DISCOLORATION OF DYE WASTEWATER BY MODIFIED UV-FENTON PROCESS WITH SODIUM PERCARBONATE

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Abstract
A modified Fenton process using sodium percarbonate (SP), as an alternative source of H2O2, and UV radiation was investigated to discoloration of dye wastewater containing Acid Green 16 (concentration 100 mg/dm3). This acid dye is characterized by the harmful effect on aquatic organisms and it may cause adverse effects in the aquatic environment. The experiments were carried out in two systems, in which two lamps were used as a UV radiation source: low pressure (system I) and medium pressure (system II). The effect of SP dosage (100-400 mg/dm3 – system I; and 100-250 mg/dm3 – system II), Fe2+/SP ratio (from 0.2 to 0.4), reaction pH (3 and 4) and reaction time (from 10 to 30 min) on colour removal efficiency was examined. The modified Fenton process was found to be very efficient for discoloration of simulated wastewater. For a system with a low pressure UV lamp the optimal doses of SP and Fe2+/SP ratio were 400 mg/dm3 and 0.2, respectively at pH 3 and 20 minutes reaction time. For a system with a medium pressure UV lamp the optimal doses of SP and Fe2+/SP ratio were 200 mg/dm3 and 0.33, respectively at pH 3 and 20 minutes reaction time. In both cases, at described conditions total visual discoloration was achieved. Better results of colour removal (concentration of Acid Green 16 was in the range of 0.64-0.96 mg/dm3) were achieved when the initial pH value equalled 3.0 than at initial pH value of 4.0 (concentration of Acid Green 16 was in the range of 0.80-6.87 mg/dm3).

Streszczenie
W procesie odbarwiania ścieków zawierających barwnik Acid Green 16 (o stężeniu 100 mg/dm³) zastosowano zmodyfikowany proces Fentona z nadwęglanem sodu, jako alternatywnym źródłem nadtlenku wodoru, wspomagany promieniowaniem UV. Barwnik ten zaliczany do grupy barwników kwasowych charakteryzuje się szkodliwym działaniem na organizmy wodne, a także może wywoływać niekorzystne zmiany w tym środowisku. Badania prowadzono w dwóch układach wyposażonych w lampy UV: niskociśnieniową (system I) i średniciśnienniową (system II). Podczas badań zastosowano dawki nadwęglanu sodu w zakresie (100-400 mg/dm³ – układ I oraz 100-250 mg/dm³ – układ II), wartości stosunku Fe2+/nadwęglan (od 0.2 do 0.4), pH reakcji (3 i 4), a także czas naświetlania (od 10 do 30 min). Zmodyfikowany proces Fentona okazał się bardzo skuteczny w odbarwianiu badanych ścieków. Dla układu I z lampą niskociśnienną najkorzystniejsza dawka nadwęglanu sodu oraz stosunek Fe2+/nadwęglan wynosiły odpowiednio 400 mg/dm³ i 0.2, przy pH=3 i czasie naświetlania 20 minut. Dla układu II (lampa średniciśnienniowa) najkorzystniejsza dawka nadwęglanu sodu wynosiła 200 mg/dm³ i stosunek Fe2+/nadwęglan 0.33, przy pH=3 i czasie naświetlania 20 minut. W obu przypadkach dla tych parametrów uzyskano wizualne odbarwienie ścieków. Lepsze efekty odbarwienia uzyskano dla pH=3 w porównaniu z pH=4 (stężenie barwnika odpowiednio 0.64-0.96 mg/dm³ i 0.80-6.87 mg/dm³).

Keywords: Fenton reagent; UV-Fenton; Acid Green 16; sodium percarbonate; Discoloration.
1. INTRODUCTION
The consumption lifestyle and an increased demand on various colored textile, paper, cosmetic and food products contributes to generation of increasing amounts of wastewater containing dyes [1]. There are many different methods for industrial wastewater treatment. One group of them are oxidation processes. Among the innovative methods of industrial wastewater treatment special interest focuses on investigations of advanced oxidation processes (AOPs). Between the various AOPs, Fenton reagent (mixture of hydrogen peroxide and ferrous iron) is one of the most effective methods of the oxidation of organic pollutants [2, 3]. Therefore, the Fenton reagent has been found to be effective in treating various industrial wastewater components including aromatic amines [4], pesticides [5, 6], surfactants [7, 8], a wide variety of dyes [9, 10] and many other substances. Fenton reagent may also be used to improve the efficiency of aerobic digestion of sewage sludge [11, 12]. For this reason, Fenton reagent has been applied to treat a variety of waste such as those associated with the chemical and textile industries [13-15]. Recently, beside the classical Fenton reagent ($\text{H}_2\text{O}_2$/ferrous salt) a lot of studies have focused especially on investigation of the Fenton process with alternative $\text{H}_2\text{O}_2$ or iron sources. Research carried out by Barbusiński [16-17] showed that these alternative sources of $\text{H}_2\text{O}_2$ could be calcium and magnesium peroxides ($\text{CaO}_2$, $\text{MgO}_2$) as well as sodium percarbonate (sodium carbonate peroxyhydrate) [18-19]. As a most reasonable in practice, it is considered to use for this purpose commercial products containing calcium peroxide (PermeOx, PermeOx Plus, Ixper 75C) and magnesium peroxide (Drillox 35M). The essence of these modifications consists in releasing $\text{H}_2\text{O}_2$ from $\text{CaO}_2$, $\text{MgO}_2$ or sodium percarbonate in acidic condition at the presence of ferrous salt. The released $\text{H}_2\text{O}_2$ reacts with $\text{Fe}^{2+}$ ions (the Fenton reaction) and generates $\text{OH}^-$ radicals which have a great oxidizing potential. For example, sodium percarbonate in the aqueous solution is decomposed into hydrogen peroxide and sodium carbonate according to the equation 1:

$$2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O} \rightarrow 2\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O}_2$$  (1)

The authors of this publication have conducted earlier studies on discoloration of wastewater using a modified Fenton process in the $\text{H}_2\text{O}_2$/swarf system. In this system heterogeneous catalyst (steel swarf), as an alternative source of iron ions, was investigated for degradation of dye Acid Green 16 [20]. The experiments were carried out in continuously-flow reactor with a column filled with steel swarf. The continuous Fenton process was found to be very efficient for discoloration of simulated wastewater.

The present study is a continuation of the use of various modifications of Fenton reagent for efficient discoloration of dye wastewater. The aim of this study was to determine the most favorable values of parameters of modified Fenton reagent, with sodium percarbonate (SP) and UV radiation (UV/SP process), in order to obtain visual discoloration of wastewater containing dye Acid Green 16. The effect of experimental factors such as SP dosage, $\text{Fe}^{2+}$/SP ratio, initial pH and reaction time was tested. UV radiation was used to increase the amount of $\text{OH}^-$ radicals such as in the UV-Fenton system.

2. MATERIALS AND METHODS
2.1. Dye Wastewater
The simulated dye wastewater was prepared by dilution of commercial dye Acid Green 16 (BORUTA-KOLOR, Poland) and meat peptone (Aminobapepton, BTL, Poland) with water. The dye was of high purity and used without further purification. Concentration of dye and peptone was 100 mg/dm$^3$ and 100 mg/dm$^3$ respectively. Thus prepared wastewater was characterized with an intensive dark-green color, high clarity and COD = 320 mg $\text{O}_2$/dm$^3$. Acid Green 16 (Fig. 1) is characterized by the harmful effect on aquatic organisms and it may cause adverse effects in the aquatic environment [20-21].

![Figure 1. Structure of the dye Acid Green 16 (C.I. 44025)](image)

2.2. Experimental Procedure
The procedure of Fenton’s reaction was as follows: the wastewater was put into reactors of 0.5 dm$^3$ volume, and then acidified with $\text{H}_2\text{SO}_4$ (1+1) to the selected values of pH, as a Fenton reaction is effective in acidic range. After that, the various amounts of sodium percarbonate (SP) and $\text{FeSO}_4\cdot7\text{H}_2\text{O}$ (1%
solution) were added and continuous magnetic stirring was applied. Next, the pH of the wastewater was again adjusted due to alkaline nature of sodium percarbonate. Prepared wastewater was introduced into a suitable reactor equipped with a low (system I) or medium (system II) pressure UV lamp. The laboratory UV reactor (Wedeco) with a low-pressure (LP) lamp (15 W) and the UV reactor (UV-Consulting Peschl) with a medium-pressure (MP) lamp (150 W) were used. After appropriate time the wastewater was neutralized with 0.1 N NaOH up to about pH 9 in order to prevent further generation of hydroxyl radicals. Then, the samples were centrifuged at 3000 rpm (2.5 min) and analyzed at the λ = 590 nm, using a WPA COLOR WAVE CO7000 Medical Colorimeter.

The scope of research was divided into three stages, which included: selection of SP dose and the reaction time, indication of the most favorable weight ratio of Fe<sup>2+</sup>/SP and the value of reaction pH (Table 1). The selection of the most favorable parameters was made on the basis of changes in dye Acid Green 16 concentration in the wastewater after the oxidation process and visual discoloration of wastewater. The concentration of the dye was measured with a colorimetric method based on a standard curve of dye [22-24].

### Table 1. Parameters of the discoloration process

<table>
<thead>
<tr>
<th>The kind of UV lamp</th>
<th>The range of SP doses, mg/dm&lt;sup&gt;3&lt;/sup&gt;</th>
<th>The range of Fe&lt;sup&gt;2+&lt;/sup&gt;/SP ratio</th>
<th>pH reaction</th>
<th>Reaction time, minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Pressure</td>
<td>100-400</td>
<td>0.2; 0.33; 0.4</td>
<td>3; 4</td>
<td>10; 20; 30</td>
</tr>
<tr>
<td>Medium Pressure</td>
<td>100-250</td>
<td>0.2; 0.33; 0.4</td>
<td>3; 4</td>
<td>10; 20; 30</td>
</tr>
</tbody>
</table>

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of SP dosage and radiation time

During the first stage of the experiment, the most favorable value of SP dose was examined. For both types of UV lamps with increasing dose of SP (at constant values of other process parameters) a gradual decrease of the concentration of dye in the treated wastewater was observed. In case of the system I, the greatest increase of process efficiency was observed when the dose of SP increased from 100 to 150 mg/dm<sup>3</sup>. At the dose of 100 mg SP/dm<sup>3</sup> the concentration of Acid Green 16 was equaled to 19.03 mg/dm<sup>3</sup> (after 10 minutes of reaction) and at the dose of 150 mg SP/dm<sup>3</sup>, the dye content was only 7.65 mg/dm<sup>3</sup> (also after 10 minutes of radiation). Further increase of SP value up to 400 mg/dm<sup>3</sup> contributed to a reduction in the concentration of dye to 0.64 mg/dm<sup>3</sup> (10 min of radiation). A similar effect of treatment efficiency was also observed in the case of the medium pressure lamp. At the dose of 100 mg SP/dm<sup>3</sup>, the concentration of Acid Green 16 was 11.17 mg/dm<sup>3</sup>, while at 150 mg SP/dm<sup>3</sup>, the concentration of the dye after the process was only 3.16 mg/dm<sup>3</sup>. Further increase in SP dose to 250 mg/dm<sup>3</sup> allowed for reducing the concentration of Acid Green 16 in the effluent to a value of 1.29 mg/dm<sup>3</sup> (10 minutes of radiation).

The obtained results concerning the effect of radiation time on the discoloration efficiency showed that the highest concentration change was achieved in the first 10 minutes of reaction for both types of UV lamps (Fig. 2 and 3). For example, in the system I (LP lamp) at the dose of 100 mg SP/dm<sup>3</sup>, the concentration of the dye was reduced from 100 to 19.03 mg/dm<sup>3</sup>. Increased reaction time contributed to further decrease in dye concentration to 13.37 and 10.53 mg/dm<sup>3</sup>, after 20 and 30 minutes of radiation respectively. A similar relationship between dye concentration and reaction time was observed in the system II (MP lamp). It was also noted that for all SP doses, in both research systems, when reaction time increased, the efficiency of discoloration also increased. This is because the longer exposure time to a UV radiation causes a larger amount of Fe<sup>2+</sup> ions produced by reduction of Fe<sup>3+</sup> ions according to the reaction [25]. It should be noted, however, that the visual discoloration of wastewater was only obtained after 20 and 30 minutes of reaction in the whole range of examined SP doses. Therefore, in further investigations the reaction time of 20 minutes was used.

Fe<sup>3+</sup> + H<sub>2</sub>O<sub>2</sub> + hν → Fe<sup>2+</sup> + OH<sup>-</sup> + H<sup>+</sup>  

(2)

The research results also showed that in the system I, higher doses of SP were required to ensure visual discoloration than in the system II (Fig. 2 and 3). When the LP lamp was used as a source of UV radiation, visual discoloration of the wastewater was achieved only at 400 mg SP/dm<sup>3</sup>. The application of the MP lamp allowed for visual discoloration of wastewater already at dose of 200 mg SP/dm<sup>3</sup>. It indicates that, the power of UV lamps plays a key role in the efficiency of UV/Fenton process. Low pressure lamps are mainly used in the disinfection process and generate radiation with a wavelength of 254 nm [26]. In contrast, medium pressure UV lamps generate radiation in length of 240-600 nm, which has a much high-
er energy. Therefore, this kind of radiation can oxidize the contaminants directly. Moreover, both types of UV lamp are often used in wastewater treatment processes, particularly in the AOPs technologies [27-30]. To further stage of research (i.e. selection of the most favorable weight ratios of Fe^{2+}/SP) doses of 400 and 200 mg/dm³ were chosen in the system with LP and MP UV lamp, respectively. Furthermore, basing on the results obtained in the first stage of the study, 20 minutes was selected as the most favorable radiation time for both systems.

3.2. Effect of Fe^{2+}/SP

In both systems, the effect of three values of the weight ratio of Fe^{2+}/SP was examined. It was shown that as the value of Fe^{2+}/SP increased, the efficiency of the purification process also increased (Fig. 4). In the system I with the LP UV lamp, visual discoloration of wastewater was obtained for Fe^{2+}/SP ratio = 0.2 and at dye concentration 0.64 mg/dm³. The increase of iron quantity (sequentially to 0.33 and 0.4 of Fe^{2+}/SP ratio) caused almost linear decrease of the dye concentration, to 0.48 mg/dm³ (Fe^{2+}/SP=0.33) and 0.32 mg/dm³ (Fe^{2+}/SP=0.4), respectively. In the system II, visual discoloration of wastewater was obtained at value of Fe^{2+}/SP ratio equal 0.33 (dye concentration = 0.96 mg/dm³). Using lower dose of iron ions did not allow to achieve the effective removal of Acid Green 16 (visual discoloration was not obtained).

In addition, it was seen that the greater efficiency of the process was observed in the system I. However, it should be noted, that in the case of the purification system with LP UV lamp the dose of SP was twice higher than in the system with MP UV lamp. Therefore, basing on the results obtained during that stage of the study as a most favorable ratio of Fe^{2+}/SP following values were chosen: 0.2 in system I and 0.33 in the system II. These were the minimum values of Fe^{2+}/SP ratio at which the visual discoloration of the wastewater was obtained.

3.3. Effect of pH

Experiments conducted in both systems showed that as reaction pH increased from 3.0 to 4.0, the efficiency of the removal of the dye Acid Green 16 decreased (Fig. 5). In the case of LP UV lamp the dye concentrations were equal to 0.64 and 0.80 mg/dm³, at pH 3.0 and 4.0 respectively. However, in the system II with MP UV lamp, the effect of pH on discoloration efficiency was much more significantly. When the process was conducted at pH 3.0 the concentration of Acid Green 16 was equal to 0.96 mg/dm³. At pH 4.0 the dye content increased up to 6.87 mg/dm³. Such differences in the effect of pH on the effectiveness of discoloration in both systems may result from the difference in SP doses. In the system I the dose of SP was twice higher than in system II. It is also known that as the pH increases quantity of H₂O₂ released from SP decreases. Generally, the higher dose of SP,
the greater quantity of H₂O₂ is released from SP into the treated wastewater. Therefore the dose of SP could have such a large impact on the process effect.

4. CONCLUSIONS

The study of treatment of synthetic dye wastewater using a modified UV-Fenton process (in the modification with sodium percarbonate) allowed to formulate the following conclusions:

• It is possible to effectively decolorize wastewater containing Acid Green 16 using the modified Fenton reagent with sodium percarbonate in combination with UV radiation.

• The type and power of the UV lamp, which is a source of radiation, has a significant impact on the effectiveness of decolorizing. In the case of MP lamp a visual discoloration of wastewater was obtained at a dose of 200 mg/ dm³. When the LP UV lamp was used, twice higher dose of SP (400 mg/dm³) was required. It can be assumed that in the case of system II beyond oxidation of the dye by Fenton reagent, direct photo-oxidation the Acid Green 16 can also occur (due to a wider range of wavelengths of the radiation emitted by the MP UV lamp).

• In both systems, the impact of individual parameters of UV-SP process on the effectiveness of decolorization of dye wastewater was noted. As the dose of SP increased, the efficiency of discoloration increased. The same impact of radiation time and Fe²⁺/SP ratio on discoloration effectiveness was observed. As the values of these parameters increased the removal of Acid Green 16 also increased.

• In the whole range of Fe²⁺/SP ratio, better results of discoloration were obtained in the system I. That phenomenon may be connected with using twice higher dose of SP in that system in comparison with system II.

• In both systems, the color removal efficiency was lower at pH 4 compared with pH 3.

• The results of the study showed that better results were obtained when system II with MP UV lamp was used. The visual discoloration of treated wastewater was achieved when following process parameters were used: dose of SP 200 mg/dm³, Fe²⁺/SP ratio 0.33, radiation time 20 minutes and pH 3.

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