

# Application of UV, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>/UV, Fe(II)/H<sub>2</sub>O<sub>2</sub> and Fe(II)/H<sub>2</sub>O<sub>2</sub>/UV process for oxidation of organic compounds in printed circuit boards wastewater

Maciej Thomas<sup>1</sup>, Krzysztof Barbusinski<sup>2</sup>, Barbara Bialecka<sup>3</sup>

1. Chemiqua Company, POLAND, Cracow, Skawinska Street 25/1, E-mail: [biuro@chemiqua.pl](mailto:biuro@chemiqua.pl)

2. Krzysztof Barbusinski, Institute of Water and Wastewater Engineering, Silesian University of Technology, POLAND, Gliwice, Konarskiego Street 18, E-mail: [Krzysztof.Barbusinski@polsl.pl](mailto:Krzysztof.Barbusinski@polsl.pl)

3. Barbara Bialecka, Department of Environmental Monitoring, Central Mining Institute, POLAND, Katowice, Plac Gwarkow 1, E-mail: [bbialecka@gig.eu](mailto:bbialecka@gig.eu)

**Abstract** – *The paper deals with possible use of acidification and UV, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>/UV, Fe(II)/H<sub>2</sub>O<sub>2</sub> and Fe(II)/H<sub>2</sub>O<sub>2</sub>/UV (Fenton and Photo-Fenton) process for purifying contaminated printed circuit boards wastewater (pH=10.5, Chemical Oxygen Demand, COD=5 980 mg O<sub>2</sub>/L, Total Organic Carbon, TOC=2 100 mg/L). Application of acidification and Photo-Fenton process was allowed to decrease COD (98.5%) and TOC (98.1%) in treated wastewater.*

**Keywords** – Advanced Oxidation Processes, Fenton, Photo-Fenton, Free radicals, Printed circuit boards wastewater, Organic compounds

## Introduction

The production of Printed Circuit Boards (PCBs), is associated with the generation of a significant amount of wastewater containing organic compounds and heavy metals (i.a. Cu, Sn, Ni) [1-2]. The source of alkaline wastewater are photochemical processes in which alkaline solutions (i.a. Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, NaOH) with the addition of anti-foaming agents are used [3-4]. The COD value of alkaline wastewater may be up to even 15 000 mg O<sub>2</sub>/L [3]. The treatment of these wastewater involves acidification (HCl or H<sub>2</sub>SO<sub>4</sub>) to precipitate insoluble polymers at pH<5. In addition, activated carbon is used and the effectiveness (COD reduction) of this method depends on many factors. The COD values in treated wastewater reported in literature (400 mg O<sub>2</sub>/L) are usually not achieved [5]. Therefore, in order to increase the reduction of COD, AOPs were applied.

## Materials and methods

Wastewater from the printed circuit board production plant was used in the study. The studies were carried out in a coagulator (500 mL) and UV photoreactor (580 mL, 11 W, Osram® Puritec HNS). In the first stage (determination of the dependence of COD change on the pH of wastewater) for the acidification of wastewater concentrated H<sub>2</sub>SO<sub>4</sub> was used. In the second stage, the wastewater after acidification and sludge filtering was subjected to UV treatment (11 W, 0-60 min), H<sub>2</sub>O<sub>2</sub> (3 g/L, 0-60 min), H<sub>2</sub>O<sub>2</sub>/UV (3 g/L, 11 W, 0-60 min), Fe(II)/ H<sub>2</sub>O<sub>2</sub> (pH=2.25, Fe(II)/H<sub>2</sub>O<sub>2</sub>=0.17, H<sub>2</sub>O<sub>2</sub> 5 g/L, 0-60 min) and Fe(II)/H<sub>2</sub>O<sub>2</sub>/UV (11 W, pH=2.25, Fe(II)/H<sub>2</sub>O<sub>2</sub>=0.17, H<sub>2</sub>O<sub>2</sub> 5 g/L, 0-60 min). During the process, samples of wastewater were taken, alkalinized (NaOH) to pH=9 and filtered by using syringe filter (0.45 μm). The remaining of H<sub>2</sub>O<sub>2</sub> was removed by using catalase before the COD determination. After that the pH (EN ISO 10523:2012), COD (ISO 15705:2005) and TOC (EN 1484: 1999) were determined.

## Results

Wastewater used in the study was characterised by alkaline reaction (pH=10.5) and high COD and TOC values (COD=5 980±900 mg O<sub>2</sub>/L, TOC=2 100±315 mg/L), which was an indication of a high content of organic compounds. In the Fig. 1 the dependence of COD and TOC on the pH of wastewater is presented. The lowest COD and TOC values were noted at pH

1-5 (790-840 mg O<sub>2</sub>/L and 315-390 mg/L respectively). Wastewater after acidification and filtering of separated sediments was characterized by low susceptibility to UV and H<sub>2</sub>O<sub>2</sub>, and changes of COD and TOC values of wastewater were small, as shown in the Fig. 2. Increased effectivity was achieved by using the UV/H<sub>2</sub>O<sub>2</sub> process. In this case, the lowest COD and TOC values (in the range of 360-365 mg O<sub>2</sub>/L and 250-255 mg/L respectively) were obtained after 50 and 60 minutes of the process. The highest effectiveness was achieved in the Fenton and Photo-Fenton process.

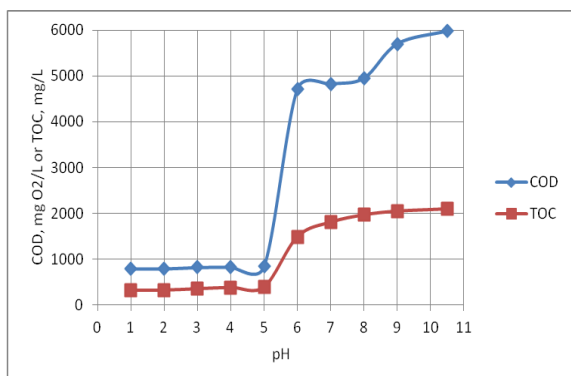


Fig.1. The changes of COD and TOC after acidification with H<sub>2</sub>SO<sub>4</sub>

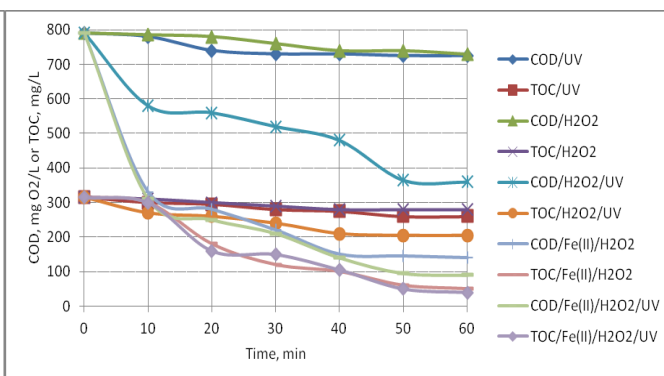


Fig.2. The changes of COD and TOC after an additional application of oxidation processes

In these cases, the lowest COD and TOC values were also obtained after 50 and 60 minutes of the process. For the Fenton process, COD values were reduced from 790 to 140 mg O<sub>2</sub>/L and for TOC from 315 to 50 mg/L. For the Photo-Fenton process, COD values were reduced to 90 mg O<sub>2</sub>/L and TOC values even to 40 mg/L. In the first stage (acidification only) the effectiveness of removal of COD and TOC reached 86.8% and 85.0%, respectively, and in the case of combining both methods (acidification and Photo-Fenton process), 98.5% and 98.1%, respectively.

### Conclusion

The wastewater acidification method (by using concentrated H<sub>2</sub>SO<sub>4</sub>) applied as a pre-treatment method allowed to remove a significant amount of organic compounds from the tested wastewater as a result of precipitation of polymers which were insoluble in an acidic environment. Pollutants remaining in wastewater were not susceptible to UV and H<sub>2</sub>O<sub>2</sub>. The highest treatment efficiency was achieved with AOPs (H<sub>2</sub>O<sub>2</sub>/UV, Fe(II)/H<sub>2</sub>O<sub>2</sub>, Fe(II)/H<sub>2</sub>O<sub>2</sub>/UV) as a result of oxidative action of hydroxyl radicals (•OH).

### References

- [1] J.-Ch. Lou, Y.-J. Huang, J.-Y. Han, "Treatment of printed circuit board industrial wastewater by Ferrite process combined with Fenton method", *Journal of Hazardous Materials*, 170, 2-3, June, 620-626, 2009.
- [2] M. Thomas, D. Zdebik, B. Bialecka, "Using Sodium Trithiocarbonate to Precipitate Heavy Metals from Industrial Wastewater – from Laboratory to Industrial Scale", *Polish Journal of Environmental Studies*, 27, 4, July, 1753-1763, 2018.
- [3] J. Michalski, "Technology and assembly of printed circuit boards", *WNT*, Warsaw, Poland 1992.
- [4] C.F. Combs, H.T. Holden, "Printed circuits Handbook. Fourth Edition", *Mc Graw-Hill*, New York, 1996.
- [5] L. Hartinger, *Handbook of wastewater and recycling technology for the metalworking industry*, *Carl Hanser Verlag*, Vienna, 1991.