

## Removal of micropollutants from water by ozonation/ biofiltration process

Bożena Seredyńska-Sobecka, Maria Tomaszewska\*, Antoni W. Morawski

*Technical University of Szczecin, Institute of Chemical and Environmental Technology, ul. Pulaskiego 10,  
70-322 Szczecin*

*email: maria.tomaszewska@ps.pl*

Received 20 February 2005; accepted 20 March 2005

### Abstract

In the paper results of studies on phenol removal by the combination of processes: ozonation and subsequent biofiltration are presented. Phenol model solution of concentration 10 mg/dm<sup>3</sup> was applied in the experiments. During oxidation process ozone doses in range of 0.7–2.5 mg O<sub>3</sub>/mg TOC were applied and contact time varied from 1 to 5 min. WG 12 granular activated carbon (Gryfskand, Poland) was used as a filter medium. Biological activity of carbon filter was obtained by circulation of surface water through the filter. During the ozonation/biofiltration studies biomass activity changed from 126 nmol PO<sub>4</sub> per g media to 86 nmol PO<sub>4</sub> per g media at the top of the filter whereas biomass activity at the bottom of filter was by 12–15% lower. In the biofiltration experiments empty bed contact time (EBCT) of the filter varied from 2.4 min to 24.0 min. The applied ozone doses and contact times of oxidant with treated water were not sufficient enough in phenol removal whereas the combination of ozonation and biofiltration processes was found to be effective to remove phenol significantly (91–100% removal effect). Chemical oxygen demand removal ranged from 58 to 93% whereas biochemical oxygen demand removal was in range of 49–85%. Total organic carbon was removed from the model solution in 38–74% depending on applied process parameters.

*Keywords:* Ozonation; Biofiltration; Phenol; Micropollutants

### 1. Introduction

Growing industrialization causes continuous increase in micropollutants penetrating

into the surface and infiltration water. Organic micropollutants are a mixture of dissolved and non-dissolved compounds which are potentially persistent in the environment and have adverse effects on human health already at low concentrations. These

\*Corresponding author.

*Presented at the Conference on Desalination and the Environment, Santa Margherita, Italy, 22–26 May 2005.  
European Desalination Society.*

substances are very often hardly-biodegradable or even non-biodegradable and remain in water for a long time. These contaminants have been reported to be mainly pharmaceutical compounds, detergents, pesticides, polycyclic aromatic hydrocarbons, surfactants, chlorinated organic compounds, esters, alcohols, glycols, aliphatic and aromatic amines and phenols. Micropollutants are removed in conventional processes of water treatment with low efficiency, therefore advanced technologies must be applied [1]. Degradation of micropollutants by chemical oxidation is always a complicated process, as its efficiency depends on the nature of the micropollutants as well as on the quality of the water (i.e. presence of natural organic matter or carbonates) [2]. Phenol was chosen as the model contaminant in this study because of being a frequent pollutant in industrial waste and it occurs in drinking water supplies [3]. This compound is considered as an important starting material for numerous intermediates in chemical industry. Phenol worldwide production is estimated to be 5 million tons per year [4]. Phenols are used extensively in the production of a large variety of aromatic compounds including, e.g. explosives, fertilizers, coke, rubber, textiles, medicines and perfumes. Phenol is also used in the petroleum, leather, paper, soap, toy, tanning dye and agricultural industries.

In the paper results of studies on phenol removal during ozonation/biofiltration process will be presented. At present, a combination of ozone oxidation and subsequent biological filtration processes is applied in some of water treatment plants as cost efficient and high performance operation. Biological activity of granular activated carbon (GAC) filters appears a few months after the commencement of the filters operation. Biological activity of carbon filters means presence of adapted microorganisms on GAC.

Ozone, due to its high oxidation and disinfection potential, has recently received much attention in water treatment technology. Ozonation of organic compounds results in formation of biodegradable organic matter, mainly carboxylic acids and carbonyl compounds, which toxicities are often unknown. Biodegradable organic matter is preferably removed on biological activated carbon (BAC), therefore it is highly recommended to use the combination of chemical oxidation and subsequent BAC filtration [2,5].

## 2. Materials and methods

Ozomatic LAB 802 ozone generator (Wedeco, Germany) was used in the experiments. The amounts of ozone generated were controlled by the oxygen flow regulation. Ozonation processes were performed in a 0.5 dm<sup>3</sup>—absorption bulb. Ozone contents in the inlet and outlet gases were determined by the iodometric procedure [6] and in water by the *o*-tolidyne method [7]. After ozonation nitrogen gas was passed through the model solution within 1 min so no residual ozone was present in the BAC feeding solution.

The model phenol solution of concentration approximately 10 mg/dm<sup>3</sup> was used in the ozonation/biofiltration experiments. Before ozonation the phenol solution was adjusted to pH approx. 7.0 with 0.5 M NaOH. Phenol concentration was analysed by 4-amino-antipyrine-ferricyanide photometric method [8]. TOC concentration was measured using Multi N/C Analyzer (Analytik Jena, Germany) with detection limit of 0.02 mg/dm<sup>3</sup>. COD<sub>Mn</sub> (chemical oxygen demand), BOD<sub>5</sub> (biological oxygen demand within 5 days), and UV<sub>254</sub> absorbance (organic compounds content measured as absorbance at 254 nm) were analysed in the same manner as recommended by the Polish Standards [9–11]. All absorbance

measurements were made on a V-530 spectrophotometer (Jasco, Japan) in 1-cm path length quartz cuvettes.

WG 12 granular activated carbon (Gryfskand, Poland) was used as a filter medium in the BAC filtration experiments. The characteristics of WG-12 given by producer is shown in Table 1. The filter used in the experiments consisted of a 3.5-cm inner-diameter glass pipe equipped with sampling ports. The bed height was approximately 20 cm. Biological activity of the carbon filter was obtained by circulation of surface water through the filter. The biofiltration experiments were performed 15 months after the commencement of the filter operation. The filter was backwashed every 2–3 weeks during 5 min by air and then during 7 min by deionized water. The biomass activity was analysed by the phospholipids extraction method. For measuring the biomass activity the granular activated carbon was taken from the top and the bottom of the filter. The arithmetic mean as the result was taken. Prior to be analysed, the samples were washed with deionized water to remove the suspended solids. For the phospholipids extraction from biomass 0.5 g of activated carbon was used. Phospholipids contained in the cell membranes were extracted during 4 h using a chloroform-methanol-water mixture with a volume ratio 1:1:0.9. Then the chloroform phase containing lipids was evaporated using nitrogen gas and subsequently the

extracted phospholipids were digested with potassium persulfate reagent at 102 °C for 2 h to release phosphates. The released phosphates were complexed with ammonium molybdate reagent and malachite green reagent and then absorbance at 610 nm was measured [12,13].

An ozonated phenol solution was used for BAC experiments. The applied ozone doses contained in range of 0.7–2.5 mg/mg TOC and contact times were in range of 1–5 min (parameters range usually applied at the intermediate oxidation step in water treatment). Three cases of ozonation of the model solutions were chosen to BAC filtration investigations: an ozone dose of 1.5 mg O<sub>3</sub>/mg TOC and a 1 min contact time, 2.5 mg O<sub>3</sub>/mg TOC and a 3 min contact time and 1.9 mg O<sub>3</sub>/mg TOC and a 5 min contact time. In the biofiltration experiments empty bed contact time varied from 2.4 min to 24.0 min. The filter was fed with a peristaltic pump. The direction of water flow was from the bottom to the top of the filter.

### 3. Results and discussion

#### 3.1. Ozonation of phenol solution

Prior to the ozonation/biofiltration experiments, preliminary study of ozonation of the model solution was performed. Ranges of the model solutions parameters and their changes after ozonation are presented in Table 2.

Table 1  
Characteristics of WG 12 carbons given by producer

Parameter	WG-12
Origin	Bituminous
Mechanical strength [%]	96.8
BET surface area (m <sup>2</sup> /g)	1260
Iodine number (mg/g)	1194
Decolorizing power (methylene blue) (cm <sup>3</sup> )	39

Table 2  
Characteristics of the model phenol solutions

Parameter	Before ozonation	After ozonation	Removal effect [%]
PH	6.95–7.06	3.76–5.39	
Temperature [°C]	19.8–25.5	20.9–25.5	
Phenol conc. [mg/dm <sup>3</sup> ]	8.76–12.23	0.13–6.70	41–99
TOC [mg/dm <sup>3</sup> ]	6.9–9.8	5.5–8.4	0–32
COD <sub>Mn</sub> [mg O <sub>2</sub> /dm <sup>3</sup> ]	10.0–20.1	5.1–16.5	10–49
BOD <sub>5</sub> [mg O <sub>2</sub> /dm <sup>3</sup> ]	6.1–14.2	4.1–11.9	–33 <sup>a</sup> –63
Absorbance UV <sub>254</sub> [l = 1 cm]	0.0989–0.1907	0.1164–0.2608	–96 <sup>a</sup> –53

<sup>a</sup>Increase in a parameter value.

Attack of ozone causes decomposition of the benzene ring in a phenol molecule [14]. Results of phenol removal during the ozonation experiments are presented in Fig. 1. The studies showed that under applied conditions phenol removal effect depended significantly on ozone dose. Contact time seemed to have lesser influence on phenol removal, but for the same ozone dose better effects of the benzene ring decomposition were obtained for the longer contact time, e.g. for the ozone dose 1.1 mg O<sub>3</sub>/mg TOC the contact time elongation from 1 to 2 min caused phenol removal effect increase from 44 to 56%.

As can be seen in Fig. 1 an application of ozone doses in range of 1.9–2.5 mg O<sub>3</sub>/mg TOC caused phenol removal effect close to

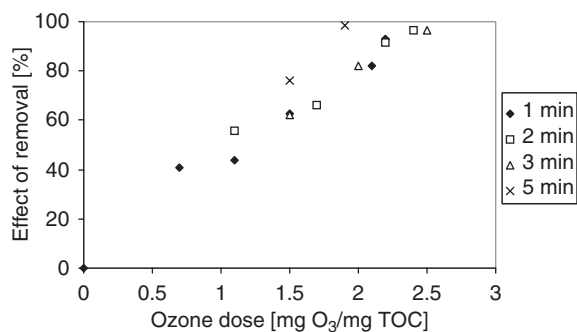


Fig. 1. Effect of phenol removal as function of ozone dose and contact time.

90%. The comparison of phenol (41–99%) and TOC (0–32%) removal (Table 2) effects showed that ozonation by-products were formed. The pH decrease down to the value of 3.76 showed out that after ozonation acidic compounds were formed.

In general, after ozonation BOD<sub>5</sub> of the model solution decreased what showed that a decrease in organic compounds concentration took place. In two cases (the ozone dose of 1.5 mg O<sub>3</sub>/mg TOC and the 1 min contact time; the ozone dose of 1.5 mg O<sub>3</sub>/mg TOC and the 3 min contact time) BOD<sub>5</sub> increases were observed (33 and 9%, respectively) and for the same cases decreases in the UV<sub>254</sub>-absorbance took place (by 17 and 53%, respectively). Generally, UV<sub>254</sub>-absorbance after oxidation was higher than for the non-ozonated solution. The applied ozone doses and contact times causes a decrease in organic compounds concentration and reduction of COD<sub>Mn</sub> in range of 10–49%.

### 3.2. Biological activity of the BAC filter

During BAC filtration experiments the biological activity of the BAC filter changed from approximately 120–80 nmol PO<sub>4</sub>/g of dry media (Fig. 2). Biological activity at the top of the filter was higher by 13–18% then at the bottom. Backwashing of the filter did not

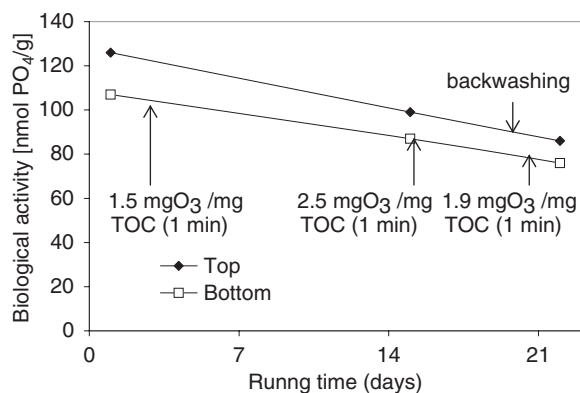


Fig. 2. Changes of biological activity of the BAC filter.

change general biological activity and its stratification within the BAC filter. The decrease in the general biological activity could be caused by less frequent feeding of the filter with surface water compared with the period of time before the biofiltration experiments.

### 3.3. Ozonation/biofiltration experiments

Our previous studies showed that application of ozonation caused significant increase in phenol removal during adsorption on granular activated carbon, therefore removal of phenol in BAC filtration process was investigated. During biofiltration of treated water contaminants are removed in two parallel processes: sorption and biodegradation [2,15].

Changes of phenol concentration are presented as an example of the BAC operation. Results of the biofiltration experiments showed that organic compounds removal effect increased with EBCT what can be seen in Fig. 3. Better results were obtained when decomposition effect of phenol was higher at the ozonation stage (Figs. 3 and 4). Phenol was totally removed only at the longest EBCT (24.0 min) when previous ozonation with the ozone dose of 1.9 mg O<sub>3</sub>/mg

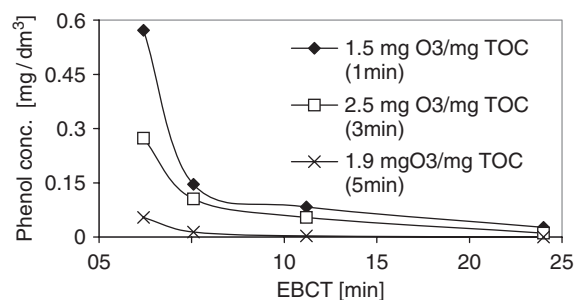


Fig. 3. Phenol concentration in the model solution after ozonation/biofiltration process.

TOC and 5 min contact time was applied. It should be mentioned that in this case phenol was removed during the ozonation process in 99% (Figs. 1 and 4a). For the ozone dose of 1.5 mg O<sub>3</sub>/mg TOC and 1 min contact time an 45% phenol removal effect was obtained (Fig. 4a). In this case, after the ozonation/biofiltration process phenol concentration in the model solution was in range of 0.572–0.027 mg/dm<sup>3</sup> depending on EBCT (summary removal effect was in range of 91.34–99.59%) (Figs. 3 and 4a). Oxidation of the model solution with the ozone dose of 2.5 mg O<sub>3</sub>/mg TOC and the 3 min contact time resulted in a 96% phenol removal and in this case after biofiltration phenol concentration in the model solution was in range of 0.273–0.011 mg/dm<sup>3</sup> (summary removal effect in range of 99.14–99.91%).

The best results of total organic carbon (range of 51–74%) and chemical oxygen demand removal (range of 75–93%) in the ozonation/biofiltration process were obtained when the lowest ozone dose 1.5 mg O<sub>3</sub>/mg TOC (1 min contact time) was applied and the GAC showed the highest biological activity (Figs. 2 and 4b,c). In this case in both the ozonated and the non-ozonated phenol solution TOC concentration were at the same level whereas a COD<sub>Mn</sub> removal during

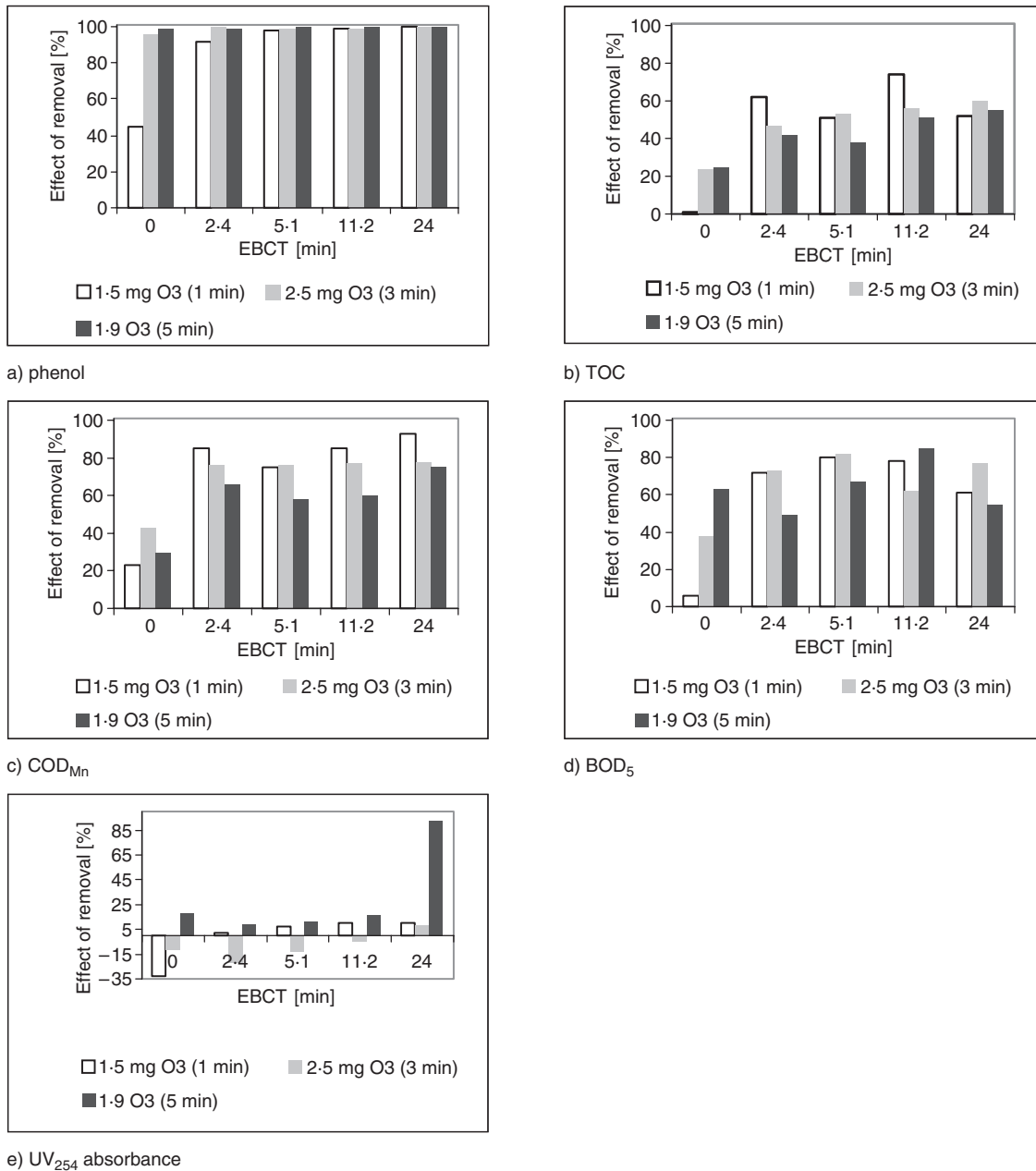


Fig. 4. Purification effect of phenol solution in ozonation/biofiltration process. a) phenol, b) TOC, c) COD<sub>Mn</sub>, d) BOD<sub>5</sub>, e) UV<sub>254</sub> absorbance.

chemical oxidation was the lowest (23%) compared with two higher ozone doses. This meant that for TOC and COD<sub>Mn</sub> removal the biofiltration process was of fundamental

importance. Generally, for phenol, TOC and COD<sub>Mn</sub> increases in removal effects with EBCT elongation were observed (Fig. 4a–c). During the ozonation/biofiltration processes

the removal effects of  $\text{COD}_{\text{Mn}}$  and  $\text{BOD}_5$  were comparable (Figs. 4c and d). A longer time was probably needed for total mineralization of organic carbon during biofiltration process. The biodegradation is a very complex process and further studies on biodegradable compounds removal should be performed.

Effect of  $\text{UV}_{254}$  absorbance removal in ozonation/biofiltration process also increased with EBCT (Fig. 4e). Even when a growth of  $\text{UV}_{254}$ -absorbance after chemical oxidation took place an increase of the summary  $\text{UV}_{254}$ -absorbance removal effects with EBCT were observed. For example, during the ozonation/biofiltration process  $\text{UV}_{254}$  absorbance removal was in range of 2–10% when ozonation with the ozone dose of 1.5 mg  $\text{O}_3/\text{mg}$  TOC and the 1 min contact time were applied (whereas during the single biofiltration process removal effects were in range of 26–32%) and for the ozone dose of 1.9 mg  $\text{O}_3/\text{mg}$  TOC and the 5 min contact time the summary  $\text{UV}_{254}$ -absorbance removal effect was in range of 9–93% (and during the single biofiltration process removal effects were in range of –10–92%). The high summary removal effect for the ozone dose of 1.9 mg  $\text{O}_3/\text{mg}$  TOC could be caused by both partial  $\text{UV}_{254}$ -absorbance removal during ozonation and enhanced biodegradation and adsorption on activated carbon processes (as the filter was backwashed of the filter just before this experiment (Fig. 2).

#### 4. Conclusions

1. Ozone dose was of dominant importance in phenol removal during the oxidation process. Contact time seemed to be less important for the purification of the model solution. Among applied ozonation process parameters the best results of phenol decomposition were obtained for the relatively small ozone dose of 1.9  $\text{O}_3/\text{mg}$

TOC and the longest 5 min contact time (99% removal effect).

2. Combination of ozonation and biofiltration of the model phenol solutions resulted in significant organic contaminants removal which was expressed by  $\text{COD}_{\text{Mn}}$ ,  $\text{BOD}_5$ , TOC and phenol concentration changes.
3. For the total phenol removal in combination of ozonation and biofiltration processes the application of proper oxidation condition (ozone dose and contact time) was of principal importance. The biofiltration process was efficient only as final purification of the model solution, following the ozonation process.

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