Removal of organic compounds from wastewater originating from the production of printed circuit boards by UV-Fenton method

Maciej Thomas¹, Barbara Białecka², Dariusz Zdebik³*

¹Chemiqua Company, Poland
²Central Mining Institute, Department of Water Protection, Poland
³Central Mining Institute, Department of Environmental Monitoring, Poland

*Corresponding author’s e-mail: dzdebik@gig.katowice.pl

Keywords: advanced oxidation process, response surface methodology, printed circuits board, wastewater, UV-Fenton

Abstract: The possibility of removing organic compounds from wastewater originating from the photochemical production of printed circuit boards by use of waste acidification and disposal of precipitated photopolymer in the first stage and the UV-Fenton method in a second stage has been presented. To optimize the process of advanced oxidation, the RSM (Response Surface Methodology) for three independent factors was applied, i.e. pH, the concentration of Fe(II) and H₂O₂ concentration. The use of optimized values of individual parameters in the process of wastewater treatment caused a decrease in the concentration of the organic compounds denoted as COD by approx. 87% in the first stage and approx. 98% after application of both processes. Precipitation and the decomposition of organic compounds was associated with a decrease of wastewater COD to below 100 mg O₂/L whereas the initial value was 5550 mg O₂/L. Decomposition of organic compounds and verification of the developed model of photopolymers removal was also carried out with use of alternative H₂O₂ sources i.e. CaO₂, MgO₂, and Na₂CO₃·1.5H₂O₂.

Introduction

Printed circuit boards (PCB), are plates made of insulating material with electrical connections and solder points, which are used for assembly of electronic subunits and provide electrical connections between the components. PCBs are components of virtually all electronic devices, including weapon systems and aviation equipment. PCB manufacturing is multi-stage, whereas the main processes (machining, photochemical and galvanic processing) are common to all types of printed circuit boards. Photochemical and galvanic processes are the primary source of wastewater and consumed technology baths. During photochemical processing, transferring the image of circuit layer from photographic film, glass or directly from data files containing the designed shape of the tracks on the copper foil takes place (LaDou 2009). Using the direct method (photoprint method) or indirect method (screen printing method), mosaic image is transferred from the block to the plate, wherein when using liquid or solid photopolymers, when they are exposed to UV light, the development of unexposed photopolymer is carried out in alkaline solutions of Na₂CO₃ or K₂CO₃ with the addition of measures to prevent the production of foam. The development process is run automatically (horizontally), whereas wastewater and consumed developing bath is produced. Similarly, the process of developing solder masks is done (Mika 1983, Michalski 1992, Coombs and Holden 1996). In both cases, the used solutions of Na₂CO₃ or K₂CO₃, and rinsing water from such processes are the source of alkaline wastewater. Furthermore, before an etching process, the washing of photopolymer takes place which is carried out in several percent hot solutions of NaOH or KOH with the addition of compounds preventing the formation of foam. Also this process is a source of alkaline wastewater (Mika 1983, Michalski 1992, Coombs and Holden 1996). Using photopolymers and masks developed in alkaline solution causes the formation of wastewater which contains a certain amount of Na₂CO₃, K₂CO₃, NaOH, KOH, anti-foam agents and particles of photopolymer and paint. The last can cause the COD of wastewater to go up to 15 000 mg O₂/L (Michalski 1992). The concentration of dissolved organic compounds in the consumed process solution is 5–10 g/L, which corresponds to COD in the range of 10 000–20 000 mg O₂/L. The wastewater may further contain 1–2 mg Cu/L, assuming that for the development of 0.15 m² of photopolymer, 1L of developer is consumed (Hartinger 1991). Other literature data also shows that the COD of wastewater from the process of developing and washing of photopolymers may be in the range of 2 390–25 678 mg O₂/L (Shipley 1994, Gliklich et al. 2006). Purification of this type of wastewater is
carried out by methods of ultrafiltration that is rarely used or by precipitation, which involves acidification of the wastewater by means of concentrated acid to pH 2–3, which results in precipitation of photopolymers, that shows good solubility only in an alkaline medium. Acidification causes precipitation of a sticky residue and after separation, pre-treated wastewater is further treated with activated carbon wherein COD is of a sticky residue and after separation, pre-treated wastewater is further treated with activated carbon wherein COD is reduced typically to 400 mg O₂/L. A further neutralization is carried out with suspension of Ca(OH)₂ or NaOH solution, and the remaining sludge is combusted in the equipment designed for incineration of such waste (Michalski 1992). Another method requires acidification of the wastewater with 10–15% HCl to pH < 2 and separation of the precipitated photopolymer by means of filtration. The acidic effluent is neutralized with 10% Na₂CO₃ to pH 5.5–7.0 and active carbon is added in an amount of 5–10 kg for 0.8 m³ of effluent. The wastewater is subjected to filtration and directed to the wastewater system (Grychtolik et al. 1990). Other authors point out that in the case of periodic methods of wastewater treatment and using acidification, precipitated sediments are of gelatinous structure and are very difficult to filter out. In such circumstances, using a commercially available acidic coagulant is necessary to induce acidification effect and obtain a fairly dense and easily sedimenting sludge. An additional problem in the case of using complex compounds in the process of commercially available baths are high concentrations of complexed compounds Cu(II) (70–350 mg/L), in contrast to conventional carbonate-based developers which can contain Cu(II) compounds in an amount of 0.2–0.3 mg/L (Keller and Goosey 1999). As shown by the literature data, the use of ultrafiltration for wastewater treatment is connected with formation of the concentrated retentate, which also has to be treated by acidification. The use of the acidification process is associated, as noted above, with the addition of HCl or H₂SO₄ wherein the literature data indicates a preferred pH range of 1–5. In this pH range, polymer particles precipitate and are polymerized or insoluble in the acidic environment, whereas the literature data referring to the assumed reduction of COD is not representative since during the acidification of the mixture of developer and stripper mixed in a volume ratio of 3:1 to about pH < 1, the COD values were obtained which corresponded to 25–30% of starting material value. What is more, recommended in many publications treatment with active carbon and given final COD value of 400 mg O₂/L, in many cases is not possible to be achieved (Hartinger 1991). Improving properties of the precipitated gelatinous photopolymer can be obtained by the addition of salts of Fe(III) or diatomaceous earth (Hartinger 1991, Goosey and Keller 1999). Purification of wastewater in question is therefore connected with the necessity of precipitation or distribution of dissolved photopolymers and precipitation of Cu(II) in a subsequent purification stage. In the technology of wastewater treatment containing organic substances, methods of advanced oxidation (AOP) are used for the decomposition of organic substances with different chemical structure present in water (Stasinakis 2008). The origins of the use of Fenton’s reagent, which is formed by the combination of salt solution of Fe(II) and H₂O₂ in acid environment, are associated with the work on the oxidation of organic acids carried out by H.J.H. Fenton, which showed a strong oxidizing properties of the mixture used in relation to tartaric acid (Dunford 2002). Later investigations continued by Haber and Weiss showed that Fenton’s reagent is characteristic for strong oxidizing properties with respect to many organic substances, and the appropriate oxidizing agent is free hydroxyl radical (OH•), characterized by high reactivity, due to its significant oxidizing potential (E⁰=2.31V) (Parson 2004). Fenton’s reaction is a radical reaction, and proceeds according to the equation (1):

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^•
\]  

The course of Fenton’s reaction, however, is more complex and associated with a number of occurring intermediate reactions (Barbusiński 2009). In the system, in addition to the generation of free radicals, reactions of their capture by radical scavengers may take place under certain conditions, which may be in the form of H₂O₂, Fe³⁺, HCO₃⁻, CO₃²⁻, PO₄³⁻, Br⁻ ions and others (Barbusiński 2003, Barbusiński 2004). Fe(II)/ H₂O₂/UV process, in which through the use of UV radiation the regeneration of Fe(II) takes place and a further quantity of OH• is formed, is a process of greater efficiency compared to the classical Fenton’s reaction, in which the Fe(III) ions are deposited in the system and the rate of oxidation process decreases. In the photocatalytic Fenton’s reaction, photoreduction of Fe(III) to Fe(II) occurs as well as photolysis of H₂O₂ according to the reactions (2) and (3):

\[
\text{Fe(OH)}^{2+} \xrightarrow{\text{hv}} \text{Fe}^{2+} + \text{OH}^•, \lambda < 580 \text{ nm}
\]  

\[
\text{H}_2\text{O}_2 \xrightarrow{\text{hv}} 2\text{OH}^-, \lambda < 310 \text{ nm}
\]

Reaction (3) plays a minor role in the process of generating an additional quantity of free radicals, hence H₂O₂ displays lower absorption capacity of photons regarding UV (Barbusiński 2006, Pouran et al. 2015). A number of studies have been carried out on use of alternative sources of H₂O₂ useful in the Fenton reaction, such as calcium peroxide (CaO₂), magnesium peroxide (MgO₂) and sodium percarbonate (Na₂CO₃·1,5H₂O₂), which usually turned out to be more efficient in wastewater treatment than the classic Fenton’s reagent, owing to the slow release of H₂O₂ from metal peroxides, even formation of radicals OH• and therefore their more efficient operation (Barbusiński 2006). Similar results in terms of increased efficiency of CaO₂ were obtained in the case of wastewater treatment from the manufacture of PCBs. When using an equivalent dose of CaO₂ in relation to H₂O₂, the COD of wastewater was obtained which is approx. 6% less than in the experiment in which a 30% solution of H₂O₂ was used (Thomas et al. 2016). Fenton’s reagent in the modification with sodium percarbonate was also used for treatment of wastewater from the production of PCBs and it showed that under the optimum conditions of the process, it is possible to reduce the COD of wastewater by 72.8% (Thomas et al. 2015). The combination of Fenton process and co-precipitation of ferrite was applied to the treatment of wastewater from the production of PCBs containing organic compounds and heavy metals. At pH 2, Fe(II) concentration of 500 mg/L, H₂O₂ concentration of 3000 mg/L and a reaction time of 60 min, the initial values of COD and TOC (406 mg O₂/L and 134 mg/L) were decreased to 84.9 mg O₂/L and 58.3 mg/L (Lou et al. 2009). The main parameters
that determine the performance of the Fenton’s reaction is pH, the concentration of Fe(II), H2O2 concentration, temperature and also the intensity and time of exposure in the case of UV-Fenton process. These parameters usually require optimization to achieve maximum efficiency of Fenton’s reaction for the given type of tested wastewater. Design of Experiments (DOE) and Response Surface Methodology (RSM), which are commonly used in chemistry, chemical technology and engineering environment are used for this purpose to optimize various kinds of processes (Zieliński 2007, Barbusiński and Fajkis 2011, Azami et al. 2012, Maha and Tony 2014, Cao et al. 2014). The aim of this study was to combine the previously used method of acidification (precipitation of significant amount of dissolved photopolymers due to their low solubility in an acidic medium), and UV-Fenton method (decomposition of the remaining photopolymers and the maximum reduction of COD wastewater) for treatment of wastewater from the photochemical treatment of printed circuit boards. The study was conducted using the methods of experiment planning (central compositional plan), while the response surface method was used for analysis and visualization of the obtained results, the construction of a mathematical model and determination of the optimum process conditions.

Materials and methods

Materials and chemical reagents
The study used raw industrial wastewater directly from the manufacturing plant of printed circuit boards located in Poland. Development of photopolymers and solder masks was carried out in 1% solution of Na2CO3 and K2CO3 to which concentrated H2SO4 was added during simultaneous fixation with concentrated H2SO4 on metal parts. Anti-foam agent was added containing ethoxylated fatty acids. Raw wastewater consisting of used development baths and rinsing waters flowed through pipelines from machines to storage tanks located at the wastewater treatment plant, where it was followed by averaging composition of wastewater. Samples of raw wastewater were taken from alkaline wastewater storage tank for 7 days. The sample of wastewater for testing in the laboratory scale was obtained by averaging the general sample. The collected sample of wastewater was not fixed, and the physicochemical composition of raw wastewater is shown in Table 1. The following were used for the study: FeSO4·7H2O (POCH, Poland), 30% H2O2, (CHEMPUR, Poland), and pH adjustment was performed using H2SO4 and NaOH with concentrations of 10%, and in the final phase of 1% (CHEMPUR, Poland). The studies used reagents of analytical purity and double-distilled water (CHEMPUR, Poland). As an alternative sources of H2O2 the following were used: CaO2 (Ixper®75C Calcium Peroxide, Solvay Chemicals International S.A), MgO2 (Ixper®35M Magnesium Peroxide, Solvay Chemicals International S.A.) and Na2CO3·1,5H2O2 (Sodium Percarbonate, Brenntag, Poland). The previous studies (Barbusiński 2006) confirmed a linear correlation between the dose of peroxides and the amount of formed H2O2 in pH range 1–5. It was confirmed by analysis (determination of H2O2 was made using manganometric method) that from 1 g of CaO2, MgO2 and Na2CO3·1,5H2O2 used in the study, in an acidic medium (pH 2, H2SO4) were released 342, 223 and 282 mg of H2O2, respectively. The content of H2O2 in the adopted research of CaO2, MgO2 and Na2CO3·1,5H2O2 was 34.2, 22.3 and 28.2%, respectively. The determination of H2O2 was made using manganometric method before the tests.

Analytical methods
Using the device Elmetron CPC411 with a combination electrode ERH-115 in compliance with PN-EN ISO 10523:2012, pH was determined. Turbidity was determined by nephelometry method using a turbidimeter CyberScan IR Turbidimeter TB1000 according to PN-EN ISO 7027-1:2016-09. COD was determined by spectrophotometry using closed tubes and spectrophotometers Spekol 1200 according to PN ISO 15705:2005, and TOC using high combustion temperature of 680°C with IR detection using analyzer TOC-LCPH by Shimadzu in compliance with PN-EN 1484:1999. Chlorides were determined by titration method according to PN ISO 9297:1994, and sulphates(VI) by weight method according to PN ISO 9280: 2002. Heavy metals (Cu, Ni, Sn) were determined using ISP-OES using spectrometer Optima 5300DV by Perkin Elmer according to PN-EN ISO 11885: 2009. The content of H2O2 in wastewater and in peroxides was determined manganometrically according to BN-89/6191-04.

Methodology of research
First, the effect of acidification with concentrated H2SO4 on the change of the value of COD was examined, in other words the efficiency of photopolymer removal from wastewater by means of the low solubility in an acidic medium. The study was conducted on a sample of raw wastewater with a volume of 1L, to which concentrated H2SO4 was added during simultaneous mixing. Subsequently the experiments were conducted under the influence of reagents, which resulted in the formed H2O2. The influence of NaOH on the efficiency of photopolymer removal from wastewater was also determined. The influence of the remaining photopolymers and the maximum reduction of COD wastewater was analyzed. The pH-adjusted wastewater was divided into six parts, where five of these were treated with peroxides at concentrations of 10%, 20%, 30%, 40%, 50% and 60% of the total volume. The sixth part was not subjected to peroxide treatment. The treatment was performed in an acidic medium (pH 2, H2SO4) in a high combustion temperature of 680°C with IR detection using analyzer TOC-LCPH by Shimadzu. The studies were conducted in triplicate, and the results obtained were averaged. The obtained results were further statistically analyzed using Statistica 13 software.

Table 1. Physicochemical parameters of wastewater from photochemical processes

| Parameter                  | Unit   | Value  |
|----------------------------|--------|--------|
| pH                         |        | 10.3   |
| Turbidity                  | NTU    | 910    |
| Chemical Oxygen Demand – COD| mg O2/L | 5550   |
| Total Organic Carbon – TOC | mg/L   | 2000   |
| Chlorides                  | mg/L   | 100    |
| Sulphates                  | mg/L   | 41     |
| Copper                     | mg/L   | 0.96   |
| Tin                        | mg/L   | 0.057  |
| Nickel                     | mg/L   | <0.02  |
measurement of pH. With the total pH values (1–9), wastewater was sampled in order to determine COD and sulphates(VI). Based on the carried out studies, the impact of HSO4\textsubscript{4} dosage on concentration of sulphates(VI) and COD values of wastewater under analysis was researched. Further studies were carried out using samples of wastewater pre-acidified to pH 3 and filtered through the filter fabric having a basis weight of 140–160 g/m\textsuperscript{2} in order to separate precipitated photopolymer. Studies using AOP, were carried out in photoreactor with a working volume of 580 ml, equipped with a UV lamp (11W, 254 nm, PURITEC® HNS, OSRAM®) arranged in the casing of quartz glass and then cooled by air supplied to the interior of the casing by a diaphragm pump, with a capacity of 400 L/h (JBL POSILENT® A400). Analysed wastewater was poured into the reactor and appropriate amounts of H\textsubscript{2}SO\textsubscript{4}, FeSO\textsubscript{4}·7H\textsubscript{2}O and H\textsubscript{2}O\textsubscript{2} were added. The content of photoreactor was stirred using a stirrer, and regulation of the temperature measurement of irradiated waste was performed and regulation of the flow rate of the air supply in such a way as to ensure constant temperature of the irradiated wastewater 18.0 ± 0.5°C. After completion of oxidation process, the wastewater samples were subjected to alkalisation with 30% NaOH to pH 10.2 in order to precipitate Fe(II) and Fe(III) in the form of Fe(OH)\textsubscript{2} and Fe(OH)\textsubscript{3}, and residual distribution of H\textsubscript{2}O\textsubscript{2}. Then, after filtration of wastewater through a membrane filter, residual values of H\textsubscript{2}O\textsubscript{2} and COD were determined. In view of the fact that the residual content of H\textsubscript{2}O\textsubscript{2} resulted in an increase in the COD of wastewater, the value of COD determined analytically was corrected. In order to standardize the results, appropriate correction was calculated by assuming for all the determined concentrations of H\textsubscript{2}O\textsubscript{2}, the theoretical value of the COD for the 1 mg of H\textsubscript{2}O\textsubscript{2} equal to 0.471 mg O\textsubscript{2}/L (Talini and Anderson 1992). A comparative study was carried out using CaO\textsubscript{2}, MgO\textsubscript{2} and Na\textsubscript{2}CO\textsubscript{3}·1,5H\textsubscript{2}O\textsubscript{2} as alternative sources of H\textsubscript{2}O\textsubscript{2}, at doses equivalent to the optimal dose of H\textsubscript{2}O\textsubscript{2} adopted after optimization testing.

**Experimental design**

The optimization of the process of removing dissolved photopolymers from industrial wastewater using photocatalytic Fenton’s reaction was performed using the response surface methodology (Plackett-Burman Experimental Design) and Statistica 10 software (StatSoft, Poland). In the first stage, on the basis of the previous studies conducted by the authors (Thomas et al. 2015, Thomas et al. 2016) and the literature (Lou et al. 2009), an analysis of previously obtained results was performed, in order to optimally select the type of dependent and independent parameters and input values to the independent parameters. The following parameters were taken into account: temperature (°C), stirring speed (rpm), irradiation time (min.), pH, the concentration of H\textsubscript{2}O\textsubscript{2} (g/L), and the concentration of Fe(II) (g/L). In the next stage, the experiment plan was established, i.e., the determination of the final values of the independent variables for which measurement of the dependent variable (COD) was performed and the amount of experiments established. The required number of experiments was carried out for the given values of the independent variables, measuring the value of the dependent variable (COD) in accordance with the adopted plan. In the last stage, the significance of the coefficients of the function describing the process was verified, suitability of the function to the research object was verified and a revised form of the function was provided. For the purposes of this study, the following designations for the dependent variable and independent variables were adopted:

\[
\begin{align*}
    x_1 & = \text{pH}, \\
    x_2 & = \text{concentration of Fe(II), g/L}, \\
    x_3 & = \text{concentration of H}_2\text{O}_2, \text{g/L}, \\
    Z & = \text{COD, g O}_2/\text{L}.
\end{align*}
\]

The mixing speed (250 rpm), irradiation time (60 min.) and temperature (18.0 ± 0.5°C) were adopted as constants. On the basis of preliminary research conducted by the authors, in which the smallest value of COD was obtained after 50–60 min. of photocatalytic Fenton’s reaction (Fe(II)/H\textsubscript{2}O\textsubscript{2}/UV) with UV light irradiation at a temperature of 18.0 ± 0.5°C, the safe, constant time of the process was assumed at 60 min. Moreover, appropriate range of H\textsubscript{2}O\textsubscript{2} doses was assumed, i.e., 4 to 6 g/L of wastewater and the molar ratio of Fe(II)/H\textsubscript{2}O\textsubscript{2} 0.11–0.20, corresponding to a concentration of Fe(II) in the range of 0.875–1.625 g/L. On the basis of preliminary studies, pH in the range of 1.75–2.75 was adopted for planning the experiment. Finally, using the determinations listed above, it was adopted:

\[
\begin{align*}
    x_1 & \in [1.75; 2.75], \\
    x_2 & \in [0.875; 1.625], \\
    x_3 & \in [4.0; 6.0].
\end{align*}
\]

It was assumed that these ranges will be subjected to regulation in the range <-1, +1>:

\[
\begin{align*}
    x_{(1)} & = 1.75, & x_{(0)} & = 2.25, & x_{(+1)} & = 2.75, \\
    x_{(-1)} & = 0.875, & x_{(0)} & = 1.25, & x_{(+1)} & = 1.625, \\
    x_{(+1)} & = 4.0, & x_{(0)} & = 5.0, & x_{(+1)} & = 6.0.
\end{align*}
\]

The adopted initial ranges of independent factors were expanded, which resulted from standardization in the range of \(-\alpha, \alpha\), instead of initially adopted standardization of \(-1, 1\), for which \(\alpha=1\). After the adoption of \(\alpha = 1.6818\) (on the basis of the experiment plan), the ranges of specified parameters adopted the following values in the plan:

\[
\begin{align*}
    x_{(1)} & = 1.41, & x_{(0)} & = 2.25, & x_{(+1)} & = 2.75, \\
    x_{(-1)} & = 0.619, & x_{(0)} & = 1.250, & x_{(+1)} & = 1.881, \\
    x_{(+1)} & = 3.318, & x_{(0)} & = 5.000, & x_{(+1)} & = 6.682.
\end{align*}
\]

The central compositional plan was adopted for the planning, as a result of which 16 experiments for three independent factors (pH, concentration of Fe(II) and H\textsubscript{2}O\textsubscript{2}) were obtained. The experiment plan and obtained results are shown in Table 2. The results of the model studies are shown in a graphic form by means of response surface plots, allowing for precise analysis of the effects of the independent variables (pH, concentration of Fe(II) and H\textsubscript{2}O\textsubscript{2}) on the value of the dependent variable (COD).

**Results and discussion**

**Precipitation of the photopolymers by acidification**

The test wastewater was characterized by a high turbidity (910 NTU), high pH value (10.3) and a high content of organic compounds expressed by COD and TOC values (5550 mg
O₂/L and 2000 mg/L, respectively). The content of heavy metals (mainly Cu) was less than 1 mg/L. A result of the slow dispensing of concentrated H₂SO₄ was intensive foaming of the wastewater with gas release (CO₂), due to the decomposition of Na₂CO₃ or K₂CO₃ present in wastewater. Together with the decreasing value of pH, precipitation of a large amount of a spongy sediment was observed. The volume of precipitated photopolymer (out of 1L of wastewater), after 30 min. of sedimentation amounted to approx. 400 mL. The precipitated viscous, amorphous sediment was separated and filtrated. The study showed that with decreasing pH of wastewater as a result of dispensing H₂SO₄, the decrease in the COD value occurred, whereas the lowest values were observed ranging from pH 4 (750–785 mg O₂/L). The greatest reduction in COD values was observed with pH within 5–6. At the same time, an increase in the sulphate(VI) concentration to a value between 4 920–5 160 at pH 3–4 was observed. As shown by the analysis of COD value changes, further dosing of H₂SO₄ (and consequently unfavourable increase in the concentration of sulphates(VI)) was not justified, because it did not cause further reduction in the COD value, as shown in Fig. 1. Wastewater pre-acidified to pH 3 and filtered through the filter fabric in order to separate precipitated purpose of photopolymers of COD value 716 mg O₂/L was used for the study.

**Degradation of photopolymers using UV-Fenton method**

Based on the data shown in Table 2, 16 experiments were conducted, including 2 experiments in the centre of the plan (for the middle values of parameters, 15C and 16C) and the

| The number of the experiment | Faktor 1 | Faktor 2 | Faktor 3 | Response |
|-----------------------------|---------|---------|---------|---------|
|                             | pH      | Fe(II), g/L | H₂O₂, g/L | COD, g O₂/L |
| 1                           | 1.75    | 0.875   | 4.000   | 0.335   |
| 2                           | 1.75    | 0.875   | 6.000   | 0.256   |
| 3                           | 1.75    | 1.625   | 4.000   | 0.398   |
| 4                           | 1.75    | 1.625   | 6.000   | 0.220   |
| 5                           | 2.75    | 0.875   | 4.000   | 0.258   |
| 6                           | 2.75    | 0.875   | 6.000   | 0.186   |
| 7                           | 2.75    | 1.625   | 4.000   | 0.290   |
| 8                           | 2.75    | 1.625   | 6.000   | 0.168   |
| 9                           | 1.41    | 1.250   | 5.000   | 0.502   |
| 10                          | 3.09    | 1.250   | 5.000   | 0.301   |
| 11                          | 2.25    | 0.619   | 5.000   | 0.399   |
| 12                          | 2.25    | 1.881   | 5.000   | 0.125   |
| 13                          | 2.25    | 1.250   | 3.318   | 0.199   |
| 14                          | 2.25    | 1.250   | 6.682   | 0.077   |
| 15                          | 2.25    | 1.250   | 5.000   | 0.080   |
| 16                          | 2.25    | 1.250   | 5.000   | 0.086   |

**Fig. 1.** The change of COD and sulphates value after addition of concentrated sulfuric acid
corresponding COD values for wastewater were obtained, also shown in Table 3. The lowest values of COD were obtained in experiments 14, 15 and 16, and the highest values in experiment 9. Table 3 shows the data sheet with estimates of ANOVA effects and model coefficients for the normalized values of the input quantities i.e. pH, concentration of Fe(II) and H₂O₂. The carried out statistical analysis showed four parameters which are statistically significant, i.e. pH(L), pH(Q), Fe(II)(L) as well as H₂O₂(L). For further analysis, all of the major linear-quadratic effects were adopted, but negligible linear-linear interaction effects were excluded from the model (1L i/o 2L, 2L i/o 3L and 2L i/o 3L) due to the higher value of the corrected coefficient of determination (R²adj) for a model in which these interactions are not considered. The results of the statistical analysis are shown in Table 3. The calculated coefficient of determination (R²), and corrected coefficient of determination (R²adj), adopted the values of 0.86 and 0.77, respectively, which indicated good adjustment of the model to experimental data. The value of the corrected coefficient of determination (R²adj =0.77) also indicated good adjustment of the model to other experimental data, describing the process of removing dissolved photopolymer from the wastewater originating from the production of PCBs, using photocatalytic Fenton’s reaction. A low mean square error value, i.e.: approx. 0.004 was obtained as a result of the analysis. Table 4 shows the results of the verification of the adequacy of the model using ANOVA, which also pointed to the importance of (Fisher’s) test the four major input parameters, i.e., pH, (L), pH (Q), Fe(II) (Q) and H₂O₂(L). Fig. 3 shows a Pareto graph presenting the estimates of standardized effects that have been grouped according to their absolute value. The vertical line represents the minimum values of statistically significant effects at the significance level α = 0.05. The data shown in Fig. 2 also indicate the importance of the four major factors, that is pH (Q), Fe (II) (Q), H₂O₂(L) and the pH(L) and the insignificance (or low significance) of the other two main factors, i.e., Fe(II)(L) and H₂O₂(Q). In order to visually verify the quality of the adjustment of experimental data derived from oxidation processes to the created model, the graph showing the dependency of the predicted values on values observed was plotted and presented in Fig. 3. The analysis of the data shown in Fig. 3 indicates a good adjustment of the experimental values to the predicted values, which demonstrates (in conjunction with the values of determination coefficients calculated for the model) that the created model is suitable for experimental data from the process of oxidation. Fig. 4 shows the change in COD values, depending on the concentration of

### Table 3. Analysis of the experiment with the central composite design using Statistica 10.

The sheet of estimators effects ANOVA model coefficients for the standardized values of the input values, at the significance level of 0.05 after excluding non-significant linear–linear interaction of effects

| Parameter | Effect | Standard Error | p-value | -95% confidence intervals | +95% confidence intervals | Factor | Standard Error of factor | -95% confidence intervals | +95% confidence intervals |
|-----------|--------|----------------|---------|--------------------------|--------------------------|--------|--------------------------|--------------------------|--------------------------|
| Constant Value | 0.084 | 0.042 | 0.076 | -0.011 | 0.179 | 0.084 | 0.042 | -0.011 | 0.179 |
| (1), pH, (L)* | -0.094 | 0.032 | 0.017 | -0.167 | -0.021 | -0.047 | 0.016 | -0.014 | -0.008 |
| pH, (Q)* | 0.218 | 0.039 | 0.000 | 0.130 | 0.307 | 0.109 | 0.020 | 0.065 | 0.154 |
| (2), Fe(II), g/L, (L) | -0.061 | 0.032 | 0.089 | -0.134 | 0.011 | -0.031 | 0.016 | -0.067 | 0.006 |
| Fe(II), g/L, (Q)* | 0.120 | 0.039 | 0.014 | 0.031 | 0.208 | 0.060 | 0.020 | 0.006 | 0.010 |
| (3), H₂O₂, g/L, (L)* | -0.096 | 0.032 | 0.015 | -0.169 | -0.023 | -0.048 | 0.016 | -0.085 | -0.012 |
| H₂O₂, g/L, (Q) | 0.032 | 0.039 | 0.433 | -0.056 | 0.121 | 0.016 | 0.020 | -0.028 | 0.060 |

* Significant value

### Table 4. Analysis of the experiment with the central composite design using Statistica 10.

Verification of the adequacy of the model using ANOVA at the significance level of 0.05, excluding the non-significant linear–linear interaction of effects

| Parameter | SS      | MS       | F       | p-value |
|-----------|---------|----------|---------|---------|
| (1), pH, (L)* | 0.030 | 0.030 | 8.576 | 0.017 |
| pH, (Q)* | 0.111 | 0.111 | 31.117 | 0.000 |
| (2), Fe(II), g/L, (L) | 0.013 | 0.013 | 3.633 | 0.089 |
| Fe(II), g/L, (Q)* | 0.033 | 0.033 | 9.362 | 0.014 |
| (3), H₂O₂, g/L, (L)* | 0.032 | 0.032 | 8.875 | 0.015 |
| H₂O₂, g/L, (Q) | 0.002 | 0.002 | 0.674 | 0.433 |

* Significant value, SS-predicted residual error sum of squares, MS-mean square, F-statistics
Fe(II) and the pH assuming a constant concentration of H₂O₂, 5.0 g/L. Model tests carried out showed that the lowest COD values were obtained with pH within the range 2.1–2.5 and Fe(II) concentration in the range 1.1–1.6 g/L, and assuming a constant concentration of H₂O₂, 5 g/L. The biggest (<0.1 g O₂/L) efficiency of organic compounds removal, expressed as COD was observed in the presented, optimum concentration ranges for the individual reactants. Apart from the ranges of concentrations, an increase in the value of COD was observed. The mathematical description of changes in COD values, after removal from the model of negligible interaction, as a function of the concentration of Fe(II) and pH, assuming a constant concentration of H₂O₂, 5 g/L, is represented by the equation (4):

\[
\text{COD (g/L)} = 3.277 - 2.061[pH] + 0.437[pH]^2 - 1.147[\text{Fe(II)}] + 0.426[\text{Fe(II)}]^2
\]  

(4)

COD (g/L) = 3.151 – 2.061[pH] + 0.437[pH]^2 – – 0.209[H₂O₂] + 0.016[H₂O₂]^2  

(5)

Fig. 5 shows the change in COD depending on the concentration of H₂O₂ and pH assuming constant concentration of the Fe(II) 1.25 g/L. On the basis of model tests, the smallest (<0.1 g O₂/L) COD value was observed in the range of pH 2.0–2.7 using concentration of H₂O₂ >4.6 g/L and a constant concentration of Fe(II) ions of 1.25 g/L. It was observed that lowering the concentration of H₂O₂ resulted in increase of COD value, similarly as increase or decrease of pH, and the efficiency of removal of organic compounds is dependent on the pH of the environment. The mathematical description of the changes of COD value after removal from the model of non-essential interactions, as a function of H₂O₂ concentration and pH, assuming a constant concentration of the Fe(II) 1.25 g/L, is represented by the equation (5):
Fig. 6 shows the change in COD value depending on the concentration of $\text{H}_2\text{O}_2$ and Fe(II) assuming a constant value of pH at 2.25. The smallest (<0.05 g $\text{O}_2$/L) COD values were observed at concentrations of Fe(II) ions in the range of 1.2–1.4 g/L and at a concentration of $\text{H}_2\text{O}_2$ >5.8 g/L and performing the process at a constant pH of 2.25. At a constant pH of 2.25, increasing or decreasing the concentration of Fe(II) ions in the reaction medium, and lowering the concentration of $\text{H}_2\text{O}_2$ resulted in the increase of the COD value and also the reduction of the efficiency of purification process. Fig. 6 allows us to notice that increasing the concentration of $\text{H}_2\text{O}_2$ above 7 g/L, resulted in a slight increase in COD. The model studies carried out result in the need for precise selection of the concentrations of various reagents in order to obtain the maximum effect of the removal of organic compounds. The mathematical description of the changes of COD value after removal from the model of non-essential interactions as a function of the concentration of $\text{H}_2\text{O}_2$ and Fe(II), and assuming a constant pH of 2.25, is represented by the equation (6):

$$\text{COD (g/L)} = 1.494 – 1.147[\text{Fe(II)}] + 0.426[\text{Fe(II)}]^2 – 0.209[\text{H}_2\text{O}_2] + 0.016[\text{H}_2\text{O}_2]^2$$  (6)

Table 5 shows critical values for the model of changes of the COD value, i.e., pH, concentration of Fe(II) ions and $\text{H}_2\text{O}_2$ concentration. The analysis carried out showed that the adopted critical values, i.e., pH of 2.36, concentration of Fe(II) ions 1.35 g/L and concentration of $\text{H}_2\text{O}_2$ 6.49 g/L correspond to the approximated value of the COD 39 mg $\text{O}_2$/L. Therefore, carrying out the oxidation process using the critical pH values and the critical concentrations of the various reagents for 60 min. irradiation with a 11W UV lamp and at a temperature of 18.0 ± 0.5°C at a stirring rate of 250 rpm, should result in obtaining the treated wastewater for which COD should be 39 mg $\text{O}_2$/L. Table 6 shows the values of determination
coefficients for the full model of removing organic compounds expressed as COD, taking into account all the major linear-square effects and linear-linear interaction effects (1L i/o 2L, 1L i/o 3L and 2L i/o 3L). To determine the approximating polynomial for the experimental data presented in Table 3, a general linear model (GLM) was adopted using the results adjusted for the intergroup system, wherein it was assumed that a polynomial II is suitable to describe the process of removing organic compounds present in the wastewater from PCB production using the Fe(II)/H₂O₂/UV system. Approximating polynomial was obtained in the form of ‘prediction equation’, which describes the change of COD value as a function of all independent factors, i.e., pH, the concentration of Fe(II) and H₂O₂ concentration, is represented by the equation (7):

\[
\text{COD (g/L) = 3.762} - 2.130[pH] + 0.437[pH]^2 - 0.879[\text{Fe(II)}] + 0.426[\text{Fe(II)}]^2 - 0.182[H_2O_2] + 0.016[pH][H_2O_2] - 0.050[\text{Fe(II)}][H_2O_2]
\]  

(7)

The calculated value of the coefficient of determination for the full model (R²=0.88) indicates a very good adjustment of the model to experimental data, while the value of the corrected coefficient of determination (R²adj=0.69) indicates a good adjustment of the model approximating the equation to the set of other experimental data from the oxidation of organic compounds in the wastewater from the production of photochemical PCB by means of Fe(II)/H₂O₂/UV system.

**Comparative study using alternative sources of hydrogen peroxide**

Comparative studies of the removal of organic compounds from the wastewater from the production of photochemical PCB, subjected to prior acidification with concentrated H₂SO₄ to pH 3 to precipitate the dissolved photopolymers were also carried out using alternative sources of H₂O₂. At the same time, the developed model of COD removal, taking critical values (Table 5) of the process, i.e., pH of 2.36, concentration of Fe(II) 1.35 g/L and concentration of H₂O₂ 6.49 g/L was subjected to experimental verification. The adopted values correspond to the projected model of COD value of 39 mg O₂/L. In comparative studies, instead of 6.49 g H₂O₂, an equivalent amounts of CaO₂, MgO₂, and Na₂CO₃·1.5H₂O₂, were used, from which 6.49 g of H₂O₂ was released due to reaction with water. In the course of the studies it has been observed that the use of suitable peroxide or sodium percarbonate instead of H₂O₂ necessitates the need to correct the pH of the wastewater to a value of 2.36 due to the increase of the pH of wastewater after addition of peroxides. During the calculation of equivalent doses of 6.49 g H₂O₂, the purity of the technical products used and the results of the manganometric analysis were taken into account. The results of the comparative tests are shown in Table 7. Based on the carried out research, in all cases wastewater was obtained which was characterized by a low COD value i.e., in the range of 55–66 mg O₂/L, but these values were not consistent with the value calculated from the model, i.e., 39 mg O₂/L. In the case of adopting H₂O₂, the obtained value was approx. 69%
higher than the value calculated from the model. In the case of using metal peroxides and sodium percarbonate, despite the fact that lower COD values were obtained, i.e., in the range of 55–58 mg O₂/L, yet they could be due to a dilution of the sample wastewater subjected to oxidation as a result of the necessary correction of pH by means of concentrated H₂SO₄. The final COD values, shown in Table 7, were also influenced by the result of the determination of the residual H₂O₂ in the sample of wastewater after oxidation. The procedure of H₂O₂ determination required prior to neutralizing the sample to pH 10.2 had an impact on the accuracy of the determination of COD by means of dichromate method. In addition, the very high contents of H₂O₂, which in connection with the value of the adjusted coefficient of determination and its correction for the full model showed a good adjustment of approximated model equation to experimental data set derived from the oxidation of organic compounds in wastewater from the photochemical production of PCB using Fe(II)/H₂O₂/UV system. Model studies made it possible to optimize the process and calculate the critical values of pH, concentrations of Fe(II) and H₂O₂ for the approximated from the model, the minimum value of COD 39 mg O₂/L. Verification of the model adjustment to the other set of experimental data derived from the oxidation process using photocatalytic Fenton’s reaction was performed experimentally well as using alternative sources of H₂O₂. As a result of performed studies, the ideal correspondence of the experimental values of COD with the COD value calculated from the model (respectively – the minimum experimental value of 55 mg O₂/L and 39 mg O₂/L), has not been obtained. Due to the impact of several factors on the final result of the determination of COD value on the basis of the obtained difference in the results and in connection with the value of the adjusted coefficient of determination (0.69), it can be concluded that the adjustment of the model was valid for the experimental data obtained. After taking into account the impact of indirect determinations on the result of COD determination and a small dilution of 1 litre wastewater sample during the process, the obtained difference of results was acceptable. The proposed wastewater treatment method enabled obtaining purified wastewater with a low content of organic compounds.

### Conclusion

The carried out studies showed the possibility of using the method of response surface for optimization process of removing organic compounds in the form of dissolved photopolymers in wastewater from the photochemical treatment of PCB using the UV-Fenton method. The use of Fe(II)/H₂O₂/UV system allowed for further reduction of COD values to less than 100 mg O₂/L. Finally, the results obtained at this stage of the research made it possible to confirm the possibility of removing organic compounds from alkaline wastewater using a combination of two successive processes, i.e.: acidification with concentrated H₂SO₄ in a first phase and applying the photocatalytic Fenton’s reaction in the second phase. Such a method for removing organic compounds reduces the amount of wastewater by approx. 87% (the first stage) and approx. 98% (after the two processes). Model tests and the obtained results of experimental studies allowed us to adjust a mathematical model which described the impact of all the independent factors on the process of COD removal from alkaline wastewater. The calculated initial values of the coefficient of determination and its correction for the full model showed a good adjustment of approximated model equation to experimental data set derived from the oxidation of organic compounds in wastewater from the photochemical production of PCB using Fe(II)/H₂O₂/UV system. Model studies made it possible to optimize the process and calculate the critical values of pH, concentrations of Fe(II) and H₂O₂ for the approximated from the model, the minimum value of COD 39 mg O₂/L. Verification of the model adjustment to the other set of experimental data derived from the oxidation process using photocatalytic Fenton’s reaction was performed experimentally well as using alternative sources of H₂O₂. As a result of performed studies, the ideal correspondence of the experimental values of COD with the COD value calculated from the model (respectively – the minimum experimental value of 55 mg O₂/L and 39 mg O₂/L), has not been obtained. Due to the impact of several factors on the final result of the determination of COD value on the basis of the obtained difference in the results and in connection with the value of the adjusted coefficient of determination (0.69), it can be concluded that the adjustment of the model was valid for the experimental data obtained. After taking into account the impact of indirect determinations on the result of COD determination and a small dilution of 1 litre wastewater sample during the process, the obtained difference of results was acceptable. The proposed wastewater treatment method enabled obtaining purified wastewater with a low content of organic compounds.

### References

Azami, M., Bahram, M., Nouri, S. & Naseri, A. (2012). A central composite design for the optimization of the removal of the azo dye, methyl orange, from wastewater using the Fenton reaction, *Journal of the Serbian Chemical Society*, 77, 2, pp. 235–246.

Barbusiński, K. (2009). Fenton Reaction – controversy concerning the chemistry, *Ecological Chemistry and Engineering S*, 16, 3, pp. 347–358.

Barbusiński, K. (2004). The intensification of wastewater treatment and stabilization of excess sludge using Fenton’s reagent, *Zeszyty Naukowe Politechniki Śląskiej*, Gliwice. (in Polish)

### Table 6. The value of the determination coefficient (R) for the full model – a method of GLM (General Linear Model)

| Parameter | Test SS for the full model relative to the SS for the rest |
|-----------|----------------------------------------------------------|
|           | R² | R² adj | SS Model | MS Model | SS Rest | MS Rest | F | p-value |
| COD, g O₂/L | 0.877 | 0.693 | 0.205 | 0.023 | 0.029 | 0.005 | 4.770 | 0.035 |

SS – predicted residual error sum of squares, MS – mean square, F – statistics

### Table 7. The results of comparative study using alternative sources of hydrogen peroxide

| The type of source of H₂O₂ | The initial concentration COD mg O₂/L | The final concentration COD mg O₂/L |
|---------------------------|--------------------------------------|-----------------------------------|
| 35% H₂O₂, Hydrogen peroxide | 718 | 66 |
| CaO₂, lxper® 75C Calcium Peroxide | 718 | 58 |
| MgO₂, lxper® 35M Magnesium Peroxide | 718 | 57 |
| Na₂CO₃·1.5H₂O₂, Sodium percarbonate | 718 | 55 |
Barbusiński, K. & Majewski, M. (2003). Discoloration of azo dye Acid Red 18 by Fenton reagent in the presence of iron powder, *Polish Journal of Environmental Studies*, 12, 2, pp. 151–155.

Barbusiński, K. (2006). Modification of the Fenton reaction using calcium and magnesium peroxides, *Wydawnictwo GIG*, Katowice 2006. (in Polish)

Barbusiński, K. & Fajkis, S. (2011). Optimization of the Fenton oxidation of wastewater generated by rape oil soapstock splitting, *Environmental Progress & Sustainable Energy*, 30, 4, pp. 620–631.

Cao, X., Lou, H., Wei, W. & Zhu, L. (2014). Treatment of tetrahydrofuran wastewater by the Fenton process: response surface methodology as an optimization tool, *Water Science and Technology*, 69, 5, pp. 1080–1087.

Coombs, C.F. & Holden, H.T. (1996). *Printed Circuits Handbook*. Fourth Edition, McGraw-Hill, New York 1996.

Dunford, H.B. (2002). Oxidations of iron (II)/(III) by hydrogen peroxide: from aquo to enzyme, *Coordination Chemistry Reviews*, 233–234, pp. 311–318.

LaDou, J. (2006). Printed circuit board industry, *International Journal of Hygiene and Environmental Health*, 209, pp. 211–219.

Lou, J-Ch., Huang, Y-J. & Han, J-Y. (2009). Treatment of printed circuit board industrial wastewater by Ferrite process combined with Fenton method, *Journal of Hazardous Materials*, 170, 2, 3, pp. 620–626.

Maha, Z.B. & Tony, A. (2014). Experimental design of photo-Fenton reactions for the treatment of car wash wastewater effluents by Response Surface Methodological Analysis, *Advances in Environmental Chemistry*, pp. 1–8.

Michalski, J. (1992). Technology and assembly of printed circuit boards, *Wydawnictwo Naukowo-Techniczne*, Warszawa 1992. (in Polish)

Mika, M. (1983). *Printed circuits board, Wydawnictwo Komunikacji i Łączności*, Warszawa 1983. (in Polish)

Hartinger, L. (1991). *Handbook of wastewater and recycling technology for the metalworking industry*, Carl Hanser Verlag, Muenchen, Wien 1991. (in German)

Gliklich, T., Gliklich, B., Pęciak, G., Stohryn, T. & Kapko, T. (2006). The project of wastewater treatment plant, pp. 1–15. INSTER Tychy 2006. (in Polish).

Shipley Company LLC (1994). Procedure WT 94-5 wastewater treatment of spent sodium hydroxide stripper for use with PEPR2400 PHOTORESIST, pp. 1–3.

Grychtolik, E., Gryglewicz, A., Gryglewicz, T., Sladki, A. & Kuryatto, M. (1990). *Wastewater treatment RISTON III*, Zakład Elektroniki Górniczej, Tychy, pp. 1–8. (in Polish)

Keller, R. & Goosney, M. (1999). *The printed circuit board industry an environmental best practice guide*, PCIF, London 1999.

Parson, S. (2004). *Advanced Oxidation Processes for Water and Wastewater Treatment*, IWA Publishing, London 2004.

PN-EN ISO 10523:2012 Water Quality. Determination of pH. PN-EN ISO 7027-1:2016-09 Water Quality. Determination of turbidity. PN-ISO 15705:2005 Water Quality. Determination of the Chemical Oxygen Demand Index. Small-scale. Sealed-tube Method.

PN-EN 1484:1999 Water Analysis. Guidelines for the determination of Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC).

PN ISO 9297:1994 Water Quality. Determination of Chloride. Silver nitrate titration with chromate indicator (Mohr’s method).

PN ISO 9280: 2002 Water Quality. Determination of sulfate. Gravimetric method using barium chloride.

PN-EN ISO 11885:2007 Water Quality. Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES).

BN-89/6191-04 Reagents. Hydrogen peroxide 30% solution.

Pouran, S.R., Azz, A.R.A. & Daud, W.M.A.W. (2015). Review on the main advances in photo-Fenton oxidation system for recalcitrant wastewaters, *Journal of Industrial and Engineering Chemistry*, 21, pp. 53–69.

Stasinakia, A.S. (2008). Use of selected advanced oxidation processes (AOPs) for wastewater treatment – a mini review, *Global NEST Journal*, 10, 3, pp. 376–385.

Thomas, M., Bialecka, B. & Zdebk, D. (2016). Treatment of wastewater from the photochemical production of printed circuit boards by using Fenton reagent after addition of calcium percarbonate, *Przemysł Chemiczny*, 11, pp. 134–139. (in Polish)

Thomas, M., Bialecka, B. & Zdebik, D (2015). Treatment of wastewater from the photochemical production of printed circuit boards by using Fenton reagent after addition of disodium percarbonate, *Przemysł Chemiczny*, 94, 6, pp. 924–929. (in Polish)

Talinli, I. & Anderson, G.K., (1992). Interference of hydrogen peroxide on the standard COD test, *Water Research*, 26, 1, pp. 107–110.  

Zieliński, R. (2007). Application of experimental design method in optimization of glucose-based surfactant production process, *Towaroznawcze Problemy Jakości*, 4, pp. 73–80.

Usuwanie związków organicznych ze ścieków pochodzących z produkcji obwodów drukowanych metodą UV-Fentona

**Streszczenie:** Przedstawiamy możliwość usuwania związków organicznych ze ścieków pochodzących z photochemicznej produkcji obwodów drukowanych przez zastosowanie w pierwszym etapie zakwaszania ścieków i usuwaniem wytrąconego fotopolimeru, a w drugim etapie metody UV-Fentona. Do optymalizacji procesu pogłębnionego utleniania zastosowano metodę powierzchni odpowiedzi dla trzech czynników niezależnych, tj.: pH, stężenia Fe(II) oraz stężenia H₂O₂. Zastosowanie zotyzmalizowanych wartości poszczególnych parametrów w procesie oczyszczania ścieków spowodowało zmniejszenie stężeń związki organicznych oznaczanych jako COD o ok. 87% w pierwszym etapie oraz ok. 98% po zastosowaniu obu procesów. Wytrącanie oraz rozkład związków organicznych związane były ze zmniejszeniem się COD ścieków do poniżej 100 mg O₂/L, przy początkowej wartości wynoszącej 5550 mg O₂/L. Rozkład związków organicznych oraz weryfikację opracowanego modelu procesu usuwania fotopolimerów przeprowadzono także z zastosowaniem alternatywnych źródeł H₂O₂, tj.: CaO₂, MgO₂, i Na₂CO₃·1,5H₂O₂.