



## Degradation and detoxification of the 4-chlorophenol by non-thermal plasma-influence of homogeneous catalysts



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### ABSTRACT

Experimental results of non-thermal plasma (NTP) utilization for degradation of 4-chlorophenol (4CP) with screening of toxicity were presented in this study. Degradation of 4CP was tested in the presence of homogeneous catalysts: hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and iron (II) (Fe<sup>2+</sup>). The rate of degradation through eight consecutive passes of the 4CP solution in the NTP reactor was considered. Products of degradation as organic acids (acetic, formic or oxalic acid) and chloride were quantified using ion chromatography (IC). *Artemia salina* was used for the toxicity screening assay in order to estimate the potential and consequences of NTP reactor application in water treatment. The measured concentration of 4CP and degradation products confirmed very efficient removal of these substances from the water during the NTP treatment with the addition of a catalyst. Concerning bioassay, a significant difference in toxicity was determined between initial solution of 4CP in comparison with the solution exposed to catalytic NTP treatment.

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## 1. Introduction

The research field of water purification has been extensively growing for the last 25 years. Rigorous pollution control and legislation in many countries resulted in an intensive search for new and efficient water treatment technologies [1]. Established techniques as coagulation, carbon adsorption, reverse osmosis, ultra-filtration and similar, as well as biological treatment, poorly remove a lot of hazardous organic compounds.

Chlorophenols (CPs) are listed among the 65 priority pollutants by the US Environmental Protection Agency – EPA [2]; most of them are toxic for humans and animals. They are faintly biodegradable and difficult to remove from the environment.

CPs are introduced into the environment due to their application in many kinds of industries, synthesis of pesticides, paints,

as well as by-products formed during bleaching of pulp and in chlorination of drinking water for disinfection. So they are frequently detected in surface water, groundwater and especially in wastewater [3].

Toxicity and bioaccumulation of CPs are directly related to their lipophilicity; an increase of the chlorination leads to increase in lipophilicity and then to a greater potential for uptake into the organism. Also, the *ortho*-substituted chlorophenols are generally of lower toxicity than the *meta*- and *para*-ones, as *ortho*-substituted chlorine seems to shield OH group, which apparently interacts with the active site in aquatic organisms [4].

The 4-chlorophenol (C<sub>6</sub>H<sub>5</sub>ClO, 4CP) is classified as hazardous substance, which may cause long-term adverse effects in the aquatic environment (Directive 67/548/EEC) [5].

CPs are resistant to biological and classical physico-chemical processes. Advanced oxidation processes (AOPs) are probably the best method for CPs removal. These processes could completely degrade chlorophenols to CO<sub>2</sub> and H<sub>2</sub>O, or to biodegradable and less toxic intermediates.

AOPs are based on the generation of highly reactive species, mainly hydroxyl radical (HO·), which has the strongest oxidation potential after fluorine (2.80V vs. NHE<sup>3</sup> in acidic media) and is able

Abbreviations: AOP, advanced oxidation processes; 4CP, 4-chlorophenol; NTP, non-thermal plasma; DBD, dielectric barrier discharge.

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to oxidize almost all organic compounds to carbon dioxide and water [6].

Hydroxyl radical is characterized with a little selectivity of attack which is a useful attribute for an oxidant used in wastewater treatment. Also, it is extremely unstable, and must be generated continuously by chemical, photochemical or electrochemical reactions. Some of the most frequently used techniques in the AOPs processes are: processes based on hydrogen peroxide ( $\text{H}_2\text{O}_2 + \text{UV}$ , Fenton and photo-Fenton) [7] photocatalysis (mainly  $\text{UV} + \text{TiO}_2$ ) [8–10] processes based on ozone ( $\text{O}_3$ ,  $\text{O}_3 + \text{UV}$  and  $\text{O}_3 + \text{catalyst}$ ) [11,12] and various combinations of all these oxidative species [13–15].

Beside the large number of studied AOPs, very promising processes are based on the use of electrical discharge technologies for elimination of harmful compounds in wastewater. These processes include contact glow discharge electrolysis (CGDE) [16], dielectric barrier discharges (DBD) [17,18] and pulsed corona discharges (PCD) [19–21].

Therefore, instead of “*ex situ*” electrical discharges for ozone production, the “*in situ*” electrical discharges in water may provide a means to utilize most of these chemically active species for water cleaning [22]. From this point of view, promising systems are those in which the discharge zone is in direct contact with the solution.

Nevertheless, during the water treatment presence of many reactive species and oxidation processes can contribute to formation of intermediates more toxic compared to parent compound. Different bioassays have been used to evaluate toxicity of the effluent [23].

The genus *Artemia* is one of the animal models used for toxicity tests in laboratory conditions as a rapid preliminary screening for the presence of biochemical activity. Different authors report the use of *Artemia* in toxicology bioassays of contaminants such as insecticides, [24] mycotoxins, [25] toxic cyanobacteria, [26] metals [27] and pharmaceuticals [28,29]. *Artemia* was also used in a battery of tests to assess the toxicity of phenolic compounds in industrial effluents [30].

The aim of this research was to examine the degradation rate and removal efficiency of 4CP by the NTP treatment in DBD reactor; to determine how external addition of  $\text{H}_2\text{O}_2$  or  $\text{Fe}^{2+}$  influences the efficiency of degradation and to measure toxicity effect after water treatment with such technology.

## 2. Experimental

### 2.1. Chemicals and methods of degradation

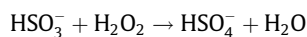
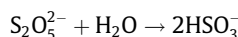
Commercial 4-chlorophenol (4CP,  $\geq 99\%$ , Sigma Aldrich, USA) is used without any further purification. The solution of 4CP, initial concentration 100 mg/L, was prepared by dissolving of 4-CP in deionized water, conductivity between 1.0 and 1.5  $\mu\text{S}/\text{cm}$ .

Three different systems for 4CP degradation were examined: 4CP/DBD (DBD treatment alone), 4CP/ $\text{H}_2\text{O}_2$ /DBD (DBD treatment with addition of  $\text{H}_2\text{O}_2$ ) and 4CP/ $\text{Fe}^{2+}$ /DBD (DBD treatment with addition of  $\text{Fe}^{2+}$ ). Solutions passed eight times through the DBD reactor which corresponds to the energy density of 45–360 kJ/L which was introduced into the solution (see 2.2).

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , Sigma Aldrich, 30% m/m) and iron(II) sulfate, ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , Merck, Germany), were used as homogeneous catalysts. Concentration of  $\text{H}_2\text{O}_2$  used in experiments was 20 mmol/L and it was added to the solution before passing through the reactor. The  $\text{Fe}^{2+}$  salt as a homogeneous catalyst was mixed very well with the 4CP. Concentration of  $\text{Fe}^{2+}$  was 5 mg/L. The initial pH values were adjusted to pH 9.00 with 0.1 M NaOH with an exception of 4CP/ $\text{Fe}^{2+}$ /DBD, where it was adjusted to 2.50 with 0.1 M sulfuric acid. All chemicals were of analytical grade.

It was noticed during the experiments that pH value was decreased after the plasma treatment. Therefore, in order to determine the influence of this effect, we tested the change of 4CP concentration with and without adjusting the pH value after each recirculation. The effect was tested for 4CP/DBD without homogeneous catalysts after 5 min of treatment time. The initial pH of the solution for both series was 9.00, and for one of them it was adjusted to pH 9.00 after each recirculation of solution. Solutions passed through the DBD reactor and the pH value was measured using pH monitor (Microcomputer pH-vision 6071, JENCO Electronics, Ltd., Taiwan). The concentration of hydrogen peroxide was measured by titanium sulfate colorimetric method using UV/VIS spectrophotometer (UV-Visible Cintra 10 spectrometer (GBC Scientific Equipment Pty Ltd., Australia). The titanium sulfate method for hydrogen peroxide was described by [31].

To determine the efficiency of 4CP degradation and production of low-weight organic acids, further degradation by residual “long-lived” active species ( $\text{H}_2\text{O}_2$ , excited-state neutral molecules, and ionic species) was stopped 5 min after each solution passed through the plasma region. Subsequent reaction was quenched by adding 0.5 g potassium metabisulfite  $\text{K}_2\text{S}_2\text{O}_5$  ( $\geq 98\%$ , Sigma Aldrich) in 50 mL of the sample:



### 2.2. NTP treatment in DBD reactor

In this research NTP treatment was performed using coaxial DBD reactor, which was operated in the air at atmospheric pressure [32]. With the application of peristaltic pump the solution of 4CP passed through the central tube to the top of the DBD reactor and then formed a thin layer over the inner electrode, therefore it was in the direct contact with plasma. Plasma above the water layer generates ozone and UV radiation; produces wide range of reactive species, excited atoms, molecules (such as  $\text{H}_2\text{O}_2$  and  $\text{O}_3$ ), electrons and ions in both gas and liquid phase. Reactor of such design was reported as successful in phenol removal from the water [33]. Electric discharges were generated in the air between the glass and the water layer at a distance of 3.5 mm, by applying a voltage of 17 kV at frequency of 200 Hz and with power of  $\sim 50$  W. The scheme of coaxial DBD is shown in Fig. 1a and described in detail by Dojčinović et al. [34]. To increase the total flow of treated solutions three discharges were connected in parallel (Fig. 1b). Plug-in power for this system of the discharges was  $\sim 150$  W.

The flow rate solution through three in parallel connected DBD reactors was 210 mL/min. During every pass through the reactor the same amount of energy density  $\sim 45$  kJ/L was introduced into the solution. Solutions were recirculated eight times (energy density 45–360 kJ/L).

### 2.3. Analytical procedures

#### 2.3.1. HPLC – concentration of the 4CP

Changes of 4CP concentration were detected on Waters 1525 Binary HPLC system, equipped with binary pump and a UV detector (Waters 2487, Dual  $\lambda$  Absorbance Detector). The column Symetry® 5  $\mu\text{m}$  C18, Waters ( $4.6 \times 150$  mm), particle size 5  $\mu\text{m}$ , length 150 mm and inner diameter 4.6 mm was used for analysis. The injection volume of the sample was 10  $\mu\text{l}$  and the flow rate of eluent was 1.0 mL/min. The compounds were eluted with a binary system of acetonitrile–water (HPLC grade, Sigma Aldrich). The mobile phase gradient was initially 30% acetonitrile, increasing

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