

MAŁGORZATA KUCHARSKA*, JEREMI NAUMCZYK*

DEGRADATION OF SELECTED CHLOROPHENOLS BY ADVANCED OXIDATION PROCESSES

This study evaluates the efficiency of O_3/OH^- , O_3/H_2O_2 , $O_3/H_2O_2/OH^-$ and H_2O_2/UV in the oxidation of 3-CP, 2,4-DCP and PCP in water solutions and synthetic domestic wastewater containing chlorophenols. The treatment efficiency follows the sequence: $PCP > 3-CP > 2,4-DCP$. The best results gave the O_3/OH^- process followed by $O_3/H_2O_2/OH^- > O_3/H_2O_2 > H_2O_2/UV$. In all cases, COD values after the process remain at 35–75% of initial value. In the case of wastewater, a significantly longer time was required for a total removal of chlorophenols (COD reduction by 36 %). During the processes many intermediates were identified, which allowed creation of degradation schemes for the chlorophenols investigated.

1. INTRODUCTION

Of all oxidation methods for wastewater purification, Advanced Oxidation Processes (AOPs) are considered to be the most effective. Although there are many papers on applying AOPs to the degradation some chlorophenols, many aspects of this process still require more detailed studies. Of all chlorophenols, PCP was most frequently used in the studies on the effectiveness of AOPs, but it is impossible to state which process is the most effective in its removal from wastewater. Researchers usually investigate only one process (in most cases O_3/OH^- , H_2O_2/UV and Fenton) and they conduct processes under different conditions (e.g. initial concentration of chlorophenol), which makes the results obtained by them non-comparable. SAPACH and VIRARAGHAVAN [1] investigated the relationship between PCP concentration and H_2O_2 dose in the H_2O_2/UV process, and they concluded that the optimal H_2O_2 dose is lower when PCP concentration is low. HONG and ZENG [2] investigated how pH influences the PCP ozonation and changes the toxicity of the solution during the process. They found that the toxicity dropped, which was concordant with the results ob-

* Faculty of Environmental Engineering, Department of Informatics and Environment Quality Research, Warsaw University of Technology, 20 Nowowiejska Street, 00-653 Warsaw, Poland. Tel.: +48 022 234 5423, e-mail: jeremi.naumczyk@is.pw.edu.pl

tained by ENGWALL et al. [3], who investigated photo-Fenton process. 2,4-DCP degradation by AOPs was comparatively less investigated. HIRVONEN and TRAPIDO [4] reported that the O_3/OH^- process is better than the H_2O_2/UV one. GRIGOROPOULOU and PHILIPPOULOS [5] compared different iron salts to be used in Fenton process – $Fe_2(SO_4)_3$ and $FeCl_3$ proved to be the best. The effectiveness of Fenton process in the case of 2,4-DCP was also investigated by BROWERS et al. [6]. The authors obtained the best results when pH was 3.5, molar ratio of H_2O_2 concentration to DCP was 4:1, and $FeSO_4$ concentration was 10–100 mg Fe/dm³. Additionally, ORMAND et al. [7] examined the effectiveness of photo-Fenton process and they observed a significant degradation of 2,4-DCP in 60 min. Despite the fact that the results are hardly comparable, it is possible to conclude that both O_3/OH^- and Fenton processes are more effective than others. 3-CP has been the least investigated of all. Only DONG and HUANG [8] ascertain that Fenton process is more effective than $UV/TiO_2/H_2O_2$. Other researchers studied the effectiveness of only one process, e.g. TANG and HUANG [9] examined Fenton process. Additionally, the kinetics of 3-CP ozonation was investigated by UTSUMI [10].

The aim of this study was to complete the knowledge of the efficiency of AOPs in removing 3-CP, 2,4-DCP and PCP. This paper compares four AOPs which have never been examined together before. Chlorophenols examined in this study were selected due to their toxicity, commonness in wastewaters, and in the case of 3-CP, limited data on them in literature.

2. MATERIALS AND METHODS

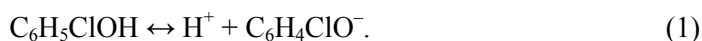
Chlorophenol solutions were prepared in deionized water with concentrations of 3-CP and 2,4-DCP of 30 mg/dm³ and PCP of 15 mg/dm³ (lower solubility in water). Synthetic wastewaters (COD of 318 mg/dm³ O₂) were prepared from the following ingredients (mg/dm³): 3-CP (23.0), 2,4-DCP (18.0), PCP (8.8), broth (150), peptone (50), urea (30), CH_3COONa (10), $CaCl_2$ (7), $NaCl$ (30), KCl (7) and $MgSO_4$ (50). Initial pH values were: 12 for the O_3/OH^- process, 7 for O_3/H_2O_2 and 3 for the H_2O_2/UV process. When chlorophenol concentration dropped to 0, the corresponding pH values (HCl was formed) were: 9, 4 and 3. The doses of H_2O_2 corresponded to chlorophenol/ H_2O_2 molar ratio: 1:1, 1:2, 1:4 and (only for H_2O_2/UV process) 1:6. Initial H_2O_2 concentration was measured iodometrically. The O_3/OH^- and O_3/H_2O_2 processes were performed in a 1 dm³ cylindrical reactor with a laboratory ozone generator (Sander). The ozone was supplied with the efficiency of 335 mg O₃/h. The H_2O_2/UV process was conducted in 1 dm³ Heraeus photoreactor, with a low pressure mercury lamp (15 W). The samples for chlorophenol, COD and (only in the case of 3-CP) phenolic index analyses were collected at specific time intervals during the experiments. The chlorophenol concentration and identification of oxidation intermedi-

ates were analyzed according to EN 12673, using GC-MS GCQ Finnigan MAT with Rtx-5MS (0.25 μm , 30 m \times 0.25 mm) capillary column and helium as carrier gas. Phenolic index was monitored using 4-aminoanthipyrine (4-AAP) method, COD – according to ISO 6060 and the consumption of ozone was determined iodometrically. All tests were performed 2–3 times.

3. RESULTS AND DISCUSSION

Of all AOPs investigated, O_3/OH^- turned out to be the most effective one. The addition of H_2O_2 ($\text{O}_3/\text{H}_2\text{O}_2/\text{OH}^-$ process) did not improve the effectiveness of the process. On the contrary – when the dose of H_2O_2 increased, the effectiveness slightly decreased. $\text{O}_3/\text{H}_2\text{O}_2$ process gave significantly worse results than O_3/OH^- and $\text{O}_3/\text{H}_2\text{O}_2/\text{OH}^-$ but slightly better than $\text{H}_2\text{O}_2/\text{UV}$.

The fact that the O_3/OH^- process had the highest efficiency in removing the chlorophenols investigated could be explained by dissociation of 3-CP in alkaline solution, according to the following reaction:



In alkaline environment, the stable structure of the molecule is disturbed, which is why the ionic forms are more highly reactive than the non-dissociated ones.

Figure 1 shows the changes in concentration of all the chlorophenols examined and the value of the phenolic index (for 3-CP) and COD (for 3-CP and 2,4-DCP) during their O_3/OH^- process.

3.1. OXIDATION OF 3-CP

The O_3/OH^- process resulted in 96% reduction of 3-CP concentration with 6 min and a total removal after 8 min. The $\text{O}_3/\text{H}_2\text{O}_2$ process (with the addition of H_2O_2 in optimal dose) brought about a 97% reduction after 45 min and a total removal of 3-CP after 55 min. During the $\text{H}_2\text{O}_2/\text{UV}$ process, the total removal of this compound was achieved after 60 min.

During the O_3/OH^- process, the value of phenolic index was decreasing significantly slower than the concentration of 3-CP (figure 1). After 6 min of the reaction, the phenolic index was reduced by 87% and after 12 min it decreased to 0. The difference between the phenolic index value and the concentration of 3-CP corresponds to by-products which react with 4-AAP (therefore containing aromatic -OH groups). The concentration of by-products was increasing for about 2 min. After 3 min of conducting the process, it exceeded the concentration of 3-CP and then it decreased, but until the end of the process, it remained higher than the concentration of 3-CP. This proves that the by-products which react with 4-AAP are more resistant to oxidation than

3-CP. This thesis is confirmed by the characteristics of the COD changes. A very slow decrease in the COD value proves that by-products are more resistant to oxidation than 3-CP. After 8 min (time of total 3-CP removal), COD decreased by 45% and after 3 h – by 51.5%. It was observed that for all parameters under analysis, the decrease in the first 6 min was very rapid, which was followed by a slow down. This phenomenon matches the consumption of O_3 , which was increasing considerably for the initial 6 min of the process, relatively slowing down afterwards.

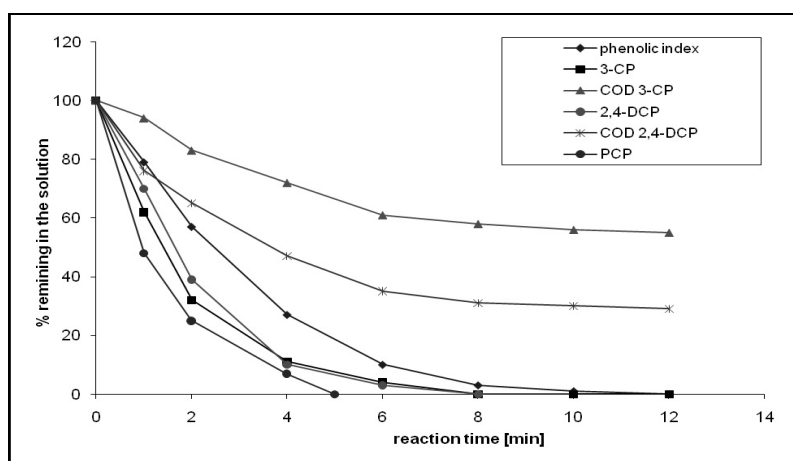


Fig. 1. Changes in concentration of chlorophenols, phenolic index and COD during O_3/OH^- process

In the O_3/H_2O_2 process, the best results were obtained at the 3-CP: H_2O_2 molar ratio of 1:2. For higher H_2O_2 doses, the process effectiveness was lower, which could be explained by the reaction of OH^\cdot with H_2O_2 leading to the decay of OH^\cdot [1]. The changes in the phenolic index remained in similar relation with the concentration of 3-CP to the one of the O_3/OH^- process, but in this case, the difference between these parameters was lower. This difference reached its maximum in the 15th min of the reaction and after about 50 min it exceeded 3-CP concentration. The total 3-CP degradation was achieved after 55 min of the process and the phenolic index value decreased to zero after 65 min. The results presented above prove that in the O_3/H_2O_2 process, oxidation of by-products (which react with 4-AAP), derived from the degradation of 3-CP, was faster than that observed in the O_3/OH^- process. The reduction of COD value achieved after 55 min (time of total 3-CP removal) was 43% and it did not improve further during the process.

The best effectiveness of the H_2O_2/UV process was observed at the 3-CP: H_2O_2 molar ratio of 1:4. As in the O_3/H_2O_2 process, higher doses of H_2O_2 resulted in a reduction of the process efficiency. The explanation of this fact could be the same as in the O_3/H_2O_2 process discussed above. The influence of H_2O_2 dose was more signifi-

cant in the case of the phenolic index value reduction than in the concentration of 3-CP, which suggests that further addition of H_2O_2 (up to optimal dose) improved oxidation of by-products derived from the degradation of 3-CP more than 3-CP itself. In this process, the decrease in the concentration of 3-CP was slower than the decrease of the phenolic index as was observed in the processes discussed before. In this case, however, the difference between those two parameters was larger. After about 20 min, the by-products concentration (which react with 4-AAP) was higher than the concentration of 3-CP remaining in the solution, and it achieved its maximum after about 30 min. This dominance was increasing during the process, at the end of which (when 3-CP was totally removed) the phenolic index value was approximately 15% of the initial value – reduction to zero was achieved after 120 min of the process. Additionally, the difference discussed above was inversely dependent on H_2O_2 dose – its higher dose resulted in the decrease of the process efficiency.

The conclusions presented above correspond with the changes in COD value observed during the process. Reduction of COD was slow, and at the end of the process (time in which all 3-CP was removed) it achieved only 25%. An increase in H_2O_2 dose resulted in the improvement of COD reduction, but this drop was significantly smaller than those observed in the case of 3-CP concentration and the phenolic index value.

3.2. OXIDATION OF 2,4-DCP

During the O_3/OH^- process, the concentration of 2,4-DCP was reduced by 97% after 6 min and it dropped to zero after 8 min. The O_3/H_2O_2 process (with optimal H_2O_2 dose) resulted in the reduction of 2,4-DCP concentration by 98% after 45 min, and a total removal was achieved after 50 min. During the H_2O_2/UV process, 2,4-DCP was removed after 45 min in 96% and after 60 min – totally. At the end of the O_3/OH^- process (time of total 3-CP removal), the reduction of COD achieved 71%. The result is much better than that in the case of 3-CP and suggests that the by-products of 2,4-DCP degradation are much more susceptible to oxidation. Extending the process to 3 h made the COD reduction reach only to 75%, which means that later by-products were more resistant to degradation. During the O_3/H_2O_2 process, the correlation between 2,4-DCP and COD reduction has quite different characteristic. After 50 min of the process (time of 2,4-DCP total removal), COD was reduced only by 43%, which testifies to a different mechanism of this process and formation of a by-product less susceptible to oxidation. The influence of H_2O_2 dose on the effectiveness of 2,4-DCP degradation in this process was rather insignificant. The best results were obtained at the molar ratio of 2,4-DCP: H_2O_2 equal to 1:1. When the addition of H_2O_2 was higher (molar ratios of 1:2 and 1:4), the results obtained were 1–2% worse. H_2O_2 dose had more significant influence on the reduction of COD value, which rose slightly when the addition of H_2O_2 was higher. The re-

sults presented above prove that the dose of H_2O_2 has a slight influence on the mechanism of this process. During the $\text{H}_2\text{O}_2/\text{UV}$ process, the best effect of 2,4-DCP degradation was observed when 2,4-DCP: H_2O_2 molar ratio was 1:4. Although the best reduction of COD value was achieved at H_2O_2 dose in a ratio of 1:6, it was slightly worse than the result obtained for H_2O_2 dose in a ratio of 1:4, which determined the dose of 1:4 as the optimal one. Reduction of COD after the time in which a total decomposition of 2,4-DCP was observed reached only 41%, which is the worst result of all processes under examination.

3.3. OXIDATION OF PCP

In the O_3/OH^- process, a total degradation of PCP was observed after 6 min. During the $\text{O}_3/\text{H}_2\text{O}_2$ process at a molar ratio of PCP: H_2O_2 equal to 1:1, the concentration of PCP was reduced by 93% after 8 min and reached zero after 12 min. On the contrary to other chlorophenols examined in this study, the increase in H_2O_2 dose did not affect the effectiveness of the process. Additionally, ozonation without H_2O_2 at pH 7 gave effect similar to those of O_3/OH^- and $\text{O}_3/\text{H}_2\text{O}_2$ processes, which means that ozone itself is sufficient for oxidation of PCP in a non-dissociated form (the one which dominates at pH 7), and the addition of H_2O_2 (transformation of a “classic ozonation” into AOP) did not improve the effectiveness of PCP degradation. The results obtained from the $\text{H}_2\text{O}_2/\text{UV}$ process are difficult to compare with the results from other processes because the PCP concentration used in this process was much lower (due to slight solubility of PCP at pH 3). However, it could be concluded that the $\text{H}_2\text{O}_2/\text{UV}$ process was the least effective. With H_2O_2 added in the optimal dose (1:4 molar ratio), the total PCP degradation occurred after 30 min.

During all the processes, a decrease in pH value was observed. In the case of the processes at pH 7 and 12, the drop was about 3 units at the end of the process, and in the case of the processes at pH 3, the drop was insignificant. For all the chlorophenols examined, during each process, initially colourless solutions turned firstly to pink (3-CP and 2,4-DCP) or light violet (PCP), then to orange (3-CP and 2,4-DCP) or violet (PCP), and to yellow at the end of the process.

Differences in the initial concentrations of the chlorophenols examined (due to differences in their solubility dependent on pH) made it difficult to compare chlorophenols directly with regard to the susceptibility to oxidation by AOPs. The investigated reactions of oxidation turned out to be first order reactions, which allowed their rate constants to be compared. According to the above-mentioned rate constants, the chlorophenols could be ordered as follows: PCP > 3-CP > 2,4-DCP. These results correspond with a tendency observed by other authors [11], [12], [13], who investigated the effectiveness of the $\text{H}_2\text{O}_2/\text{UV}$ process in removing some other chlorophenols as well. Some authors report that if the number of chlorine atoms in the molecule

of chlorophenol rises, its susceptibility to oxidation is also higher, due to the exceeded rate of the aromatic ring dechlorination [14]–[16]. Phenolic group and chlorine atom in the aromatic ring are *ortho*- and *para*-directing substituents. OH^\bullet radicals are then supposed to attack the aromatic ring in those positions. Additionally, OH^\bullet attacks the positions in the ring not occupied by chlorine atom, which means that fewer chlorine atoms in the ring promote the susceptibility of chlorophenol to oxidation. However, the result obtained in this study shows that the mechanisms of reactions are more complicated, and the effectiveness of the process depends also on other parameters, such as the place of chlorine atom substitution in the ring and the forms of chlorophenol (ionic or molecular) dependent on the pH value.

3.4. GC-MS ANALYSIS

In each process of 3-CP oxidation, some by-products were identified, among others, 1-chloro-3,5-bis(1,1-dimethylo)-2-(2-propenyloxy) benzene, 2,2'-methyl bis[3,4,6-trichloro-dimethylo] phenol, cyclopropane[3,4]-cyclohepta-[1,2-a] naphthalene, and 2,3,6-trichlorobenzoic acid. It is difficult to compare these results with those obtained by other authors, because there is almost no data covering this problem. Beside the above-mentioned by-products, some authors detected also: chloroorobenzenodiols, chlorodihydroxybiphenols, dichlorodihydroxybiphenols [4], catechol and pyrocatechol [16], chlorodihydroxybenzene, chlorocatechol, chlorohydroquinone [17] as by-products of monochlorophenol oxidation.

During oxidation 2,4-DCP the following by-products were identified: 4-chloro-1-naphthalenole, 4,6-dichloro-1,2-benzenodiole, 2,5-dichloro-1,4-benzenodiole and 1-chloro-2,6-dimethoxynaphthalene. Some researchers observed formation of 1,4-hydroquinone, chlorohydroquinone, catechol, 2-chlorohydrochinone [4], [16], polychlorinated chlorobenzenes, hydroxylated and chlorinated dibenzenes, and tri- and tetrachlorodihydroxybiphenyls [4].

In the case of PCP, among main by-products of oxidation the following were identified: 2,3,5,6-tetrachloro-*p*-benzoquinone, 1-chloro-3,5-bis(1,1-dimethyloethylo)-2-(2-propenyloxy) benzene and lower substituted chlorophenols, e.g. 2,4-DCP. These results correspond to the results presented by other authors, who additionally identified: 3,4,5-trichloro-3-cyclopentene-1,2-dion, tetrachlorophenol and carboxylic acids: 3-chloro-2-hydroxy-3-metonyl-2-propenoic, 2-chloromaleic and oxalic acid [2] as by-products.

Based on the results obtained in this study, an oxidation scheme for 3-CP and 2,4-DCP has been created (figures 2 and 3) and confirmed the scheme of PCP oxidation proposed by HONG and ZENG [2].

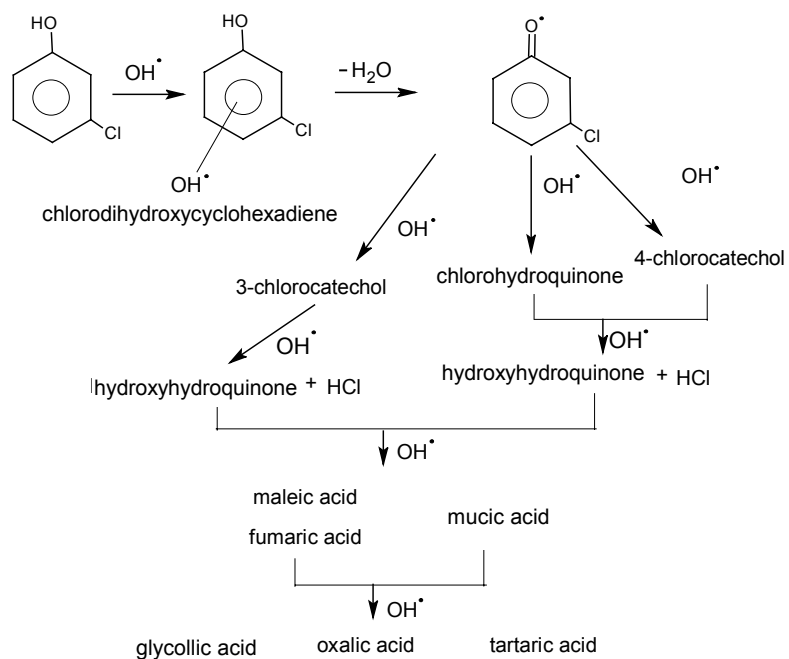


Fig. 2. A possible scheme for oxidation of 3-CP

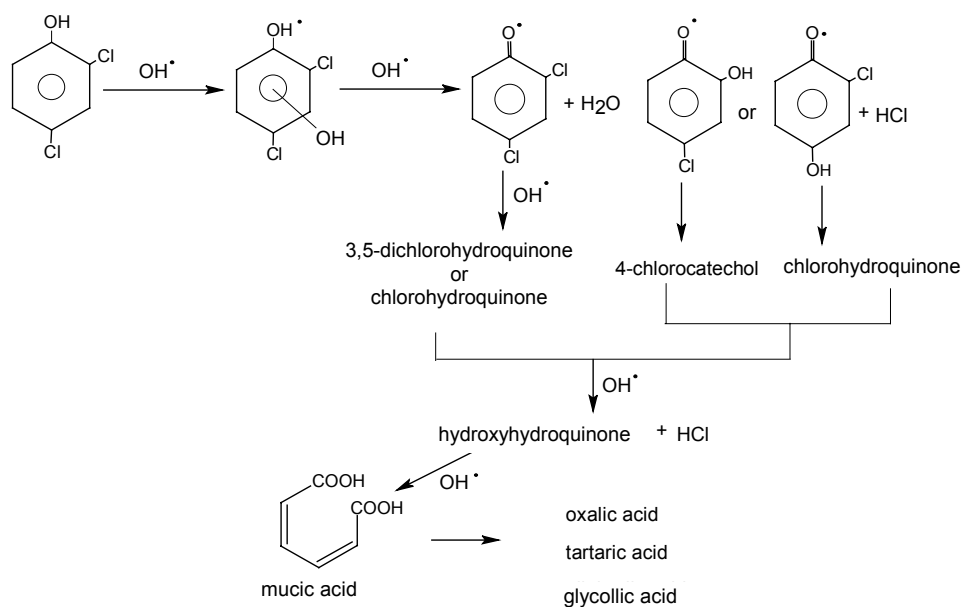


Fig. 3. A possible scheme for oxidation of 2,4-DCP

3.5. WASTEWATER PURIFICATION

The time in which all the chlorophenols investigated were removed from the wastewater was longer than in the case of water – 14 min of the process. At this time, COD value decreased by 36%. As calculated from the previous results, a drop of COD value equivalent for 3-CP oxidation was 48%, and for 2,4-DCP – 70%. These results suggest that easily biodegradable compounds were more resistant to oxidation by AOPs than chlorophenols, and they did not affect significantly the effectiveness of chlorophenol oxidation.

BIBLIOGRAPHY

- [1] SAPACH R., VIRARAGHAVAN T., *J. Environ. Sci.*, 1997, A32, 2355–2366.
- [2] HONG P.K.A., ZENG Y., *Water Res.*, 2002, 36, 4243–4254.
- [3] ENGWALL M.A., PIGNATELLO J.J., GRASSO D., *Water. Res.*, 1999, 33, 1151–1158.
- [4] HIROVEN A., TRAPIDO M., HENTUNEN J., TARHANEN J., *Chemosphere*, 2000, 41, 1211–1218.
- [5] GROGOROPOLOU H., PHILIPPOPOULOUS C., *Wat. Sci. Tech.*, 1997, 36, 151–154.
- [6] BOWERS A.R., GADDIPATI P., ECKENFELDER JR., MONSEN R.M., *Wat. Sci. Tech.*, 1989, 21, 477.
- [7] ORMAD M.P., OVEKKEIRO J.L., *Applied Cat. B*, 2001, 32, 157–166.
- [8] DONG C., HUANG C.P., *Aquatic Chemistry*, 1993, ACS.
- [9] TANG W., HUANG C.P., *Waste Managm.*, 1995, 15, 615–622.
- [10] UTSUMI H., HAN Y.-H., ICHIKAWA K., *Water Res.*, 2003, 37, 4924–4928.
- [11] MOZA P.N., FYTIANOS K., SAMANIDOU V., *Bull. Environ. Contam. Toxicol.*, 1988, 41, 678–682.
- [12] TRAPIDO M., VERESSININA Y., HENTUNEN J., HIRVONEN A., *Environ. Technol.*, 1997, 18, 325–332.
- [13] HUGUL M., APAK R., DEMIRCI S., *J. Hazard. Mat.*, 2000, B77, 193–208.
- [14] BENITEZ J.F., BELTRAN-HEREDIA J., ACERO J.L., RUBIO F.J., *Chemosphere*, 2000, 41, 1271–1277.
- [15] CHEN J.N., NI C.H., *Proceedings of the International Regional Conference of IOA*, Poitiers, France, 49.1–49.4.
- [16] PERA-TITUS M., GARCIA-MOLINA V., BANOS A.M., GIMENEZ J., ESPLUGAS S., *Appl. Catalys. B, Environmental*, 2004, 47, 219–256.
- [17] JUNG OH-JIN, *Bull. Korean. Chem. Soc.*, 2001, 22.

ROZKŁAD WYBRANYCH CHLOROFENOLI
ZA POMOCĄ WYSOKOEFEKTYWNYCH PROCESÓW UTLENIANIA

Oceniano efektywność procesów O_3/OH^- , O_3/H_2O_2 , $O_3/H_2O_2/OH^-$ i H_2O_2/UV w usuwaniu 3-CP, 2,4-DCP i PCP z wody oraz ze ścieków bytowo-gospodarczych zanieczyszczonych chlorofenolami. Badane związki pod względem podatności na degradację można uszeregować następująco: PCP > 3-CP > 2,4-DCP. Najlepsze wyniki uzyskano dla procesu O_3/OH^- , gorsze dla procesów $O_3/H_2O_2/OH^- > O_3/H_2O_2$, a najgorsze dla procesu H_2O_2/UV . We wszystkich przypadkach wartość ChZT na końcu procesu wносиła 35–75% wartości początkowej. Czas potrzebny do całkowitego usunięcia chlorofenoli ze ścieków był znacznie dłuższy, a ChZT obniżyło się o 36%. W czasie procesów zidentyfikowano wiele produktów pośrednich utleniania, co umożliwiło sporządzenie schematów utleniania badanych chlorofenoli.