Petroleum and Coal

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STUDY OF PHENOL DEGRADATION PATHWAY DURING ELECTROMEDIATED MINERALIZATION

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Received September 9, 2016; Accepted November 2, 2016

Abstract

A new process of electromediated oxidative degradation of phenol and its main intermediate – hydroquinone has been studied. The oxidizers complex has been generated by passing direct current through sulfuric acid solutions containing phenols. To qualitative and quantitative analysis of reaction intermediates a gas chromatography and UV spectroscopy have been used. These analyses have shown total mineralization of toxic products of phenol and hydroquinone and the decay rate constants have maximum values at current density 0.6 A/cm^2. Moreover, the values of pseudo first-order rate constants are comparable to rate constants for non-thermal plasma treatment. According to UV-spectroscopy, the main intermediate of phenol oxidation is *p*-benzoquinone, which has not been identified by GC/MS. In any case, the both phenol and hydroquinone have been successively degraded to carbon dioxide and water at these conditions.

Keywords: phenol; hydroquinone; electromediated oxidation; kinetics.

1. Introduction

The study of phenol oxidation is important from two points of view. Firstly, phenol and substituted phenolic compounds are extremely toxic and namely nonbiodegradable pollutants. The sources of phenolic wastewaters are paint, pharmaceutical and coal industries, pesticide manufacture and others. In the case of storage and inappropriate ways of disposal, for example, an incineration, a subsequent slow release of toxic compounds leads to localized soil and groundwater contamination, and, thus, it represents long-term environmental threats. Secondly, phenol oxidation by different reagents has been widely studied, the intermediates and values of the decay rate constants are well-known.

Among varieties of disposal technologies chemical deactivation/detoxification, providing the opportunity to reduce a toxic chemical to a non-toxic state is considered to be a universal method. Effective mineralization of phenolic toxicants can be achieved by ozonation [1-4], AOPs [5-7], electrochemical oxidation [8-11]. In recent years, innovative advanced oxidation processes (AOPs) using persulfate ($S_2O_8^{2-}$, PS) to generate sulfate radicals (SO_4^{2-}) for degradation and eventual mineralization of refractory organic pollutants have received increasing interest. Sulfate radical is known as a strong one-electron oxidant for its high standard redox potential (E^0 = 2.6 V vs. normal hydrogen electrode (NHE)) being similar to that of the hydroxyl radical (HO·) with E^0 = 2.8 V vs. NHE [12]. Nevertheless, pure reagents application is restricted in their flammability and explosion hazard. Besides, the electricity applied for oxidizers synthesis is cheaper than the equivalent quantity of oxidizers.

In this work persulfate ions and sulfate, radicals are electrogenerated by anodic oxidation of sulfuric acid and sulfates. Moreover, these active reagents are applied to oxidize phenolic toxicants in situ. Such type of electrooxidation could be characterized as indirect (or mediated) electrolysis, where organic pollutants do not exchange electrons directly with the anode surface but rather through the mediation of some electroactive species regenerated there, which act as intermediaries for electrons shuttling between the electrode and organic compounds [13].

The motivation of the present work was to study the application of indirect electrochemical oxidation for phenol-saturated solutions mineralization in detail. The most challenging task was the aromatic ring destruction. In this regard, the study of anodic electrochemical treatment of solutions containing phenol and its first intermediate – hydroquinone was carried out. To qualitative and quantitative analysis of reaction intermediates a UV spectroscopy and gas chromatography with a selective ion detector was used. Those analyses showed total mineralization of toxic products of phenol and hydroquinone. Furthermore, the pseudo first-order rate constants were determined and compared with rate constants for non-thermal plasma treatment [17].

2. Experimental

Chemicals: H_2SO_4 – ACS reagent, 95.0-98.0%, used as 30 % aqueous solution; phenol – for technical purposes; hydroquinone – for technical purposes; ethylacetate – HPLC Plus, for HPLC, GC, and residue analysis, 99.9%; distilled water – pH 5.50 ÷ 6.60.

In the study, the peroxydisulfuric, peroxomonosulphuric (Caro's) acids and their salts were electrogenerated by anodic oxidation of sulfuric acid and sulfates, and then they oxidized the dissolved substance without its isolation.

Oxidation of sulfuric acid solutions (30 % mass.) containing 1 g/dm^3 phenol in 80 ml was carried out in an electrolytic cell with the lead electrodes (S_e=10 cm^2) in amperostatic conditions. The electrochemical installation had been previously described [14]. At these conditions, the high yield of peroxydisulfuric and peroxomonosulphuric acids was observed.

The phenol and hydroquinone decomposition during electrolysis was monitored by UV/vis spectrometer «Evolution – 60» equipped with a quartz cell to collect the UV absorption spectra without phenol or hydroquinone extraction from the sulfuric acid solution. The sampling rate was 10 min and volume – 20 µL diluted into 2 ml distilled water. Such volume allows keeping volume current density as a constant.

To study oxidation products in detail gas chromatograph Agilent 7820 with an ion-selective detector Agilent 5975 was used. In that case, sample preparation included necessary extraction of organic substances from the sulfuric acid solution to avoid SO_4^{2-} ions presence that could damage a chromatographic column. The best solvent for the phenol and hydroquinone extraction was ethyl acetate. The counted effectiveness of its extraction was 75%. Quantitative determination of phenol and hydroquinone during electrolysis was carried out by the absolute calibration method using a calibration curve.

Infrared spectra of sediments were detected by Simex FT-801.

3. Results and disussion

Earlier the efficient appliance of this oxidative system for phenol, nitro- and chloro- derivatives destruction with chemical oxidation demand (COD) measuring has been shown [15]. In this study, it is important to make a comparative analysis of UV-spectra and GC-MS data. The UV difference spectra collected during electrolysis of phenol and hydroquinone are shown in Fig. 1 (a, b), respectively.

Initially, UV-spectra normally has 2 peaks of absorbance at 210 nm and 270 nm for phenol, 210 nm and 290 nm for hydroquinone [16]. It can be seen that after 10 min electrolysis the absorption peak at 245 nm begins to appear. This fact indicates the formation of p-benzoquinone – the main oxidation intermediate. Increasing and broadening of the absorption band in the range from 200 to 230 nm confirms that the oxygen-containing compounds such as carboxylic and dicarboxylic acids are formed.

According to the GC MS analysis, only hydroquinone as the main intermediate is identified. However, it may be a consequence of a sample pre-treatment procedure. Besides, dicarboxylic acids and carboxylic acids such as butane, crotonic and acetic acids are detected.

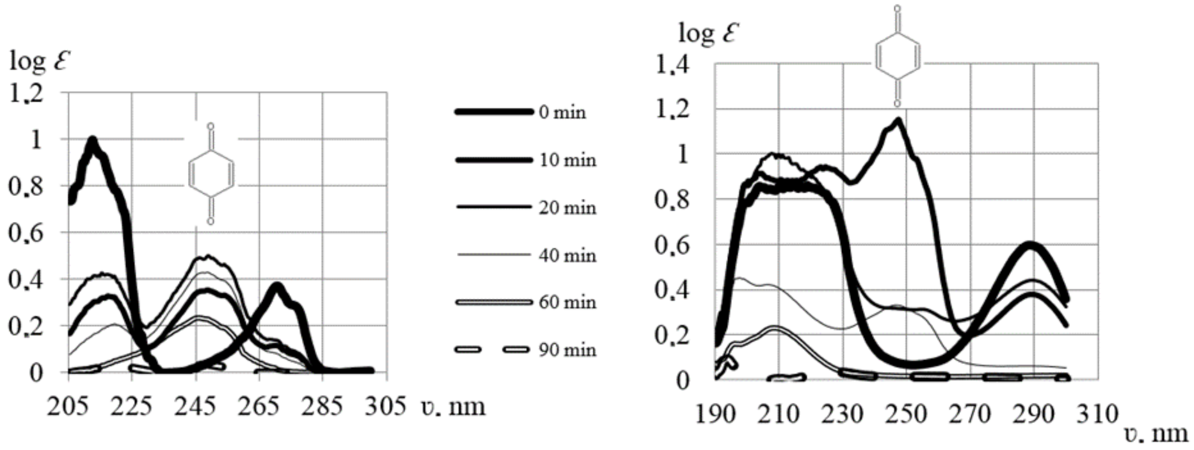

Fig. 1. Initial UV-spectrum of phenol (a) and hydroquinone (b) and their evolution during electrolysis

Complete phenol mineralization and its intermediate, hydroquinone, are confirmed by UV-spectroscopy and GC-MS as well. For complete mineralization of phenol and hydroquinone, it is necessary around 1.5÷2 h.

The kinetic analysis of the phenol and hydroquinone oxidation by the electrogenerated oxidizing system is carried out according to a pseudo first-order reaction. Since it is assumed that phenol concentration is in excess, the rate constant of this reaction can be determined as an observed constant. We have evaluated the decay rate constant basing on UV-spectra in comparison with GC-MS data according to the equation: $ln\frac{[C]_0}{[C]_t} = -k \cdot t$. The results are shown in Fig. 2.

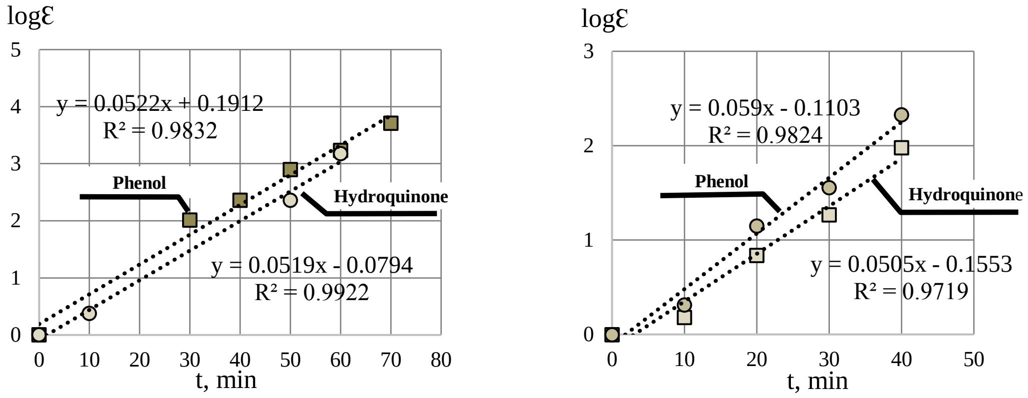

Fig. 2. Parity plots of decay rate constant for phenol and hydroquinone based on UV-spectra (a) and GC-MS data (b)

Therefore, the values of rate constants are 0.052 min^{-1} (UV) and 0.059 min^{-1} (GC-MS) for phenol; 0.052 min^{-1} (UV) and 0.051 min^{-1} (GC-MS) for hydroquinone. Rate constants calculated according to the data of both methods had an identical order and correlated with each other rather good. In addition, further current density growth till 1 A/cm^2 does not allow achieving considerable decay rate constant increasing. Thus, current density 0.6 A/cm^2 is considered to be reasonable.

Moreover, our kinetics data have been compared with the data on obtaining phenol by mineralization in water in a catalytic non-thermal plasma reactor [17], which is considered to be one of the advanced oxidation processes. Non-thermal plasma can produce UV radiation, shock waves, ions (H^+, H_3O^+, O^-, OH^-), molecular species (O_3, H_2O_2), reactive radicals (such as $O^\bullet$, $H^\bullet$, $OH^\bullet$) that are capable of mineralizing the pollutant. In particular, the phenol solutions with initial concentrations from 50 to 100 ppm are treated and the rate constants, calculated by the same equation, are equal from 0.125 to 0.084 min^{-1}. As a matter of fact, a pretty close value of decay rate constants have been obtained, but the initial concentration is 770 ppm.

Besides, it is known that phenol dimers can be formed by oxidative polymerization [18-19]. Nevertheless, the analysis of sediments after electrolysis shows obtaining lead sulfate only. However, if an electrolyte has been used 10 times, another type of sediment is formed. The infrared spectrum of such sediment is well correlated with IR spectra of the film formed by phenol electrooxidation obtained by Gattrell M, Kirk DW [20] (Fig. 3).

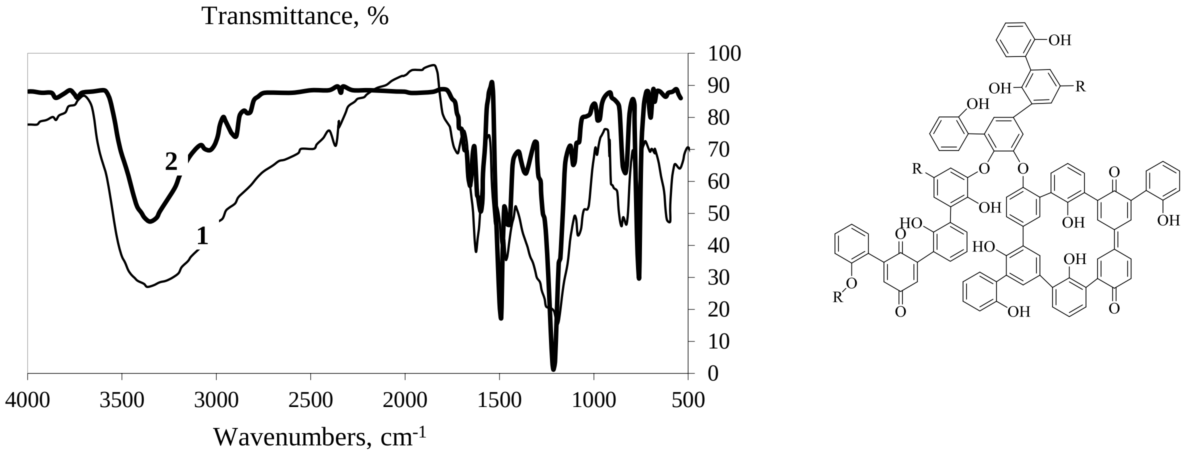

Fig. 3. Infrared spectra of sediments produced during phenol electrooxidation: (1) – present results; (2) – results obtained by Gattrell M and Kirk DW [20]

The wide and strong absorption band at 3350 cm^{-1} identifies the formation of polynuclear aromatic hydrocarbons with numerous hydrogen bonds. Thus, a good correlation between these spectra indicates that the obtained sediment is similar to the polymeric structure mentioned in this work [20].

4. Conclusions

Oxidation of phenol in an acidic aqueous solution in an electrochemical cell with lead electrodes leads mainly to the formation of p-benzoquinone, dicarboxylic and carboxylic acids. Complete phenol and hydroquinone mineralization have been achieved at current density – 0.6 A/cm^2. The method efficiency has been evaluated by two analytical methods, such as UV-spectroscopy and gas chromatography – mass spectrometry, according to the calculations of oxidation rate constants. The comparison of rate constants with non-thermal plasma treatment has shown the similarity of rate constants that means the similarity of process mechanisms. Also, it has been identified that the reasonable treatment process time is 120 min.

Acknowledgments

This work was partially supported by the Ministry of Education and Science of the Russian Federation (project 'Science' No. 4.2569.2014/K).

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