Phenol degradation in water whirling around DC arc

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Abstract: DC plasma torch with adjustable arc power was used for the degradation of phenol dissolved in water. The plasma torch involves the combination of a gas stabilized anode part and a water stabilized arc part. Water whirl surrounds the arc in the water stabilized arc part and is formed by tangential injection/ejection of water. Phenol dissolved in water circuit used for arc stabilization in concentration of 100 mg/l and its degradation byproducts were analyzed by means of HPLC with UV and fluorescence detection. Experimental results show that approximately 90% of phenol was removed from aqueous solution in comparison with its initial concentration in 40l water circuit after 25 minutes plasma treatment (electric power in plasma: 40 kW), while byproducts concentrations increased during experiment. Some basic chemical mechanisms of degradation are suggested.

Keywords: Plasma, phenol, degradation, DC plasma torch, benzoquinone.

1. Introduction

Is water a commodity or a human right? Such a question was formed by Maeve Shearlaw from Guardian [1]. Whether the answer is "yes" or "no", nothing can change the fact that water purification has taken a more and more important role during last decades. The very special technique of water purification is the usage of electrical discharge. This paper describes the usage of DC electrical discharge surrounded by water whirl (also called Gerdien arc [2]) for these purposes.

The main features of Gerdien arc are very high plasma temperatures and thus high intensity of short wave ultraviolet radiation. Water flows with high flow rate in a thin layer around the arc column. Such configuration results to the fact that all water flowing through the torch passes the positions with high level of ultraviolet radiation.

2. Experiment

Experiments were carried out with the plasma torch with the arc power of 40 kW (200 A, 200 V). The cathode part of the arc column is created by an arc stabilized by argon flow, argon plasma enters the chamber with Gerdien arc, where the arc column is stabilized by a direct contact with water vortex, which surrounds the arc (Fig.1). Argon flow rate was set up to 22.5 slm during the experiments. Water with the flow rate of 18.5 l/min circulates around the arc in the layer depth of 1 mm at the distance of 3 mm from the centreline of high temperature arc column. The centreline plasma temperature that was measured by optical emission spectroscopy is over 15 000 K [3]. Water is injected tangentially into the arc chamber under constant pressure and flow rate and evaporates at the rate of 15 g./min   that is insignificant amount due to the volume of a water tank and the duration of the experiment.

Fig. 2 presents simplified scheme of the system for controlling of water entry and output pressures and for measurement of temperatures and flow rates. A sampling point is located between the water tank and the plasma torch (water with dissolved phenol flows from the water tank through the sampling point to the plasma torch).
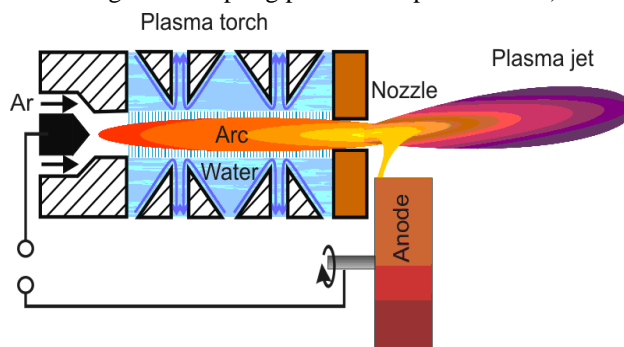

Fig. 1 Schema of hybrid stabilized plasma torch
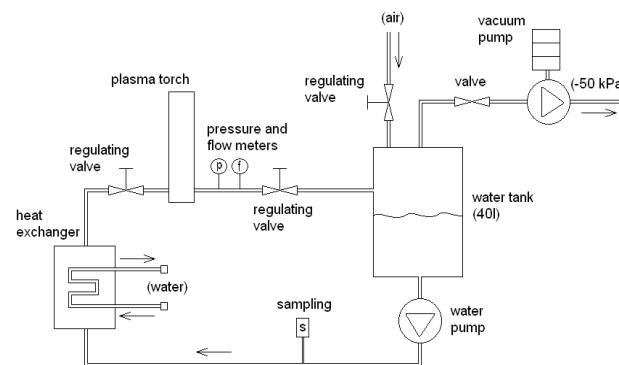
Fig. 2 Simplified scheme of plasma torch water system

Phenol degradation has been frequently studied in many papers [4, 5], sometimes with the presence of various additives in water [6–8].

This paper deals with the non-catalytic degradation of phenol dissolved in water in the amount of 100 mg/l (approximately 1 mmol/l).

The HPLC analysis of phenol (PH) and its aromatic degradation products (hydroquinone (HQ), catechol (CC), 1,4-benzoquinone (BQ), hydroxyhydroquinone (HHQ), hydroxybenzoquinone (HBQ), muconic acid (MUC) – see Fig. 3) has been carried out on column Supelcosil LC-18 (2.1 mm ID, 25 cm length, 5μm) by means of UV a fluorescent detection.
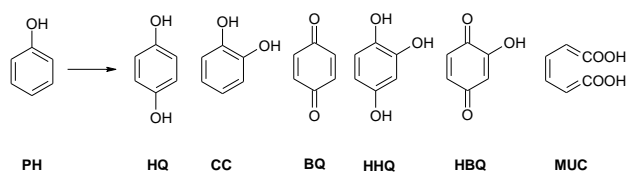
Fig. 3 Phenol and its aromatic degradation derivates - terminology

3. Results

Phenol concentration decreased from 100 mg/l to 10 mg/l during 25 minutes experiment that means the reduction of phenol concentration by 90 % (Fig . 4).
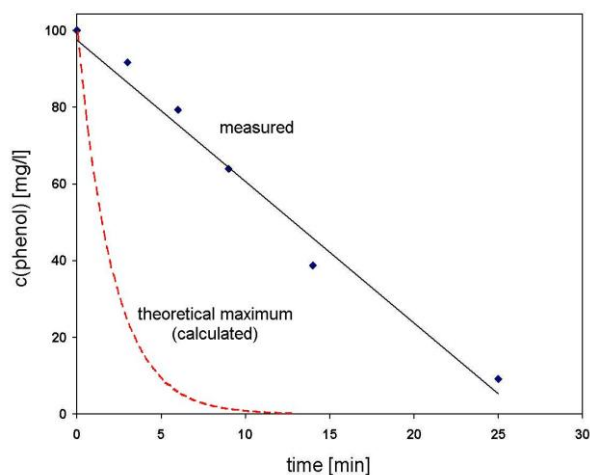
Fig. 4. Decreasing phenol concentration in aqueous solution (points with linear trend), dash line stands for the calculated theoretical maximum of phenol degradation

The linear trend of measured data tempts to the zero-order kinetics of the degradation but first-order would be more probable [8]. The measured data are influenced by

many effects obviously. First of all, the 40 liters water tank with initial phenol concentration of 100 mg/l is continuously diluted by water flow treated by plasma (18.5 l/min). Simple theoretical calculation assumes that phenol passing the arc column is degraded with the efficiency of 100%:

$$\frac{dC}{dt} = -\frac{R}{V}C_0 \tag{1}$$

where t, R, C_0 and V are time, water flow rate (18.5 l/min), initial phenol concentration (100 mg/l) and the volume of the water tank (40 l), respectively. The calculated decrease of phenol concentration shows out much faster degradation than the measured one is. Secondly, OH˙ radicals are formed by the plasma and their concentration in water circuit probably increases in the beginning of the experiment, because it has been measured that H_2O_2 concentration during the experiments increases. OH˙ radicals play important role in phenol degradation process and their lower concentration during first minutes of the experiments might cause a certain delay of the phenol degradation.

1,4-benzoquinone as a known product of phenol degradation was also analyzed (Fig. 5)
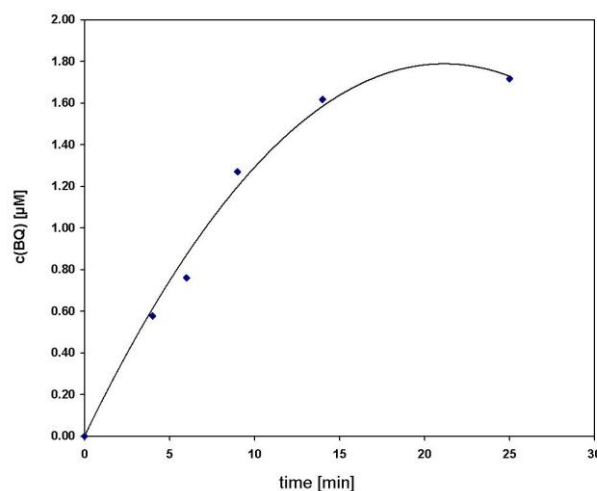
Fig. 5 Kinetics of 1,4-benzoquinone (BQ) during phenol degradation

Other known phenol degradation derivates such as hydroquinone, catechol, muconic acid etc. were not detected at all and even the concentration of 1,4-benzoquinone was due relatively fast phenol concentration decrease relatively low. Maximal 1,4-benzoquinone concentration reaches approximately 0,02 mg/l and the mole ratio of initial phenol concentration to maximal 1,4-benzoquinone concentration is 1:0.16.
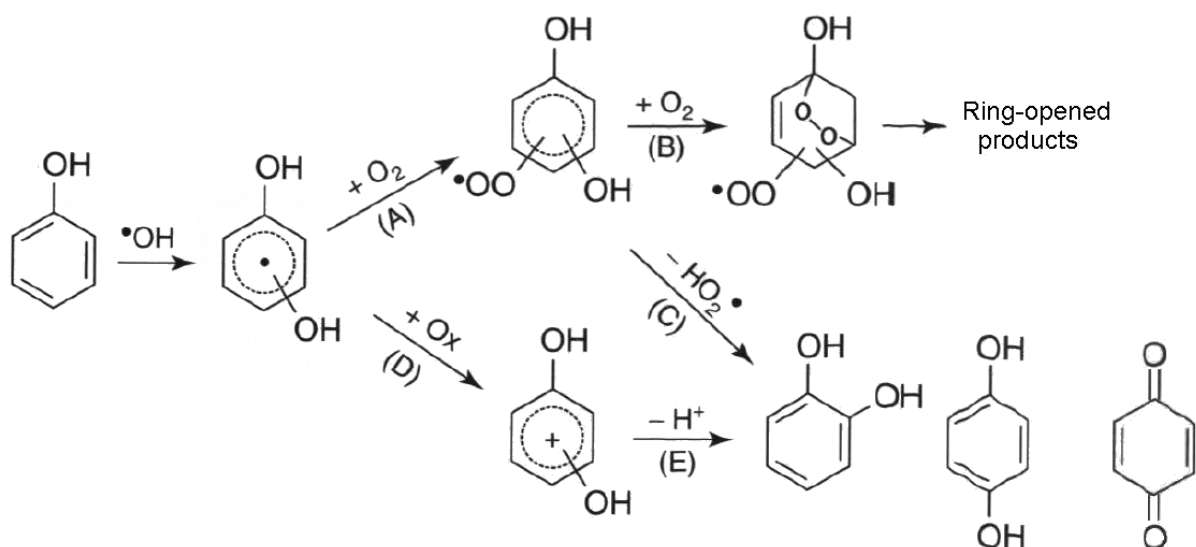
Fig. 6 Mechanism of OH. radical attack on phenol ring [8]

The absence of common phenol derivates mentioned above incites to the photocatalytic degradation way, where the main degradation derivates are just 1,4-benzoquinone (detected), catechol (not detected) and pyrogallol (benzene-1,2,3-triol, not analyzed) [9].

Phenol degradation probably proceeds synergetically by two mechanisms:

- OH. radical attack on phenol ring
- direct phenol photolysis

Further experiments including pyrogallol analysis, TIC + TOC measurements, pH measurement and dissolved oxygen measurement should bring more light into the experiment that looks very simple at the first sight.

The comparison of energetic costs in water treatments facilities is always a tough task, because there is the wide range of model substances, experiments are carried out with different concentrations and mechanisms, with or w/o catalyst, etc. Approachable results usually differ from ones to thousands of kWh/m^3, in the case of simply degradable compound with low efficiency [10] to the case of sonochemical degradation of more stable compounds [11] for example, respectively.

The energy consumption of the described experiment is 417 kWh/m^3 with the 90 % removal of dissolved phenol. If we increased the efficiency of the process (for instance by the adding of catalyst), we could reach theoretical maximum energy consumption of 36 kWh/m^3 due to relatively high flow rate through the plasma torch, but such a value would need adjustment of the water circuit to a non-cyclic water flow trough the plasma torch at least.

4. Summary and Conclusions

The flow of the aqueous solution of phenol without any catalyst was treated by the direct contact with an electrical arc in the plasma torch employing Gerdien stabilization of the arc by a water whirl. Such a unique configuration enables the water flow to meet the high level of UV radiation.

The concentration of phenol was decreased to 10 % with comparison to initial concentration after 25 minutes of plasma treatment.

The described experiment is energetically demanding, but the configuration of Gerdien arc offers the outstanding parameters for water treatment resulting from the small distance between relatively high power DC arc and the water flow.
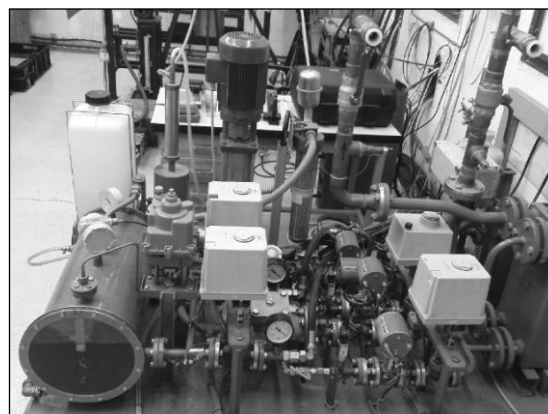

Fig. 7 Water circuit with the 40 liter water tank (bottom left)

5. References

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