

**NON-THERMAL PLASMA INDUCED DECOMPOSITION  
OF 2-CHLOROPHENOL IN WATER \*****P. Lukeš<sup>1\*</sup>, M. Člupek\*, V. Babický\*, P. Šunka\*, G. Winterová<sup>†</sup>, V. Janda<sup>†</sup>***\* Institute of Plasma Physics, Academy of Sciences of the Czech Republic  
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Application of non-thermal plasma produced by pulsed corona discharge in water for degradation of 2-chlorophenol has been investigated in reactor with the needle-plate geometry of electrodes. It was shown that decomposition of 2-chlorophenol by the discharge can be referred essentially to the oxidation by hydroxyl radical and it can be described by the first order kinetics. The complete removal of  $500 \mu\text{mol.l}^{-1}$  2-chlorophenol by the discharge was attained in the presence of ferrous ions with the energy efficiency of  $3.5 \times 10^{-3} \mu\text{mol.J}^{-1}$ . Chlorohydroquinone, chlorobenzoquinone, 3-chlorocatechol and catechol were detected as the primary decomposition products.

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**1 Introduction**

The removal of hazardous organic pollutants from groundwater and wastewater is one of the critical and urgent topics in the environmental research. Since many of these pollutants are biologically rather resistant, the applications of common water clarification treatments are often not efficient. Great attention is, therefore, focused on so-called advanced oxidation processes (AOPs) that are based on generation of highly reactive species, especially hydroxyl radicals, which are capable to oxidize virtually any organic in the solution. Among a number of AOPs studied, non-thermal plasmas produced by different types of electrical discharges have recently attracted particular interest as an alternative method of water treatment. The pulsed high voltage discharges generated directly in water have been demonstrated to initiate a variety of chemical and physical effects. These include intense ultraviolet radiation, overpressure shock waves, high electric field and, in particular, formation of chemically active species such as  $\text{OH}\cdot$ ,  $\text{H}\cdot$  and  $\text{O}\cdot$  radicals and hydrogen peroxide  $\text{H}_2\text{O}_2$  molecules [1-3]. These physical and chemical processes can subsequently act on biological cells and chemical compounds dissolved in water. Magnitude of their contributions strongly depends upon the pulse power of the discharge and also solution conductivity. Previously, pulsed corona discharges in water have been shown to be effective at

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degrading a number of small organic compounds including phenol [4-8] and organic dyes [9-11], and at deactivating of microorganisms in water [12].

In the present paper we report the results of degradation of 2-chlorophenol by means of pulsed streamer corona discharge in water focusing on the identification and quantitative determination of primary aromatic byproducts and also to discuss the fundamental mechanisms of plasma induced degradation of given chlorophenol.

## 2 Experimental apparatus and methods

Apparatus for generating of pulsed streamer corona discharge in liquid phase was described in detail in [6]. Briefly, electrode system of the needle-plate geometry immersed in a cylindrical glass vessel (volume 1150 ml) was used with the needle-plate distance of 28 mm. Needle electrode was made from mechanically sharpened tungsten wire and the ground electrode was from stainless steel. A pulsed high voltage applied to the needle was provided by a pulse power supply. It consists of a variable voltage 0-30 kV DC source, a low inductance storage capacitor ( $C=7$  nF) equipped with a high-frequency filter to reduce electromagnetic interference and a rotating double spark gap giving the maximum pulse repetition frequency of 100 Hz. Reaction vessel was cooled by water circulation system ( $T=3^{\circ}\text{C}$ ) to ensure a constant temperature in the reactor ( $\sim 13^{\circ}\text{C}$ ). A magnetic stirring bar at the bottom of the reactor provided sufficient solution mixing.

The concentrations of 2-chlorophenol and its aromatic by-products in the solution were measured using a Hewlett Packard high-performance liquid chromatograph HP 1050 equipped with a  $5\ \mu\text{m}$   $\text{C}_{18}$  reverse phase column (25 cm long, 3 mm i.d., Vydac). A two-solvent gradient elution program was used. Solvent A consisted of 1% acetic acid and 99% water and solvent B was 100% acetonitrile. The mobile-phase flow rate of  $0.3\ \text{ml}\cdot\text{min}^{-1}$  was used. The phenols were determined using HP 1050 multiple wavelength detector (250, 274 and 290 nm) and simultaneously with HP 1046A fluorescence detector (excitation and emission wavelengths 271 and 297 nm, respectively). Identification and quantitative analysis were based on peaks retention times and calibration method with standard solutions. Chloride ion concentration was obtained using a Theta 90 Model ISE 103 Cl chloride ion selective electrode coupled with a Theta 90 Model RE 405/ i argent chloride reference electrode.

## 3 Results and Discussion

Fig. 1 shows the time dependence of the degradation of  $500\ \mu\text{mol}\cdot\text{l}^{-1}$  2-chlorophenol (2-CP) by the pulsed corona discharge in aqueous solution of two different compositions. Line (a) corresponds to the degradation of 2-CP by the discharge in the solution of dilute sulfuric acid ( $100\ \mu\text{mol}\cdot\text{l}^{-1}$ ) and line (b) demonstrates 2-CP removal in the solution containing  $250\ \mu\text{mol}\cdot\text{l}^{-1}$   $\text{FeSO}_4$ . Initial solution conductivity of  $100\ \mu\text{S}\cdot\text{cm}^{-1}$  and the applied voltage of the positive polarity of 21 kV with the pulse repetition rate of 35 Hz (mean power input 54 W) were used in each case. As it follows from Fig. 1, the degradation of 2-CP was notably accelerated in the presence of ferrous ions in the solution. For given conditions 50% degradation of 2-chlorophenol was attained after 12 min (removal efficiency  $6.3 \times 10^{-3}\ \mu\text{mol}\cdot\text{J}^{-1}$ ) and more than 98% after 50 min ( $3.5 \times 10^{-3}\ \mu\text{mol}\cdot\text{J}^{-1}$ ) in the presence of ferrous ions whereas only slow degradation

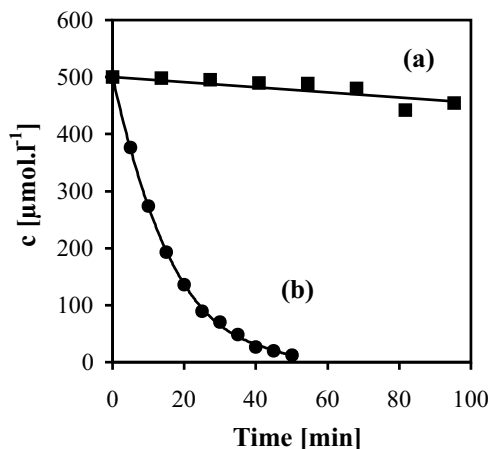


Fig. 1. Degradation of 2-CP by pulsed corona discharge in (a)  $100 \mu\text{mol.l}^{-1}$   $\text{H}_2\text{SO}_4$  and (b)  $250 \mu\text{mol.l}^{-1}$   $\text{FeSO}_4$ .

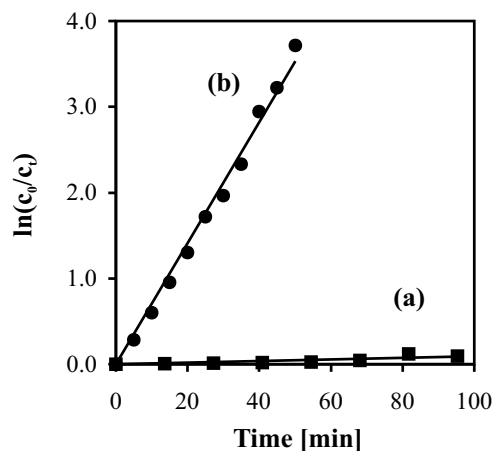


Fig. 2. First-order plot for degradation of 2-CP by pulsed corona discharge in (a)  $100 \mu\text{mol.l}^{-1}$   $\text{H}_2\text{SO}_4$  and (b)  $250 \mu\text{mol.l}^{-1}$   $\text{FeSO}_4$ .

of 2-CP was obtained in the solution of dilute sulfuric acid ( $1.9 \times 10^{-4} \mu\text{mol.l}^{-1}$ ). The same effect of iron on the efficiency of the pulsed corona discharge process was observed previously during degradation of phenol [5-7]. As hydrogen peroxide is produced by the discharge, the effect of iron addition is assumed to be mainly in an increased concentration of  $\text{OH}\cdot$  radicals due to decomposition of  $\text{H}_2\text{O}_2$  in Fenton-type reactions by ferrous and ferric ions [13,14].

Regression analysis of the concentration curves of 2-CP versus treatment time by the discharge indicated that the decomposition rate of 2-CP can be described by first order kinetics with respect to 2-CP concentration  $\ln \frac{c_0}{c_t} = k_0 \cdot t$  where  $c_0$  and  $c_t$  are concentrations of 2-chlorophenol at times 0 and  $t$ ,  $k_0$  is first order rate constant and  $t$  is treatment time. For each set of data concerning the decay of 2-CP in the solution of sulfuric acid (a) or with addition of ferrous ions (b) straight lines with good correlation were obtained, as demonstrated in Fig. 2. The calculated first order rate constants of 2-CP degradation by the discharge under the same experimental conditions as in Fig. 1 were  $1.5 \times 10^{-5} \text{ s}^{-1}$  and  $1.2 \times 10^{-3} \text{ s}^{-1}$  for the case (a) and (b), respectively.

Fig. 3 shows the formation of aromatic by-products during the degradation of  $500 \mu\text{mol.l}^{-1}$  2-chlorophenol by the pulsed corona discharge in the presence of  $250 \mu\text{mol.l}^{-1}$   $\text{FeSO}_4$ . Chlorinated dihydroxybenzenes ( chlorohydroquinone (CHQ), chlorobenzoquinone (CBQ), and 3-chlorocatechol (3-CCC) ) were detected as the main primary products and catechol (CC) as chlorine free aromatic by-product was identified in minor amount (Fig. 4). Further disappearance of these intermediates in later treatment times suggests that the decomposition pathway of 2-chlorophenol by the discharge proceeded to the oxidative ring cleavage resulting in the formation of aliphatic products and dechlorination. This is supported by the results obtained from measurement of chloride ions release when  $293 \mu\text{mol.l}^{-1}$  of chlorides was determined in the treated solution after complete degradation of 2-chlorophenol substrate (approximately 60% dechlorination).

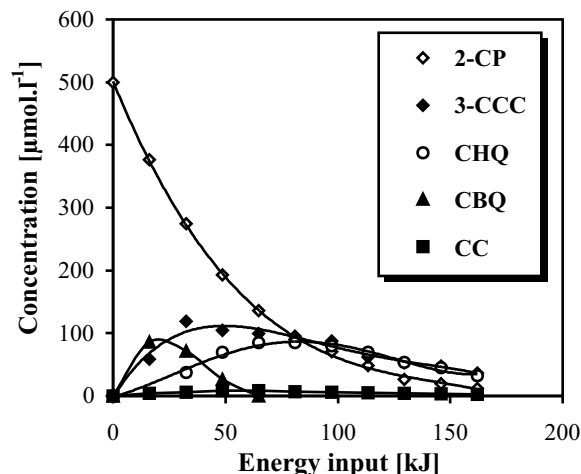


Fig. 3. Degradation of  $500 \mu\text{mol.l}^{-1}$  2-chlorophenol by pulsed corona discharge and formation of aromatic by-products in the presence of  $250 \mu\text{mol.l}^{-1}$   $\text{FeSO}_4$ . Applied voltage 21 kV, power input 54 W, initial solution conductivity  $100 \mu\text{S.cm}^{-1}$ .

From the pattern of formed products (Fig. 4) it is apparent that the decomposition of 2-chlorophenol by the pulsed corona discharge can be referred essentially to the oxidation by the hydroxyl radical. When  $\text{OH}\cdot$  radical reacts with the aromatic hydrocarbons predominantly by the electrophilic addition on the  $\text{C}=\text{C}$  double bonds at aromatic ring, initially  $\text{OH}$  adducts (chlorodihydroxycyclohexadienyl radicals (CDHCD)) are produced as the main transients (Fig. 5, path A). Consequently, in the presence of oxygen CDHCD $\cdot$  radical may form organoperoxyl radical. The decay of such transients leads largely through the elimination of  $\text{HO}_2\cdot$  radical to the hydroxylated products of 2-CP or also to the direct fragmentation of aromatic ring of 2-CP [14-16]. The isomeric distribution of formed chlorodihydroxybenzenes indicates that the hydroxylation of 2-chlorophenol was preferably at the *ortho* and *para* positions to the phenolic group. This is consistent with the electron-donating character of  $\text{OH}$ - and  $\text{Cl}$ - groups and the electrophilicity of hydroxyl radical. Although both substituents ( $\text{OH}$ -,  $\text{Cl}$ -) are *ortho/para* directors of the elec-

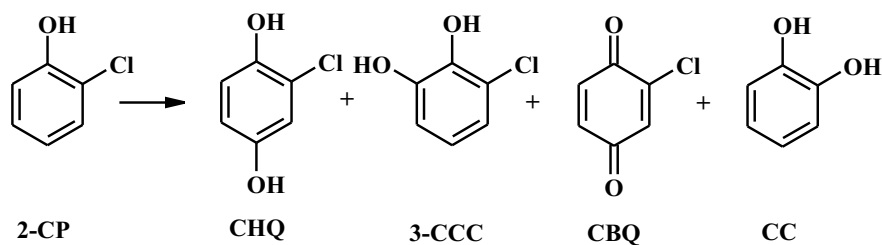


Fig. 4. Identified aromatic by-products formed during degradation of 2-CP by pulsed corona discharge.

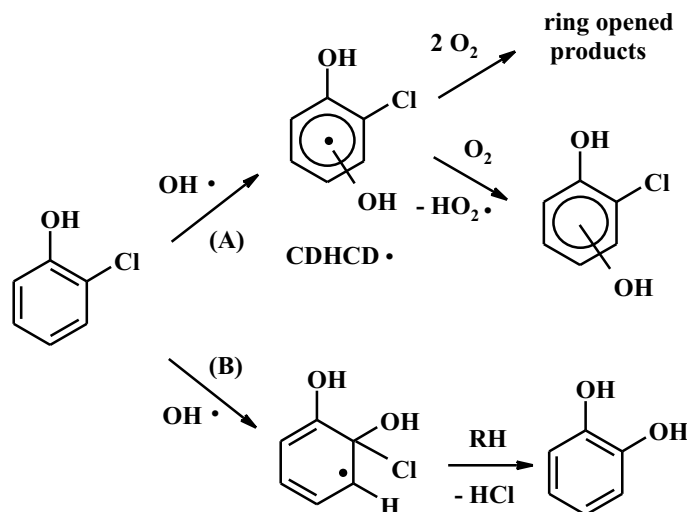


Fig. 5. Scheme of 2-CP oxidation by OH· radical attack.

trophilic substitution, the further OH· attack is directed in the *ortho/para* positions with respect to the OH group, which has a higher electron donating capacity than the chlorine. The small amount of catechol identified as a chlorine free aromatic by-product is derived from the OH· attack on the chloro-position of 2-chlorophenol (Fig. 5, path B) [15]. On the other hand, the initial formation of chlorobenzoquinone in place of chlorohydroquinone indicates possible oxidation of 2-chlorophenol also by HO<sub>2</sub>· radical in coupling reaction with phenoxy radicals [16]. The fast loss of CBQ from the reaction mixture is possibly due to shifting the redox equilibrium of CBQ/CHQ system during the experiment.

#### 4 Conclusions

Conversion of 2-chlorophenol and formation of oxidized reaction by-products by pulsed streamer corona discharge in needle-plate electrode geometry have been determined. Chlorohydroquinone, chlorobenzoquinone, 3-chlorocatechol and catechol were detected as the primary 2-chlorophenol decomposition products. It was shown that the decomposition of 2-chlorophenol by the discharge can be referred essentially to the oxidation by hydroxyl radical and it can be described by the first order kinetics. The attack of hydroxyl radical was strictly on *ortho* and *para* positions to the phenolic OH-group, due to the electron-donating character of phenolic OH group and the electrophilicity of the OH· radical.

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