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A comparison of electrooxidation of phenol on boron doped diamond and mixed metal oxide anodes

DJURICIC T.[1], PROSEN H.[2], KRAVOS A.[2], MICIN S.[3] and MALINOVIC B.N.[1*]

[1]University of Banja Luka, Faculty of Technology, Stepe Stepanovica 73, 78000 Banja Luka, Bosnia and Herzegovina
[2]University of Ljubljana, Faculty of Chemistry and Chemical Technology, Vecna pot 113, 1000 Ljubljana, Slovenia
[3]University of Banja Luka, Faculty of Security Studies, Zivojina Misica 10a, 78000 Banja Luka, Bosnia and Herzegovina

*corresponding author:
e-mail: borislav.malinovic@tf.unibl.org

Abstract. Phenolic compounds are widespread in wastewater from various industries. Since the phenols are potentially carcinogenic for humans and hazardous for the environment, their presence in wastewater raises concerns. In this paper electrooxidation process was used for treatment of synthetical prepared wastewater containing phenol. Initial phenol concentration in wastewater was 50 mg/L with addition of different supporting electrolytes (NaCl, Na_2SO_4, H_2SO_4). The treatment was performed in a batch electrochemical reactor at constant current density of 20 mA/cm^2. Boron doped diamond (BDD) and mixed metal oxide (MMO) anode materials were examined, and stainless steel was used as cathode. Phenol concentration before and after treatment was determined by standard spectrophotometric method with 4-aminoantipyrine, while transformation products were identified by different chromatographic methods. Experiments have shown that the treatment is very efficient and with low energy consumption, wherein the phenol removal efficiency mostly depends on the duration of treatment and the type of supporting electrolyte.

Keywords: BDD, MMO, removal efficiency, 4-aminoantipyrine

1. Introduction

Phenols as a group of organic pollutants are widespread in wastewater from oil, dyes, pesticides and pharmaceutical industries. Since phenols are very toxic, their presence in wastewater raises concerns. There are many treatments for their removal such as electrochemical oxidation (EO), as one of the advanced oxidation processes (AOPs) (Hurtado et al. 2016). EO is used to remove contaminants from wastewater because it has significant advantages, is eco-friendly and based on the *in situ* production of the hydroxyl radical as strong oxidation agent. For EO treatment most important parameter is selection of anode material which can be "active" (low oxygen evolution overpotential, e.g., mixed-metal oxide - MMO) and "inactive" electrodes (high oxygen evolution overpotential, e.g., boron doped diamond - BDD) and which determine the mechanism of electrooxidation (De Battisti and Martínez-Huitle 2018; Malinović et al. 2021). MMO anodes are made by coating a substrate, such as titanium, with several types of metal oxides (RuO_2, IrO_2 or PtO_2).

EO of phenol in batch reactor ($\gamma_{0(phenol)}$=100 mg/L) using different MMO anodes (Ti/Pt, Ti/IrO_2-Ta_2O_5, Ti/Ta_2O_5-SnO_2-IrO_2, Ti/RuO_2 and Ti/IrO_2-RuO_2) showed that Ti/Pt anode was the most effective (99.5%). Ti/RuO_2 and Ti/IrO_2-RuO_2 also showed high efficiency (*Ef*) with 87.1% and 84.7% efficiency after 8 h of treatment in 0.1 M Na_2SO_4 supporting electrolyte solution at current density, j=31 mA/cm^2 (Barisci et al. 2017). By-products benzoquinone, hydroquinone, pyrocatechol, maleic acid and oxalic acid were observed, while the concentration of pyrocatechol and oxalic acid increased at an early stage and decreased after 6 h of treatment with Ti/IrO_2-RuO_2 anode. Two independent studies of five different electrochemical treatments showed that electro-Fenton was the most efficient, followed by direct EO with BDD on Nb substrate anode which showed better results than MMO (Ru-MMO) anode (Yavuz, Koparal, and Ogutveren 2010; Ye and Li 2016). Phenol removal of 99.53% ($\gamma_{0(phenol)}$=192.9 mg/L) was obtained in direct EO at the current density of 5 mA/cm^2 for 40 min (conductivity was 15.63 mS/cm). A comparison of BDD on Si substrate and PbO_2 anodes was also performed on the basis of measurements of Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) in reactor with electrolyte recirculation (Weiss, Groenen-Serrano, and Savall 2008). BDD anode showed better efficiency and during the electrolysis less intermediates were formed with BDD compared to PbO_2. After 5 h of treatment with BDD under a current density of j=47 mA/cm^2, 99% of the phenol was removed with an energy consumption of 42.55 kWh/kg$_{phenol}$.

Oliveira *et al.*, (2018) studied EO of phenolic wastewaters from cashew-nut processing industry, while Britto-Costa and Ruotolo (2012) studied model phenolic wastewater for performance of BDD and MMO (Ti/RuO_2-TiO_2) anodes and showed that BDD has the best performance by applying 100 mA/cm^2 for 6 h treatment, which removed 100% of COD for real wastewater ($\gamma_{0(phenol)}$=1.3 mg/L) and model wastewater by applying 50 mA/cm^2 for 8 h

treatment, which removed almost 90% of COD in presence of 607 mg/L Cl^- ($\gamma_{0(phenol)}$=210 mg/L) where the energy consumption was in the range from 51 to 269 kWh/kg_{phenol}.

Due to the presence of chloride ions in the wastewater during the electrolytic process, unwanted by-products can be generated. Chromatographic experiments revealed the formation of by-products resistant to degradation, and *L. sativa* bioassays showed that the wastewater was toxic, especially when treated with MMO (Oliveira et al. 2018). Previous studies have proven the presence of many by-products of phenol electrooxidation: hydroquinone, catechol, benzoquinone, followed by maleic, oxalic and formic acids (Weiss, Groenen-Serrano, and Savall 2008).

Other important parameters are the type of electrolyte (supporting electrolyte), initial phenol concentration, current density, reactor construction, etc. Supporting electrolytes have a primary role to provide good conductivity of wastewater, and at the same time reduce energy consumption. They can also provide strong oxidizing agents by electrogeneration, such as active chlorine species (Malinović et al. 2021).

Although chlorides are used as supporting electrolyte for phenol degradation (Yavuz, Koparal, and Ogutveren 2010; Britto-Costa and Ruotolo 2012), toxic organochlorinated species have been reported as by-products (Santos, Afonso, and Dutra 2010; Oliveira et al. 2018). For this reason, other supporting electrolytes such as Na_2SO_4 (Hurtado et al. 2016; Barisci et al. 2017) or H_2SO_4 (Weiss, Groenen-Serrano, and Savall 2008; Yavuz, Koparal, and Ogutveren 2010) have been used in many studies.

In this paper, a comparison of two types of electrodes (BDD and MMO) as anodes using different supporting electrolytes was performed. Efficacy was monitored as phenol removal efficiency. The influence of supporting electrolytes was followed by energy consumption and analysis of phenol degradation byproducts for both selected anode types and supporting electrolytes.

2. Materials and methods

To prepare the model wastewater, phenol, 99.5% (Centrohem, Serbia) was dissolved in distilled water to a concentration of 50 mg/L. As supporting electrolytes different chemicals were used: NaCl, 99.5% (LachNer), Na_2SO_4, 99% (LachNer) and H_2SO_4, 96% (LachNer). The experimental part presents the application of EO process in a batch electrochemical reactor, made of polyester and distance between electrodes was 2 cm. All experiments were performed at an ambient temperature, with the initial wastewater volume of 400 cm^3 and stirred by a magnetic stirring bar (300 rpm). The applied anodes were BDD on a Nb substrate (Metachem, Germany) and MMO (mixtures of oxides of IrO_2 and RuO_2 on a Ti substrate, Metachem, Germany). Useful area of both anodes was 28.26 cm^2, and the stainless steel (SS) plate was used as cathode (EN 1.4301/AISI 304). The electrolysis was performed at j=20 mA/cm^2. Different supporting electrolytes were used in different concentrations (2 g/L NaCl, 2 g/L Na_2SO_4 and 2.5 mL/L 2 M H_2SO_4) in order to achieve approximately the same conductivity (≈ 3 mS/cm).

The concentration of phenol in samples of model wastewater during treatment was determined by standard spectrophotometric method with 4-aminoantipyrine (Bridgewater et al. 2012) and high-performance liquid chromatographic method with diode-array detector (HPLC-DAD). Degradation products were identified by HPLC-DAD and liquid chromatography-tandem mass spectrometry (LC-MS/MS) with negative electrospray ionization. Volatile products were extracted by solid-phase microextraction (CAR-PDMS fiber) and determined by gas chromatography-mass spectrometry (SPME GC-MS) in total ion current mode. Organic acids were identified by ion chromatography (IC).

3. Results and discussion

Results of phenol removal by EO are expressed by removal efficiency, E_f, in percent calculated by the following equation (1), where γ_i and γ_f are initial and final concentration of phenol in mg/L. The energy consumption (EC) per mass of removed phenol (m) was calculated for applied current (I) using equation (2) after electrolysis time (t) and average cell voltage (U):

$$E_f = ((\gamma_i - \gamma_f) / \gamma_i) \cdot 100 \quad (1)$$

$$EC = \Delta U \cdot I \cdot t / m_{phenol} \quad (2)$$

The phenol removal efficiency was researched depending on the anode materials and supporting electrolytes as a function of electrolysis duration. For 60 min of treatment by using BDD and NaCl the highest phenol removal efficiency (E_f=99.9%) was achieved. Almost the same removal efficiency was achieved with Na_2SO_4 (Ef=99.3%) and H_2SO_4 (E_f=94.8%) but with 160 min of treatment (Fig. 1). Figure 2 shows that the MMO anode has much lower efficiency than BDD under the same electrolysis conditions. The highest efficiency was also achieved in the presence of NaCl as supporting electrolyte and in 120 min the efficiency was 48.23%.

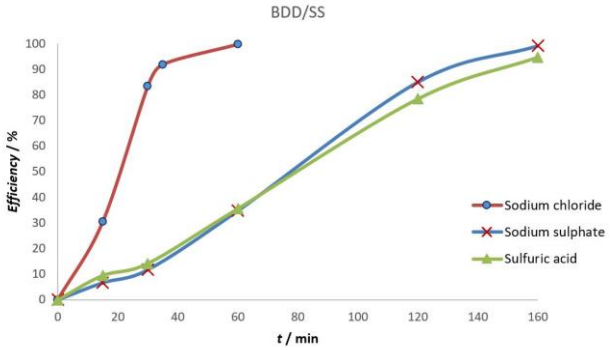

Figure 1. The impact of supporting electrolyte on phenol degradation with BDD anode and SS cathode ($\gamma_{0(phenol)}$=50 mg/L, j=20 mA/cm^2, stirring 300 rpm)

The advantages of BDD anode over MMO for phenol removal by EO have been confirmed in other available studies (Britto-Costa and Ruotolo 2012). However, used MMO anode (Ti/IrO_2-RuO_2) has lower efficiency than other types of MMO for treatment of phenol such as Ti/RuO_2 (Barisci et al. 2017) and Ti/RuO_2-TiO_2 (Oliveira et al. 2018).

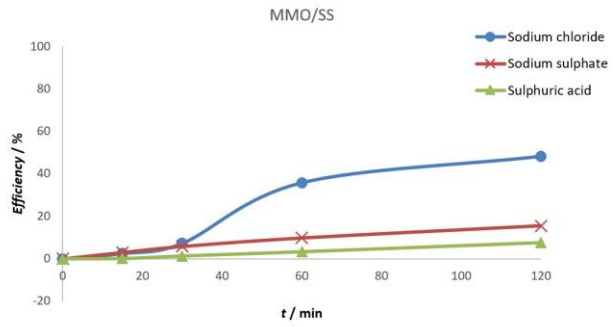

Figure 2. The impact of supporting electrolyte on phenol degradation with MMO anode and SS cathode ($\gamma_{0(phenol)}$=50 mg/L, j=20 mA/cm^2, stirring 300 rpm)

Different degradation products were identified depending on the supporting electroyte and type of anode. In NaCl, 2,4-dichlorophenol was identified during treatment with BDD, but was absent after 1 h, while it was present at relatively high concentration after 2 h of EO with MMO. With both electrodes, some other chlorinated products were found, mainly chloroform and other chlorinated alkanes. Oxalic, malonic, maleic, and acetic acid were found after the end of treatment. With Na_2SO_4 and H_2SO_4 as supporting electrolytes, chlorinated products were absent. Main identified compounds at both anodes were benzoquinone, hydroquinone, pyrone and furan derivatives, as well as oxalic, acetic, and formic acid.

The lowest energy consumption was recorded in the presence of NaCl, and at an efficiency of 99.9% it was 116.62 kWh/kg$_{phenol}$. Figure 3 shows that EC depends on the achieved efficiency for NaCl as supporting electrolyte and the amount of NaCl, so in the study of Santos, Afonso, and Dutra (2010) same efficiency was achieved (99.9%), but in the presence of 20 g/L NaCl, energy consumption was 7.33 kWh/kg$_{phenol}$.

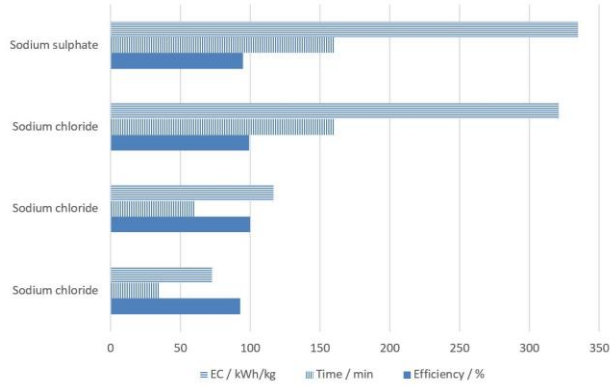

Figure 3. Energy consumption, time and efficiency for EO with BDD anode and SS cathode (NaCl: t=35, 60 min, E_f=92.7, 99.9%, EC=72.82, 116.62 kWh/kg$_{phenol}$; Na_2SO_4: t=160 min, E_f=99.3%, EC=320.88 kWh/kg$_{phenol}$; H_2SO_4: t=160 min, E_f=94.8%, EC=335.02 kWh/kg$_{phenol}$)

Some studies have shown very high energy consumption as in the case of treatment of phenolic wastewaters from cashew-nut processing industry with BDD anode by applying 20 mA/cm^2 where the energy consumption was 5769 kWh/kg$_{phenol}$ (E_f=92.3%, $\gamma_{0(phenol)}$=1.3 mg/L) (Oliveira et al. 2018). In the study by Britto-Costa and Ruotolo (2012) energy consumption was in the range from 51 to 269 kWh/kg$_{phenol}$, which is similar to our study.

4. Conclusions

In addition to the anode material, the choice of supporting electrolyte plays a very important role for the electrooxidation which is an effective treatment for the degradation of phenols with low energy consumption. The best results of phenol removal, 99.9% in 60 min of treatment, were achieved with BDD anode and NaCl as supporting electrolyte which leads to the formation of organochlorinated by-products. We can also conclude that excellent results have been achieved with BDD anode and Na_2SO_4 and H_2SO_4 as supporting electrolyte (99.3% and 94.8% in 120 min of treatment) and which we recommend due to the occurrence of less toxic by-products. MMO compared to BDD achieves much lower efficiency, except in the presence of NaCl, 48.23% for 120 min of treatment. It is a known fact that mixed IrO_2-RuO_2 coating is used for the production of chlorine and hypochlorite, which leads to indirect electrooxidation of phenols in presence of NaCl.

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