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DEGRADATION OF AQUEOUS PHENOL SOLUTIONS BY COAXIAL DBD REACTOR

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Abstract. Solutions of 2-chlorophenol, 4-chlorophenol and 2,6-dichlorophenol in bidistilled and water from the river Danube were treated in plasma reactor. In this reactor, based on coaxial dielectric barrier discharge at atmospheric pressure, plasma is formed over a thin layer of treated water. After one pass through the reactor, starting chlorophenols concentration of 20 mg/l was diminished up to 95%. Kinetics of the chlorophenols degradation was monitored by High Pressure Liquid Chromatography method (HPLC).

1. INTRODUCTION

Chlorophenols are important intermediers during synthesis of pesticides, herbicides and dyes. Also, they have arisen in the chlorination process of water with high organic carbon concentration. The chlorophenols are very toxic materials for humans and animals. They are even more toxic than phenols. The chlorophenols are most often found in natural and waste waters. In this paper we have given the demonstration of degradation efficiency for 2-chlorophenol, 4-chlorophenol and 2,6-dichlorophenol by plasma reactor based on a coaxial dielectric barrier discharge (DBD), see Kuraica et al. 2004, Manojlovi et al. 2006. DBD plasma reactor was used for direct water ozonation, see Gottschalk et al. 2000, Tajima et al. 2001. The chlorophenols degradation dynamics were tested in synthetic waters, see Andreozzi et al. 1999, Benitez et al. 2000, in bidistilled water and water from the river Danube, taken near Belgrade. These waters were used as matrix waters. The coaxial DBD as a plasma reactor system operates in the air at atmospheric pressure. In the reactor one of the dielectric layers is the flowing water. This reactor is very efficient because the plasma that is formed abovewater has, except ozone, also UV radiation and radicals (e.g. OH·), excited atoms (e.g. O·) and molecules, electrons and ions. Existence of so many reactive species in plasma and in water is the reason why electrical discharges that have plasma in direct contact with water solutions are very interesting for many researches. There are several discharges in which plasma is formed above water, like corona above water, see e.g. Grabowski et al. 2006, Lukes et al. 2005, or DBD above water, see Bubnov et al. 2006.

2. EXPERIMENTAL SETUP

A schematic diagram of experimental setup is shown in Fig. 1. Water flows up through a vertical hollow cylindrical electrode (diameter 21.5 mm) and flows down making a thin dielectric film over the electrode. Discharge is generated in air within 4 mm gap between the dielectric and the water layer by applying voltage up to 20 kV, as shown in Fig. 1. Plasma produced in coaxial DBD reactor is typical for silent (filamentary) discharges and consists of numerous micro discharges (filaments). Ozone generated in this discharge sustained in the gap between outer glass barrier electrode (diameter 30 mm; thickness 1.5 mm) and flowing water layer as inner barrier electrode of coaxial DBD reactor. High voltage at 50 Hz is applied between the inner, grounded stainless steel electrode and outer metal electrode 40 cm in length. To increase the water flow through the reactor (∼150 ml/min) three coaxial DBD units are connected parallel, as shown in Fig. 1. The process of chlorophenols degradation was tested with several synthetic samples prepared by dissolving of analytical grade 2-chlorophenol, 4-chlorophenol and 2,6-dichlorophenol in bidistilled water and water from Danube, with chemical oxygen demand (COD) between 92 and 105 mg O2/l, and pH from 6.2 to 6.5. Amount of 5 l of synthetic water (20 mg/l corresponding phenol concentration) was prepared per sample, and it was instantly treated with DBD. The concentration of dissolved and residual ozone was determined by standard methods, see e.g. Eaton et al. 1995, (for dissolved ozone the iodometric method and for residual ozone the indigo colorimetric method). Residual ozone concentration was determined by photometer (PC 22, LOVIBOND), and original reagents indigo- trisulfonate in pills were used. The chlorophenol concentration was determined by chromatographic method by HPLC (Agilent1100 Series), under these conditions: colon LiChrospher 100 RP-18 (250 × 4 mm, 5 μm) Agilent Technologies; UV detector; A (H_2O) and B (MeCN) solutions; sample volume 50 ml at 280 nm wavelength. The chlorophenol concentration has been determined before plasma treatment, and after the plasma treatment, every 5 min for the first 20 min; after 1 h, and after 24 h. During the monitoring of degradation process, synthetic samples were kept in well closed vessels with no gas exchange with atmosphere. The increase of 2,6-dichlorophenol degradation is obtained with another passing of the sample trough the DBD plasma reactor (recirculation after 1 h).

3. EXPERIMENTAL RESULTS AND DISCUSION

Change of the concentrations of 2-chlorophenol in bidistilled water and real water samples from Danube with time is presented in Fig. 2a. The concentration of 2-chlorophenol decreases significantly during ozonation, and then decreases slowly. In bidistilled water after 24 h, concentration of 2-chlorophenol is 0.01 mg/l, i.e. degradation of 2-chlorophenol is 99.95%. Corresponding results for Danube water are 1.05 mg/l with degradation of 94.8%. Change of the concentrations of 4-chlorophenol in bidistilled water and Danube water with time is represented in Fig. 2b. From Fig. 2b one can see a significant decrease of 4-chlorophenol concentration in bidistilled water during DBD treatment and after 5 min. During further time degradation, concen-

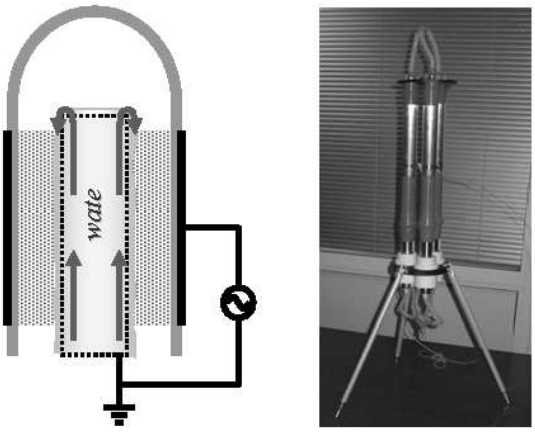

Figure 1: Schematic picture of coaxial DBD and photo of three parallel connected DBDs.

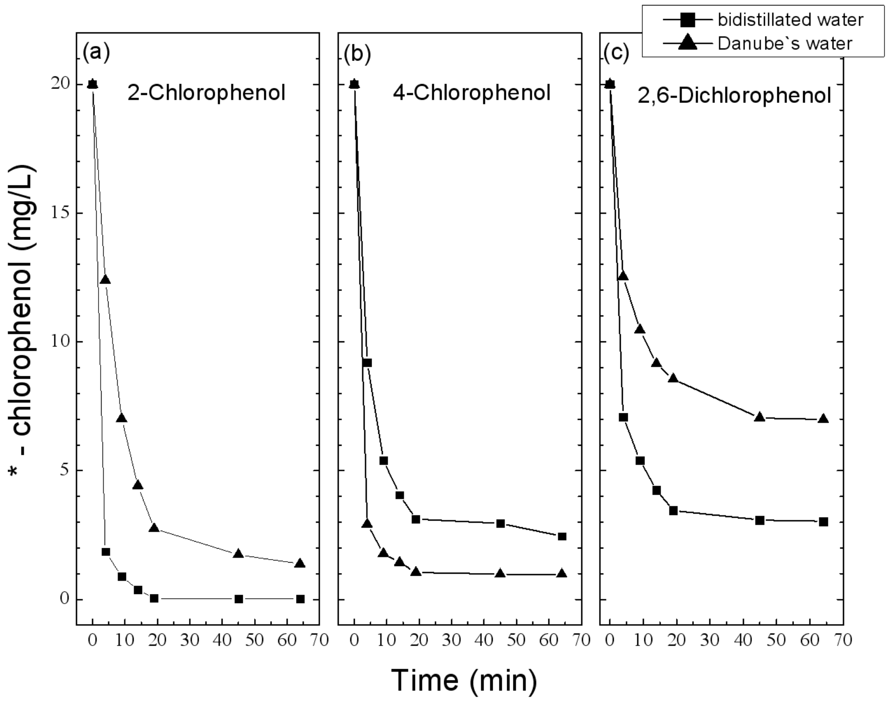

Figure 2: Change of the concentrations of (a) 2-chlorophenol, (b) 4-chlorophenol, and (c) 2,6-dichlorophenol in bidistilled water and Danube water with time degradation.

tration change is relatively small. The percentage of removed 4-chlorophenol after 24 h for bidistilled water is 96%, and for Danube water 89.8%. Change of the concentrations of 2,6-dichlorophenol in bidistilled water and Danube water with time is represented in Fig. 2c. The percentage of removed 2,6-dichlorophenol after 24 h for bidistilled water is 85%, and for Danube water 74.6%. With recirculation after 1 h, 2,6-dichlorophenol is removed for bidistilled water for 93.8%, and for Danube water 90.2%. With the recirculation, better results are obtained. These results can be explained by higher stability of 2,6-dichlorophenol for reaction with OH radical, i.e. smaller number of places for possible reactions according to previously published results, see Tang et al. 1996.

The 2,6-dichlorophenol is more resistant towards ozone compared to 2-chlorophenol and 4-chlorophenol. The percentage of phenol removal from Danube water was considerably lower than the corresponding value for bidistilled water. Lower removal of chlorophenols from sample prepared with Danube water could be explained by protective effect of fulvic and humic acids which also reacted with ozone. During the experiments, although the total oxidation capability was high, residual ozone concentration was low. Therefore, we have assumed that active species was hydroxyl radical (OH·), which is in accordance with previously published results obtained when nonthermal plasma was in contact with water solutions, see Lukes et al. 2005. The DBD plasma reactor construction enabled synergetic effect for advanced oxidation process: simultaneous exposition of water layer to ionized gas and to UV emission from the electric discharge, see Legrini et al, 1993. UV light induces homolyses of O_3 and subsequent production of OH·, radicals by the reaction of O· with water, see Glaze et al. 1987. Small concentration of residual ozone, and large concentration of, so called "dissolved ozone", could be explained in this way. The proposed mechanism of reactions of hydroxyl radical with chlorophenol was previously described, see e.g. Lukes et al. 2003, Long et al. 2007. The chlorophenols undergo two types of reactions. One is chlorine substitution and other is hydroxylation in ortho or para positions. Reaction of substitution is much slower and this is possible explanation for less efficient degradation of 2,6-dichlorophenol. The obtained quinoness undergo further degradation through dicarboxylic acids resulting finally in carbon dioxide production.

4. CONCLUSION

The coaxial DBD with flowing water as one of the dielectric layers has been used as the plasma reactor for treatment of water with high content of chlorophenols. In the experiments performed at laboratory level, with 2-chlorophenol, 4-chlorophenol and 2,6-dichlorophenol dissolved in bidistilled water, after 24 h, 99.95%, 96.0% and 85.0% of chlorophenols were removed, respectively. Corresponding values for Danube water were significantly smaller: 94.8%, 89.8% and 74.6%. With recirculation after 1 h, 2,6-dichlorophenol was removed 93.8% and 90.2% in bidistilled and Danube water, respectively.

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