned above in an acid environment is 2.8 V, which is the highest oxidizing potential among all of the known oxidants [15,16]. There are plenty of publications in the scientific literature, that describe the Fenton process as one of the most effective methods for the treatment of wastewaters generated during different technological processes, such as the production of chemicals, insecticides, dyes, explosives, refining waste and fuel stations, as well as the other industrial wastewaters generated in the coke industry, or during the production of plastics, adhesives and wood impregnates [11,17–20]. The entire course of the oxidation process can be controlled by changing one of the key factors of the reaction, such as pH, temperature or doses of the reagents. Among the mentioned factors one of the most important is a pH value of the reaction mixture, which determines the form of the oxidant and oxidized compounds, as well as the whole reaction mechanism. Another important aspect of the process is its temperature, which significantly affects the rate of the reaction – the rate constant increases with temperature according to the logarithmic function. Last but not least factor is a dose of the oxidizing agent and its contact time with the oxidized substances, most often increase of those two factors that lead to the increase of the overall efficiency of the oxidation processes [3].

Thanks to its effectiveness and popularity there is a constantly growing interest in developing new methods of the classic Fenton reaction modifications [21–25]. Mentioned modifications to the Fenton process includes many different changes that can lead to the acceleration of free radicals formation, such as using the visible and ultraviolet radiation (photo Fenton reaction) or conducting the process with simultaneous ozonation of the environment [26]. Another important modification techniques that are worth to mention are innovative methods using a Solar Photo Fenton reactions [27–31] and electro-Fenton processes [32–35]. Effectiveness of wastewater treatment using the Fenton reaction depends on several process parameters, such as the mentioned specific ratio of $COD/Fe^{2+}/H_2O_2$, appropriate pH value of the reaction mixture (in the range 3–5), sufficient reaction time and a suitable temperature. Another important aspect is to ensure appropriate mixing conditions of the whole reaction mixture, which is especially important in the case of the reactions conducted in two-phase systems. However, maintaining the appropriate temperature and pH values is often considered as one of the hardest and crucial factors, hindering the effective oxidation of hardly biodegradable pollutants by the Fenton reaction. Ensuring an appropriate pH value of the reaction environment, within the mentioned range, that allows for the effective decomposition of hydrogen peroxide to $OH^{\bullet}$ radicals, is an easy task only at the very beginning of the Fenton process. It is because, during the oxidation reaction, more and more intermediate products are formed, mostly in the form of organic acids, which caused a significant decrease of pH value, often much lower than 3, which in turn, can reduce the effectiveness of oxidation of pollutants. A similar problem can occur in the situation of sudden temperature increase, which can be caused by a faster decomposition of substrates in the strongly acidic environment [22]. For the wastewater treatment processes conducted by Fenton reaction in the systems with a pH value below 1, a one-time pH correction is often insufficient, which leads to serious problems with maintaining a constant and optimal pH value during the whole reaction cycle. It is because, after adjusting the reaction mixture pH to a value between 3 and 5, another addition of the Fenton's reagents, which are Fe^{2+} and H_2O_2, leads to further decrease of the pH values and once again can cause a decrease of the process efficiency. That is why, one of the main tasks of the presented study was to carry out a more stable Fenton reaction in a continuous, flow system, with constant dosing of all necessary reagents to maintain an optimal pH value (i.e., pH: 3.5–4.5) and temperature within the whole reaction time.

2. Materials and methods

The analysis of the organic pollutants removal effectiveness was conducted for technological wastewater from non-ferrous metallurgy processes. Mentioned wastewaters were generated in the processes of wet dust removal from blast furnace gas in one of the Polish industrial smelter. Those solutions were characterized by strongly acidic pH, high COD_{Cr} and TOC values, tawny brown colour, very specific irritating odour and also a high concentration of metals, especially arsenic. The initial solution used during the study was an acidic (pH = 0.4), technological wastewaters (TW) with COD_{Cr} and TOC values 66 g O_2/L and 18 g/L respectively. Moreover, a concentration of three different metals was also analysed during the study, the initial concentration was 5.17, 3.47 and 1.67 g/L, respectively, for arsenic, zinc and lead.

Currently, due to the lack of an efficient treatment technique, the stream of the mentioned wastewater is combined with the other wastewater effluents generated during the other processes and then directed to the collective industrial wastewater treatment plant. However, due to the very high COD_{Cr} and TOC concentration, it strongly increased the final concentration of organic matter in the combined wastewater stream, which in turn increases the overall cost of treatment. That is why the company is trying to find a way of efficient pre-treatment of that specific wastewater stream. In the scientific literature, there are some reports about possible processes and methods that could be used for that purposes such as flocculation, adsorption or coagulation and electrocoagulation processes [36–38]. However, the operating costs of that processes are usually too high, comparing with the obtained results, especially in the case of wastewater with very high COD_{Cr} and TOC concentrations. That is why, a main task during the presented studies was to conduct a Fenton reaction in a way that will allow for the significant reduction of total organic carbon (TOC) and chemical oxygen demand (COD_{Cr}) in the analysed wastewaters, which are a measure of the content of organic compounds and suspensions in water and sewage. Another equally important aspect was to minimize the content of mineral suspensions and inorganic compounds in the final solutions. After the oxidation process, those parameters were established as a basis for the evaluation of conducted oxidation process efficiency. Chemical analyses were performed in accordance with the appropriate standards and good laboratory practice, by using an atomic emission spectroscopy methods for metal concentration analyses in liquid samples. On the other hand, metal analyses in the sludges generated within the Fenton processes were conducted by using a X-ray fluorescence spectrophotometer.

The oxidation process was carried out by using Fenton's reagent (H_2O_2/Fe^{2+}), where hydrogen peroxide was added as a perhydrol directly without any dilution (an estimation equal 1 mL = 370 mg of pure H_2O_2 was assumed). Meantime, iron (Fe^{2+}) was added to the reaction system in the form of solid iron(II) sulphate heptahydrate powder or solutions prepared based on it. A suspension of $Ca(OH)_2$ was used to correct the pH value of the reaction mixture during the process. An appropriate range of the reagent ratios and doses was established during the preliminary studies, and it was related to specific parameters of the treated technological wastewaters and literature studies in that subject. That ratio can be related with a specific nature of the reacting mixture, because depending on the initial COD_{Cr} value, pH of the solution and other aspects, Fenton reaction may need a higher concentration of Fe^{2+} to ensure optimal reaction conditions. The efficiency of the analysed oxidation process was concerned as a reduction of COD_{Cr} or TOC mass (Ef_Q) and concentration (Ef_C), and defined in the following formula, proposed by the authors:

$$\mathrm{Ef}_Q = \frac{V_p C_p - V_k C_k}{V_p C_p} \times 100\% \tag{2}$$

where Ef_Q – mass efficiency of the process [%]; V_p – volume of initial solution [L]; V_k – volume of final solution [L]; C_p – initial concentration of analysed compound [g/L]; C_k – final concentration of analysed compound [g/L].

As it was mentioned, the experiment was conducted in three different ways, first one was a classic cyclic Fenton reaction conducted in batch reactors, the second was a continuous Fenton reaction that was performed in a simple single-step flow reactor. The last one was a two-step continuous Fenton reaction with two separate rectors and a continuous flow throughout the whole system. In that case, analyses were conducted in two different volume reactors with agitators and reagent tanks with necessary pumping systems. Reactors were connected by hoses, so at the end of the oxidation process effluent from the first reactor, was transferred as an influent to the second reactor, where additional portions of reagents were added to the reaction mixture. To better illustrate a system used in this part of the study, a scheme of that installation was presented at the figure below (Fig. 1).

During the whole treatment process reaction time and the pH value in both reactors were kept at a constant level, respectively: 3–4 h and pH: 3.5–4.0. All reagents in both reactors were dosed directly under the agitator, and the stream of technological wastewater was introduced to first reactor with a constant flow rate, equal 0.3 L/h. The continuity of the two-step process of technological wastewater treatment, with a constant reaction time of approximately 3–4 h (in each of the reactors), was obtained by appropriate choice of flow rates for all streams of reagents and a constant collection of the oxidized and purified reaction mixture calculated as:

$$\vec{V}_{\mathrm{eff}} = \vec{V}\left(\mathrm{TW+Fe^{2+}}\right) + \vec{V}\left(\mathrm{H_2O_2}\right) + \vec{V}\left(\mathrm{Ca(OH)_2}\right) \tag{3}$$

where $\vec{V}_{\mathrm{eff}}$ – volume flow at the outlet of the reactor [L/h]; $\vec{V}\left(\mathrm{TW+Fe^{2+}}\right)$ – volume flow of TW including Fe^{2+} doses, entering the reactor [L/h]; $\vec{V}\left(\mathrm{H_2O_2}\right)$ – volume flow of perhydrol, entering the reactor [L/h]; $\vec{V}\left(\mathrm{Ca(OH)_2}\right)$ – volume flow of $Ca(OH)_2$ suspension, entering the reactor [L/h].

Thanks to that it was possible to easily adjust the flow rate at the pump collecting treated wastewaters from the reactors, so that the sums of the volumetric flow rates at the inlet and outlet of the systems were the same. Moreover, an

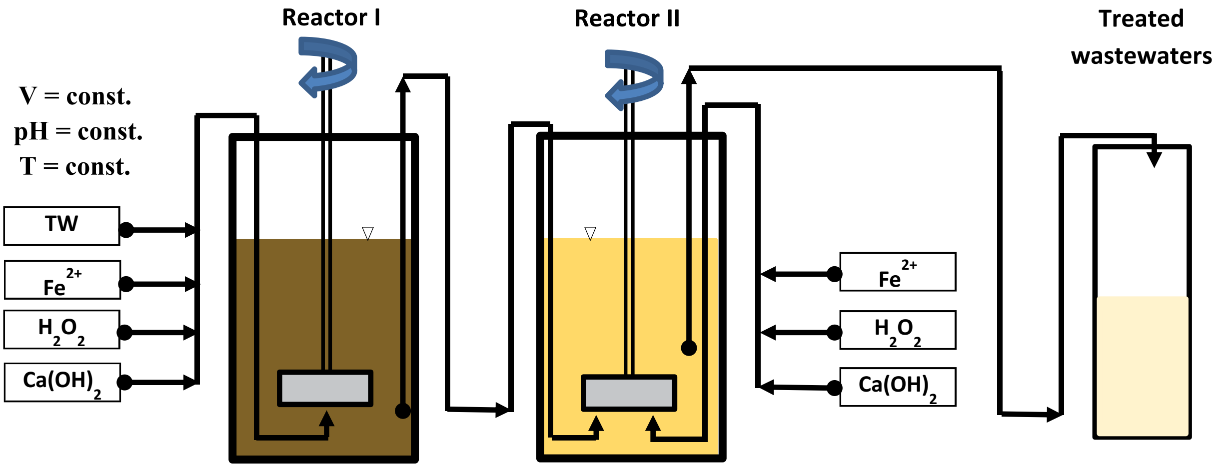

Fig. 1. Schematic illustration of the experimental system used for a two-step continuous Fenton process.

appropriate mixing of the reaction mixture led to avoiding the precipitates accumulation in the reaction system, and the sludge formed during the Fenton process was filtered from the treated wastewaters after leaving the analysed reaction system. Thus, the designed reaction system, after a sufficiently long time of operation, can be considered as a typical example of a system operating in a continuous mode. Another important parameter reported for the final two-step Fenton processes is the average oxidation state (AOS) known also as the mean oxidation number of carbon (MOC). This parameter can be calculated by using a common formula [39,40]:

$$\mathrm{AOS} = 4 - 1.5\frac{\mathrm{COD_{Cr}}}{\mathrm{TOC}} \tag{4}$$

AOS – average oxidation state; $\mathrm{COD_{Cr}}$ – chemical oxygen demand [mg/L]; TOC – total organic carbon [mg/L].

Based on the calculated AOS value, it is possible to estimate the oxidation number for the carbons atoms present in the organic matter characterized by the TOC parameter. According to the literature, the lowest possible value of the AOS parameter can be –4, and it is for the compounds with the lowest possible oxidation number of its carbon atoms, with occurs only for the methane (CH_4) particles. On the other hand, the maximum oxidation number of the carbon atoms can be 4 and it occurs only in two compounds which are CO_2 and urea [41]. So, every other organic compound has to have an AOS value between –4 and 4, and the highest that value is, the more oxidized are the carbon compounds in the solution. Thus, in general, during the oxidation processes, the value of AOS parameters should increase with the duration of the process [39].

2.1. Analytical methods and apparatus used during the experiment

- The $\mathrm{COD_{Cr}}$ analysis was performed based on the ISO norm: ISO 6060:1989 Water quality – Determination of the chemical oxygen demand. Due to the possible interference of chlorides, present in the analyzed samples, appropriate amounts of mercury(II) sulfate were calculated, as it is recommended in the mentioned ISO norm [42]. To ensure an appropriate concentration of mercury sulphates in the analysed solution and decrease the necessary amount of the reagent, it was added to the sample after a previous dilution. Moreover, residual H_2O_2 can also influence the results of $\mathrm{COD_{Cr}}$, but according to the literature, most of the studies in this field was performed for solutions with a $\mathrm{COD_{Cr}}$ value below 1 g/L [43]. Wastewaters analyzed within the presented experiments has a $\mathrm{COD_{Cr}}$ value around 65 g/L, so, it was assumed, that even if some of the H_2O_2 particles were still stable in the parameter of conducted Fenton process after so long time, its influence on the obtained $\mathrm{COD_{Cr}}$ results was negligible. However, to avoid possible interferences of residual H_2O_2 on the results of $\mathrm{COD_{Cr}}$ analysis, the sample solution was alkalized and left for at least 24 h. After that time it was analyzed using the previously described methods. According to the literature that procedure should allow to completely eliminate any possible influence of the H_2O_2 on the $\mathrm{COD_{Cr}}$ analysis of the samples [44,45].
- Analysis of TOC was performed in the external accredited laboratory by using an automated Total Organic Carbon Analyser by SHIMADZU (Kyoto, Japan).
- The concentration of metals in the analysed wastewater, both before and after the Fenton process, was determined by the ICP OES technique, using an Optima 5300 V Spectrometer by Perkin Elmer (Waltham, USA).
- pH analyses were made according to the Polish norm entitled "Testing of pH, acidity and alkalinity – Determination of the pH of water and wastewater with specific electrolytic conductivity of 10 microsiemens/cm and above, by the electrometric method".
- Other apparatus used during the experiment was as follow:
- Peristaltic pomp Masterflex L/S series by Cole-Parmer (Vernon Hills, USA).
- Different glass reactors with a volume of 2, 3 and 5 L, equipped with mechanical stirrers.
- Digital pH analyzers CP-401 by Elmetron (Zabrze, Poland).

- Mechanical stirrers RW 16 basic by IKA (Staufen, Germany).
- Other basic laboratory equipment like laboratory scales and balances, fume hoods, etc.

All of the reagent used during the study, such as iron(II) sulfate heptahydrate, calcium hydroxide, hydrogen peroxide (35%) were at least ACS pure and provided by VWR (Radnor, USA). The anti-foaming agent used as an addition to the reaction mixture was bought from the Nalco Water (Naperville, USA) company and was labelled as the anti-foaming agent number 71135.

3. Results

3.1. Cyclical system (batch reactors) – determination of a proper ratio of COD_{Cr}:H_2O_2:Fe^{2+}

First tests were conducted in a 5-L glass reactor equipped with a paddle agitator with a stator. To that reactor, a 1,000 mL of the analysed solution was introduced to perform an oxidation process. by the following addition of the necessary reagents, which were a solid $FeSO_4·7H_2O$ and 30% hydrogen peroxide added to the solution in portions. The portioning of the peroxide doses was imposed by the rapid increase of the reaction mixture temperature ($60 < T \leq 90$) and equally instant foaming of the reaction solution. Stabilization of the reaction solution at the temperature level around 60°C was achieved by extending the dosage of hydrogen peroxide in time however, the addition of the entire H_2O_2 dose did not exceed 120 min. Initial tests were performed for a different COD_{Cr} (g O_2):H_2O_2 (g):Fe^{2+} (g) ratios, which were related to the COD_{Cr} value in the initial solution, including the ratios1.0:(0.1–2.5):(0.1–1.25). Oxidation processes were analysed in 7 h cycles and a COD_{Cr} value of the samples were analysed after 1, 2, 4 and 7 h of the oxidation process, with continuous mixing of the sample. The acidic character of the oxidized solutions was hindering a stabilization of the process in the optimal pH range, which led to a decrease in the overall process efficiency. Hence, one of the tests was conducted with a simultaneous stabilization of the pH value of the reaction mixture, by dosing of a suspension of $Ca(OH)_2$, with each portion of the reagents introduced to the reactor. Changes in the COD_{Cr} value in the analysed systems presented as a function of the oxidation process time were shown in Fig. 2.

Based on the data presented in the figure a clear influence of the reagent dose on the overall efficiency of the process can be found. That is why in the further study two best reagent ratio between COD_{Cr}:H_2O_2:Fe^{2+} equal 1:2:1 and 1:2.5:1.25 were a starting point for the next experiments. However, the most significant increase in the COD_{Cr} removal was obtained when the process was conducted in the pH value between 3.3–4.4, which confirms a clear influence of pH value on the process efficiency. That is why in all of the further tests an appropriate alkalization of the reaction mixture was performed to achieve optimal conditions for a Fenton reaction. Moreover, analysis of the data in Fig. 2 proves that in the case of non-alkalized reaction systems, the vast majority of the Fenton reaction occurs

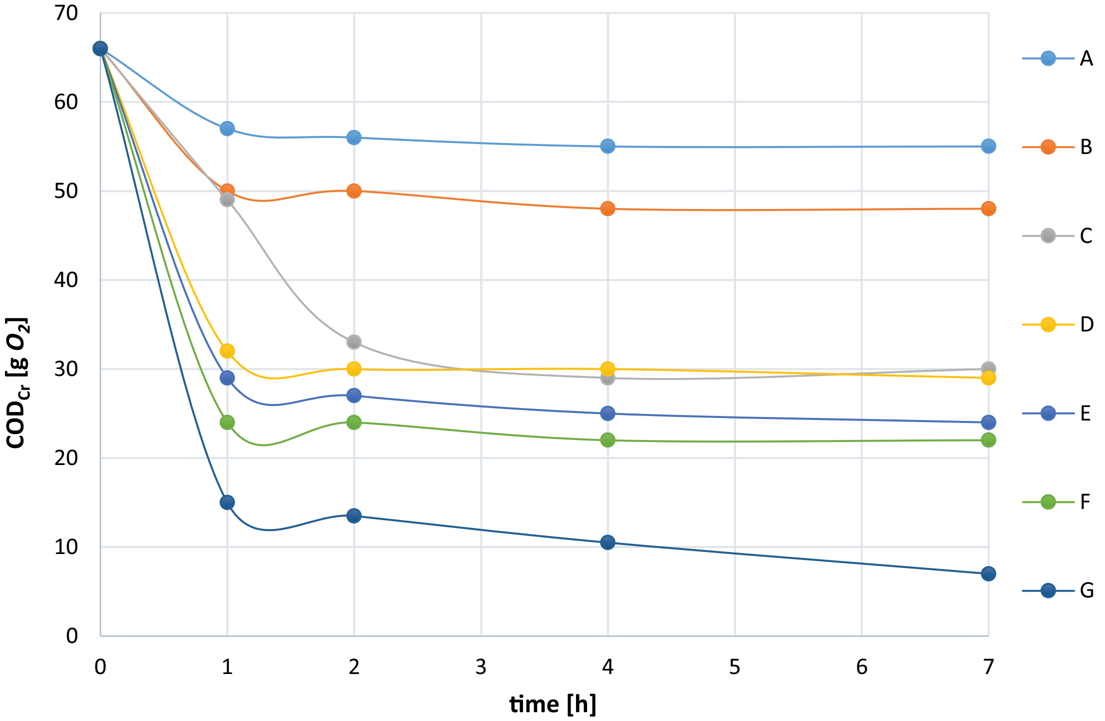

Fig. 2. COD_{Cr} changes vs. process oxidation H_2O_2/Fe^{2+} in time. A – COD_{Cr} (g O_2):H_2O_2 (g):Fe^{2+} (g) = 1.0:0.1:0.1; B – COD_{Cr} (g O_2):H_2O_2 (g):Fe^{2+} (g) = 1.0:0.5:0.5; C – COD_{Cr} (g O_2):H_2O_2 (g):Fe^{2+} (g) = 1.0:1.0:1.0; D – COD_{Cr} (g O_2):H_2O_2 (g):Fe^{2+} (g) = 1.0:1.5:1.0; E – COD_{Cr} (gO_2):H_2O_2 (g): Fe^{2+} (g) = 1.0:2.0:1.0; F – COD_{Cr} (g O_2): H_2O_2 (g): Fe^{2+} (g) = 1.0:2.5:1.25; G – COD_{Cr} (g O_2):H_2O_2 (g):Fe^{2+} (g) = 1.0:2.5:1.25 (with pH correction).

in the first one or two hours of the process. But for the system with the alkalized reaction mixture, a clear reduction of COD_{Cr} value took place even after mentioned two hours. It can be easily explained by the fact, that at a pH below 2, cations of $[H_3O_2]^+$ are formed which slow down the process of hydroxyl radicals generation and after the mentioned time, the amount of the free radicals in solution is too low to effectively oxidize rest of the organic compounds [46]. So, for alkalized systems, it was decided to conduct a Fenton reaction for at least four hours but for the better result, a six-hour system was also analysed. Besides the discussed reduction of the COD_{Cr} value during the purification of technological wastewater, continuous Fenton reaction allows also for significant removal of lead, arsenic and zinc. In the presented study 90% of lead, 76% of arsenic and 16% of zinc were removed. Mentioned decrease in the metal concentration in a final solution, to the following values: Pb – 0.18 g/L As – 1.2 g/L Zn – 2.9 g/L, was a consequence of the solid phase precipitation, with a predominant share of iron (49%) and arsenic (4.0%). Moreover, a decrease in the concentration of the mentioned impurities in the reaction mixture was associated with a colour change from tawny brown to the orange-yellow and a slight reduction in odour nuisance was also observed. Although in general, it is much easier to control all of the operational conditions in batch reactors, for the analysed TW sustenance of the optimal conditions was extremely difficult. It was mainly because of the very violent foaming of the solution after the addition of even very small doses of the reagents. Moreover, even the addition of a larger amount of the anti-foaming agents to the reaction mixture did not help to avoid the mentioned problem. That, combined with a large increase of the mixture temperature, led to the overheating of the reaction and enforced to take frequent breaks in dosing even at the very slow speed of the pumps. That is why, it was decided, that instead of often waiting for a descend of the foam it can be better to conduct the whole process in a continuous system, where the influent stream will be kept at a very low level, but no more breaks in the process will be needed after the stabilization of the whole process. Thank to that it was possible to find optimal flow rates of the TW influent and reacting agents solutions allowing to maintain a stable temperature and relatively small amount of the generated foam.

3.2. Single-step continuous system

During the studies on a single-step continuous Fenton reaction system, two variables were considered as crucial for the analysed process: reaction time and a ratio of $COD_{Cr}:H_2O_2:Fe^{2+}$ [g]. Changes of those two parameters were made by the modification and a proper adjustment of the speed and thus the efficiency of dosing pumps. The doses of the reagents were calculated based on the COD_{Cr} value in the initial solution of process wastewater introduced into the reactor per time unit. The Fenton oxidation process was conducted for the following ratios of the reagents: $COD_{Cr}:H_2O_2:Fe^{2+}$ equal 1.0:2.5:1.25 and 1.0:2.0:1.0, for 3 and 6 h. During the whole process, stirrers in the reactor and reagent mixing tanks were kept at a constant speed, and the iron sulphate was dissolved directly in the technological wastewater (TW) in the appropriate quantity that allowed to maintain a constant $COD_{Cr}:Fe^{2+}$ ratio in the solution. All of the solutions used during the experiment, such as technological wastewater (TW) with the addition of Fe^{2+} ions, hydrogen peroxide and $Ca(OH)_2$ suspension were introduced to the reactor, directly under the paddle stirrer equipped with a stator. A stream of oxidized and purified final solution was withdrawn from the higher part of the reactor by a peristaltic pump so the volume of the reaction mixture in the reactor was set at a constant level equal to 2,000 mL. Control of the reaction time was possible by regulating a stream of the initial solution, (TW containing Fe^{2+}) introduced to the reactor, to which the size of the remaining reagent streams (H_2O_2 and $Ca(OH)_2$) was related. Stream of the $Ca(OH)_2$ suspension with a concentration of 200 g/L was calculated to ensure an optimal pH value of the reaction mixture at the level $3.5 \leq pH \leq 4.5$. During the whole time of the process, the following parameters were monitored constantly: volume of the influent and effluent streams, temperature and pH value of the reaction mixture. Each of the experimental cycle (for different reagent ratios) included approximately 30 h of continuous operation of the system, conducted in three 10-h working periods. The streams obtained after the process were transferred to vacuum filtration, and the resulting sediments were dried to constant weight in the oven at about 100°C. In each experimental cycle, first 20 h of the system's operation were treated as achieving the steady state of the system. So, only combined filtrates and sediments from the last 10-h period were analysed and considered as reliable experimental results and reported in the table below (Table 1).

Comparing obtained mass efficiency of the continuous Fenton process with that in a batch mode, an important decrease can be observed. On the other hand, changes between the mentioned efficiency in systems with the same initial reagent ratios after 4 and 6.5 h are much lower than it was in the case of cyclic processes. Despite the lower efficiency of the process conducted in continuous flow systems, the advantages of such solution, compared with the cyclic one, are as follows:

- Reduction (even complete elimination) of foaming problems of the reaction mixture
- Reduction of the optimal reaction time from 7 to 4 h
- Stabilization of the pH of the reaction mixture at the desired (optimal) level
- Stabilization of the temperature of the reaction mixture at the level of 50°C–60°C

To better analyse and evaluate different aspects of using flow reactors for the Fenton process, additional qualitative and quantitative analyses of sludges generated in the process was also made, and the results of those analyses were summarized in Table 2.

An interesting observation was made at the overall amount of solid wastes generated in the process, because for both initial reagents ratios, final concentration of sludge in the reaction mixture was decreasing with a time of the reaction. It is a reason why, the reaction time should be longer, cause generation of solid waste is one of the most important disadvantages of the whole Fenton process.

Last but not least aspect analysed on this stage of the study was decolourization of the wastewaters after the continuous Fenton process. Results of that colour removal in systems with a different initial ratios of the reagents after 6 h of the process are presented in Fig. 3.

Comparison of the colour changes shows that initial reagent ratio equal to 1:2.5:1.25 leads to a better decolourization of the analysed solution. Similar observation was also made in case of odour reduction between the treated and untreated samples of wastewaters, however, only partial reduction of odour nuisance was observed.

3.3. Two-step continuous system

For two-step systems, eight different cycle modes were conducted, and each of them covered five working days. However, for each cycle, first 20 h of the process was treated as stabilization of the system conditions and parameters. That stabilization stage after every change in the reagent ratios was crucial for obtaining a steady state of the system, which in turn, was necessary for appropriate analysis of the reaction parameters and its efficiency. Stabilization of the systems was carried out following the principles of continuous operation, leaving in each of the reactors 1 L of reaction mixtures from the previous research cycle. Effluents were collected from the reactors only after reaching the appropriate level for each of them, that is, 2.0 L for the first reactor and 2.6 L for the second reactor.

Although an optimal reagent ratio was established before at the following values (COD_{Cr}:H_2O_2:Fe^{2+}) 1:2:1 and 1:2.5:1.25, in the two-step Fenton process, reagents could be added to the reactors at the 1st and 2nd step of the oxidation process with different ways. That is why the two-step Fenton process was analysed in eight modes with different initial reagent doses, and different ways of adding the

Table 2
Chemical composition of sludge from the technological wastewater oxidation process (TW) in a continuous single-step system

Parameter	Reagents ratio COD_{Cr}:H_2O_2:Fe^{2+} [g]			
	1.0:2.5:1.25	1.0:2.5:1.25	1.0:2.0:1.0	1.0:2.0:1.0
Reaction time, h	3.9	6.2	3.8	6.5
Quantity, $g_{d.m.}$/L	411	351	347	319
Humidity, %	31	32	32	31
As, %	1.0	0.88	0.76	0.79

Table 1
The quality of filtrates from the wastewater oxidation process (TW) in a continuous single-step system

Parameter	Technological wastewater	Reagents ratio COD_{Cr}:H_2O_2:Fe^{2+} [g]			
		1.0:2.5:1.25	1.0:2.5:1.25	1.0:2.0:1.0	1.0:2.0:1.0
Reaction time, h	–	3.9	6.2	3.8	6.5
pH value	0.4	3.7	3.7	3.7	3.7
Colour	Tawny brown	Yellow	Yellow	Yellow	Yellow
Odour	Intensive characteristic	Slightly characteristic	Slightly characteristic	Slightly characteristic	Slightly characteristic
COD_{Cr}, g O_2/L	66.0	13.6	14.6	15.4	13.4
Ef_Q, %	–	56	58	51	55
Arsenic, g/L	3.47	1.5	1.59	1.58	1.61
Zinc, g/L	0.08	0.037	0.038	0.039	0.039
Lead, g/L	1.67	0.061	0.124	0.028	0.114

Fig. 3. Difference in colour removal for single-step continuous process (for the ratio 1:2:1 – A and for ratio 1:2.5:1.25 – B).

reagent to the system. In "mode I" Fe^{2+} was added fully in the first step of the process, with half of the H_2O_2 dose, and rest of the calculated H_2O_2 were added at the beginning of the second step of the reaction. For "mode II" and "mode III" substrates were added in the assumed ratio at the first step of the process, then at the beginning of the second step, COD_{Cr} analysis was conducted again and an additional amount of the reagent with the same ratios was added. That is why in those modes overall doses of the reagent spent on both steps of the process were the highest. In "mode IV" and "mode V" half doses of Fe^{2+} and H_2O_2 were added at the beginning of each step, assuming the reagent ratio analogical to that from "mode II" and "mode III". "Mode VI" assumed addition of the whole Fe^{2+} in the first step and precisely half of the previously calculated H_2O_2 analogously to the "mode I" but with a different doses of reagents. The last two modes were conducted similarly as a mode IV and V, but with different final regent ratios. Final reagent ratios reported in Table 3 were calculated based on the overall doses of reagents introduced to the system in both first and second step of the process, thus because of the different flow rates they could differ from the initially assumed values. Moreover, presented results show clearly, that the best COD_{Cr} decrease was obtained for the system working in IV and V mode, where the percentage mass efficiency of the Fenton reaction was almost 77% and 75%, respectively. Lower efficiency was obtained for the systems working in mode II and III where reagent dose was calculated at the beginning of each step, based on the COD_{Cr} concentration in the influent. Another very important aspect related to that fact is a relatively lower amount of the reagents necessary for the effective treatment of analysed wastewater. That difference was the clearest in the case of systems working in mode II and IV, where also a better COD_{Cr} removal efficiency was obtained despite the reduction of overall reagent dose by 40% for H_2O_2 and 33% for Fe^{2+}. For a better comparison of results obtained in different modes analyse during the study, an extended report was summarized in Table 3, including differences in the selected parameters after each oxidation step.

For a two-step, Fenton process despite the usual COD_{Cr} analysis, changes of additional parameters such as TOC and selected metals concentration were also analysed. Thanks to that it was possible to confirm a high performance of the studied systems in the removal of organic and inorganic pollutants from the treated wastewaters. According to the presented experimental results in a two-step continuous Fenton process of the analysed technological wastewater, in the best operation mode, it was possible to reduce the values of COD_{Cr} from 66 to approximately 7 g O_2/L and TOC from 18 to about 2.5 g/L, which gives a mass efficiency value EfQ of the process, respectively, 77% and almost 65%. Both COD_{Cr} and TOC removal were the best for the continuous Fenton reactions working in the modes II – V. That was probably a result of the appropriate reagent ratio allowing for effective generation of free radicals during the whole oxidation process. Moreover, analysis of the data presented in the table proves that the oxidation process was conducted correctly and the AOS parameter of the final solution was clearly higher compared with the crude TW. However, the increase in the AOS value was different in each of the analysed modes, which proves that combination and the order of reagent addition can have an important impact on the course of the oxidation reactions. To better evaluate the Fenton processes conducted in different modes, additional analyses

Table 3
Process effectiveness and parameters of filtrate quality after the two-step oxidation TW in a continuous system

Parameter	TW	Stage	Mode I	Mode II	Mode III	Mode IV	Mode V	Mode VI	Mode VII	Mode VIII
H_2O_2/COD_{Cr} ratio	–	Final	3.76	3.71	2.59	2.19	1.89	2.48	1.15	0.99
Fe/COD_{Cr} ratio	–	Final	1.25	1.82	1.34	1.22	0.96	1.25	0.61	0.58
pH	0.4	2nd	3.7	3.8	3.7	3.7	3.6	3.7	3.7	3.6
COD_{Cr}, g O_2/L	66.0	1st	13.3	16.2	14.6	13.7	17.6	15.2	19.7	24
		2nd	12	6.4	7.4	7.3	7.9	9.8	9.1	10.1
TOC, g/L	18.0	1st	4.11	4.95	5.11	3.87	5.36	4.64	6.22	7.08
		2nd	3.87	2.33	2.68	2.76	3.04	3.44	3.20	3.84
AOS	–1.50	1st	–0.85	–0.91	–0.28	–1.31	–0.93	–0.91	–0.75	–1.08
		2nd	–0.65	–0.12	–0.14	0.03	0.11	–0.27	–0.27	0.06
Arsenic, mg/L	5,170	1st	0.38	0.32	0.7	1.2	2.1	–	–	–
		2nd	0.28	0.21	0.3	0.2	3.4	0.5	0.7	1.4
Zinc, g/L	3.47	1st	1.28	1.15	1.4	1.8	1.9	–	–	–
		2nd	1.2	0.8	1.0	1.0	1.2	1.5	1.4	1.3
Lead, mg/L	1,670	1st	26.0	11.0	62.0	280	324	–	–	–
		2nd	19.0	4.3	9.0	21.0	106	56.0	97.0	160.0
Fe consumption, kg/L	n.a.	2nd	0.4	0.59	0.44	0.4	0.31	0.41	0.26	0.19
H_2O_2 consumption, kg/L	n.a.	2nd	0.62	0.61	0.43	0.36	0.31	0.41	0.25	0.17
COD_{Cr} removal effectiveness, %	n.a.	2nd	61.0	67.3	73.3	76.9	75.0	72.3	71.3	69.3

of the sludges was also made. In Table 4, a brief summary, of the most important parameters for the generated solid wastes, was presented.

Data presented in Table 4 are slightly different than it could be expected, based on the removal of the selected metals from TW during the oxidation process. It is mainly because except the overall metal removal from the oxidized solution an amount of generated sludge is also an important factor that can affect at final metals concentrations in the sludge dry mass. Thus, even though one of the best arsenic removal results was obtained for a mode II, due to the significantly larger amount of the generated sludge during the process, as concentration in the sludge, in this mode was the lowest from all of the analysed systems. That is why in order to reduce the amount of generated solid wastes during the process, it was concluded that the best operating modes for a two-step Fenton process were modes III – V, which assure a good treatment condition with a simultaneous low quantity of generated sludge. Last, important parameters analysed during the process was odour and colour reduction. In Table 3, a short information about observed changes was also reported, but to better illustrate TW colour changes at each step of the process, photo of the TW samples where set together at the figure below (Fig. 4).

Table 4
Quantities and quality of process sludge, after the second step oxidation TW in a continuous system for the chosen reaction types

Parameter	Mode I	Mode II	Mode III	Mode IV	Mode V
Quantity, $g_{d.m.}$/L of TW	244	327	286	285	281
Humidity, %	26.0	28.6	29.4	32.0	26.2
Arsenic, %	1.6	1.3	1.4	1.7	1.8
Zinc, %	0.2	0.2	0.2	0.1	0.2
Lead, %	0.4	0.3	0.4	0.4	0.4

As it was presented, colour removal in a two-step continuous Fenton reaction was much better compared with a single-step process. Also, for each of the conducted processes in a different mode, clear changes between each step

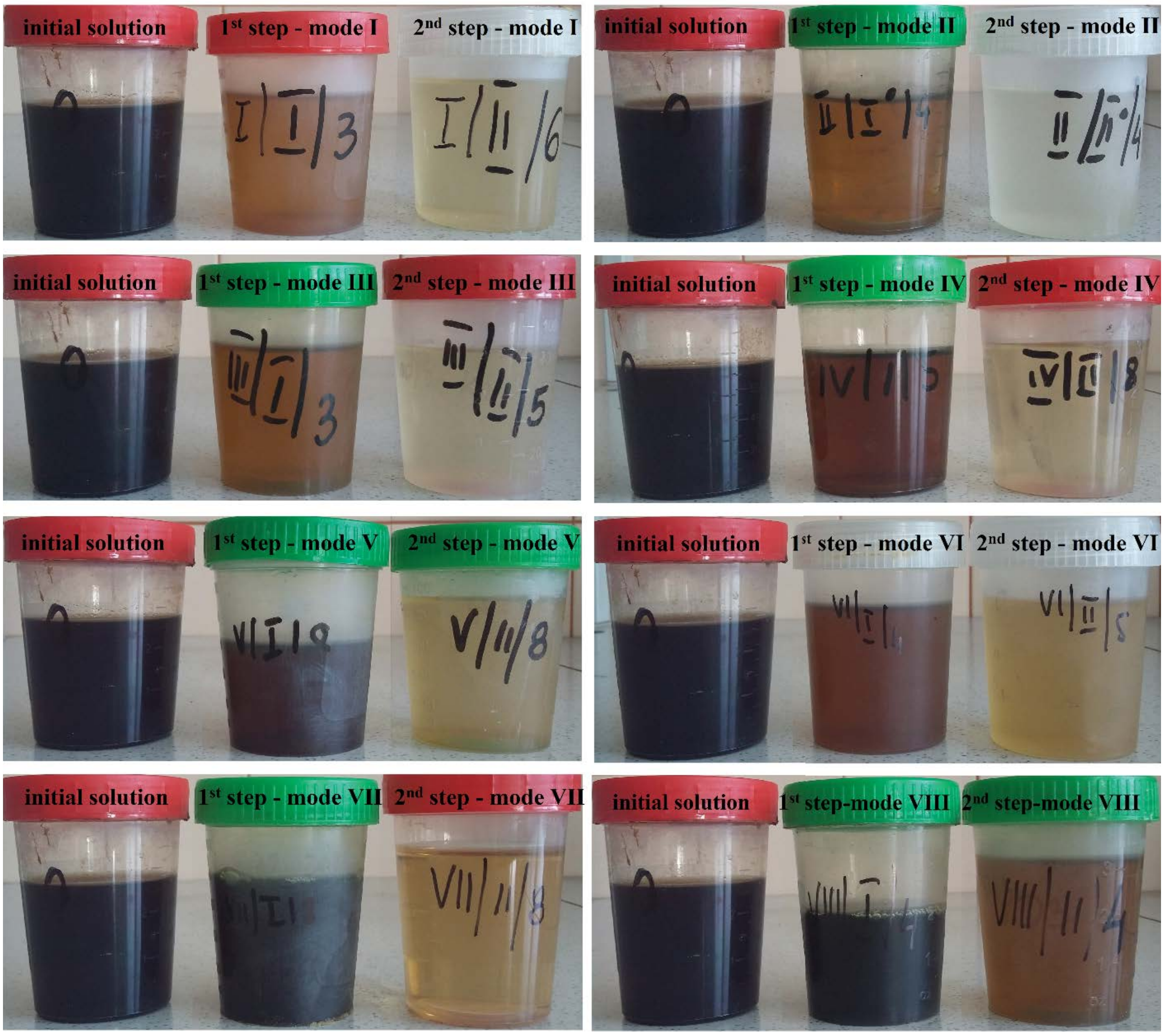

Fig. 4. Comparison of TW decolourization by different modes of two-step continuous Fenton process.

can be found. Best results in terms of colour removal were obtained for systems working in mode II and III, which is an interesting observation, due to the fact, that for that modes overall doses of the reagents were the highest, but COD_{Cr} removal was lower than in a case of systems working in mode IV and V. It proves, that there are no straight relations between the changes of odour and colour properties of the TW and COD_{Cr} removal during the oxidation process.

4. Discussion

To confirm an important influence of the reagent initial ratio on the efficiency of the Fenton reaction and COD_{Cr} reduction from the reaction mixture, a correlation table was prepared, by using a standard MS Excel analytical tool pack (Table 5).

Based on the presented statistical analysis, a clear correlation between the reagent ratio was observed both in the case of Fe^{2+} and H_2O_2. Moreover, an important fact is that ratio between H_2O_2 and Fe^{2+} is also correlated with the efficiency of analyzed Fenton reaction. J. Guilford observed that influence of reagent ratios on the COD_{Cr} removal can be classified as a high and very high correlation, showing that overall efficiency of the process is strongly dependent on mentioned reagent doses [47]. Another important conclusions and crucial experimental results have been discussed in this part. In the table below, a summary of the oxidation results based on the mass efficiency of COD_{Cr} removal in the analyzed technological wastewater before and after the Fenton process were presented (Table 6).

In the case of continuous systems, the obtained values of COD_{Cr} removal in two-step systems, operating based on corresponding ratios of the reagent doses, are much higher compared with a single-step system. Additionally, based on the presented results for cyclic systems with simultaneous control of pH conditions, the degree of COD_{Cr} reduction is almost the same. Thus, all of the continuous process advantages, discussed in Section 3.2, clearly prove the legitimacy and high application potential of the proposed solutions and modifications. Moreover, as it was proven before, Fenton reaction conducted as a continuous process has many indisputable advantages, for example, more stable parameters of the process, shorter reaction time, higher overall efficiency of the process, etc. However, one of the most important is a fact, that continuous Fenton reaction leads to a significant reduction of precipitates which are the most important solid wastes that are generated within the process. To better illustrate these observations, simple histograms of generated precipitates are shown in Figs. 5 and 6.

Table 5
Correlation table of initial reagent ratios influence on the overall COD_{Cr} removal

	COD_{Cr} removal	H_2O_2/ COD_{Cr}	Fe^{2+}/ COD	H_2O_2/ Fe^{2+}
COD_{Cr} removal	1			
H_2O_2/COD_{Cr} ratio	0.91	1		
Fe^{2+}/COD_{Cr} ratio	0.94	0.90	1	
H_2O_2/Fe^{2+} ratio	0.77	0.93	0.70	1

Table 6
Summary of COD_{Cr} removal efficiency for different treatment systems with corresponding ratios of the reagents

Tb	Time	Batch reactors	Single-step mode	Two-step mode
1:2:1	4 h	43%*	51%	–
1:2:1	6–7 h	45%*	55%	Mode 3: 73.3% Mode 4: 76.9% Mode 6: 72.3%
1:2,5:1,25	4 h	72%	56%	–
1:2,5:1,25	6–7 h	77%	58%	mode 5: 75%

Presented data compares the precipitates amounts generated during the processes working in the initial reagent ratios equal 1:2:1, it can be found, that almost 19% lower sludges are generated in the two-step continuous systems than in the analogue system conducted in the simple batch reactor. A similar situation occurs in the systems working with an initial reagent ratio equal to 1:2.5:1.25, which was presented below.

In the second of the analysed reagent ratios, differences in sludge precipitation between cyclic and continuous systems were slightly lower and after the exactly the same amount of reaction time it was about 12% less precipitates generated in two-step continuous process. Last but not least aspect of two-step continuous analysis was an economical aspect of the process, cause with different doses and thus different amounts of the necessary reagents, a different overall mass efficiency was obtained. That is why based on the data presented in Table 3 a brief summary of the overall economic efficiency of the process is presented in Fig. 7.

Values presented in Fig. 7 were calculated as the final usage of H_2O_2 or Fe^{2+} in grams needed to remove 1 g of COD_{Cr} from 1 L of TW in each of the analysed two-steps continuous process modes. Based on the presented data, the most economical advantageous process was the one that was performed at the mode VIII. It was caused mostly by the very low final doses of both reagents added to the reacting mixture, not by a higher removal of COD_{Cr}. However, considering a mass efficiency removal equal to 69% as satisfactory, it could be possible to significantly reduce the operational costs of the Fenton process installation. On the other hand, comparison of four modes (modes II – V) that were considered before as the most promising due to the very high efficiency of COD_{Cr} removal and excellent decolourization degree, shows that equally divided reagent doses led to a significant reduction of the process costs. Thus, for future solutions, mode IV and V seems to be the best way of treating this kind of wastewater by the Fenton process.

5. Conclusions

Treatment processes of solutions characterized by a high COD_{Cr} and TOC values and a strongly acidic character (pH < 1), based on the Fenton reaction in a cyclic system undergo in very changing conditions of pH and temperature,

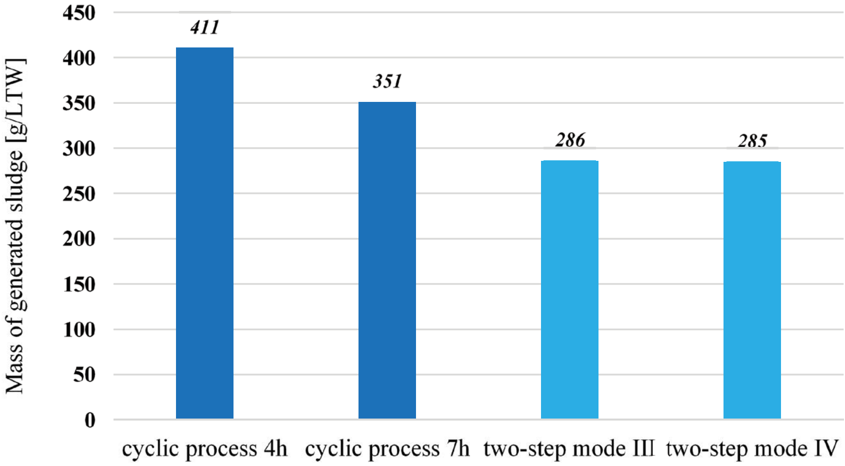

Fig. 5. Amount of sludges generated during the continuous Fenton process in one and two-steps, at the same initial reagent ratio equal (COD_{Cr}:H_2O_2:Fe^{2+}) 1:2:1.

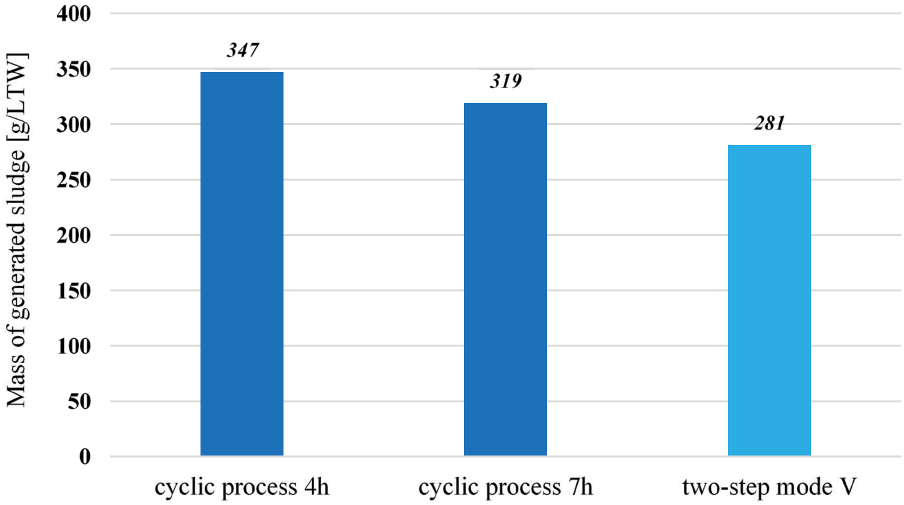

Fig. 6. Amount of sludges generated during the continuous Fenton process in one and two-steps, at the same initial reagent ratio equal (COD_{Cr}:H_2O_2:Fe^{2+}) 1:2.5:1.25.

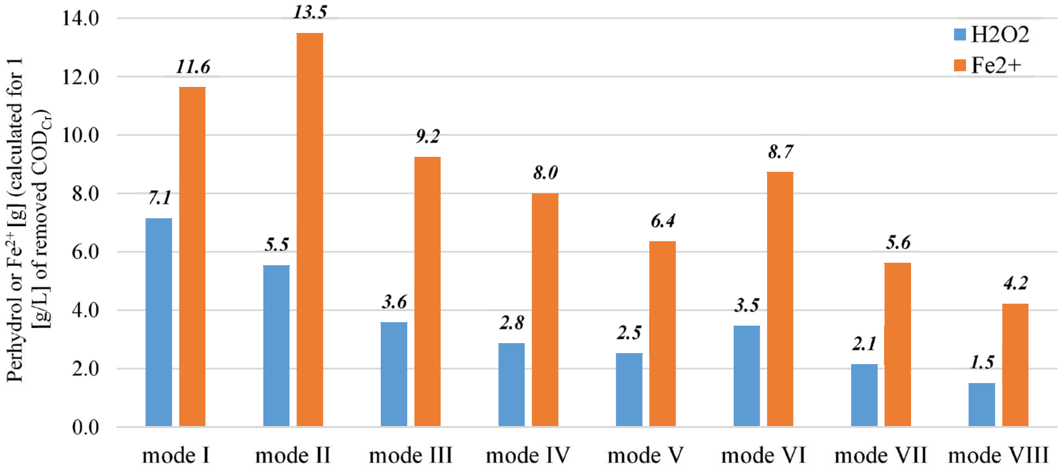

Fig. 7. Amount of 35% H_2O_2 and Fe^{2+} reagent spent for the treatment method, calculated per 1% of removed COD_{Cr} in a different modes of two-step continuous Fenton process.

resulting from the addition of the necessary reagents. In those systems, maintaining a stable pH value at the level of 3.5 ≤ pH ≤ 4.5 during the whole process requires a continuous intervention with the pH correcting agents (such as $Ca(OH)_2$). The phenomenon of intense foaming and temperature increase of the reaction mixture, often above 70°C, occurring in that conditions, has a significant adverse effect on the process.

However, in the presented study, it was proven that the modification of the Fenton reaction, by conducting it in a continuous system may lead to a significant improvement in the efficiency of this method. That result was even better in the case of two-step continuous process, which can shorten the reaction time and allows to reduce the COD_{Cr} and TOC parameters of the solution by 77% and 65%, respectively. The continuous system and its gradation allow to substantially reduce or even eliminate the phenomenon of foaming of the reaction mixture during the process.

Moreover, in those conditions, it was much easier to stabilize the temperature at the level of 40°C–50°C and remove the colour and odour nuisance from the oxidized solution. Another advantage of performing Fenton reaction in the continuous mode is a significant increase in the removal of selected metals from the solution. Using a two-step continuous system leads also to a significant reduction of sludge amounts generated during the process, in both of the analysed reagent dose systems. Thus, it can be concluded, that using a two-step reaction process, allows not only to reduce the COD_{Cr} value without increasing the costs and amounts of the reagent but also to generate less solid wastes during the whole Fenton process.

References

[1] J. Wąsowski, A. Piotrowska, Rozkład organicznych zanieczyszczeń wody w procesach pogłębionego utleniania, Ochr. Środowiska., nr 2 (2002) 27–32.

[2] A. Kowal, M.Ś. Bróż, Oczyszczanie wody. Podstawy teroretyczne i technologiczne, procesy i urządzenia, 6th ed., Wydawnictwo Naukowe PWN, Warszawa, 2009.

[3] A.M. Anielak, Chemiczne i fizykochemiczne oczyszczanie ścieków, Wydawnictwo Naukowe PWN, Warszawa, 2007.

[4] C.K. Duesterberg, T.D. Waite, Process optimization of fenton oxidation using kinetic modeling, Environ. Sci. Technol., 40 (2006) 4189–4195.

[5] H. Zhang, H.J. Choi, C.P. Huang, Optimization of Fenton process for the treatment of landfill leachate, J. Hazard. Mater., 125 (2005) 166–174.

[6] A. Goi, M. Trapido, Hydrogen peroxide photolysis, Fenton reagent and photo-Fenton for the degradation of nitrophenols: a comparative study, Chemosphere, 46 (2002) 913–922.

[7] S.M. Kim, A. Vogelpohl, Degradation of organic pollutants by the photo-Fenton-process, Chem. Eng. Technol., 21 (1998) 187–191.

[8] B. Utset, J. Garcia, J. Casado, X. Domènech, J. Peral, Replacement of H_2O_2 by O_2 in Fenton and photo-Fenton reactions, Chemosphere, 41 (2000) 1187–1192.

[9] A.G. Chakinala, P.R. Gogate, A.E. Burgess, D.H. Bremner, Treatment of industrial wastewater effluents using hydrodynamic cavitation and the advanced Fenton process, Ultrason. Sonochem., 15 (2008) 49–54.

[10] M. Wang, G. Yang, H. Feng, Z. Lv, H. Min, Optimization of Fenton process for decoloration and COD removal in tobacco wastewater and toxicological evaluation of the effluent, Water Sci. Technol., 63 (2011) 2471–2477.

[11] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater., 98 (2003) 33–50.

[12] P. Riesz, T. Kondo, C.M. Krishna, Free radical formation by ultrasound in aqueous solutions. A spin trapping study, Free Radical Res. Commun., 10 (1990) 27–35.

[13] D.H. Geske, A.H. Maki, Electrochemical generation of free radicals and their study by electron spin resonance spectroscopy; the nitrobenzene anion radical, J. Am. Chem. Soc., 82 (1960) 2671–2676.

[14] A.G.G. Mata, S.V. Martínez, A.Á. Gallegos, M. Ahmadi, J.A.H. Pérez, F. Ghanbari, S.S. Martínez, Recent overview of solar photocatalysis and solar photo-Fenton processes for wastewater treatment, Int. J. Photoenergy, 2017 (2017) 8528063, doi: 10.1155/2017/8528063.

[15] K. Barbusiński, Intensyfikacja procesu oczyszczania ścieków i stabilizacji osadów nadmiernych z wykorzystaniem odczynnika Fentona, Zesz. Nauk. Inżynieria Środowiska/Politech. Śląska. z., 50 (2004) 7–169.

[16] Y. Wang, Y. Sun, W. Li, W. Tian, A. Irini, High performance of nanoscaled Fe_2O_3 catalyzing UV-Fenton under neutral condition with a low stoichiometry of H_2O_2: kinetic study and mechanism, Chem. Eng. J., 267 (2015) 1–8.

[17] C.L. Hsueh, Y.H. Huang, C.C. Wang, C.Y. Chen, Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system, Chemosphere, 58 (2005) 1409–1414.

[18] E. Brillas, J.C. Calpe, J. Casado, Mineralization of 2,4-D by advanced electrochemical oxidation processes, Water Res., 34 (2000) 2253–2262.

[19] B. Gözmen, M.A. Oturan, N. Oturan, O. Erbatur, Indirect electrochemical treatment of Bisphenol A in water via electrochemically generated Fenton's reagent, Environ. Sci. Technol., 37 (2003) 3716–3723.

[20] A. Krzysztoszek, J. Bogacki, J. Naumczyk, Study on removal of heavy metals from landfill leachate by Fenton's process and modified Fenton's process, Sci. Rev. – Eng. Environ. Sci., 51 (2011) 36–42.

[21] J. Długosz, Metoda Fentona i jej modyfikacje w oczyszczaniu odcieków – praca przeglądowa, Arch. Gospod. Odpad. i Ochr. Środowiska. Vol. 16, n (2014) 33–42.

[22] A. Janda, T. Marcinkowski, Modification possibilities for oxidation effectiveness of hard degradable organic pollutants, Ochr. Środowiska., 41 (2019) 47–53.

[23] F. Fu, Q. Wang, B. Tang, Effective degradation of C.I. Acid Red 73 by advanced Fenton process, J. Hazard. Mater., 174 (2010) 17–22.

[24] D. Kulikowska, Charactarization of organics and methods treatment of leachate from stabilized municipal landfills, Ecol. Chem. Eng. S, 16 (2009) 389–402.

[25] J. Perkowski, M. Sidor, Badania rozkładu niejonowych związków powierzchniowo czynnych w wybranych procesach pogłębionego utleniania, Ochr. Środowiska. R. 29, nr (2007) 18–25.

[26] S.S.A. Amr, H.A. Aziz, New treatment of stabilized leachate by ozone/Fenton in the advanced oxidation process, Waste Manage., 32 (2012) 1693–1698.

[27] V.J.P. Vilar, T.F.C. V Silva, M.A.N. Santos, A. Fonseca, I. Saraiva, R.A.R. Boaventura, Evaluation of solar photo-Fenton parameters on the pre-oxidation of leachates from a sanitary landfill, Sol. Energy, 86 (2012) 3301–3315.

[28] S.G. Michael, I.M. Kordatou, V.G. Beretsou, T. Jäger, C. Michael, T. Schwartz, D.F. Kassinos, Solar photo-Fenton oxidation followed by adsorption on activated carbon for the minimisation of antibiotic resistance determinants and toxicity present in urban wastewater, Appl. Catal., B, 244 (2019) 871–880.

[29] S. Papoutsakis, S.M. Cuevas, N. Gondrexon, S. Baup, S. Malato, C. Pulgarin, Coupling between high-frequency ultrasound and solar photo-Fenton at pilot scale for the treatment of organic contaminants: an initial approach, Ultrason. Sonochem., 22 (2015) 527–534.

[30] S. Foteinis, J.M. Monteagudo, A. Durán, E. Chatzisymeon, Environmental sustainability of the solar photo-Fenton process

for wastewater treatment and pharmaceuticals mineralization at semi-industrial scale, Sci. Total Environ., 612 (2018) 605–612.

[31] M. Khandarkhaeva, A. Batoeva, M. Sizykh, D. Aseev, N. Garkusheva, Photo-Fenton-like degradation of bisphenol A by persulfate and solar irradiation, J. Environ. Manage., 249 (2019) 109348, doi: 10.1016/j.jenvman.2019.109348.

[32] G. Matyszczak, K. Krzyczkowska, A. Fidler, A novel, two-electron catalysts for the electro-Fenton process, J. Water Process Eng., 36 (2020) 101242, doi: 10.1016/j.jwpe.2020.101242.

[33] D. Gümüş, F. Akbal, Comparison of Fenton and electro-Fenton processes for oxidation of phenol, Process Saf. Environ. Prot., 103 (2016) 252–258.

[34] H. Liu, C. Wang, X. Zhong, X. Xuan, C. Jiang, H. Cui, A novel electro-fenton process for water treatment: reaction-controlled pH adjustment and performance assessment, Environ. Sci. Technol., 41 (2007) 2937–2942.

[35] S. Qiu, D. He, J. Ma, T. Liu, T.D. Waite, Kinetic modeling of the electro-fenton process: quantification of reactive oxygen species generation, Electrochim. Acta, 176 (2015) 51–58.

[36] A. Shahedi, A.K. Darban, F. Taghipour, A.J. Zanjani, A review on industrial wastewater treatment via electrocoagulation processes, Curr. Opin. Electrochem., 22 (2020) 154–169.

[37] X. Meng, S.A. Khoso, F. Jiang, Y. Zhang, T. Yue, J. Gao, S. Lin, R. Liu, Z. Gao, P. Chen, L. Wang, H. Han, H. Tang, W. Sun, Y. Hu, Removal of chemical oxygen demand and ammonia nitrogen from lead smelting wastewater with high salts content using electrochemical oxidation combined with coagulation–flocculation treatment, Sep. Purif. Technol., 235 (2020) 116233, doi: 10.1016/j.seppur.2019.116233.

[38] S. Li, W. Wang, Y. Liu, W. Zhang, Zero-valent iron nanoparticles (nZVI) for the treatment of smelting wastewater: a pilot-scale demonstration, Chem. Eng. J., 254 (2014) 115–123.

[39] N. Jaafarzadeh, F. Ghanbari, M. Moradi, Photo-electro-oxidation assisted peroxymonosulfate for decolorization of acid brown 14 from aqueous solution, Korean J. Chem. Eng., 32 (2015) 458–464.

[40] M. Ahmadi, F. Ghanbari, S.M. Bidgoli, Photoperoxi-coagulation using activated carbon fiber cathode as an efficient method for benzotriazole removal from aqueous solutions: modeling, optimization and mechanism, J. Photochem. Photobiol., A, 322–323 (2016) 85–94.

[41] F. Vogel, J. Harf, A. Hug, P.R.V. Rohr, The mean oxidation number of carbon (MOC)—a useful concept for describing oxidation processes, Water Res., 34 (2000) 2689–2702.

[42] E.R. Burns, C. Marshall, Correction for chloride interference in the chemical oxygen demand test, J. (Water Pollut. Control Fed., 37 (1965) 1716–1721.

[43] I. Talinli, G.K. Anderson, Interference of hydrogen peroxide on the standard cod test, Water Res., 26 (1992) 107–110.

[44] L. Gu, J.Y. Nie, N. Zhu, L. Wang, H.P. Yuan, Z. Shou, Enhanced Fenton's degradation of real naphthalene dye intermediate wastewater containing 6-nitro-1-diazo-2-naphthol-4-sulfonic acid: a pilot scale study, Chem. Eng. J., 189–190 (2012) 108–116.

[45] Y. Wang, W. Li, A. Irini, A novel and quick method to avoid H_2O_2 interference on COD measurement in Fenton system by Na_2SO_3 reduction and O_2 oxidation, Water Sci. Technol., 68 (2013) 1529–1535.

[46] Y. Flores, R. Flores, A.A. Gallegos, Heterogeneous catalysis in the Fenton-type system reactive black 5/H_2O_2, J. Mol. Catal. A Chem., 281 (2008) 184–191.

[47] R. Falk, A.D. Well, Many faces of the correlation coefficient, J. Stat. Educ., 5 (1997) 11910597, doi: 10.1080/10691898.1997.11910597.