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Electrodegradation of Phenol Through Continuous Electrolysis of Synthetic Wastewater on Platinized Titanium and Stainless Steel Anodes

Grazyna Piotrowska and Boguslaw Pierozynski[*]

Department of Chemistry, Faculty of Environmental Management and Agriculture, University of Warmia and Mazury in Olsztyn, Plac Lodzki 4, 10-727 Olsztyn, Poland
[*]E-mail: bogpierozynski@yahoo.ca, boguslaw.pierozynski@uwm.edu.pl

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This paper reports on the process of phenol electrodegradation realized through continuous electrolysis of synthetic wastewater. Oxidative degradation of phenol is examined by means of a laboratory size, self-made electrolyser for different anode/cathode configurations, various electrical parameters and phenolic wastewater compositions. Monitoring of phenol decomposition (along with quantitative identification of reaction products) in wastewater is carried-out by means of instrumental HPLC/MS method in function of electrolysis time, also in relation to specific energy consumption.

Keywords: Phenol electrodegradation; Phenol electrooxidation; PhER; Wastewater electrolysis; HPLC/MS analysis

1. INTRODUCTION

Phenolic compounds present severe toxicity to industrially-based (e.g. produced by refineries and drug manufacturing plants) wastewaters [1-9]. Electro-oxidation is one of the most attractive methods for the degradation of phenolic compounds. Formerly published works on this topic covered examination of numerous phenolic chemicals on a number of electrode materials, including: noble and semi-noble (Pt, Ir, Ru), transitional metals and their oxides (Ti, Sb, Sn, Pb) under different experimental conditions [1, 6, 8, 9-12]. In addition, an advanced boron-doped diamond (BDD) anode was shown [13, 14] to exhibit significant catalytic properties towards phenol electrodegradation in synthetic wastewaters. BDD anodes proved to exhibit not only superior chemical and mechanical stability to other commonly used materials, but also extended overpotential for oxygen evolution reaction. However, very high capital cost and large energy consumption prevent commercial application of this type of anodes in wastewater treatment plants [13, 14].

This paper makes a continuation of recently published scientific articles on phenol electrooxidation reaction (PhER) from this laboratory [15-17]. It is concerned with the continuous process of phenol electrodegradation, examined by means of a laboratory-made electrolyser unit (energized by a dc power supply). Here, phenol oxidation is studied for different anode and cathode configurations, various electrical parameters and synthetic wastewater compositions. Monitoring of a phenol decomposition process (along with quantitative evaluation of reaction products) is performed by means of commonly used, instrumental HPLC/MS analysis [18-20] in function of electrolysis time and in relation to specific energy consumption.

2. EXPERIMENTAL

A PMMA-made, 750 cm^3 of working volume, wastewater electrolysis cell (external dimensions: 179×87×91 mm; wall thickness: 9 mm) used in this work, is illustrated in Fig. 1 below.

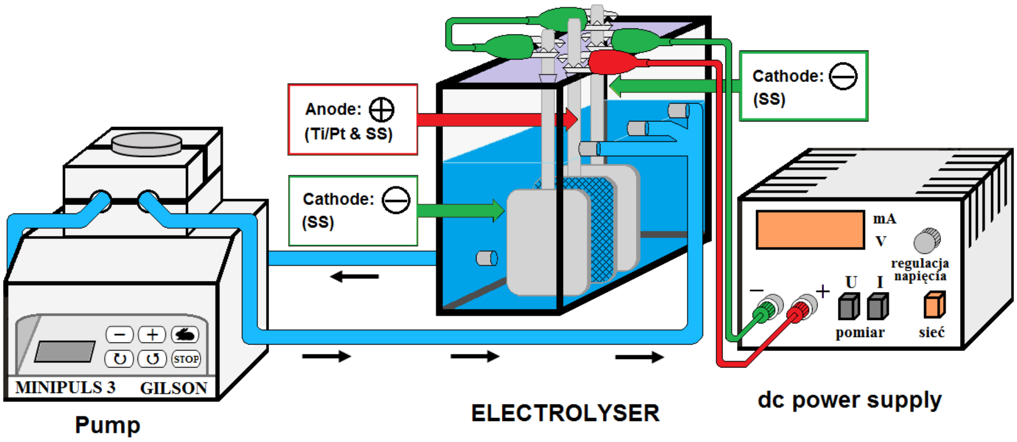

Figure 1. Schematic diagram of electrochemical phenol degradation system for synthetic wastewater, as follows: electrolyser unit; Ti/Pt anode; SS cathodes; Gilson Minipuls 3 peristaltic pump; wastewater recirculation line; dc power supply with electrical connections.

The electrolyser contains a single anode (platinized titanium Ti/Pt: 6×12 mm mesh; 1 mm thickness; 61% of open area; 60×53 mm geometrical size: S_A= 25.7 cm^2; Pt coating's thickness: 3 µm, prepared at Silesian University of Technology or a stainless-steel SS electrode: AISI 321: 62×51×0.5 mm: S_A= 64.3 cm^2) positioned in a middle part and two cathodes (stainless-steel electrodes: AISI 321: 49×39×2 mm) located at two sides of the electrolyser. A distance between anode and cathode is *ca*. 20 mm, which translates to 40 mm between the two cathodes. Prior to being installed in the electrolyser, stainless steel electrodes were polished with emery paper down to 2000 grade, de-greased with acetone and rinsed with ultra-pure water (18.2 MΩ cm Millipore Q3 UV water purification system was used). On the other hand, Ti/Pt anode was thoroughly rinsed with ultra-pure water. The electrolyser was operated at room temperature in a wastewater recirculation mode (at a rate of *ca*. 20 mL min^{-1}), enabled through the application of Gilson Minipuls 3, peristaltic pump (see all details in Fig. 1 below). The wastewater electrolysis cell was galvanostatically energized by means of a laboratory 10V/2A dc power supply, with periodic (every 30 minutes) recording of a resulting voltage parameter. Synthetic wastewater solution was prepared by dissolving Na_2SO_4: 0.015 and 0.030 M (Polish Chemical Compounds, p.a.) using Millipore ultra-pure water source with initial phenol (Sigma-Aldrich, >99 %) concentrations on the order of 1×10^{-4} M (9.4 mg dm^{-3}) and 1×10^{-3} M (94.1 mg dm^{-3}).

A primary analysis of phenol content in wastewater was carried-out spectro-photometrically with 4-aminoantipyrine [21, 22], where for every studied object four independent wastewater samples (5, 10, 20 and 40 cm^3) were collected for initial solution and after 2, 4, and 6 hours of electrolyser's continuous operation. Statistical analysis was performed by means of Fisher's least significant difference: LSD method ($\alpha= 0.05$).

In addition, the process of phenol electrodegradation was subjected to a quantitative assessment of the reaction products/intermediates by means of the combined HPLC/MS analysis, carried-out for an initial concentration of phenol: 1×10^{-4} M and electrolyte conductivity of 5 mS cm^{-1}, after 2 and 6 hours of continuous electrolysis, performed at 100 and 200 mA (SS cathode and Ti/Pt anode were used). Hence, micro-HPLC (LC 200, Eksigent, Canada) system was combined with QTRAP 5500 mass spectrometer (AB SCIEX, Canada), equipped with an ESI ion source, triple quadrupole and ionic trap. Reaction products were separated by means of Halo C18 (2.7 µm, 0.5×50 mm) chromatographic column (Eksigent, Canada) at 45 ^{o}C for the mobile phase flow of 20 µL min^{-1}. Both qualitative and quantitative analyses were conducted based on the MRM (Multiple Reaction Monitoring) method. The quantitative analysis was performed through the application of linear calibration curves ($R^2= 0.992$), based on a series of dilutions of respective standards.

The process of phenol electrodegradation was examined on the following objects/ configurations:

I. 2×Cathodes: SS; Anode: Ti/Pt; I= 100 mA; pH= 7.0; κ= 5.0 mS cm^{-1}; [Ph]= 1×10^{-4} M
II. 2×Cathodes: SS; Anode: Ti/Pt; I= 200 mA; pH= 7.0; κ= 5.0 mS cm^{-1}; [Ph]= 1×10^{-4} M
III. 2×Cathodes: SS; Anode: Ti/Pt; I= 100 mA; pH= 7.0; κ= 5.0 mS cm^{-1}; [Ph]= 1×10^{-3} M
IV. 2×Cathodes: SS; Anode: Ti/Pt; I= 200 mA; pH= 7.0; κ= 5.0 mS cm^{-1}; [Ph]= 1×10^{-3} M
V. 2×Cathodes: SS; Anode: Ti/Pt; I= 100 mA; pH= 7.0; κ= 2.5 mS cm^{-1}; [Ph]= 1×10^{-4} M
VI. 2×Cathodes: SS; Anode: SS; I= 100 mA; pH= 7.0; κ= 5.0 mS cm^{-1}; [Ph]= 1×10^{-4} M
VII. 2×Cathodes: SS; Anode: SS; I= 200 mA; pH= 7.0; κ= 5.0 mS cm^{-1}; [Ph]= 1×10^{-4} M.

3. RESULTS AND DISCUSSION

Fig. 2 below illustrates the effect of electrolysis time for phenol-based synthetic wastewater on the content of phenol, examined on various objects (electrolyser configurations), denoted as I, II, VI and VII for an initial phenol concentration of 1×10^{-4} M (*ca*. 9.4 mg dm^{-3}).

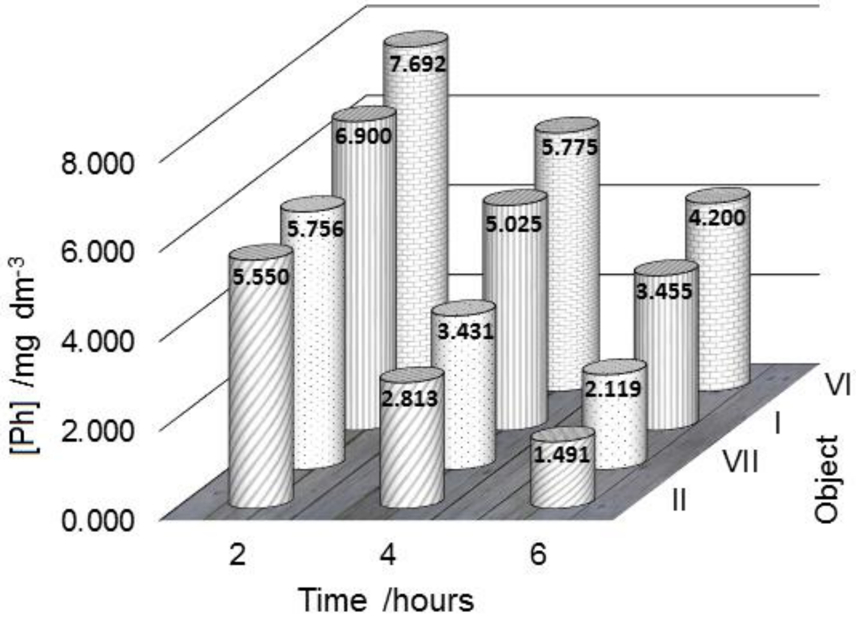

Figure 2. Influence of electrolysis time on the content of phenol in synthetic wastewater for various (**I**, **II**, **VI** and **VII**) examined objects/configurations (initial phenol concentration: 1×10^{-4} M).

Here, objects I and II refer to electrolyser's configuration having two stainless steel-made cathodes and a single, Ti/Pt anode, with dc current settings of 100 mA (anodic current-density: j_A= 3.9 mA cm^{-2}) and 200 mA (j_A= 7.8 mA cm^{-2}), correspondingly (pH= 7.0 and C= 5.0 mS cm^{-1}). On the other hand, a respective difference in configuration between object pairs (I, II) and (VI, VII) is related to the replacement of Ti/Pt anode for the former pair by a stainless steel anode for the latter case.

Hence, object II combining two SS cathodes with the platinized titanium mesh anode in between proves to be the most effective configuration of the electrolyser for the process of electrodegradation of phenol present in synthetically made wastewater. Here, imposition of 7.8 mA cm^{-2} anodic current-density over 6 hours enables to radically reduce the content of phenol in wastewater, from an initial value of 9.4 to about 1.5 mg dm^{-3}, at the expense of 5.3×10^{-3} KWh of consumed electrical energy (see Table 1).

Table 1. Average current and voltage parameters, and energy consumption obtained upon continuous, 6-hour electrolysis of phenol-based synthetic wastewater.

Object	Current/ mA	Voltage/ V	Consumed energy/ KWh
I	109	3.69	2.4×10^{-3}
II	208	4.28	5.3×10^{-3}
III	106	3.58	2.3×10^{-3}
IV	208	4.30	5.4×10^{-3}
V	112	4.33	2.9×10^{-3}
VI	111	3.29	2.2×10^{-3}
VII	211	3.91	4.9×10^{-3}

The above translates to about 84% reduction of initial phenol concentration (compare the respective results given in Fig. 2 and Fig. 3). However, it should be stressed that nearly 41% reduction of phenol content was already achieved after first 2 hours of the electrolysis (see Fig. 3). For the same electrolyser's configuration, but examined at half current-density (3.9 mA cm^{-2}), a final phenol content in wastewater after 6 hours of electrolysis came to about 3.4 mg dm^{-3}, which could be translated to over 63% reduction of initial phenol concentration and 2.4×10^{-3} KWh of consumed energy.

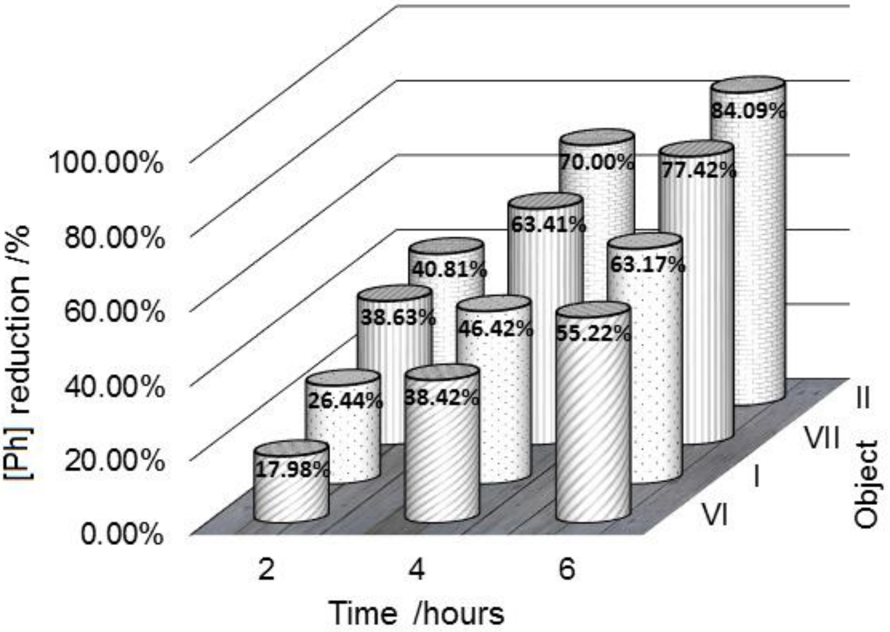

Figure 3. Influence of electrolysis time on the reduction of phenol concentration in synthetic wastewater for various (**I**, **II**, **VI** and **VII**) examined objects/configurations (initial phenol concentration: 1×10^{-4} M).

On the other hand, the replacement of platinized titanium anode by the SS-made anode significantly (adversely) affected the phenol electrodegradation process. Thus, for the configuration denoted as object VII (with current set at 200 mA or 3.1 mA cm^{-2}), 6 hours of continuous wastewater electrolysis led to the reduction of phenol content on the order of 77% (*ca*. 2.1 mg dm^{-3} of phenol remaining in processed wastewater). For the object VI configuration (100 mA or *ca*. 1.55 mA cm^{-2}), the respective parameters for phenol removal came to about 55% and 4.2 mg dm^{-3} (see again Figs. 2 and 3). It should be stressed however that the phenol degradation results produced on the objects denoted as VI and VII were associated correspondingly with similar energy consumptions as those generated on the objects I and II (see Table 1 for details).

Furthermore, Figs. 4 and 5 present the influence of wastewater conductivity on the phenol content and the reduction of phenol concentration upon continuous electrolysis (carried-out on Ti/Pt anode), correspondingly. Thus, when electrolytic conductivity becomes reduced to 2.5 mS cm^{-1} (50% of its initial value, see object V in Figs. 4 and 5), imposition of 100 mA for 6 hours of continuous electrolysis (understandably) results in similar phenol purification effects to those previously obtained for the object I (compare the remaining content of phenol at *ca*. 3.6 mg dm^{-3} and its nearly 62%

concentration reduction for the object V with *ca*. 3.4 mg dm^{-3} and 63% parameters recorded for the object I, see again Figs. 4 and 5). However, a severe diminution of the conductivity for the object V resulted in a considerable increase of an average voltage parameter from 3.69 to 4.33 V, which can be translated to energy consumption being increased by about 20% (Table 1).

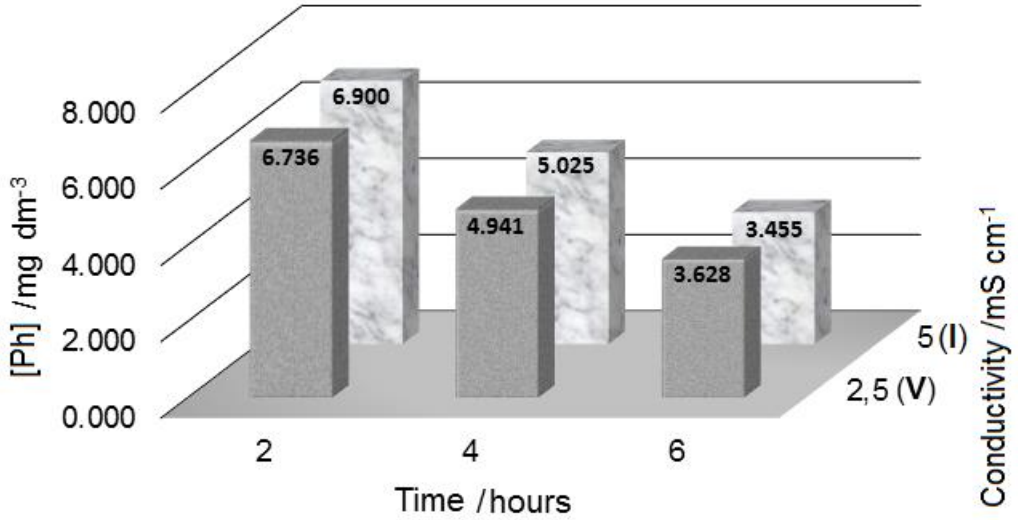

Figure 4. Influence of purification time and electrolytic conductivity of synthetic wastewater on the phenol content (initial phenol concentration: 1×10^{-4} M, employed current: 100 mA; objects **I** and **V**).

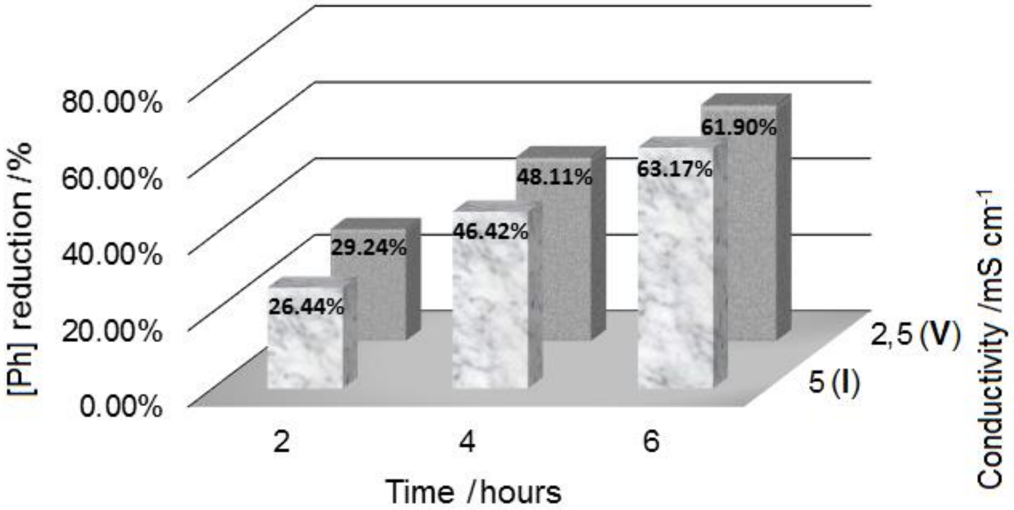

Figure 5. Influence of purification time and electrolytic conductivity of synthetic wastewater on the reduction of phenol concentration (initial phenol concentration: 1×10^{-4} M, employed current: 100 mA; objects **I** and **V**).

On the other hand, a radical increase of phenol concentration in synthetically prepared wastewater from 10^{-4} M (9.4 mg dm^{-3}) to 10^{-3} M (94.1 mg dm^{-3}) caused significant inhibition of anodic phenol electrooxidation process. So, in this case acquisition of 200 mA (Ti/Pt anode with current-density of 7.8 mA cm^{-2}) for 6 hours resulted in a depletion of phenol content from 94.1 to about 45.3 mg dm^{-3} (only *ca*. 52% concentration reduction), at the expense of 5.4×10^{-3} KWh of consumed energy. At the same time, analogous parameters recorded at half current-density (3.9 mA cm^{-2}) came to *ca*. 63.3 mg dm^{-3}, 33% and 2.3×10^{-3} KWh, respectively (see objects denoted as III and IV in Figs. 6 and 7, and Table 1 for details). Considerable impediment of the PhER (recorded upon a 10-fold increase of initial phenol concentration in wastewater) most likely results from the fact that under severe experimental conditions reactive catalyst surface could become subjected to self-inhibition effects, due to extended formation of polymeric films on the electrode surface [6, 23].

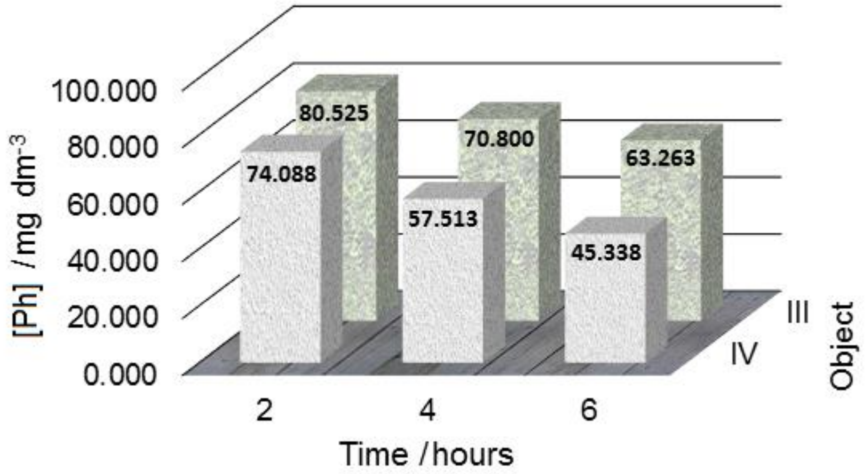

Figure 6. Influence of electrolysis time on the content of phenol in synthetic wastewater for objects denoted as **III** and **IV** (initial phenol concentration: 1×10^{-3} M).

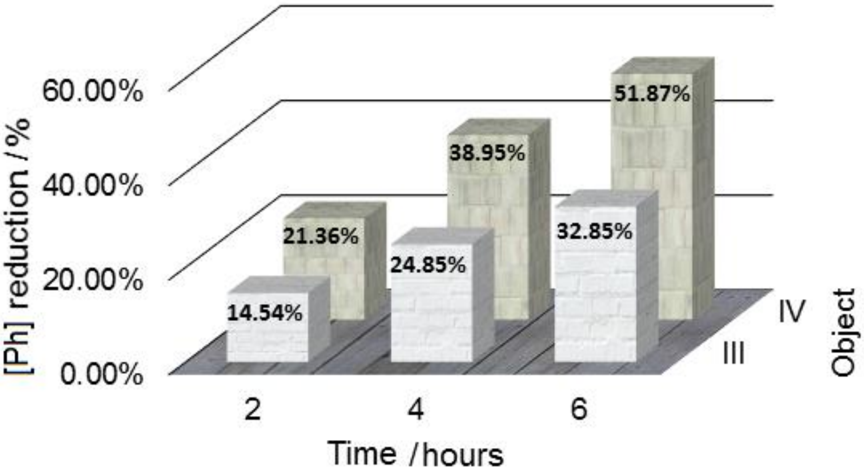

Figure 7. Influence of electrolysis time on the reduction of phenol concentration in synthetic wastewater for objects denoted as **III** and **IV** (initial phenol concentration: 1×10^{-3} M).

In summary, the most effective configuration of the electrolyser to perform the process of electrodegradation of phenol in sulphate-based synthetic wastewater proved to be the object denoted as II, which combined the application of platinized titanium (DSA) anode placed between two stainless-steel cathodes and the following operating parameters: j_A= 7.8 mA cm^{-2}, pH= 7.0, κ= 5.0 mS cm^{-1}, [Ph]= 1×10^{-4} M/9.4 mg dm^{-3} and t= 2, 6 hours. This laboratory electrolysis setup would require about 618 and 894 kWh of electrical energy in order to electrochemically degrade 1 kg of phenol, based on the calculations carried-out for 2 and 6 hours of continuous electrolysis, correspondingly. It is then evident (also refer to Figs. 2 and 3) that the efficiency of the PhER becomes significantly reduced along with a progress of the process of electrolysis (a partial result of surface contamination by electrosorbed phenol oxidation by-products). Nevertheless, taking into account the set concentration of phenol in wastewater at 1×10^{-4} M, the above-derived amounts of electrical energy should be sufficient to treat over 100 m^3 of phenol-based industrial wastewater. Furthermore, similar energy consumption levels (595 and 897 kWh) were correspondingly recorded for analogous, but the stainless-steel based anode configuration of the electrolyser (the object denoted as VII), carried-out at the anodic current-density of 3.1 mA cm^{-2} (compare with j_A= 7.8 mA cm^{-2} for the Ti/Pt anode above). These comparative results imply that for the platinized titanium anode, operated at significantly higher anodic current-density value, the efficiency of oxygen evolution reaction (OER) considerably intensified, at the expense of parallel phenol electrooxidation reaction [24].

Similar works on the process of electrocatalytic degradation of phenol were published by Li et al. [8] (Ti/RuO_2-Pt and Ti/IrO_2-Pt anodes), Dos Santos et al. [12] (Ti/RuO_2 anode) and by Berenguer et al. [24] (Pt/Ru-doped Ti/SnO_2-Sb anodes). For example, in Ref. 24 the presented energy consumption levels for the removal of 1 kg of phenol are fundamentally lower (83 to 629 kWh per 1 kg of phenol removed for an anodic current-density of 10 mA cm^{-2}, see Table 5 there for details) than those recorded in this work. However, it should be stressed that all experimental electrolysis work in Ref. 24 was carried-out in highly-conductive (and rather unrealistic for wastewater plant conditions), 0.5 M NaOH solution (compare with 0.03 M Na_2SO_4 electrolyte used in this work). Similarly, highly conductive 0.34 M NaCl solution (and comparatively 0.34 M Na_2SO_4) was employed for all electrolysis tests described in Ref. 12, where sodium sulphate supporting electrolyte was found radically less effective in the PhER than sodium chloride solution. In this work, sodium chloride was not used as a base of supporting solution in order to avoid the formation of chlorinated intermediates and electrolysis by-products.

Table 2. Quantitative evaluation of PhER intermediates produced from phenol-based synthetic wastewater, identified by means of HPLC/MS analysis.

Average content of PhER intermediates/ mol dm^{-3}					
Sample	Phenol	Maleic acid	Hydroquinone	Catechol	p-benzoquinone
1	1.4×10^{-6}	9.0×10^{-8}	2.4×10^{-5}	1.7×10^{-5}	9.1×10^{-5}
2	1.9×10^{-6}	1.7×10^{-7}	1.5×10^{-5}	1.1×10^{-5}	5.2×10^{-4}
3	5.6×10^{-6}	1.4×10^{-7}	1.6×10^{-5}	1.5×10^{-5}	2.0×10^{-4}
4	5.0×10^{-6}	2.5×10^{-7}	7.8×10^{-6}	8.0×10^{-6}	8.9×10^{-5}

In addition, the combined HPLC/MS analysis was conducted on four pre-electrolyzed samples (Sample 1: I= 100 mA, t= 2 hours; Sample 2: I= 100 mA, t= 6 hours; Sample 3: I= 200 mA, t= 2 hours; Sample 4: I= 200 mA, t= 6 hours), 20 hours after completion of the electrolysis process. Thus, electrooxidation of phenol led to the formation of a series of intermediates, including: hydroquinone, catechol, p-benzoquinone and maleic acid (it should be noted that oxalic acid was not instrumentally detected due to its low molecular mass). These substances were properly identified in the respective chromatograms, which can be seen in Figs. 8a and 8b.

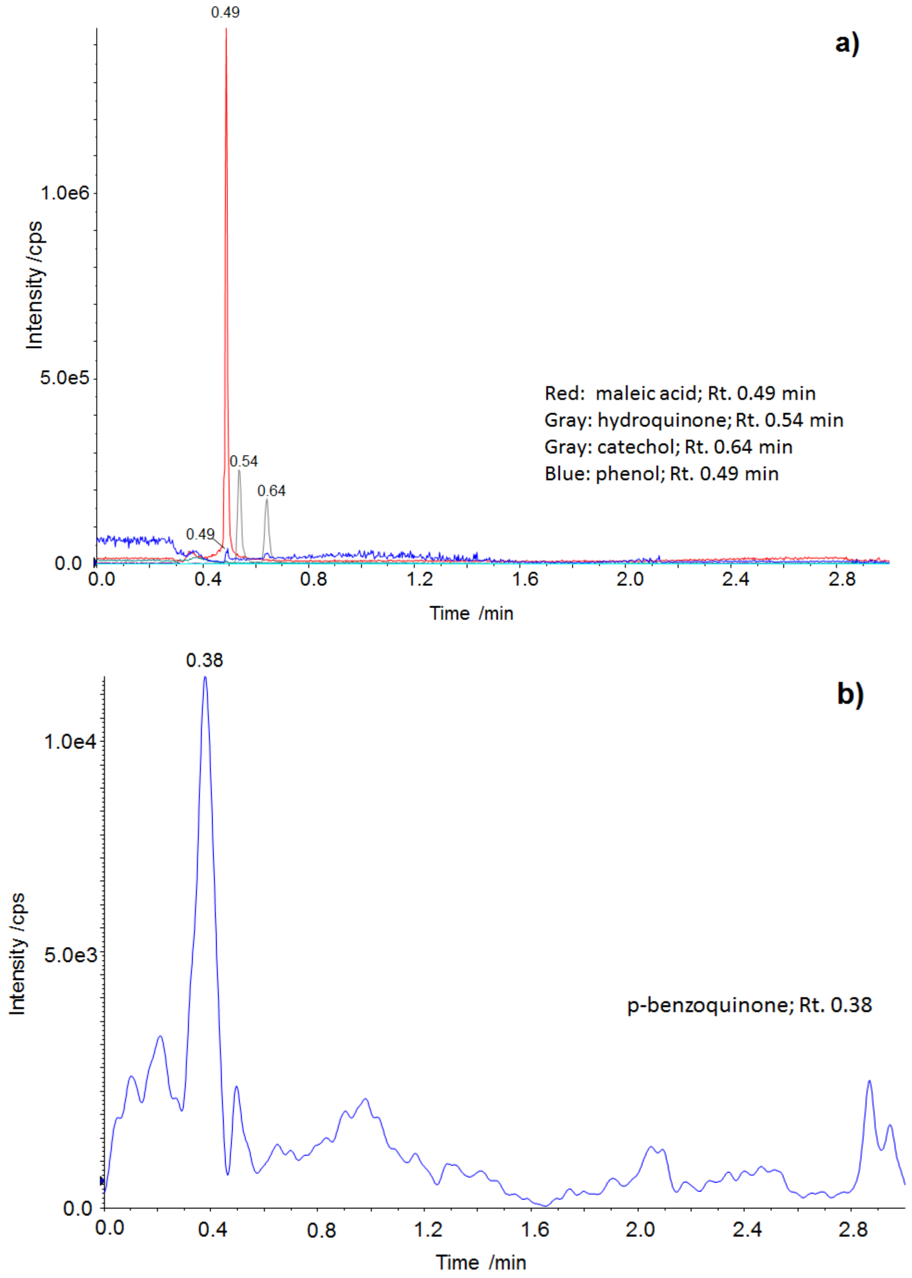

Figure 8. HPLC chromatograms recorded for phenol-based, electrolyzed synthetic wastewater exhibiting detected phenol electrooxidation products: A) phenol, hydroquinone, catechol and maleic acid; B) p-benzoquinone.

Most importantly, Table 2 above presents quantitative HPLC/MS evaluation of all identified reaction intermediates. Hence, 20 hours after the completion of electrolysis trials, all electrolyzed wastewater samples contained very small amounts of phenol $(1.4\text{-}5.6)\times10^{-6}$ M and traces of maleic acid (*ca*. 10^{-7} M). On the other hand, average concentrations of hydroquinone, catechol and p-benzoquinone came to about 1.6×10^{-5} M, 1.1×10^{-5} M and 2.2×10^{-4} M, respectively. Interestingly, the instrumentally-derived concentration of phenol is significantly lower than that immediately recorded after completion of the electrolysis (e.g. by 3.2× when residual concentration of phenol for Sample 4 in Table 2: 5.0×10^{-6} M is compared with 1.6×10^{-5} M for the object denoted as II in Fig. 2). Thus, it is most likely that initially formed phenoxy radicals might trigger a chain reaction [25], finally leading in time to increased formation of oxidation intermediates, including carboxylic acids and CO_2 (see a schematic diagram of phenol electrodegradation process in Fig. 9).

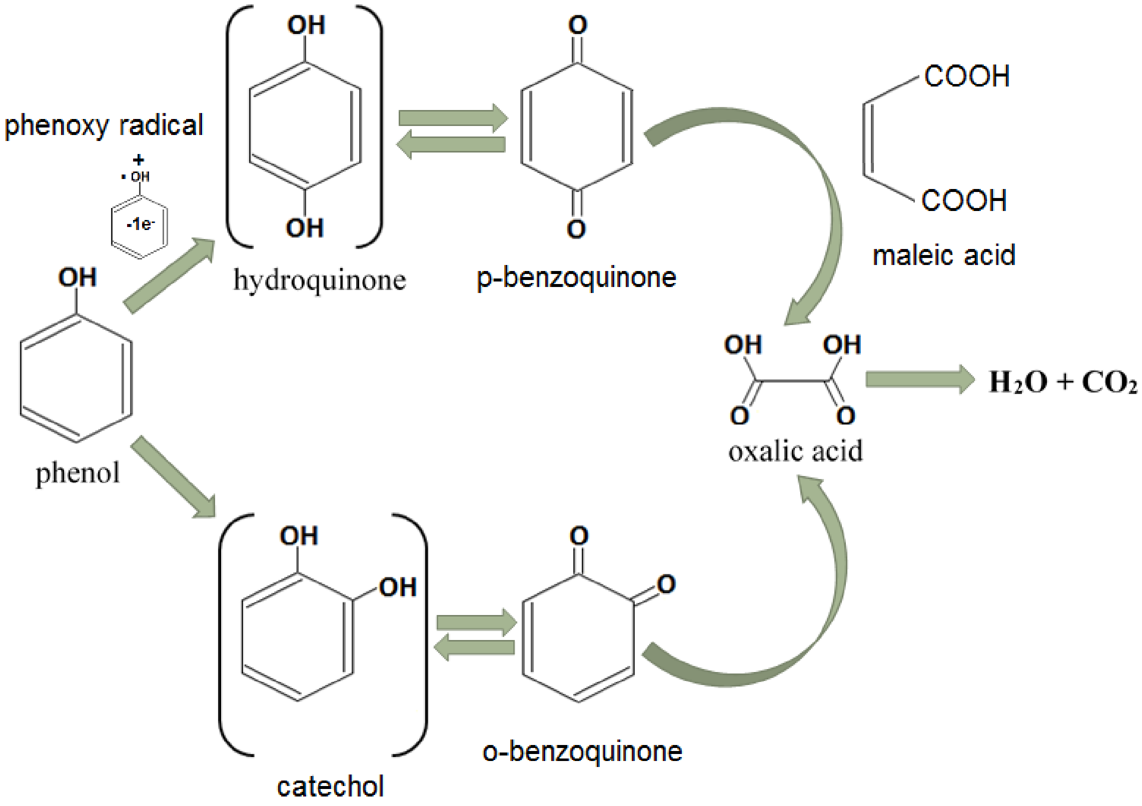

Figure 9. Schematic diagram of electrochemical phenol degradation process [16].

However, the most important information obtained from the HPLC/MS instrumental analysis is that phenol electrooxidation process carried-out on platinized titanium anode (under experimental conditions employed in this work) proceeds with predominantly preserved ring structure, where the formation of final phenol oxidation products (maleic and oxalic acids, and CO_2) is quite limited.

4. CONCLUSIONS

Both platinized titanium and stainless steel anodes proved to be effective in electro-degradation of phenol, carried-out via continuous electrolysis of synthetically made, sulphate-based wastewater.

The laboratory electrolysis setup (for both anode configurations) would require about 600 and 900 kWh of electrical energy in order to degrade 1 kg of phenol, in reference to 2 and 6-hour electrolysis process, respectively. Such high energy demand is a consequence of both electrolyser's design and relatively low conductivity (sodium sulphate) of wastewater base (comparatively to examination of Cl^- and OH^--based solutions by other authors). Catalyst surface contamination by electrosorbed phenol oxidation by-products is responsible for a recorded efficiency drop in time of phenol electrooxidation reaction. In addition, operation of Ti/Pt anode at respectively higher anodic current-density than that for SS electrode results in intensification of a parasitic, anodic oxygen evolution reaction.

Main instrumentally-detected products of PhER included: hydroquinone, catechol, p-benzoquinone and maleic acid. After completion of electrolysis process these intermediates might undergo further oxidation via a chain reaction, initiated by originally generated phenoxy radical species. Supplementary examinations of phenol electrooxidation reaction would involve optimization work on the process of continuous electrolysis of phenol-based synthetic wastewater, primarily in relation to anode type and electrode distances, and modification of electrolyte composition. The aim of further work would be both to optimize energetics of the process, as well as to substantially increase the yield of carboxylic acids and carbon dioxide.

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