

DEGRADATION OF 4-CHLOROPHENOL USING WATER FALLING FILM DBD REACTOR

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Abstract. In this paper we present experimental results of degradation of 4-chlorophenol using falling film dielectric barrier discharge (DBD) reactor. Degradation of 100 ml/L water solution of 4-chlorophenol was examined using catalysts in four different set of conditions: DBD, DBD/H₂O₂, DBD/TiO₂ i DBD/Fe²⁺. Kinetics of the 4-chlorophenol degradation in several successive passes trough the reactor was monitored using HPLC. Changes in concentrations of carbon that originate from products of degradations like acetic, formic and oxalic acids and changes in concentrations of carbon calculated on basis of degraded 4-chlorophenole are presented.

1. INTRODUCTION

Today, water treatment deserves more and more attention especially waste water treatment. Goal of the waste water treatment is to remove hazardous contaminates from water. There are many processes for water treatment: chemical, physical and biological treatment and combination of them (Droste 1997). Chlorphenoles are contaminants with toxicity for humans and animals. They are non biodegradable and their removal is not simple. Chlorophenoles are intermediers in synthesis of many pesticides, herbicides, fungicides, insecticides and paints. They have anti-bacterial activity so they are used for disinfection in some cases. In process of water chlorination they arise as products of phenol chlorination. So they could be found in surface water, groundwater and especially in wastewater.

Chlorophenoles are bioaccumulative and their bioaccumulation increase with substitution on phenol ring. *Ortho*-substituted chlorophenoles are less toxic than *meta*- and *para*-substituted derivatives. Standard techniques for water treatment as coagulation, carbon adsorption, reverse osmosis, ultrafiltration and similar could not remove chlorphenoles. Advanced oxidation processes (AOPs) are one of alternatives for their removal. These processes could completely degrade chlorphenoles to carbon-dioxide or to biodegradable and less toxic intermediers. AOPs are

based on free radicals (hydroxy radicals) formations which have the strongest oxidation potential after fluorine (Tang 2004)

The aim of this research was to examine different conditions for degradation of 4-chlorophenol. Degradation was performed with AOPs using non-thermal plasma reactor based on coaxial dielectric barrier discharge with water film. In this investigation we examine the influence of barrier discharge on several of 4-chlorophenol solutions.

2. EXPERIMENTAL SETUP

Starting concentration of 4-chlorophenol was 100 mg/L (56.06 mg/L carbon). Four different sets of conditions were examined: DBD, DBD/H₂O₂, DBD/TiO₂ and DBD/Fe²⁺, where DBD notifies influence of barrier discharge on water solutions. Starting pH values were adjusted to pH 9.00 with NaOH and only in case DBD/Fe²⁺ pH was adjusted to pH 3.50 with sulphuric acid. Solutions were passing eight times through the DBD reactor. Concentration of undegradating 4-chlorophenol was determined by HPLC technique. Degradations products, formic, acetic and oxalic acid were quantified using ion chromatography.

Coaxial DBD reactor used in our investigation was designed as a nonthermal plasma reactor operated at atmospheric pressure (Kuraica *et al.* 2004). In this reactor water formed thin layer which is in direct contact with plasma, see Figure 1. Reactor of such design was successful in phenol removal from water (Manojlović *et al.* 2006, Dojčinović *et al.* 2008). It is very efficient because plasma which is generated above water generates ozone and UV radiation. It also produces free radicals as ·OH, excited atoms O, molecules, electrons and ions. Schematic of DBD is shown on Figure 1. Cylindrical reactor was prepared with Pyrex tubes with internal diameter of 28.5 mm and length of 600 mm. Outer electrodes were made with aluminum foil which is sealed on outer glass tube on 400 mm length. Inner electrodes were stainless steel with 21.3 mm diameter cylinder. Barrier discharge was generated between inner metal electrode and outer glass tube which was dielectric in our system.

Solutions of 4-chlorophenols were passed on the top of reactor through inner electrodes using peristaltic pump. Flow rate through three parallel connected DBD reactors were 210 mL/min. Solutions were recirculated eight times. Electric discharge was generated in air with 3.5 mm gap between glass electrodes and water film by applying voltage up to 20 kV on 200 Hz and with 150 W power.

Solution of 4-chlorophenol, concentration 100 mg/L, was prepared by dissolution of p.a. 4-Chlorophenol purchased from Aldrich. Concentration of hydrogen peroxide used in experiments was 20 mmol/L. It was added in solution before passing solution through reactors. TiO₂ (AEROXIDE® TiO₂ P25 Degussa) were used in experiments with TiO₂. Concentrations of TiO₂ in suspension were 1 g/L. Concentration of Fe²⁺ was 5 mg/L. In one pass of solution through three parallel DBD reactors with flow rate of 210 mL/min energy of about 18 kJ/L was introduced in solution.

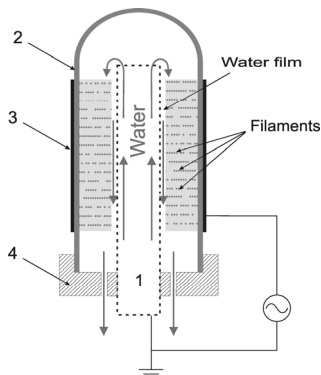


Figure 1: Schematic picture of coaxial falling film DBD reactor. 1 – iner electrode, 2 – glass tube, 3 – outer electrode, 4 – plastic holder.

3. RESULTS AND DISCUSION

Changes of 4-chlorophenol concentrations in various solutions during treatment in DBD reactor are presented in Figure 2. Starting degradation was best in DBD reactor without any addition, where for one pass and energy of about 18 kJ/L, degradation of 4-chlorophenol of about 28 % was achieved. In the second pass in all four examined systems and energy of 36 kJ/L achieved degradations were around 30 %. Further passing of solutions through reactors show that best results were obtained in solution with Fe^{2+} where degradations of about 5 to 10 % per pass were obtained.

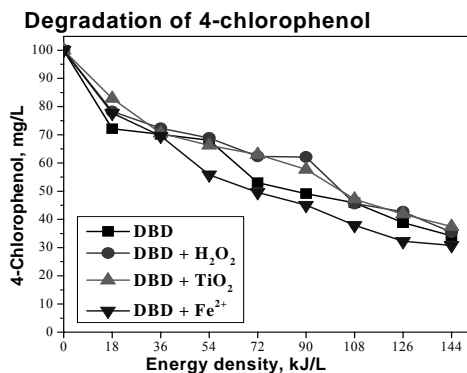


Figure 2: Change of concentration during the 4-chlorophenol degradation in different systems in the DBD reactor.

Changes in concentrations of carbon that originate from some products of degradations like acetic, formic and oxalic acids and changes in concentrations of carbon calculated on basis of degraded 4-chlorophenole is shown in Figure 3. Sum of carbon concentrations calculated from all identified species is also shown. In all cases, concentrations of 4-chlorophenol decrease with increased number of pass.

On the other hand, concentration of oxalic acid (product of degradation) at first increases and then decreases. In all cases where degradations were catalyzed we can see that catalyst favored total degradation and that concentration of acetic and formic acid as final products of degradation remained unchanged. Lowest concentration of degradation products were obtained in DBD/Fe²⁺. Iron(II) is homogeneous photocatalyst which dominantly catalyze degradation of organic acid which are capable to create complexes with iron(II) (Andreozzi *et al.* 2006).

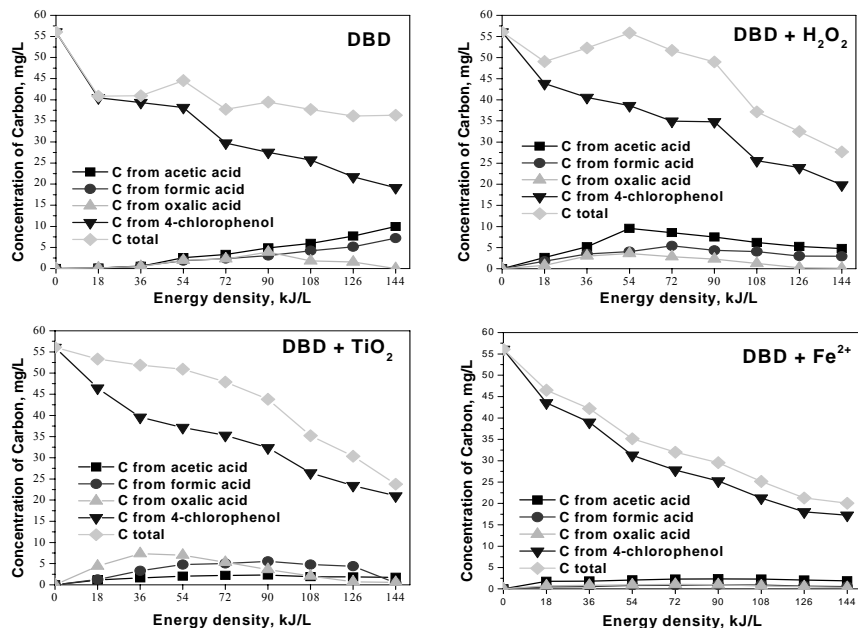


Figure 3: Change of carbon concentration in different systems during the degradation of 4-chlorophenol in the DBD reactor.

References

- Andreozzi, R., Canterino, M., Marotta, R.: 2006, *Water Research*, **40**, 3785.
- Dojčinović, B. P., Manojlović, D., Roglić, G. M., Obradović, B. M., Kuraica, M. M., Purić J.: 2008, *Vacuum*, **83**, 234.
- Droste, R. L.: 1997, *Theory and practice of water and wastewater treatment*, John Wiley & Sons, New York, , pp. 219-234.
- Kuraica, M. M., Obradović, B. M., Manojlović, D., Ostojić, D. R., Purić, J.: 2004, *Vacuum*, **73**, 705.
- Manojlović, D., Ostojić, D. R., Obradović, B. M., Kuraica, M. M., Krsmanović, V. D., Purić, J.: 2006, *Desalination*, **213**, 116.
- Tang, W. Z.: 2004, *Physicochemical Treatment of Hazardous Waste*, Lewis Publishers.