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

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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 H_2O_2 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 O_2/L whereas the initial value was 5550 mg O_2/L. Decomposition of organic compounds and verification of the developed model of photopolymers removal was also carried out with use of alternative H_2O_2 sources i.e. CaO_2, MgO_2, and $Na_2CO_3 \cdot 1,5H_2O_2$.

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 Na_2CO_3 or K_2CO_3 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
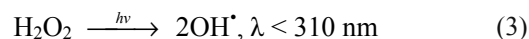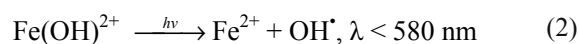
produced. Similarly, the process of developing solder masks is done (Mika 1983, Michalski 1992, Coombs and Holden 1996). In both cases, the used solutions of Na_2CO_3 or K_2CO_3 and rinsing water from such processes are the source of alkaline wastewater. Furthermore, before an etching process, the washing 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 Na_2CO_3, K_2CO_3, 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 O_2/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 O_2/L. The wastewater may further contain 1–2 mg Cu/L, assuming that for the development of 0.15 m^2 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 O_2/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 reduced typically to 400 mg O_2/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% Na_2CO_3 to pH 5.5–7.0 and active carbon is added in an amount of 5–10 kg for 0.8 m^3 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 H_2SO_4, wherein the literature data indicates a preferred pH range of 1–5. In this pH range, polymer particles precipitate andare 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 O_2/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 H_2O_2 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 (E^0=2.31V) (Parson 2004). Fenton's reaction is a radical reaction, and proceeds according to the equation (1):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^· \qquad (1)$$

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 H_3O^+, Fe^{2+}, HCO_3^-, CO_3^{2-}, PO_3^{2-}, Br ions and others (Barbusiński 2003, Barbusiński 2004). Fe(II)/H_2O_2/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 H_2O_2 according to the reactions (2) and (3):

$$Fe(OH)^{2+} \xrightarrow{hv} Fe^{2+} + OH^·, \lambda < 580 \text{ nm} \qquad (2)$$

$$H_2O_2 \xrightarrow{hv} 2OH^·, \lambda < 310 \text{ nm} \qquad (3)$$

Reaction (3) plays a minor role in the process of generating an additional quantity of free radicals, hence H_2O_2 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 H_2O_2 useful in the Fenton reaction, such as calcium peroxide (CaO_2), magnesium peroxide (MgO_2) and sodium percarbonate ($Na_2CO_3 \cdot 1,5H_2O_2$), which usually turned out to be more efficient in wastewater treatment than the classic Fenton's reagent, owing to the slow release of H_2O_2 from metal peroxides, even formation of radicals OH· and therefore their more efficient operation (Barbusiński 2006). Similar results in terms of increased efficiency of CaO_2 were obtained in the case of wastewater treatment from the manufacture of PCBs. When using an equivalent dose of CaO_2 in relation to H_2O_2, the COD of wastewater was obtained which is approx. 6% less than in the experiment in which a 30% solution of H_2O_2 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, H_2O_2 concentration of 3000 mg/L and a reaction time of 60 min, the initial values of COD and TOC (406 mg O_2/L and 134 mg/L) were decreased to 84.9 mg O_2/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), H_2O_2 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 Na_2CO_3 and K_2CO_3 to which anti-foam agent was added containing ethoxylated fatty acids. Raw wastewater consisting of used development baths and rinsing waters flew 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: $FeSO_4 \cdot 7H_2O$ (POCH, Poland), 30% H_2O_2, (CHEMPUR, Poland), and pH adjustment was performed using H_2SO_4 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 H_2O_2 the following were used: CaO_2 (Ixper®75C Calcium Peroxide, Solvay Chemicals International S.A), MgO_2 (Ixper®35M Magnesium Peroxide, Solvay Chemicals International S.A.) and $Na_2CO_3 \cdot 1,5H_2O_2$ (Sodium Percarbonate, Brenntag, Poland). The previous studies (Barbusiński 2006) confirmed a linear correlation between the dose of peroxides and the amount of formed H_2O_2 in pH range 1–5. It was confirmed by analysis (determination of H_2O_2 was made using manganometric method) that from 1 g of CaO_2, MgO_2 and $Na_2CO_3 \cdot 1,5H_2O_2$ used in the study, in an acidic medium (pH 2, H_2SO_4) was released 342, 223 and 282 mg of H_2O_2 respectively. The content of H_2O_2 in the adopted research of CaO_2, MgO_2 and $Na_2CO_3 \cdot 1,5H_2O_2$, was 34.2, 22.3 and 28.2%, respectively. The determination of H_2O_2 was made using manganometric method before the tests.

Analytical methods

Using the device Elmetron CPC411 with a combination electrode ERH-11S 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 680ºC with IR detection using analyzer TOC-L$_{CPH}$ 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 H_2O_2 in wastewater and in peroxides was determined manganometrically according to BN-89/6191-04.

Methodology of research

First, the effect of acidification with concentrated H_2SO_4 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 H_2SO_4 was added during simultaneous

Table 1. Physicochemical parameters of wastewater from photochemical processes

Parameter	Unit	Value
pH	–	10.3
Turbidity	NTU	910
Chemical Oxygen Demand – COD	mg O_2/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 H_2SO_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/m² 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_2SO_4, $FeSO_4 \cdot 7H_2O$ and H_2O_2 were added. The content of photoreactor was stirred at a constant speed of 250 rpm. Simultaneously, continuous 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 $Fe(OH)_2$ and $Fe(OH)_3$ and residual distribution of H_2O_2. Then, after filtration of wastewater through a membrane filter, residual values of H_2O_2 and COD were determined. In view of the fact that the residual content of H_2O_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_2O_2, the theoretical value of the COD for the 1 mg of H_2O_2 equal to 0.471 mg O_2/L (Talinli and Anderson 1992). A comparative study was carried out using CaO_2, MgO_2 and $Na_2CO_3 \cdot 1,5H_2O_2$ as alternative sources of H_2O_2, at doses equivalent to the optimal dose of H_2O_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_2O_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:

x_1 – pH,
x_2 – concentration of Fe(II), g/L,
x_3 – concentration of H_2O_2, g/L,
Z_1 – COD, g O_2/L.

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_2O_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_2O_2 doses was assumed, i.e., 4 to 6 g/L of wastewater and the molar ratio of Fe(II)/H_2O_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:

$$x_1 \in <1.75; 2.75>,$$
$$x_2 \in <0.875; 1.625>, \quad (1)$$
$$x_3 \in <4.0; 6.0>$$

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

$$
\begin{array}{lll}
x_{1(-1)} = 1.75 & x_{1(0)} = 2.25 & x_{1(+1)} = 2.75, \\
x_{2(-1)} = 0.875 & x_{2(0)} = 1.25 & x_{2(+1)} = 1.625, \quad (2) \\
x_{3(-1)} = 4.0 & x_{3(0)} = 5.0 & x_{1(+1)} = 6.0.
\end{array}
$$

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

$$
\begin{array}{lll}
x_{1(-\alpha)} = 1.41 & x_{1(0)} = 2.25 & x_{1(+\alpha)} = 2.75; \\
x_{2(-\alpha)} = 0.619 & x_{2(0)} = 1.250 & x_{2(+\alpha)} = 1.881; \quad (3) \\
x_{3(-\alpha)} = 3.318 & x_{3(0)} = 5.000 & x_{1(+\alpha)} = 6.682
\end{array}
$$

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_2O_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_2O_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

O_2/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 H_2SO_4 was intensive foaming of the wastewater with gas release (CO_2), due to the decomposition of Na_2CO_3 or K_2CO_3 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 H_2SO_4, the decrease in the COD value occurred, whereas the lowest values were observed ranging from pH 4 (750–785 mg O_2/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 H_2SO_4 (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 O_2/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

Table 2. Experimental conditions and results of central composite design

| The number of the experiment	Variables			Response
	Faktor 1	Faktor 2	Faktor 3	
	pH	Fe(II), g/L	H_2O_2, g/L	COD, g O_2/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
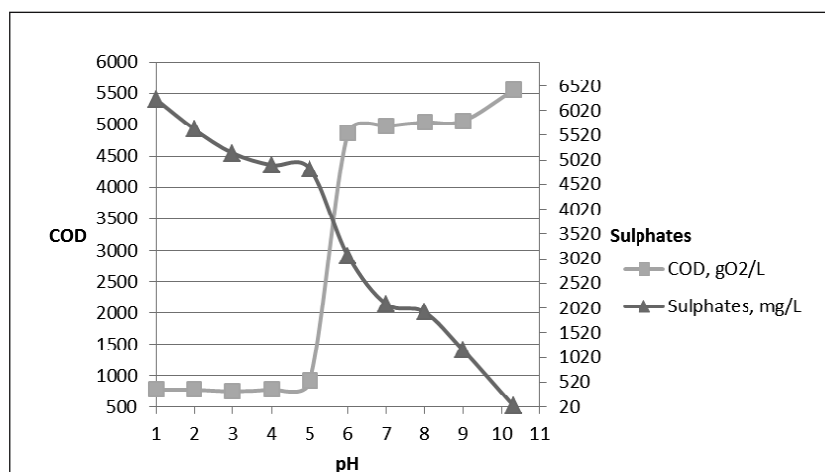
Fig. 1. The change of COD and sulphates value after addition of concentrated sulfuric acid

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 H_2O_2. The carried out statistical analysis showed four parameters which are statistically significant, i.e. pH(L), pH(Q), Fe(II)(L) as well as H_2O_2(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, 1L i/o 3L and 2L i/o 3L) due to the higher value of the corrected coefficient of determination (R^2_{adj}) 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 (R^2), and corrected coefficient of determination (R^2_{adj}), 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 (R^2_{adj}=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 H_2O_2(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 $\alpha = 0.05$. The data shown in Fig. 2 also indicate the importance of the four major factors, that is pH (Q), Fe (II) (Q), H_2O_2(L) and the pH(L) and the insignificance (or low significance) of the other two main factors, i.e., Fe(II)(L) and H_2O_2(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	The evaluation of the effects, COD, g O_2/L, R^2=0.8633, R^2_{adj}=0.7722, 3 parameter, 1 block, 16 experiments, MS=0.0036								
	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	-0.084	-0.011
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	0.016	0.104
(3), H_2O_2, g/L, (L)*	-0.096	0.032	0.015	-0.169	-0.023	-0.048	0.016	-0.085	-0.012
H_2O_2, 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	The evaluation of the effects, COD, g O_2/L, R^2=0.8633, R^2_{adj}=0.7722, 3 parameter, 1 block, 16 experiments, MS=0.0036			
	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), H_2O_2, g/L, (L)*	0.032	0.032	8.875	0.015
H_2O_2, 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 H_2O_2 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 H_2O_2 5 g/L. The biggest (<0.1 gO_2/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 H_2O_2 5 g/L, is represented by the equation (4):

$$COD\ (g/L) = 3.277 - 2.061[pH] + 0.437[pH]^2 - 1.147[Fe(II)] + 0.426[Fe(II)]^2 \quad (4)$$

$$COD\ (g/L) = 3.151 - 2.061[pH] + 0.437[pH]^2 - 0.209[H_2O_2] + 0.016[H_2O_2]^2 \quad (5)$$

Fig. 5 shows the change in COD depending on the concentration of H_2O_2 and pH assuming constant concentration of the Fe(II) 1.25 g/L. On the basis of model tests, the smallest (<0.1 gO_2/L) COD value was observed in the range of pH 2.0–2.7 using concentration of H_2O_2 >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 H_2O_2 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 H_2O_2 concentration and pH, assuming a constant concentration of the Fe(II) 1.25 g/L, is represented by the equation (5):
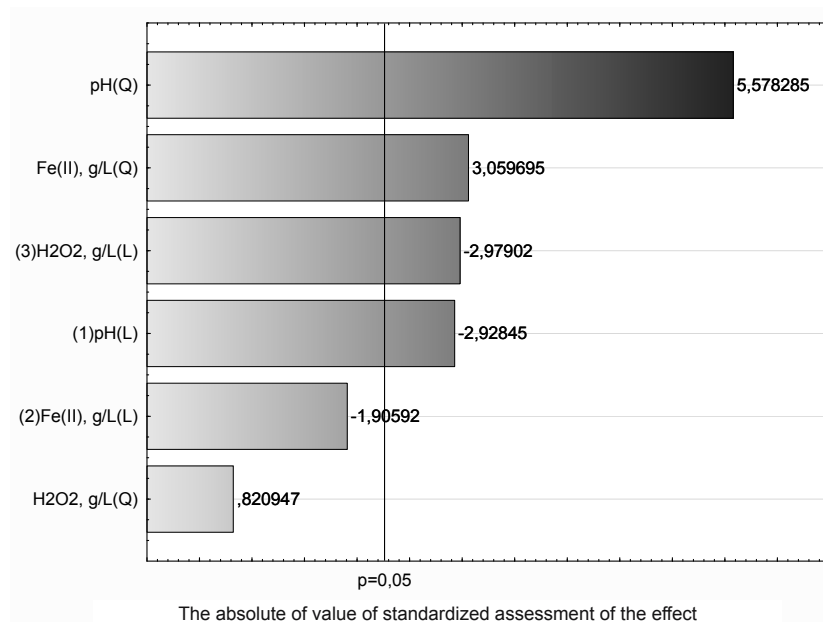

Fig. 2. Pareto chart – the absolute value of standardized assessment of the effects (COD, g/L, 3 value, 1 block, 16 experiments, MS=0.0036)
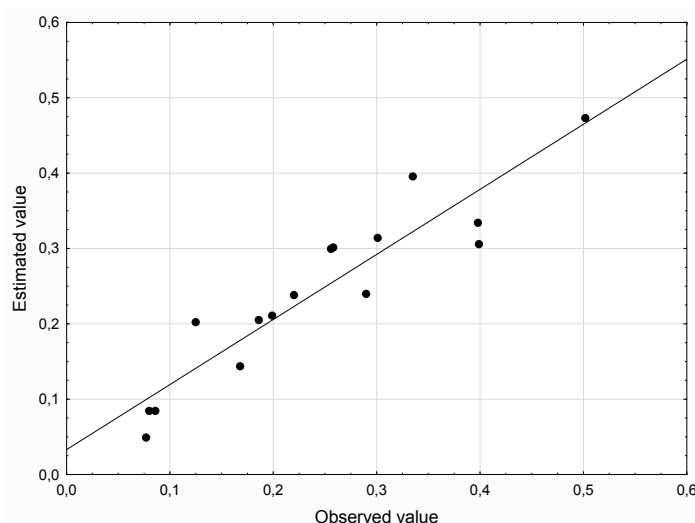

Fig. 3. Estimated vs. observed values plots (COD, g/L, 3 value, 1 block, 16 experiments, MS=0.0036)

Fig. 6 shows the change in COD value depending on the concentration of H_2O_2 and Fe(II) assuming a constant value of pH at 2.25. The smallest (<0.05 gO_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 H_2O_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 H_2O_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 H_2O_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 H_2O_2 and Fe(II), and

assuming a constant pH of 2.25, is represented by the equation (6):

$$COD\ (g/L) = 1.494 - 1.147[Fe(II)] + 0.426[Fe(II)]^2 - 0.209[H_2O_2] + 0.016[H_2O_2]^2 \quad (6)$$

Table 5 shows critical values for the model of changes of the COD value, i.e., pH, concentration of Fe(II) ions and H_2O_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 H_2O_2 6.49 g/L correspond to the approximated value of the COD 39 mg 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 $18.0 \pm 0.5°C$ at a stirring rate of 250 rpm, should result in obtaining the treated wastewater for which COD should be 39 mg O_2/L. Table 6 shows the values of determination
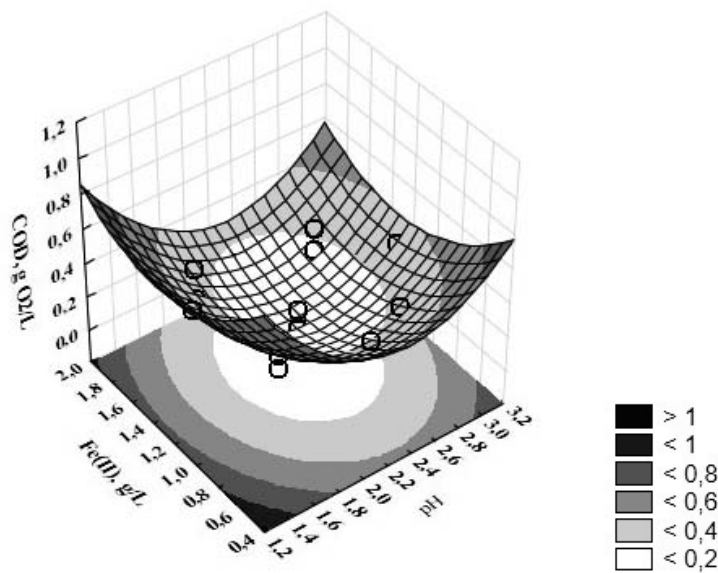

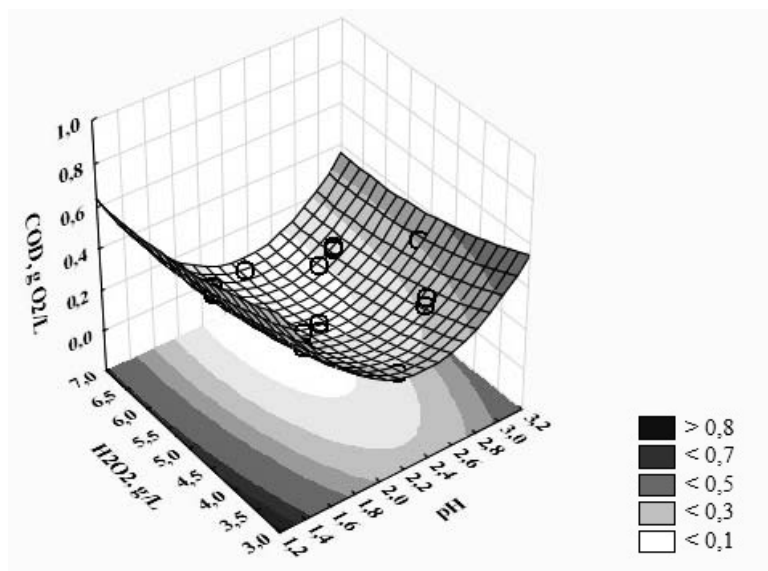**Fig. 4.** Response surface plot for COD removal (g O_2/L) with respect to pH and Fe(II)

Fig. 5. Response surface plot for COD removal (g O_2/L) with respect to pH and H_2O_2

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)/H$_2$O$_2$/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 H$_2$O$_2$ concentration, is represented by the equation (7):

$$COD\ (g/L) = 3.762 - 2.130[pH] + 0.437[pH]^2 - \\ - 0.879[Fe(II)] + 0.426[Fe(II)]^2 - 0.182[H_2O_2] + \\ + 0.016[H_2O_2]^2 - 0.009[pH][Fe(II)] + \\ + 0.016[pH][H_2O_2] - 0.050[Fe(II)][H_2O_2]$$

(7)

The calculated value of the coefficient of determination for the full model (R^2=0.88) indicates a very good adjustment of the model to experimental data, while the value of the corrected coefficient of determination (R$^2_{adj}$=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)/H$_2$O$_2$/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 H$_2$SO$_4$ to pH 3 to precipitate the dissolved photopolymers were also carried out using alternative sources of H$_2$O$_2$. 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 H$_2$O$_2$ 6.49 g/L was subjected to experimental verification. The adopted values correspond to the projected model of COD value of 39 mg O$_2$/L. In comparative studies, instead of 6.49 g H$_2$O$_2$, an equivalent amounts of CaO$_2$, MgO$_2$, and Na$_2$CO$_3$·1,5H$_2$O$_2$, were used, from which 6.49 g of H$_2$O$_2$ 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 H$_2$O$_2$ 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 H$_2$O$_2$, 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 O$_2$/L, but these values were not consistent with the value calculated from the model, i.e., 39 mg O$_2$/L. In the case of adopting H$_2$O$_2$, the obtained value was approx. 69%
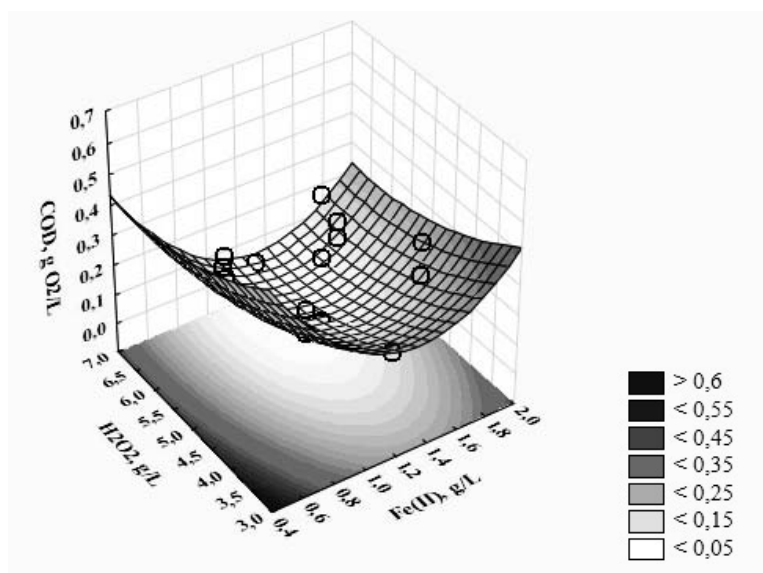

Fig. 6. Response surface plot for COD removal (g O$_2$/L) with respect to Fe(II) and H$_2$O$_2$

Table 5. The critical values (pH, Fe(II), H$_2$O$_2$) for the approximated value of COD (0.039 g O$_2$/L), excluding the non-significant linear-linear interaction of effects

Parameter	The critical values for COD, g O$_2$/L, estimated value for COD = 0.039		
	The measured minimum value	The critical value	The measured maximum value
pH	1.41	2.36	3.09
Fe(II), g/L	0.619	1.346	1.881
H$_2$O$_2$, g/L	3.318	6.494	6.682

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							
	R^2	R^2_{adj}	SS Model	MS Model	SS Rest	MS Rest	F	p-value
COD, g O_2/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 H_2O_2	The initial concentration COD mg O_2/L	The final concentration COD mg O_2/L
35% H_2O_2, Hydrogen peroxide	718	66
CaO_2, Ixper® 75C Calcium Peroxide	718	58
MgO_2, Ixper® 35M Magnesium Peroxide	718	57
$Na_2CO_3 \cdot 1.5H_2O_2$, Sodium percarbonate	718	55

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 O_2/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 H_2SO_4. The final COD values, shown in Table 7, were also influenced by the result of the determination of the residual H_2O_2 in the sample of wastewater after oxidation. The procedure of H_2O_2 determination required prior to neutralizing the sample to pH of 10.2 had an impact on the accuracy of the determination of H_2O_2 and consequently on the final COD value (the determined COD value was subtracted by the correction regarding the contents of H_2O_2, which influenced the overestimation of the results obtained by dichromate method). In addition, the very determination of COD by means of dichromate method was associated with expanded uncertainty of ± 15% for the COD≥50 mg O_2/L. Based on the obtained results and taking into account the limitations of the analytical methods applied, it cannot be clearly inferred that there is greater photocatalytic efficiency of Fenton's reaction with regard to the treated wastewater when metal peroxides and sodium percarbonate are used.

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)/H$_2$O$_2$/UV system allowed for further reduction of COD values to less than 100 mg O$_2$/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 H$_2$SO$_4$ 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)/H$_2$O$_2$/UV system. Model studies made it possible to optimize the process and calculate the critical values of pH, concentrations of Fe(II) and H$_2$O$_2$ for the approximated from the model, the minimum value of COD 39 mg O$_2$/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 H$_2$O$_2$. 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 O$_2$/L and 39 mg O$_2$/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.

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

Streszczenie: Przedstawiono możliwość usuwania związków organicznych ze ścieków pochodzących z fotochemicznej produkcji obwodów drukowanych przez zastosowanie w pierwszym etapie zakwaszania ścieków i usuwaniem wytrąconego fotopolimeru, a w drugim etapie metody UV-Fentona. Do optymalizacji procesu pogłębionego utleniania zastosowano metodę powierzchni odpowiedzi dla trzech czynników niezależnych, tj.: pH, stężenia Fe(II) oraz stężenia H_2O_2. Zastosowanie zoptymalizowanych wartości poszczególnych parametrów w procesie oczyszczania ścieków spowodowało zmniejszenie stężania związków 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 O_2/L, przy początkowej wartości wynoszącej 5550 mg O_2/L. Rozkład związków organicznych oraz weryfikację opracowanego modelu procesu usuwania fotopolimerów przeprowadzono także z zastosowaniem alternatywnych źródeł H_2O_2, tj.: CaO_2, MgO_2, i $Na_2CO_3 \cdot 1,5H_2O_2$.